# A Theoretical Approach to Molecular Design: Planar-Tetracoordinate Carbon 

by
Danne René Rasmussen, BSc (Hons) Syd.

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THE AUSTRALIAN NATIONAL UNIVERSITY

## Declaration

The work reported in this thesis is entirely my own and contains no material written or published by any other person, except where due reference has been made. It has not been submitted for any other degree or diploma at any university or other institution. The work presented in this thesis was carried out at the Research School of Chemistry at The Australian National University under the supervision of Professor Leo Radom.

## List of Publications

Parts of the work described in this thesis have been published:
(1) Octaplane: A saturated hydrocarbon with a remarkably low ionization energy leading to a cation with a planar tetracoordinate carbon atom

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(2) Planar Carbon Story

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The article entitled "Planar tetracoordinate carbon in a neutral saturated hydrocarbon: Theoretical design and characterization" appeared as the lead communication in the 19th issue of Angewandte Chemie for 1999 with the frontispiece reproduced on page (iv). This article was discussed in Chemical and Engineering News in their Science/Technology Concentrates section on October 11, 1999 (CEN 1999, 77(41), 81). The article "Hemispiroalkaplanes: Hydrocarbon cage systems with a pyramidal tetracoordinate carbon atom and remarkable basicity" is to appear on the cover of Chemistry - A European Journal later in 2000. An impression of the cover appears on page (v).

## COMMUNICATIONS



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A mock-up of the cover of Chemistry - A European Journal for the issue in which will appear the article "Hemispiroalkaplanes: Hydrocarbon cage systems with a pyramidal tetracoordinate carbon atom and remarkable basicity": Rasmussen, D. R.; Radom, L. Chem. Eur. J. 2000, 6, page numbers not yet known.

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## The Essence ...

Using the power of modern supercomputers and quantum mechanical methods for solving the fundamental equations for describing chemical systems, a range of hydrocarbon cage systems designed to have good potential for containing a planartetracoordinate carbon atom have been examined. Exact planarity at a central tetracoordinate carbon atom is achieved in the molecules dimethanospirooctaplane and dimethanospirobinonaplane. These are the first neutral saturated hydrocarbons predicted to contain an exactly planar tetracoordinate carbon atom. The recommended synthetic target is dimethanospirobinonaplane (pictured below).



#### Abstract

A number of novel hydrocarbon cage systems have been designed and characterized using ab initio molecular orbital calculations at the MP2 and B3-LYP levels. In particular, equilibrium structures for five families of molecules, hemialkaplanes, hemispiroalkaplanes, alkaplanes, spiroalkaplanes and dimethanospiroalkaplanes, have been examined in detail with the aim of designing a saturated hydrocarbon with a planar-tetracoordinate carbon atom and with a view to identifying appropriate synthetic targets.

The hemialkaplanes and hemispiroalkaplanes are constructed from a spiropentane or neopentane subunit, respectively, which is capped by a cyclic hydrocarbon. The hemispiroalkaplanes are predicted to contain a pyramidal-tetracoordinate carbon atom possessing a lone pair of electrons. Protonation at this apical carbon atom is found to be highly favorable, resulting in a remarkably high basicity for a saturated hydrocarbon. The proton affinities of the hemispiroalkaplanes are calculated to be more than $1170 \mathrm{~kJ} \mathrm{~mol}^{-1}$, even greater than those for the diamine "proton sponges".

The alkaplanes and the spiroalkaplanes, which are constructed by bicapping a neopentane or spiropentane subunit, respectively, with a pair of cyclic hydrocarbons, show unprecedented flattening of a tetracoordinate carbon atom. Linking the spiroalkaplane caps with methano bridges gives the dimethanospiroalkaplanes, two of which, dimethanospirooctaplane and dimethanospirobinonaplane, achieve exact planarity at the central carbon atom. They are the first neutral saturated hydrocarbons predicted to contain an exactly planartetracoordinate carbon atom. This has been achieved through structural constraints alone. The electronic structure at the central carbon atom results in a highest occupied molecular orbital corresponding to a $p$-type lone pair. Consequently, the adiabatic ionization energies for octaplane, spirooctaplane and dimethanospirooctaplane (approximately 5 eV ) are predicted to be similar to those of lithium and sodium - incredibly low for a saturated hydrocarbon.

Some consideration has been given to likely pathways for unimolecular decomposition for all species. Predicted structures, heats of formation and strain energies for all the novel hydrocarbons are also detailed. Tetramethylhemispirooctaplane and dimethanospirobinonaplane are identified as the preferred synthetic targets.


## Summary

A summary of previous work directed towards the design, synthesis and understanding of compounds that might contain a planar-tetracoordinate carbon atom is given in Chapter 1. Both the electronic and structural approaches to achieving this goal are examined. Considerable success has been previously achieved with the electronic approach, which has enabled the synthesis of a number of organometallic compounds which contain a pla-nar-tetracoordinate carbon atom. The majority of these molecules rely on the incorporation of the planar-tetracoordinate carbon atom into a $\pi$-bonding system and have an electronic configuration of $\sigma^{n} \pi^{2}$ (where $n=3-4$ ) at carbon rather than the $\sigma^{2} \pi^{2}$ configuration predicted for square-planar methane. Synthetic work directed towards forming planartetracoordinate carbon via the structural approach has centered on the fenestranes. However, despite considerable attention, little progress has been made towards the goal of achieving an exactly planar-tetracoordinate carbon atom. Our own calculations on the [4.4.4.4]- and [5.5.5.5]fenestrane isomers are included to illustrate how these molecules are unlikely to ever lead to planar-tetracoordinate carbon.

Chapter 2 gives a brief description of the theoretical methods used in the present work and some observations are made concerning the computational resources required.


I


II

In Chapter 3 we explore, using ab initio molecular orbital calculations at the MP2 and B3LYP levels, the hemialkaplanes (I) ${ }^{\dagger}$ and hemispiroalkaplanes (II), which are constructed by capping a spiropentane or neopentane subunit, respectively, with a cyclic hydrocarbon. The hemialkaplanes capped by a larger ring are predicted to exert considerable flattening

[^0] molecules are labelled with Arabic numerals (e.g. 2).
at the apical carbon atom ( $\alpha_{\text {plan }}=9.6-10.0^{\circ}$ ) but are not expected to be particularly stable due to the presence of overlong $\mathrm{C}-\mathrm{C}$ bonds (with lengths of $1.7 \AA$ or more). The hemispiroalkaplanes are characterized by a pyramidal-tetracoordinate carbon atom possessing a lone pair of electrons. Protonation at this apical carbon atom is found to be highly favorable, resulting in a remarkably high basicity for a saturated hydrocarbon. The proton affinities of the hemispiroalkaplanes are calculated to be more than $1170 \mathrm{~kJ} \mathrm{~mol}^{-1}$, even greater than those for the diamine "proton sponges". Consideration of the strain energies suggests that tetramethylhemispirooctaplane or tetramethylhemispirobinonaplane should be the preferred synthetic targets. Some consideration of likely pathways for unimolecular decomposition has been given, with reference to the calculated vibrational normal modes and experimental evidence from unimolecular rearrangements of bridged spiropentanes.


Molecules which we have named alkaplanes (III), spiroalkaplanes (IV) and dimethanospiroalkaplanes (V) are examined in Chapter 4. The alkaplanes and the spiroalkaplanes, which are constructed by bicapping a neopentane or spiropentane subunit, respectively, with a pair of cyclic hydrocarbons, show unprecedented flattening of a tetracoordinate carbon atom ( $\alpha_{\text {plan }}=5-9^{\circ}$, and $\alpha_{\text {plan }}=3-4^{\circ}$, respectively). In addition, the spiroalkaplanes with an eight-membered primary-ring cap are calculated to have structures without any particularly long $\mathrm{C}-\mathrm{C}$ bonds and to have a low barrier to inversion at the central carbon atom ( $\left.\Delta \mathrm{E}_{\text {plan }}=4-13 \mathrm{~kJ} \mathrm{~mol}^{-1}\right)$. Examination of the structures and strain energies of these larger spiroalkaplanes suggests that they are likely to be good synthetic targets. Linking the caps of these larger spiroalkaplanes with methano bridges gives the dimethanospiroalkaplanes. Two of the molecules so formed, dimethanospirooctaplane (1) and
dimethanospirobinonaplane (2), achieve exact planarity at the central carbon atom. They are the first neutral saturated hydrocarbons predicted to contain an exactly planar-tetracoordinate carbon atom. This has been achieved through structural constraints. The electronic structure at the central carbon atom results in a highest occupied molecular orbital corresponding to a $p$-type lone pair. This loosely bound pair of electrons leads to predicted adiabatic ionization energies for octaplane, spirooctaplane and dimethanospirooctaplane of approximately 5 eV - values similar to those for lithium and sodium and incredibly low for a saturated hydrocarbon.


1


2

Some consideration has been given to likely pathways for unimolecular decomposition. The probable existence of a low-lying triplet surface in the alkaplanes suggests that these molecules will not be good synthetic targets. On the other hand, the spiroalkaplanes and dimethanospiroalkaplanes are not expected to have a low-lying triplet surface and a preliminary examination of the cleavage of what is expected to be the weakest $\mathrm{C}-\mathrm{C}$ bond suggests a reasonable barrier to decomposition. Predicted structures, heats of formation and strain energies are detailed. Dimethanospirobinonaplane (2) is found to have the lowest strain of the dimethanospiroalkaplanes and is suggested as the preferred synthetic target for synthesis of a saturated hydrocarbon with an exactly planar-tetracoordinate carbon atom.

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## CD-ROM Contents

The present work is stored in electronic format as a Portable Document Format (PDF) file on the included CD-ROM (inside back cover) with the name 'thesis.pdf'. The version included on the CD-ROM is complete, including all data in Appendix $C$ (i.e. with all the GAUSSIAN archive files not included in the printed matter). The electronic versions of this work have the advantage that they are fully hyperlinked, allowing easy navigation between the contents, lists, and citations and the associated text.

Different versions for print and screen use are included in the directories so labelled. Further, versions which have been optimized for color, grayscale and single- or double-sided use are also included.

In addition, Fortran source code for the program to calculate $\alpha_{\text {plan }}$, which is detailed in Appendix B, is included in files 'alpha.f' and 'eigen.f'.

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Figure 1-5. Structural representations and relative energies (in $\mathrm{kJ} \mathrm{mol}^{-1}$ ) at the MP2/6-311+G(3df,2p)//MP2/6-31G(d) level for all-cis-[5.5.5.5]fenestrane (1-52) and all-trans-[5.5.5.5]fenestrane (1-53).

## Chapter 2 <br> Theoretical Methods

Figure 2-1. MP convergence on the energy typically oscillates to some degree.
Figure 2-2. MCSCF techniques define an active space and determinants resulting from excitations within this space are then included in the SCF procedure.
Figure 2-3. Pople diagram illustrating the progression of ab initio methods to the exact solution to the time-independent Schrödinger equation (under the Born-Oppenheimer approximation).

## Chapter 3

Hemialkaplanes - Pyramidal Carbon
Figure 3-1. Orbital interaction diagram showing the molecular orbitals in pyra-midal-tetracoordinate carbon formed from the interaction of a carbon atom with a pair of $\mathrm{C}=\mathrm{C}$ double bonds.
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Figure 3-6. Structural parameters (MP2/6-31G(d) values in bold type, B3-LYP/6$31 \mathrm{G}(\mathrm{d})$ values in plain text, all values in $\AA$ or degrees) for protonated hemioctaplane $\left(\mathbf{3}-\mathbf{1}-\mathbf{H}^{+}\right)$, hemispirobioctaplane $\left(\mathbf{3}-\mathbf{4}-\mathbf{H}^{+}\right)$, hemispirooctaplane $\left(\mathbf{3}-5-\mathbf{H}^{+}\right)$, hemispirobinonaplane $\left(\mathbf{3}-\mathbf{6}-\mathbf{H}^{+}\right)$, and tetramethylhemispirooctaplane (3-24- $\mathbf{H}^{+}$). The apical angle shown is $360-\theta_{\mathrm{x} 0 \mathrm{x}}$, i.e. the outer angle made by $\mathrm{x}, \mathrm{C}^{0}$ and $\mathrm{x} .{ }^{32}$
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## Chapter 4 <br> Alkaplanes - Planar Carbon

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Figure 4-3. The lowest-energy planar methane structure is found to have $C_{2 v}$
Figure 4-3. The lowest-energy planar methane structure is found to have $C_{2 v}$
symmetry. Open-shell $D_{4 \mathrm{~h}}$ structures have downhill in-plane modes that lead to dissociation into $\mathrm{CH}_{3}{ }^{+}+\mathrm{H}^{*}$. MRCI+Q/AV5Z// UCCSD(T)/6-311+G(3df,2p) energies (in $\mathrm{kJ} \mathrm{mol}^{-1}$ ) are relative to the tetrahedral ground-state singlet. Where appropriate, the number of imaginary frequencies ( $\mathrm{n} i$ ) is indicated.
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Figure 4-5. Structural parameters (MP2/6-311+G(2d,p)(red) ${ }^{38}$ values in bold type, B3-LYP/6-31G(d) values in plain text) for hexaplane (4-31), heptaplane (4-33), and $S_{4}$ symmetry octaplane (4-27). All unique bond lengths and $\mathrm{H}-\mathrm{H}$ close contacts ( $\AA$ ) are shown. The most highly distorted CCC angles and the distortion from planarity, $\alpha_{\text {plan }}$, $\left({ }^{\circ}\right)$ are also given.
Figure 4-6. Structural parameters (MP2/6-311+G(2d,p)(red) ${ }^{38}$ values in bold type, B3-LYP/6-31G(d) values in plain text, all values in $\AA$ or degrees) for spirohexaplane (4-39), spirobiheptaplane (4-40) and the two spiroheptaplane isomers (4-41 and 4-42). All unique bond lengths are shown. The most distorted CCC angles and the distortion from planarity at $\mathrm{C}^{0}, \alpha_{\text {plan }}$, are given. The angles and bond lengths around the central $\mathrm{C}(\mathrm{C})_{4}$ subunit for $\mathbf{4 - 4 2}$ are also shown.
Structural parameters (MP2/6-311+G(2d,p)(red) values in bold type, B3-LYP/6-31G(d) values in plain text, all values in $\AA$ or degrees) for spirobioctaplane (4-43), spirooctaplane (4-28) and spirobinonaplane (4-44). All unique bond lengths, any $\mathrm{H}-\mathrm{H}$ close contacts, and the most distorted CCC angles are shown. The distortion from planarity at $\mathrm{C}^{0}, \alpha_{\text {plan }}\left({ }^{\circ}\right)$, is also given.
Figure 4-8. Structural parameters (MP2/6-311+G(2d,p)(red) ${ }^{38}$ values in bold type, B3-LYP/6-31G(d) values in plain text, all values in $\AA$ or
degrees) for dimethanospirobioctaplane (4-47), dimethanospirooctaplane (4-29), and dimethanospirobinonaplane (4-48). All unique bond lengths and some close-contact distances ( $\AA$ ) are shown. CCC angles significantly distorted from the tetrahedral ideal and the distortion from planar-tetracoordination at $\mathrm{C}^{0}, \alpha_{\text {plan }}\left({ }^{\circ}\right)$, are also given.
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Figure 4-10. An iso-surface of the highest occupied molecular orbital (HOMO) of dimethanospiro[2.2]octaplane (4-29) (the iso-surface is drawn at $0.080 e \AA^{-3}$ ).
Figure 4-11. Structural parameters (MP2/6-311+G(2d,p)(red) ${ }^{38}$ values in bold type, B3-LYP/6-31G(d) values in plain text, all values in $\AA$ or degrees) for octaplane radical cation $\left(\mathbf{4 - 2 7 ^ { + + }}\right)$, spirooctaplane radical cation $\left(\mathbf{4 - 2 8}{ }^{\mathbf{+}}\right)$, and dimethanospirooctaplane $\left(\mathbf{4 - 2 9}{ }^{\boldsymbol{+}}\right)$. All unique bond lengths and some close-contact distances ( $\AA$ ) are shown. Angles significantly distorted from the tetrahedral ideal are also given.
Figure 4-12. $\quad$ Structural parameters (MP2/6-31G(d) values in bold type, B3-LYP/6$31 \mathrm{G}(\mathrm{d})$ values in plain text, all values in $\AA$ or degrees) for triplet octaplane (triplet-4-27) and triplet spirooctaplane (triplet-4-28). Selected bond lengths and the dissociated CC distance are shown. Selected angles are also given. The two-dimensional structural elements show a top-down view of a slice of the molecule through the central $\mathrm{C}(\mathrm{C})_{4}$ and $\mathrm{C}(\mathrm{CH})_{4}$ regions.
Figure 4-13. Calculated potential energy curves for homolytic $\mathrm{C}^{0}-\mathrm{C}^{\alpha}$ bond cleavage in dimethanospirooctaplane (4-29) determined at the O -UMP2(fc)/6-31G(d) and $\boldsymbol{\square}$ - UB3-LYP/6-31G(d) levels are given as relative energy, $E_{\text {rel }},\left(\mathrm{kJ} \mathrm{mol}^{-1}\right)$ against $\mathrm{C}^{0}-\mathrm{C}^{\alpha}$ bond length, $r\left(\mathrm{C}^{0}-\mathrm{C}^{\alpha}\right)$ $(\AA)$. Optimized geometries at fixed values of $r\left(\mathrm{C}^{0}-\mathrm{C}^{\alpha}\right)$ were determined at the UB3-LYP/6-31G(d) level.

## Appendix A <br> Nomenclature

## Appendix B <br> A Planarity Measure

Figure B-1. The deviation from planar-tetracoordination in the central $\mathrm{C}^{0}\left(\mathrm{C}^{\alpha}\right)_{4}$ moiety of the alkaplanes can be determined by finding the plane through $\mathrm{C}^{0}$, defined by the normal to the plane, $\hat{\mathbf{u}}$, which minimizes the sum of squared distances $d_{i}$ made by the unit vectors $\hat{\mathbf{u}}_{i}$ with the plane.

## Appendix C <br> Computational Data

## List of Molecules

## Chapter 1

## Schematics

| 1-I | Fenestranes (symmetric) |
| :--- | :--- |
| 1-II | Erker's Olefinic Compounds |
| 1-III | Fenestranes (atom labels) |
| 1-IV | Paddlanes |
| 1-V | Alkaplanes |
| 1-VI | Spiroalkaplanes |
| 1-VII | Dimethanospiroalkaplanes |
| Molecules |  |

1-1 2,3,4,5-tetraboraspiropentane
1-2 1,1-dilithiocyclopropane
1-3 3,3-dilithio-1,2-diboracyclopropane
(deloc-4,5,6,7,8)-spiro[2.5]octa-1,5,7-trien-4-ylium

1-4 bowlane
1-5 octaplane
1-6 spiro[2.2]octaplane
1-7 dimethanospiro[2.2]octaplane
1-8 3,3-dilithiocyclopropene
1-9 diboracyclopropane
1-VIII Fenestranes (general)
1-IX Fenestranes (three fused rings)
1-X Paddlanes (experimental)
1-XI Hemialkaplanes
1-XII Hemispiroalkaplanes
1-XIII Bridged spiropentanes

1-10 difluorodilithiomethane
1-11 dilithiomethane
1-12 $\quad \mathrm{CB}_{2} \mathrm{H}_{4}$ (preferred isomer)
1-13 difluorodilithiomethane (pyramidal)
1-14 difluorodilithiomethane (preferred isomer)
1-15 1,1-dilithioethene
1-16 1,2-dilithioethene
1-17 2,3-diboraspiropentane
1-18 1,2-diborabicyclo[1.1.0]butane
1-19 1,2-diboraspiro[2.2]pent-4-ene
1-20 $\quad \mathrm{C}_{2} \mathrm{~B}_{2} \mathrm{H}_{4}$ (cis-isomer)
1-21 $\quad \mathrm{C}_{2} \mathrm{~B}_{2} \mathrm{H}_{4}$ (trans-isomer)
1-22 phenyllithium dimer
1-23 [(2,6-dimethoxyphenyl)lithium] ${ }_{2}$
1-24 [8-(dimethylamino)-1-naphthyllithium $\left.\cdot \mathrm{Et}_{2} \mathrm{O}\right]_{2}$
1-25 Cotton's $\mathrm{V}_{2}$ complex $\mathbf{1 - 5}$
1-26 Buchwald's $\mathrm{Zr}_{2}$ Complex
1-27 Erker's neutral complexes
1-28 Erker's cationic complexes
1-29 Chisholm's ditungsten adducts
1-30 Cotton's ditungsten complexes
1-31 $\mathrm{Pd}_{2}$ and $\mathrm{H}_{2} \mathrm{CCCPh}$ complex
1-32 $\mathrm{Pd}_{2}$ and $\mathrm{CS}_{2}$ complex
1-33 $\left[\mathrm{WRe}_{2}\left(\mathrm{C}_{5} \mathrm{Me}_{5}\right)(\mathrm{O})(\mathrm{CO})_{8}(\mathrm{CCPh})\right]$
1-34 $\quad\left[\mathrm{Re}_{4} \mathrm{C}(\mathrm{CO})_{15} \mathrm{I}\right]^{-}$
1-35 Siebert's dicobalt complexes
1-36 unsaturated [3.5.5.5]fenestrane
1-60
1-61
1-62
1-63
1-6
1-65 [1.1.1.1]paddlane
1-66 [2.2.2.2]paddlane
1-67 hexa-3-ene-1,5-diyne
1-68 Dodziuk's unsaturated paddlane
1-69 heteroatomic paddlanes from synthesis
1-70 all-carbon skeleton, unsaturated paddlanes from synthesis
1-71 Dodziuk's hemidodecaplane
1-72 Dodziuk's bisbowlane

1-73 tricyclo[4.1.0.0 ${ }^{1,3}$ ]heptane
1-74 benzotricyclo[4.1.0.0. ${ }^{1,3}$ hept-4-ene
1-75 tricyclo[5.1.0.0 $0^{1,3}$ ]octane
1-76 7,7-dichloro-2,5,5,8,8-pentamethyltricyclo[5.1.0.0 ${ }^{1,3}$ ]octane
1-77 tetracyclo[6.1.0.0 $0^{1,3} .0^{4,6}$ ]undecane

## Chapter 2

## Schematics

none
Molecules
2-1 dimethanospiro[2.2]octaplane
2-2 spiro[2.2]octaplane

## Chapter 3

## Schematics

3-I Paddlanes
3-II Alkaplanes
3-III Hemialkaplanes
3-IV Spiroalkaplanes
3-V Hemispiroalkaplanes
Molecules
3-1 hemioctaplane (bowlane)
3-2 hemihexaplane
3-3 hemibiheptaplane
3-4 hemispirobioctaplane (perp)
3-5 hemispirooctaplane
3-6 hemispirobinonaplane (perp)
3-7 all-trans-[4.4.4.4]fenestrane
3-8 all-cis-[5.5.5.5]fenestrane
3-9 all-cis-[4.4.4.5]fenestrane derivative
3-10 [3.4.3]fenestrane-ketene (tricyclo[3.1.0.0 ${ }^{1,3}$ ]hexane-ketene)
3-11 [3.3.3]fenestrane (tricyclo[2.1.0.0 ${ }^{1,3}$ ]pentane)
3-12 [3.5.3]fenestrane (tricyclo[4.1.0.0 ${ }^{1,3}$ ]heptane)
3-13 [3.6.3]fenestrane (tricyclo[5.1.0.0 ${ }^{1,3}$ ]octane)
3-14 4,5-benzotricyclo[4.1.0.0 ${ }^{1,3}$ hept-4-ene
3-15 pyramidane
3-16 Dodziuk's hemidecaplane
3-17 Dodziuk's hemiundecaplane
3-18 Dodziuk's hemidodecaplane
3-19 $\mathrm{Fe}_{4} \mathrm{C}$ core compounds
3-20 $\quad\left[\left(\mathrm{Ph}_{3} \mathrm{PAu}\right)_{5} \mathrm{C}^{+}\right.$
3-21 C bound to cyclohexa-1,4-diene
3-22 $\quad \mathrm{C}$ bound to norbornadiene
3-23 C bound to bicyclo[2.2.2]octa-2,5-diene
3-24 tetramethylhemispirooctaplane
3-25 hemibihexaplane
3-26 hemibioctaplane
3-27 hemibinonaplane
3-28 hemispirobutaplane

1-78 Baird's bridged spiropentane (tetracyclo[3.3.1.0 $0^{2,4} .0^{2,8}$ nonane)
1-79 3-vinyl-7,7-dibromobicyclo[4.1.0]heptane
1-80 tricyclo[3.1.0.0 $0^{1,3}$ ]hexane-4-ketene
$1-81$
1-82
tricyclo[3.1.0.0 $0^{1,3}$ ]hexane
tricyclo[2.1.0.0 $0^{1,3}$ ]pentane

2-3 dimethanospiro[2.2]binonaplane

3-VI Fenestranes (four fused rings)
3-VII Fenestranes (three fused rings)
3-VIII Hemialkaplanes (parameters)
3-IX Hemispiroalkaplanes (parameters)

3-29 hemispirobihexaplane (perp)
3-30 hemispirobihexaplane (par)
3-31 hemispirohexaplane (perp)
3-32 hemispirohexaplane (par)
3-33 hemispirobiheptaplane (perp)
3-34 hemispirobiheptaplane (par)
3-35 hemispirobioctaplane (par)
3-36 hemispirobinonaplane (par)
3-37 syn-tricyclo[4.2.0.0 ${ }^{2,5}$ ]octa-3,7-diene
3-38 ring opened hemispirobinonaplane
3-39 cyclopropane
3-40 tetrahedrane
3-41 spiropentane
3-42 [1.1.1]propellane
3-43 prismane
3-44 cubane
3-45 tetrakis(tert-butyl)tetrahedrane
3-46 cyclobutane
3-47 bicyclo[2.2.0]hexane
3-48 cyclohexane
3-49 norbornane (bicyclo[2.2.1]heptane)
3-50 cis-bicyclo[3.3.0]octane
3-51 cyclooctane
3-52 bicyclo[3.3.1]nonane
3-53 [3.4.3]fenestrane (tricyclo[3.1.0.0 $\left.0^{1,3}\right]$ hexane)
3-54 tetracyclo[3.3.1.0 $0^{2,4} .0^{2,8}$ ]nonane (Baird's hydrocarbon)
3-55 hydrocarbon parent of isodrin
3-56 tetradehydrotetraquinane isomer of the hydrocarbon parent of isodrin

## Chapter 4

## Schematics

| 4-I | [l.m.n]Fenestranes (three fused rings) |
| :--- | :--- |
| 4-II | [k.l.m.n]Fenestranes (four fused rings) |
| 4-III | Paddlanes |
| 4-IV | Hemialkaplanes |


| 4-V | Hemispiroalkaplanes |
| :--- | :--- |
| 4-VI | Alkaplanes |
| 4-VII | Spiroalkaplanes |
| 4-VIII | Dimethanospiroalkaplanes |

## Molecules

4-1 2,3,4,5-tetraboraspiropentane
4-2 1,1-dilithiocyclopropane
4-39 spiro[2.2]hexaplane
4-3 3,3-dilithio-1,2-diboracyclopropane
4-4 1,1-dilithioethene
4-5 1,2-dilithioethene
4-6 2,3-diboraspiropentane
4-7 1,2-diborabicyclo[1.1.0]butane
4-8 1,2-diboraspiro[2.2]pent-4-ene
4-9 $\quad \mathrm{C}_{3} \mathrm{~B}_{2} \mathrm{H}_{4}$ (cis-isomer)
4-10 $\quad \mathrm{C}_{3} \mathrm{~B}_{2} \mathrm{H}_{4}$ (trans-isomer)
4-11 Chisholm's ditungsten adducts
4-12 Siebert's dicobalt complexes
4-13 Cotton's $V_{2}$ complex
4-14 Buchwald's $\mathrm{Zr}_{2}$ Complex
4-15 Erker's neutral complexes
4-16 [3.5.3.5]fenestrane
4-17 an all-cis-[4.4.4.5]fenestrane derivative
4-40 spiro[2.2]biheptaplane
4-41 a spiro[2.2]heptaplane isomer
4-42 another spiro[2.2]heptaplane isomer
4-43 spiro[2.2]bioctaplane
4-44 spiro[2.2]binonaplane
4-45 [3.5.3]fenestrane or tricyclo[4.1.0.0 ${ }^{1,3}$ ]heptane

4-18 all-trans-[4.4.4.4]fenestrane
4-46 tetracyclo[3.3.1.0 $\left.0^{2,4} .0^{2,8}\right]$ nonane (Baird's hydrocarbon)
4-47 dimethanospiro[2.2]bioctaplane
4-48 dimethanospiro[2.2]binonaplane
4-49 cyclopropane
4-50 cyclobutane
4-51 cyclopentane
4-52 cyclohexane
4-53 cyclooctane
4-54 bicyclo[3.3.1]nonane
4-19 [5.5.5.5]fenestrane
4-20 an unsaturated fenestrane ([5.6.5.6]fenestraoctaene)
4-21 another unsaturated fenestrane ([5.5.5.5]fenestrahexaene)
4-22 [2.2.2.2]paddlane
4-23 an unsaturated paddlane
tetrahedrane
4-56 pyramidane
4-57 [1.1.1]propellane
4-58 spiropentane
4-59 prismane

4-24 hemioctaplane (bowlane)
4-60

4-25 [3.4.3]fenestrane (tricyclo[3.1.0.0 ${ }^{1,3}$ ]-
4-61 tetramethyltetrahedrane hexane)

4
4-63 pagodane
4-26 [3.3.3]fenestrane (tricyclo[2.1.0.0 $\left.0^{1,3}\right]$ pentane)
rane
4-65 bicyclo[2.2.0]hexane
4-66 cycloheptane
4-27 octaplane $\left(S_{4}\right)$
4-67
4-28 spiro[2.2]octaplane
4-29 dimethanospiro[2.2]octaplane
4-30 bihexaplane
4-31 hexaplane
4-68 cis-bicyclo[3.3.0]octane
4-69 a bis-methano-bridged [1.1.1.1]pagodane
4-70 [1.1.1.1]isopagodane
4-32 biheptaplane
4-71 [2.2.1.1]isopagodane
4-33 heptaplane
4-72
4-34 bioctaplane
4-35 octaplane $\left(D_{2}\right)$
4-73 a dibenzo derivative of the isodrin parent a dibenzo derivative of the isodrin parent
hydrocarbon
4-74 a syn dimeric benzene derivative of birdcage hydrocarbon
4-36 binonaplane
4-37 hemibioctaplane
4-75 a syn dimeric benzene derivative of hemispirobioctaplane

## Appendix A

## Schematics

A-I Fenestranes (three rings)
A-II Fenestranes (four rings)

## Molecules

A-1 a [4.4.4.5]fenestrane
A-2 a [3.5.3.5]fenestrane
A-3 a [4.5.5.5]fenestrene
A-4 a [5.5.5.5]fenestratetraene
A-5 pyramidane
A-6 windowpane
A-7 staurane
A-8 octaplane

## Chapter 1 Planarizing Distortions at Carbon

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### 1.1 Introduction

In 1874 it was suggested independently both by van't $\mathrm{Hoff}^{1}$ and le $\mathrm{Bel}^{2}$ that the arrangement in space of the substituents at a tetracoordinate carbon is such that they form a tetrahedral geometry. Van't Hoff wrote that, ${ }^{\dagger}$
"... theory is brought into accord with the facts if we consider the affinities of the carbon atom directed toward the corners of a tetrahedron of which the carbon atom itself occupies the center."

Similarly, le Bel, who was considering the same problem of isomerism in the fatty acids, wrote that,

[^1]"... we are obliged to admit that the four atoms A occupy the angles of a regular tetrahedron, whose planes of symmetry are identical with those of the whole molecule $\mathrm{MA}_{4}$; in this case no bisubstitution product can have rotatory power."

These concepts quickly propelled structural chemistry into the three-dimensional realm which today seems only too natural. Remarkably, van't Hoff was attacked vehemently for his theory by Hermann Kolbe. ${ }^{\dagger}$ Kolbe $^{3}$ called it a "play of imagination" which "forsakes the solid ground of fact and is quite incomprehensible to the sober chemist." It is likely that Kolbe's tirade was the inspiration for van't Hoff's inaugural address as professor of chemistry in Amsterdam, which dealt with the role of the "imaginative faculty" in science.

It was almost 100 years later before the very real prospect of exceptions to what has become the van't Hoff/le Bel precept was seriously considered. In 1970, Hoffmann, Alder and Wilcox ${ }^{4}$ proposed in their seminal work on this subject, that it might be possible to stabilize a structure in which the four substituents attached to a tetracoordinate carbon atom are arranged in a plane. There ensued a great interest in the possibility of planar-tetracoordinate carbon.

At first examination it was clear to Hoffmann et al. that because molecules with a simple chiral center at carbon do not racemize we should expect that an achiral geometry, such as a planar one, will lie at least $250 \mathrm{~kJ} \mathrm{~mol}^{-1}$ above the tetrahedral form. Their initial calculations suggested that the barrier to inversion was in fact considerably greater than this proposed lower limit and that it was unlikely that a simple carbon compound could be found that actually prefers a planar arrangement. It was suggested, instead, that the possibility of a planar geometry at tetracoordinate carbon might arise, in a more indirect fashion, as the transition structure involved in non-dissociative racemization of a suitably substituted methane derivative.

However, the challenge had been laid and a search to find systems which might contain planar-tetracoordinate carbon began. Some degree of success came very quickly with the work of Pople, Schleyer and coworkers, published in $1976 .{ }^{5}$ They identified a number of small lithium- and boron-containing molecules (which included 1-1-1-3) that were predicted from ab initio calculations to prefer a planar-tetracoordinate geome-

[^2]try. These simple structures have, however, proven to be difficult to synthesize (see Section 1.4.1 on page 9). At about the same time experimental work began which was

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directed towards the synthesis of the fenestranes (1-I), and related hydrocarbons ${ }^{6,7}$ that were expected to induce planarizing distortions at the central tetracoordinate carbon atom. Experimental success was then achieved in Erker's group ${ }^{8}$ where a facile route was found to organometallic compounds with a planar carbon center which is clearly associated with four substituents, two of which are metals (1-II). ${ }^{\dagger}$


1-I


1-II

Lack of success in achieving significant planarizing distortions at a quaternary carbon in purely organic systems (such as 1-I) and the difficulty in synthesizing candidates of a purely organic nature led to a lull in this approach to planar-tetracoordinate carbon. However, it had always been recognized that the search for planar-tetracoordinate carbon was the sort of problem for which computational chemistry was well suited. ${ }^{4}$ Computational techniques allow for the examination of a wide range of molecules, each of which might take years to synthesize in a laboratory. Exploitation of this computational approach led to the identification by McGrath, Radom and Schaefer of bowlane

[^3]$(1-4)^{9}$ as a purely organic molecule with considerable flattening at a tetracoordinate carbon atom. Since then we have proposed other target molecules, including octaplane (15), ${ }^{10}$ and spiro[2.2]octaplane (1-6). ${ }^{11}$ Finally, we have identified dimethanospiro[2.2]octaplane (1-7) ${ }^{12}$ as the first saturated hydrocarbon predicted to contain a planar-tetracoordinate carbon atom.


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This endeavour has proven to be well served by the use of both van't Hoff's "imaginative faculty" and detailed analysis. Previous work in the search to locate structures containing a planar-tetracoordinate carbon, their relevance to the present work, and further analysis by us that relates directly to these compounds, are described in detail in the remainder of this Chapter.

### 1.2 Inversion of Methane

Because methane is the simplest possible tetracoordinate carbon molecule, it serves as a good first model for examining the issues involved in designing a molecule containing a planar-tetracoordinate carbon atom. Many researchers have examined methane from the slightly different perspective of a model for the inversion (or, in the case of methane itself, the automerization) process at tetracoordinate carbon, which was thought originally to proceed via a square-planar transition structure (Figure 1-1).

Monkhurst ${ }^{13}$ was the first to examine inversion of tetracoordinate carbon theoretically, although he was preempted by a brief paper on the deformation of a general $\mathrm{AH}_{4}$ species by Saturno. ${ }^{14}$ Monkhurst proposed that inversion may occur either through a planar or a pyramidal structure. Using methane as a model he then determined, via approximate electronic structure calculations, that the planar structure was lower in energy than the pyramidal structure and that the barrier to inversion was of the order of


Figure 1-1. The automerization of methane, initially thought to proceed via a $D_{4 \mathrm{~h}}$ structure is expected to proceed via a pyramidal-like structure.
$1000 \mathrm{~kJ} \mathrm{~mol}^{-1}$. With such a large barrier, dissociation and recombination would clearly be the preferred pathway. Many workers ${ }^{4,15-17}$ (including Hoffmann, Alder and Wilcox) made estimations of the difference in energy between the planar and tetrahedral geometries $\left(\Delta \mathrm{E}_{\mathrm{PT}}=\mathrm{E}_{\text {Planar }}-\mathrm{E}_{\text {Tetrahedral }}\right)$ in methane which ranged from 600 to $1000 \mathrm{~kJ} \mathrm{~mol}^{-1}$.

In 1977, Minkin et al. ${ }^{18}$ used a number of methods including HF calculations employing a double-zeta basis to show that in fact the pyramidal $C_{4 \mathrm{v}}$ symmetry structure is expected to be lower in energy than the planar $D_{4 \mathrm{~h}}$ structure. This preference was noted by others ${ }^{19}$ and led to the elucidation in 1993 by Gordon and Schmidt ${ }^{20}$ of the preferred route for the hypothetical classical inversion (automerization) of methane, which is seen to proceed via a pyramidal-type structure with $C_{\mathrm{s}}$ or possibly $C_{4 \mathrm{v}}$ symmetry (Figure 1-1).

The most accurate calculations published to date for the relative energies of the various methane geometries come from the work of Pepper and coworkers. ${ }^{21}$ Like Gordon and Schmidt before them, they find that the lowest-energy, planar structure for methane does not have four equivalent hydrogen atoms and $D_{4 \mathrm{~h}}$ symmetry, as had been supposed, but has $C_{2 \mathrm{v}}$ symmetry and a structure that suggests a complex between $\mathrm{CH}_{2}$ and $\mathrm{H}_{2}$ (reminiscent of the structure ${ }^{22}$ for $\mathrm{CH}_{4}^{2+}$ ). Further, they find that the energy of the
$C_{2 \mathrm{v}}\left(D_{4 \mathrm{~h}}\right)$ symmetry, planar structure relative to the tetrahedral geometry is about 510 (546) $\mathrm{kJ} \mathrm{mol}^{-1}$ (after correction for the zero-point vibrational energy (ZPVE)). This is significantly higher than the homolytic dissociation energy of the $\mathrm{C}-\mathrm{H}$ bond in methane $\left(435 \mathrm{~kJ} \mathrm{~mol}^{-1}\right) .{ }^{23}$ Further, the $C_{\mathrm{s}}\left(C_{4 \mathrm{v}}\right)$ symmetry transition structure for the automerization process is found to lie 440 (437) $\mathrm{kJ} \mathrm{mol}^{-1}$ above the tetrahedral ground state (after correction for ZPVE). This is very close in energy to the homolytic dissociation energy of the $\mathrm{C}-\mathrm{H}$ bond ( $435 \mathrm{~kJ} \mathrm{~mol}^{-1}$ ) and suggests that classical inversion without bond cleavage might in fact be possible under certain conditions.

Most recently, Yoshizawa and coworkers ${ }^{24}$ have shown using B3-LYP calculations that this barrier can be reduced to $180-200 \mathrm{~kJ} \mathrm{~mol}^{-1}$ when methane is complexed to a transition metal cation (such as $\mathrm{Fe}^{+}, \mathrm{Co}^{+}, \mathrm{Ni}^{+}$or $\mathrm{Cu}^{+}$). They suggest that inversion of stereochemistry at a carbon atom in catalytic reactions on hydrocarbons should be possible. They found this catalyzed inversion to proceed via a $C_{\mathrm{s}}$ symmetry structure, much like that of the uncatalyzed process.

It seems that pyramidal geometries at tetracoordinate carbon may, in general, be lower in energy than planar geometries (see also Section 1.3 below). A pyramidal geometry at tetracoordinate carbon is unusual in itself. Molecules with a pyramidal tetracoordinate carbon atom are considered further in Chapter 3.

### 1.3 Designing Planar Carbon

It was Hoffmann and coworkers ${ }^{4}$ who initiated attempts to explicitly design systems in which a planar-tetracoordinate carbon would be preferred over the usual tetrahedral arrangement. Hoffmann and coworkers clearly recognized the audacity of their proposal. They wrote,

> "Attempts to subvert something as basic to organic chemistry as the tetrahedral tetracoordinate carbon atom should perhaps be viewed as acts appropriately described by the Yiddish word chutzpah and/or the Greek hubris."

Their caution was based, at least in part, on calculations which had determined the energy difference $\Delta \mathrm{E}_{\mathrm{PT}}=\mathrm{E}_{\text {Planar }}-\mathrm{E}_{\text {Tetrahedral }}$ in methane to be anywhere from 600 to 1000 $\mathrm{kJ} \mathrm{mol}^{-1}$, values ${ }^{4,15-17}$ much greater than Hoffmann's proposed lower limit of 250 $\mathrm{kJ} \mathrm{mol}^{-1}$. Clearly, overcoming the preference for a tetrahedral geometry would be for-
midable. Consideration of the difference $\Delta \mathrm{E}_{\mathrm{PT}}=\mathrm{E}_{\text {Planar }}-\mathrm{E}_{\text {Tetrahedral }}$ shows that it can be reduced either by lowering $\mathrm{E}_{\text {Planar }}$ or by raising $\mathrm{E}_{\text {Tetrahedral }}$. Raising $\mathrm{E}_{\text {Tetrahedral }}$ can be achieved by devising polycyclic structures in which a tetrahedral arrangement at the central carbon is made unfavorable on steric grounds. Hoffmann's initial suggestion ${ }^{4}$ for this approach was based on a symmetric fenestrane skeleton (1-I where $n<3$ ). This can be considered as a structural approach, which relies on a rigid covalent bonding regime to apply constraints on the positioning of the substituents to carbon. This approach is explained in greater detail in Section 1.5 on page 19. The alternative, lowering $\mathrm{E}_{\text {Planar }}$, requires replacement of hydrogen in methane with substituents that in some way electronically favour a planar bonding arrangement.



Figure 1-2. The electronic structure of square-planar methane showing the $p$-type lone-pair (HOMO) and six C-H bonding electrons.

Examination of the electronic structure of square-planar methane (Figure 1-2) reveals that the highest occupied molecular orbital (HOMO) $\left(\mathrm{a}_{2 \mathrm{u}}\right)$ is expected to be a $p$ -
type lone pair, while the remaining six valence electrons are involved in forming four $\sigma$ deficient $\mathrm{C}-\mathrm{H}$ bonds. Other ways to describe the bonding of the hydrogens to carbon have been suggested. One way sees square-planar methane as a resonance hybrid of structures that have a pair of regular C-H bonds and a three-center two-electron (3c-2e) bond between the remaining hydrogens and carbon. Our full-valence MCSCF calculations suggest that a unique five-center six-electron (5c-6e) bonding scheme is more appropriate. Whatever the best bonding description, it is clear that substituents which are strong $\sigma$-donors and/or $\pi$-acceptors (when bound with the correct orientation) will stabilize a planar over the tetrahedral geometry.

This electronic approach to designing molecules with a planar-tetracoordinate carbon atom has seen much activity and has had considerable success. Work in this area is summarized in the next section (Section 1.4 on page 9).

One other issue that becomes apparent when examining the electronic structure of methane, is the low-lying lowest unoccupied molecular orbital (LUMO). This has led some workers ${ }^{17,19 b}$ to suggest that the lowest state of planar methane (and its derivatives ${ }^{5,27 \mathrm{~b}}$ ) may be a triplet (or perhaps an open-shell singlet biradical) species. Calculations by Schleyer and coworkers ${ }^{19 \mathrm{c}}$ on a range of isoelectronic $\mathrm{AH}_{4}$ systems $\left(\mathrm{BH}_{4}^{-}, \mathrm{CH}_{4}\right.$, $\mathrm{NH}_{4}^{+}, \mathrm{AlH}_{4}^{-}, \mathrm{SiH}_{4}$ and $\left.\mathrm{PH}_{4}^{+}\right)$showed that only planar $\left(D_{4 \mathrm{~h}}\right) \mathrm{BH}_{4}^{-}$preferred the triplet state and then by only $40 \mathrm{~kJ} \mathrm{~mol}^{-1}$ (at the MP2/6-31G(d)//HF/6-31G(d) level) over the lowest-energy, pyramidal singlet. But the method used is expected to overstate the stability of the triplet and they suggest that the singlet probably is the lowest-energy state in this case as well. However, the HOMO in the preferred singlet states of planar $\mathrm{BH}_{4}^{-}$, $\mathrm{AlH}_{4}^{-}, \mathrm{SiH}_{4}$ and $\mathrm{PH}_{4}{ }^{+}$is the $\mathrm{b}_{1 \mathrm{~g}}$ orbital. Only $\mathrm{CH}_{4}$ and $\mathrm{NH}_{4}{ }^{+}$prefer the $\mathrm{a}_{2 \mathrm{u}} \mathrm{HOMO}$ (see Figure 1-2). Interestingly, pyramidal ( $C_{4 \mathrm{v}}$ ) singlet structures are preferred by $\mathrm{CH}_{4}, \mathrm{NH}_{4}^{+}$ and $\mathrm{PH}_{4}^{+}$but not by $\mathrm{BH}_{4}^{-}, \mathrm{AlH}_{4}^{-}$and $\mathrm{SiH}_{4}$. A detailed examination of the three lowest electronic states of square-planar ( $D_{4 \mathrm{~h}}$ ) methane was carried out by Gordon and Schmidt ${ }^{20}$ using multireference techniques. They also found that the singlet with an $\mathrm{a}_{2 \mathrm{u}}$ HOMO (p-type lone pair) is preferred over both the triplet and the open-shell singlet.

Although there is considerable evidence to suggest that planar-tetracoordinate carbon will indeed prefer a closed-shell singlet state with a $p$-type lone pair, it is possible that when hydrogen is replaced by other substituents the preferred electronic configuration may alter.

### 1.4 Electronic Stabilization

Initial suggestions of structures that exploited electronic stabilization at a planartetracoordinate carbon included a number of structures which either surrounded a central carbon atom with an annulene perimeter or incorporated the target atom into a delocalized $\pi$-system. Further attempts at designing molecules with a planar-tetracoordinate carbon atom involved calculations on structures which successively replaced the hydrogens of methane with $\sigma$-donors and/or $\pi$-acceptors like Li and B to form small polar organometallic molecules. Later attempts involved the use of transition metal substituents, and structures of this nature then began to show up incidentally from X-ray structure analyses.

Although there are a few notable exceptions, most of the compounds synthesized to date which achieve planar-tetracoordination at carbon do so by associating a fourth ligand in the plane of an already planar, $\mathrm{sp}^{2}$-hybridized carbon atom. In this way, the planar-tetracoordinate carbon is stabilized to a large extent by direct incorporation into a $\pi$-system. As has been pointed out by Siebert and Gunale, ${ }^{25,26}$ this removes the $p$-type lone-pair. It has been shown that in these molecules the carbon atom contributes a single electron to the $\pi$-system and three electrons to $\sigma$-bonding rather than the two and two split seen in square-planar methane (the electronic configuration at the planar carbon is $\sigma^{3} \pi^{1}$ rather than $\sigma^{2} \pi^{2}$ ). By removing the $p$-type lone pair, these compounds are greatly stabilized but are no longer expected to show properties which result from an electronic structure like that of square-planar methane.

Electronically-stabilized, planar carbon compounds (whether purely theoretical or experimentally isolated) can be separated into a number of distinct groups which are discussed in detail below.

### 1.4.1 Lithium and Boron Substituents

Pople, Schleyer and coworkers ${ }^{5}$ identified through HF/4-31G calculations, six small, polarorganometallic molecules that appeared to prefer a planar arrangement at the central tetracoordinate carbon atom (1-1-1-3 and 1-8-1-10). All these molecules have either two lithium and/or two boron substituents, both of which appear to have a very strong stabilizing effect on the planar geometry. This was predicted by Hoffmann ${ }^{4}$


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from his examination of the electronic structure of methane. Dilithiomethane (1-11) was found to be border-line because the planar and tetrahedral-like $\left(C_{2 v}\right)$ structures were of similar energy. More accurate calculations ${ }^{27,28}$ on dilithiomethane (1-11) indeed indicated that there is little difference in the energy of the two geometrical isomers. Our best calculations, at the $\operatorname{CCSD}(\mathrm{T}) / \mathrm{AVTZ}$ level, indicate that the planar-tetracoordinate geometry is indeed a minimum but the tetrahedral geometry is also a minimum and is slightly preferred $\left(5 \mathrm{~kJ} \mathrm{~mol}^{-1}\right)$. Further, the barrier to conversion of the planar into the


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$1-9$


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1-11
tetrahedral-like geometry is very small (about $3 \mathrm{~kJ} \mathrm{~mol}^{-1}$ ). 3,3-Dilithiocyclopropene ( $\mathbf{1 -}$ 8) has not been analyzed further in the literature. However, our calculations, at the MP2/6-311+G(2d,p) level, indicate that it is unstable with respect to dissociation. Diboracyclopropane (1-9) has received further attention ${ }^{29}$ and the planar-tetracoordinate structure is found to be a transition structure. The preferred isomer of $\mathrm{CB}_{2} \mathrm{H}_{4}$ has a B-B bond bridged by hydrogen and $\mathrm{CH}(\mathbf{1 - 1 2})$. Further investigation of dilithiodifluoromethane (1-10) showed that very strong F-Li interactions lead to a pyramidal geometry (1-13) where a carbon atom sits on a $(\mathrm{LiF})_{2}$ base. ${ }^{30}$ More recently, Sorger and Schleyer ${ }^{31}$ have re-examined most of these molecules at the B3-LYP/6-311++G(d,p) level. In this work they find that $\mathbf{1 - 1 3}$ is a transition structure and that the preferred isomer is in fact $\mathbf{1 - 1 4}$. Schleyer also identified four new, lithium- and boron-containing species (1-15-1-18) ${ }^{32}$ that are predicted to contain planar-tetracoordinate carbon. Most



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1-16


1-17


1-18
recently, Gribanova, Minkin and Minyaev ${ }^{33}$ have identified, through MP2(full)/6$31++\mathrm{G}(\mathrm{d}, \mathrm{p})$ calculations, a number of isomers of 1,2-diboraspiro[2.2]pent-4-ene (1-


1-19

$1-20$


1-21

19-1-21) as also containing a planar-tetracoordinate carbon atom. In summary, it appears that there are ten small, lithium- and boron-containing species that have been identified as containing a planar-tetracoordinate carbon center (1-1-1-3 and 1-15-121). ${ }^{\dagger}$ Unfortunately, attempts at synthesis of the lithiated compounds has been frustrated by aggregation and lithium solvation effects (which disrupt the predicted planar-tetracoordination). ${ }^{34}$ In fact, it seems unlikely that any of the small lithiated species identified

[^4]so far will exist as discrete compounds and attention seems to have turned to aggregations of these and similar species. ${ }^{34}$



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1-24

Lithiated compounds in which the target carbon atom for planar-tetracoordination is incorporated into an aromatic ring have also been considered. ${ }^{35}$ These molecules are expected to aggregate into dimers (at least) and typical examples are [(2,6-dimethoxyphenyl)lithium $]_{2}$ (1-23) and $\left[8 \text {-(dimethylamino)-1-naphthyllithium } \cdot \mathrm{Et}_{2} \mathrm{O}\right]_{2}$ Semi-empirical calculations of unsolvated dimers ${ }^{35 \mathrm{a}}$ indicated that both 1-23 and the phenyllithium dimer (1-22) should prefer planar-tetracoordination at the lithiated carbon. X-ray crystal structure analysis of 1-23 showed further aggregation into tetramers which are stacked one on top of the other and rotated $90^{\circ}$. A tetracoordinate carbon environment can be discerned within these tetramers that has only minimal distortion from planar-tetracoordination (the distortion angle was given as $11^{\circ}$ ). However, the coordination at the ipso-carbon is actually five-fold. X-ray structure analysis of $\mathbf{1 - 2 4}$ (which does not aggregate into tetramers) shows a tetracoordinate environment about the lithiated carbon atoms that has only minimal distortion from planarity (again an angle of $11^{\circ}$ was reported). ${ }^{34 \mathrm{c}}$ No phenyllithium-type compound has yet been synthesized which has absolute planar-tetracoordination at the lithiated carbon.

Phenyllithium-type compounds (e.g. 1-22-1-24) and the lithiated ethylene species 1-15 and 1-16 fall into the group of compounds that have a planar-tetracoordinate carbon incorporated into a $\pi$-system. The other eight molecules containing a planar-tetracoordinate carbon, 1-1-1-3 and 1-17-1-21, do not rely on direct incorporation into a $\pi$-system and are expected to have the characteristic $p$-type lone-pair HOMO.

### 1.4.2 Dimetallic Complexes

The vast majority of compounds identified to date with a planar-tetracoordinate carbon atom have two metal ligands. Most of these compounds also make use of incorporation of the target carbon atom into a $\pi$-system.

### 1.4.2.1 Complexed Aromatics

Although they did not report it at the time, ${ }^{\dagger}$ Cotton et al. ${ }^{36}$ were the first to determine the crystal structure of a compound which has a planar-tetracoordinate carbon. The divanadium complex $\mathbf{1 - 2 5}$, which has four 1,3-dimethoxy-substituted phenyl groups coordinated to a triple-bonded $\mathrm{V}_{2}$ unit, has two planar-tetracoordinate carbon environments associated with the two carbon atoms ( $\mathrm{C}^{\text {ipso }}$ ) which are bonded to vanadium. It was Keese et al. ${ }^{6}$ who first pointed out the planar-tetracoordination at $\mathrm{C}^{\text {ipso }}$ in 1-25.

Buchwald et al. have identified a substituted 1,3-bis(dicyclopropenylzirconium) complex ${ }^{37}$ (1-26) in which a pair of $\mathrm{Cp}_{2} \mathrm{Zr}$ moieties form 3-center 2-electron (3c-2e) bonds with $\mathrm{C}^{\text {ipso }}$ and a neighboring aromatic carbon atom. The orientation of these Zr moieties is stabilized by a bridging methyl group so that (excluding the Cp groups) all atoms other than hydrogen lie in a plane which is only very slightly disturbed from exact planarity. Interestingly, the aromatic system remains intact; the $\mathrm{C}^{i p s o}-\mathrm{C}^{\alpha}$ bond-lengths (1.39 and $1.40 \AA$ ) are only slightly increased from the aromatic ideal.


1-25

$1-26$

[^5]These two compounds, in similar fashion to 1-22-1-24, rely on incorporation of the target carbon atom ( $\mathrm{C}^{i p s o}$ ) into an aromatic $\pi$-system. Calculations by Poumbga, Bénard and Hyla-Kryspin on 1-25 and 1-26 have shown that the planar-tetracoordinate carbon atom ( $\mathrm{C}^{\text {ipso }}$ ) in each of these compounds bears a formal negative charge and has a $\sigma^{4} \pi^{1}$ configuration rather than the $\sigma^{2} \pi^{2}$ configuration of square-planar methane. ${ }^{26 c}$ In these compounds, stabilization is believed to depend on $\sigma$-electron density donation from the aromatic ligand to in-plane, empty, metal $d$-orbitals with metal-metal bonding character. ${ }^{25}$

### 1.4.2.2 Olefinic Complexes

The most numerous examples, by far, of synthetically isolated compounds exhibiting a planar-tetracoordinate carbon atom fall into the category which is best described as complexes of an ethylene subunit. These compounds (1-27 and $\mathbf{1 - 2 8}{ }^{\dagger}$ ) can be either neutral or cations and are characterized by a relatively undisturbed $\mathrm{C}=\mathrm{C}$ double bond ${ }^{26 a, b}$ (with a normal $\mathrm{C}=\mathrm{C}$ double-bond bond length) and a pair of metallic substituents (one must be either $\mathrm{Ti}, \mathrm{Zr}$ or Hf and the other may be either $\mathrm{B}, \mathrm{Al}$ or Ga for neutral species or Zr or Hf for the cationic species). The metal centers are bridged by either a methyl, ethyl or alkynyl ligand through a $3 \mathrm{c}-2 \mathrm{e}$ bond, or by chlorine through a pair of regular two-center two-electron ( $2 \mathrm{c}-2 \mathrm{e}$ ) bonds. Erker and coworkers ${ }^{8,38-40}$ have elucidated facile, and quite general, routes to the synthesis of these compounds (1-27 and 1-28 ${ }^{41}$ ) and as a result have identified many species based on this formula. ${ }^{*}$

In all of these compounds, the $\mathrm{sp}^{2}$-hybridized planar-tetracoordinate carbon is involved in a $3 \mathrm{c}-2 \mathrm{e}$ bond with the pair of metals $\left(\mathrm{M}^{1}, \mathrm{M}^{2}\right)$. Stabilization in these $d^{0}$ compounds was found ${ }^{26 a, b}$ to involve strong $\sigma$-acceptor character at $\mathrm{M}^{1}$ and no delocalization of the $\pi$-electron density at the planar-tetracoordinate carbon.

Although the stabilization of the planar-tetracoordinate geometries is clearly quite different to that in compounds 1-27 and 1-28, both 1,1-dilithioethene (1-15) and 1,2-dilithioethene $(\mathbf{1 - 1 6})^{32}$ can also be considered as members of the dimetallic olefinic category. Despite a normal $\mathrm{C}=\mathrm{C}$ double-bond bond length (calculated at the CCSD/DZP

[^6]


$M^{1}, M^{2}=Z r, H f$
$R^{1}=\mathrm{Me}, \mathrm{Et}, \mathrm{Pr}, \mathrm{Ph}, \mathrm{Bz}$
$R^{2}=\mathrm{Me}, \mathrm{CC}-\mathrm{Me} ; \mathrm{L}=\mathrm{CC}-\mathrm{R}$
1-28
level to be $1.36 \AA$ ) in the 1,1 -dilithioethene isomer (1-15), it was found that the $\mathrm{C}=\mathrm{C}$ double bond was highly polarized, with electron density moved away from the planartetracoordinate carbon. Further, the two lithium substituents each donate an electron to the ethylene fragment leaving a purely electrostatic lithium interaction. Similarly, in the case of the 1,2 -dilithioethene isomer (1-16), lithium bonding was found to be almost entirely ionic in nature. Clearly, lithium is not acting as a $\pi$-acceptor but is a strong $\sigma$ donor, and incorporation of the planar-tetracoordinate carbon into a $\pi$-system stabilizes the perpendicular $p$-orbital.

### 1.4.2.3 Allene Adducts and Analogues

Chisholm and coworkers ${ }^{42}$ reported a ditungsten allene adduct (1-29) in which the terminal allene hydrogens are parallel (instead of the uncomplexed perpendicular arrangement). Further, on complexation the $\mathrm{C}-\mathrm{C}$ bond lengths have increased to a normal C-C single-bond length and the geometry of the tetracoordinate bonding at the central carbon atom is planar. The bonding is unique. Allene was found to be acting as a


1-29

a $X=Y=N-R$
$b X=O ; Y=N-P h$
$1-30$
four-electron donor in a manner that completely disrupts the allene $\pi$-bonding. All four
electrons are donated through in-plane orbitals and the perpendicular p-orbital at the central carbon is empty, allowing for positive overlap with filled metal-metal bonding orbitals.

Compounds of a similar nature (1-30) were identified earlier by Cotton and coworkers. ${ }^{43}$ In these analogous complexes, it has been pointed out ${ }^{42}$ that the bonding description need not be the same because the substituents at nitrogen lie roughly in the plane of the $\mathrm{X}-\mathrm{C}-\mathrm{Y}$ and $\mathrm{W}-\mathrm{W}$ planes (the lone-pair on nitrogen, and possibly oxygen, appears to be involved in the $\mathrm{X}-\mathrm{C}-\mathrm{Y}$ to $\mathrm{W}-\mathrm{W}$ bonding).

Two other complexes that are somewhat similar to 1-29 are worth noting, 1-31 and 1-32. These dipalladium complexes have a pair of formally $d^{8} \mathrm{Pd}$ centers connected via a 2 c -2e bond. In 1-31, ${ }^{44}$ compounds described as $\mu-\eta^{3}$-allenyl/propargyldipalladium complexes, the allenyl/propargyl unit is complexed to the dipalladium moiety in a way that puts the allenyl/propargyl carbon atoms, the two palladium atoms, the two phosphorous atoms and the bonding atom of ligand X , all in a plane. The $\mathrm{C}-\mathrm{C}$ bonds in these complexes are short ( $1.26-1.40 \AA$ ) and the three carbon atoms almost lie in a line ( $\angle \mathrm{CCC} \approx 175^{\circ}$ ). Reactivity studies and preliminary calculations suggest that the cen-


1-31


1-32
tral tetracoordinate carbon atom (which is formally planar-tetracoordinate) has a high electron density. The cation complex 1-32 ${ }^{45}$ appears to be an analogue of $\mathbf{1 - 3 0}$ and has the characteristic $\mu-\eta^{2}: \eta^{2}$ bonding, in this case between the $\mathrm{CS}_{2}$ and $\mathrm{Pd}_{2}$ moieties. Once again, the carbon atom at the center is planar-tetracoordinate with only very slight deviations from exact planarity. The nature of the electronic structure at the planar-tetracoordinate carbon has not been analyzed but it seems likely that it is similar to that in $\mathbf{1 - 3 0}$.

### 1.4.2.4 Other Transition-Metal Complexes

There have been a number of other reports of transition-metal complexes that contain a planar-tetracoordinate carbon atom. The cluster compound $\left[\mathrm{WRe}_{2}\left(\mathrm{C}_{5} \mathrm{Me}_{5}\right)(\mathrm{O})\right.$

a $\mathrm{R}=\mathrm{Ph}$
b $\mathrm{R}=\mathrm{C}(\mathrm{Me}) \mathrm{CH}_{2}$
1-33

$(\mathrm{CO})_{4}$

1-34
$\left.(\mathrm{CO})_{8}(\mathrm{CCPh})\right](\mathbf{1 - 3 3})^{46}$ is of the complexed ethylene type. An examination of the structure shows that the $\mathrm{C}-\mathrm{C}$ bond is effectively a $\mathrm{C}=\mathrm{C}$ double bond (1-33a, $1.31 \AA$ and $\mathbf{1 -}$ 33b, $1.34 \AA$ ). The other three substituents to the planar-tetracoordinate carbon atom are the three metal centers, $\mathrm{W}\left(\mathrm{C}_{5} \mathrm{Me}_{5}\right)(\mathrm{O}), \operatorname{Re}(\mathrm{CO})_{4}$, and $\operatorname{Re}(\mathrm{CO})_{4}$. This three-transitionmetal complex has an acetylide ligand in a unique $\mu-\eta^{1}: \eta^{1}: \eta^{2}$-bonding mode. Beringhelli et al. ${ }^{47}$ have reported a unique tetrarhenium anion cluster $\left[\mathrm{Re}_{4} \mathrm{C}(\mathrm{CO})_{15} \mathrm{I}\right]^{-}(\mathbf{1 - 3 4})$. This complex does not have a planar-tetracoordinate carbon atom but the central carbon atom, which is in a tetrahedral-like environment, is considerably flattened from the tetrahedral ideal $\left(\angle \operatorname{ReCRe}=162^{\circ}\right)$.

An intriguing group of dicobalt complexes (1-35) has been identified by Siebert and Gunale. ${ }^{25,48}$ These compounds are essentially complex-stabilized diborylcarbenes. The central carbon atom is found to exist in a planar-tetracoordinate environment. Calculations on the electronic structure ${ }^{26 \mathrm{~d}}$ of the planar-tetracoordinate carbon revealed a $\sigma^{3.9} \pi^{1.4}$ configuration, while the electronic configuration of the bare diborylcarbene was found to be $\sigma^{3.0} \pi^{1.5}$. On these grounds, Siebert and Gunale argue that the stabilization of the pla-nar-tetracoordinate carbon by Co is as was envisaged by Hoffmann, ${ }^{4}$ i.e. $\sigma$-donation and $\pi$-acceptance, although they point out that there appears to be a push-pull effect between the two Co centers (so one Co acts as a $\sigma$-donor while the other acts as a $\sigma$ acceptor). ${ }^{48}$ It seems likely that the two boron groups attached to the planar-tetracoord-

a $\mathrm{Ar}=\operatorname{Dur}$ (2,3,5,6-tetramethylphenyl)
b Ar $=$ Mes (2,4,6-trimethylphenyl)
1-35
inate carbon atom also act as $\sigma$-donor $/ \pi$-acceptors, explaining the difference of $\sigma$ and $\pi$ densities (in the bare diborylcarbene) from that of the ideal square-planar carbon in methane (which should have a $\sigma^{2} \pi^{2}$ configuration).

### 1.4.3 Annulenes

Hoffmann's initial paper on the stabilization of planar-tetracoordinate carbon suggested many structures based on the idea of surrounding a central tetracoordinate carbon atom with an annulene perimeter (for example 1-36-1-39). The intention here was

1-36

$1-37$

$1-38$

1-39
to make some use of structural constraints applied through the $\sigma$-framework and also to derive some stabilization through delocalization of the $p$-type lone pair through the annulene perimeter. It was shown quite conclusively by both Gleiter and coworkers ${ }^{49}$ and Schleyer and coworkers ${ }^{50}$ that such delocalization does not occur and any distortion from the tetrahedral ideal is purely a result of the structural constraints resulting from the $\sigma$-framework.

In a similar approach, which, like the annelation approach, tries to incorporate the

$1-40$

$1-41$

$1-42$
potentially planar-tetracoordinate carbon into a $\pi$-electron system, Hoffmann suggested structures like the cations 1-40 and 1-41. MNDO/2 calculations by Schoeller ${ }^{51}$ indicated that $\mathbf{1 - 4 0}$ and $\mathbf{1 - 4 2}$ have a greatly reduced preference for the tetrahedral-like geometry (the $\Delta \mathrm{E}_{\mathrm{PT}}$ values for $\mathbf{1 - 4 0}$ and $\mathbf{1 - 4 2}$ are 65 and $95 \mathrm{~kJ} \mathrm{~mol}^{-1}$, respectively). Despite the potential for achieving planar-tetracoordinate carbon in a cation of this nature, this approach to planar-tetracoordinate carbon has not been pursued further. However, compounds like 1-40 (in which the target carbon atom is not much distorted from the tetrahedral ideal) have been the subject of more recent investigation. ${ }^{52}$

### 1.5 Structural Approach

This approach is the antithesis of the electronic approach. It relies almost exclusively on defining a suitably rigid bonding environment about the planar-tetracoordinate carbon atom. Because there would appear to be no question of significant electronic stabilization in a saturated hydrocarbon, these compounds form an excellent vehicle for the examination of structurally-constrained planar-tetracoordinate carbon.

The first step in devising a scheme to apply structural constraints to the positions of the four atoms bonded to a tetracoordinate carbon atom involves linking the four substituents together to give a polycyclic compound (Figure 1-3). In the tetrahedral ideal, the atoms bond to carbon with XCX angles of $109.5^{\circ}$. Shortening the links or 'straps' between the substituents X will reduce the XCX angle ( $\alpha$ in Figure 1-3). In a squareplanar geometry these angles are reduced to $90^{\circ}$. In other, less symmetrical, planar geometries the four XCX angles will add to $360^{\circ}$. Hydrocarbon systems of this type are a special type of polycyclic system (1-III) in which the central quaternary carbon atom, $\mathrm{C}^{0}$, is common to all rings and the four carbon atoms bonded to it, $\mathrm{C}^{\alpha}$, are each com-


A


B


C

Figure 1-3. The structural approach to forming planar-tetracoordinate carbon involves binding the substituents at carbon. If the 'straps' are 'tight' enough, the XCX angles are reduced from $\mathbf{A}$, the tetrahedral ideal of $109.5^{\circ}$ to $\mathbf{B}$, the square-planar ideal of $90.0^{\circ}$. It is likely that a less symmetric planar geometry, $\mathbf{C}$, will result.
mon to a pair of rings. Compounds based on this structural motif have been labelled the fenestranes (see Section 1.5.2 on page 24).


1-III


1-IV

From a simplistic viewpoint, rings of less than six carbon atoms are needed to apply any planarizing distortion at the central quaternary carbon atom. ${ }^{4}$ Cyclohexane is effectively unstrained, with CCC angles close to the tetrahedral ideal, and so cannot be expected to aid in reducing the opposite $\mathrm{C}^{\alpha} \mathrm{C}^{0} \mathrm{C}^{\alpha}$ angles at the central carbon at all. However, because of configurational problems associated with fusing four six-membered rings at a single atom, some distortion from the tetrahedral ideal in this structure should be expected. Cyclopentane, cyclobutane and cyclopropane, however, all have CCC angles less than $109.5^{\circ}$. Fused ring systems of type 1-III with combinations of three-, four- and five-membered rings are expected to exhibit a flattened central tetracoordinate carbon atom.

The main problem with this approach is that it can never actually achieve planartetracoordinate carbon except by coincidence. To achieve planar-tetracoordination, a
symmetrical bonding environment, which results in a plane of symmetry through the central $\mathrm{C}^{0}\left(\mathrm{C}^{\alpha}\right)_{4}$ subunit, is required. In structures of type 1-III, the four carbon atoms, $\mathrm{C}^{\alpha}$, bonded to the central carbon atom, $\mathrm{C}^{0}$, have two other bonds to carbon $\left(\mathrm{C}^{\alpha}-\mathrm{C}^{\beta}\right)$ and one to hydrogen. Because of the constraints on the orientation of the $\mathrm{C}^{\alpha}-\mathrm{C}^{\beta}$ bonds (a result of the pericyclic ring fusion at $\mathrm{C}^{0}$ ), the only way to achieve a symmetric environment at the central carbon, which contains a plane of symmetry through the $\mathrm{C}^{0}\left(\mathrm{C}^{\alpha}\right)_{4}$ subunit, is to make the four $\mathrm{C}^{\alpha}$ atoms also planar-tetracoordinate. Since this is likely to be energetically prohibitive, a different approach is needed.

In many ways, the fenestrane approach is a two-dimensional approach to a threedimensional problem. Clearly, a more three-dimensional structural design is necessary. The largely 'lateral' forces imposed by reducing the $\mathrm{C}^{\alpha} \mathrm{C}^{0} \mathrm{C}^{\alpha}$ angles need to be supplemented, or replaced, by perpendicular constraints (i.e. a bonding regime that constrains the positions of the $\mathrm{C}^{\alpha}$ atoms from moving perpendicularly to the potential plane at $\mathrm{C}^{0}$ ). A cage of some kind is required.

One attempt to devise such a cage, in which the lateral forces applied in the fenestrane approach are completely replaced by perpendicular constraints, can be seen in the small-ring paddlanes (1-IV). In these cage compounds, the target planar carbon atom is no longer central. Instead, a pair of bridgehead carbon atoms are subjected to planarizing distortions through their connection to one another. If such compounds are indeed stable, this should prove to be quite an effective way of applying the necessary perpendicular constraints. Bowlane ${ }^{9}(\mathbf{1 - 4})$ acts in a similar manner to produce a single bridgehead carbon atom which is considerably flattened. ${ }^{\dagger}$ However, the bonding environment at the potentially planar-tetracoordinate carbon $\left(\mathrm{C}^{0}\right)$ is again not symmetrical and cannot be symmetrical.

The only way to obtain a truly planar-tetracoordinate carbon atom is to place it in a bonding arrangement that allows for the possibility of an identical spatial arrangement of the atoms both above and below the proposed plane. This is a necessary but not sufficient condition for planar-tetracoordination at carbon. Octaplane (1-5), first suggested by McGrath and Radom, ${ }^{10}$ takes this approach. By attaching equivalent cyclooctane rings both above and below the central $\mathrm{C}^{0}\left(\mathrm{C}^{\alpha} \mathrm{H}\right)_{4}$ moiety, it is possible to define a plane

[^7]
$1-4\left(C_{2 v}\right)$


1-5 $\left(S_{4}\right)$
of symmetry through this central subunit without requiring undue distortion of the remaining tetracoordinate carbon atoms. In octaplane (1-5), the perpendicular constraints applied in bowlane are effectively duplicated on both sides of the central $\mathrm{C}(\mathrm{CH})_{4}$ subunit. This approach leads to remarkable flattening at $\mathrm{C}^{0}$ but not planarity; the ground state singlet is found to prefer distortion to $S_{4}$ symmetry with a tetrahedrally distorted central-quaternary carbon atom. The forces involved in constraining the positions of the $\mathrm{C}^{\alpha}$ atoms are not enough to overcome the preference for distortion at $\mathrm{C}^{0} .^{\dagger}$


In examining other alkaplanes (1-V) (see Chapter 4), we have explored variations on the exact nature of the perpendicular constraints used to hold the four $\mathrm{C}^{\alpha}$ atoms in position. However, in all the alkaplanes of type $\mathbf{1 - V}$ no use is made of the 'lateral'-type forces that are present in the fenestranes. The spiro[2.2]alkaplanes (1-VI), by introducing bonds between adjacent pairs of $\mathrm{C}^{\alpha}$ atoms, introduce an effect that can be considered as 'lateral' in nature. However, unlike the case for the fenestranes, the spiroalkaplanes do not have a set of four small, fused rings, and so the effect is perhaps better likened to the beneficial effect of incorporating a potentially planar-tetracoordinate carbon

[^8]atom into a three-membered ring (see Section 1.5.1 on page 23).

The spiroalkaplanes ( $\mathbf{1 - V I ) ~ e x h i b i t ~ i m p r o v e d ~ f l a t t e n i n g ~ a t ~ t h e ~ c e n t r a l ~ c a r b o n ~ a t o m ~}$ over the alkaplanes (1-V) but fail to achieve a completely planar-tetracoordinate carbon atom. However, exact planarity at the central, tetracoordinate carbon atom results when the two caps, the cycloalkane units above and below the central $\mathrm{C}(\mathrm{C})_{4}$ subunit, are linked by a pair of bridging methano groups to form the dimethanospiroalkaplanes (1VII), dimethanospiro[2.2]octaplane (1-7) and dimethanospiro[2.2]binonaplane (1-43). ${ }^{\dagger}$ This remarkable result is detailed in Chapter 4.


1-7 $\left(D_{2 \mathrm{~h}}\right)$

$1-43\left(D_{2 \mathrm{~h}}\right)$

The most important aspects of previous studies which have examined the flattening of planar-tetracoordinate carbon through structural means alone are outlined below. In some cases, results from our own calculations are quoted where they further clarify the discussion and no other recent results are available.

### 1.5.1 The Effect of Small Rings

The beneficial effect of incorporating a target planar-tetracoordinate carbon atom into a small, preferably three-membered, ring was first recognized by Pople, Schleyer and coworkers. ${ }^{5}$ This effect appears to be due to the alleviation of the repulsive steric interactions that result if four non-bonding substituents are placed in a plane. The majority of the compounds already mentioned which have a planar-tetracoordinate carbon take advantage of this effect, 1-1-1-3, 1-9, 1-15-1-21 and 1-25-1-35. In fact, the only exceptions are possibly dilithiomethane (1-11), which has an ambiguous geom-

[^9]etry, and the phenyllithium dimers (1-22-1-24), which lose their planar-tetracoordinate geometry on complexation of solvent to lithium. Clearly this effect is significant and worth due consideration when designing systems that aim to achieve planar-tetracoordinate carbon.

### 1.5.2 Fenestranes

The first saturated hydrocarbons to be examined for flattening at the central, quaternary carbon atom from a synthetic approach were the [k.l.m.n]fenestranes (1-VIII). The term fenestrane was initially given by Georgian ${ }^{53}$ to the symmetric [4.4.4.4]fenestrane $(\mathbf{1 - 4 4})(k, l, m, n=4)$ for its resemblance to a window. ${ }^{\dagger}$ As was indicated by Hoffmann, ${ }^{4}$


1-VIII


1-44


1-IX
these compounds (where $k, l, m, n<6$ ), are the intuitive first suggestions for constraining the geometry at carbon. When the fused rings are smaller than six-membered, they must start to exert some angle strain on the central carbon atom; flat five-membered rings have the ideal angle of $108.0^{\circ}$ for the included CCC angles, which is less than the tetrahedral ideal of $109.5^{\circ}$. However, it is possible for molecules with three fused rings at a central atom to exert some planarizing distortion at the central carbon atom. Molecules of this type are often labeled as [l.m.n]fenestranes (1-IX). The origin of the planarizing distortion at the central carbon atom in the [l.m.n]fenestranes is not the same as the 'strapping' effect referred to above for the [k.l.m.n]fenestranes but results from the orientation in which the rings are fused. An [l.m.n]fenestrane may be seen as two (overlapping) bicyclo[x.y.0]alkane subunits. These bicyclo[x.y.0]alkane subunits may be either cis- or trans-fused. For example, [4.4.4]fenestrane, can be considered as two overlapping bicyclo[2.2.0]hexane subunits. These bicyclo[2.2.0]hexane subunits can be either cis- and trans-bicyclo[2.2.0]hexane (1-45 and 1-46, respectively). Generally, trans-fused, small rings cause considerable angle strain at the bridgehead carbon atoms which are common to the two rings. Thus, trans,trans-[4.4.4]fenestrane (or simply $t, t$ -

[^10][4.4.4]fenestrane) ( $\mathbf{1 - 4 7})^{\dagger}$ might be expected to exhibit considerable distortion from the tetrahedral ideal at the central carbon $\left(\mathrm{C}^{0}\right)$. This same effect also applies to the [k.l.m.n]fenestranes (1-VIII).


Considerable effort has gone into analyzing and synthesizing the fenestranes, particularly in the groups of Keese, ${ }^{6,54-56}$ Agosta, ${ }^{7,57}$ Wynberg ${ }^{58}$ and Smit. ${ }^{59}$ Wiberg ${ }^{60}$ and Minkin ${ }^{61}$ have also made important contributions, although mostly theoretical. Cook and coworkers ${ }^{62}$ have concentrated on making unsaturated fenestranes. One aspect that has become clear in all the work on the fenestranes is that to effect considerable distortion at the central carbon atom from the tetrahedral ideal requires exploitation of the increased strain that results from incorporation of trans-fused bicyclo[x.y.0]alkane subunits.


1-48a ( $C_{4 \mathrm{v}}$ )


1-49 $\left(D_{2 d}\right)$

Initial interest in the fenestranes centered around [4.4.4.4]fenestrane. Liebman and Greenberg ${ }^{63}$ proposed a pyramidal structure for the all-trans ${ }^{\ddagger}$ isomer ( $\mathbf{1 - 4 8}$ ) and sug-

[^11]gested that this isomer may well be lower in energy than the all-cis isomer (1-49). Schleyer and coworkers ${ }^{64}$ determined MNDO geometries for the all-cis and all-trans isomers and Schulman, Sabio and Disch ${ }^{65}$ determined HF/STO-3G optimized structures. In both cases symmetry was imposed and the nature of the resulting stationary points were not examined through analysis of the force constant matrix. Our calcula-


1-48

$1-49$

$1-50$


1-51
tions at the MP2/6-311+G(3df,2p)//MP2/6-31G(d) level indicate that the $C_{4 \mathrm{v}}$ symmetry structure (1-48a) proposed up until now for the all-trans isomer (1-48) is not a minimum on the potential energy surface but represents a transition structure connecting two equivalent $C_{2 \mathrm{v}}$ symmetry structures (1-48b). An examination of the [4.4.4.4]fenestrane

$C_{2 \mathrm{v}}$
$\mathrm{E}=18.0$
1-48b

$1-49$


$1-50$

$C_{\mathrm{s}}$
$\mathrm{E}=-60.0$
1-51

Figure 1-4. Structural representations and relative energies (in $\mathrm{kJ} \mathrm{mol}^{-1}$ ) at the MP2/ $6-311+\mathrm{G}(3 \mathrm{df}, 2 \mathrm{p}) / / \mathrm{MP} 2 / 6-31 \mathrm{G}(\mathrm{d})$ level of the four isomers of [4.4.4.4]fenestrane.
potential energy surface revealed three other minima which correspond to the all-cis (149), trans,cis,trans,cis (1-50), and trans,cis,cis,cis (1-51) isomers. No other local minima which are [4.4.4.4]fenestrane isomers could be found. ${ }^{\dagger}$ Perhaps surprisingly, the lowest-energy isomer is found to be the $C_{\mathrm{s}}$ symmetry, trans,cis,cis,cis isomer (1-51).

[^12]This result is less surprising when the geometries are examined in detail. The trans,cis,cis,cis isomer (1-51) has the least deformation at the central carbon atom while the most strained isomer ( $\mathbf{1 - 5 0}$ ) has the most flattened central tetracoordinate carbon (Figure 1-4).

The smallest, fully-symmetric fenestrane to be synthesized is the all-cis isomer of [5.5.5.5]fenestrane ( $\mathbf{1 - 5 2}$ ) (also called staurane). ${ }^{54}$ The structure of this $D_{2}$ symmetry

molecule has been determined by electron-diffraction ${ }^{54 \mathrm{f}}$ and it was found that distortion in the bonding at the central carbon atom from the tetrahedral ideal is minimal; the $\mathrm{C}^{\alpha, 1} \mathrm{C}^{0} \mathrm{C}^{\alpha, 3}$ angle is widened from the tetrahedral ideal of $109.5^{\circ}$ to $116.2^{\circ}$ (in a planartetracoordinate fenestrane this angle would be $180^{\circ}$ ). Keese has determined structures

$D_{2}$

$$
\begin{gathered}
E=0.0 \\
\mathbf{1 - 5 2}
\end{gathered}
$$


$D_{2 \mathrm{~d}}$
$\mathrm{E}=582.3$
$1-53$

Figure 1-5. Structural representations and relative energies (in $\mathrm{kJ} \mathrm{mol}^{-1}$ ) at the MP2/ $6-311+\mathrm{G}(3 \mathrm{df}, 2 \mathrm{p}) / / \mathrm{MP} 2 / 6-31 \mathrm{G}(\mathrm{d})$ level for all-cis-[5.5.5.5]fenestrane (1-52) and all-trans-[5.5.5.5]fenestrane (1-53).
for all isomers of [5.5.5.5]fenestrane using MNDO calculations ${ }^{60,54 \mathrm{a}}$ and finds that the all-trans isomer (1-53) has a remarkably flattened central, tetracoordinate carbon
$\left(\angle \mathrm{C}^{\alpha, 1} \mathrm{C}^{0} \mathrm{C}^{\alpha, 3}=178.0^{\circ}\right)$. Our calculations ${ }^{\dagger}$ at the MP2/6-31G(d) level give a similar result. However, we find that the $\mathrm{C}^{\alpha, 1} \mathrm{C}^{0} \mathrm{C}^{\alpha, 3}$ angle for this $D_{2 \mathrm{~d}}$ symmetry molecule ( $\mathbf{1}$ $\mathbf{5 3}$ ) is $164.1^{\circ}$. Further, $\mathbf{1 - 5 3}$ is calculated to be $582.3 \mathrm{~kJ} \mathrm{~mol}^{-1}$ higher in energy than $\mathbf{1 -}$ 52 (calculated at the MP2/6-311+G(3df,2p)//MP2/6-31G(d) level) and, as can be seen from the orientation of the hydrogens at the peripheral bridgehead carbon atoms $\left(\mathrm{C}^{\alpha}\right)$, these molecules differ only by inversion at $\mathrm{C}^{0}$. Because of the considerable flattening at $\mathrm{C}^{0}$ in 1-53, this barrier is not expected to be particularly large (we calculate it to be about $25 \mathrm{~kJ} \mathrm{~mol}^{-1}$ ). Given the very large thermodynamic preference for $\mathbf{1 - 5 2}$ and the low barrier for conversion of $\mathbf{1 - 5 3}$ to $\mathbf{1 - 5 2}$, it seems likely that synthesis of $\mathbf{1 - 5 3}$ will prove prohibitively difficult.

A number of workers ${ }^{66,66}$ have had success in incorporating a single trans-fused bicyclo[x.y.0]alkane subunit into small-ring fenestranes. In particular, cis,trans,cis,cis-[4.5.5.5]- and trans,cis,cis,cis-[5.5.5.5]fenestrane derivatives have been prepared (1$\mathbf{5 4} \mathbf{- 1 - 5 7}$ ). The X-ray crystal structures of all the cis,trans,cis,cis-[4.5.5.5]fenestrane derivatives show similar geometries at the central carbon atom; 1-54 has angles across the central carbon of $131.1^{\circ}$ and $120.2^{\circ}, \mathbf{1 - 5 5}$ yields angles of 132.4 and $119.5^{\circ}$, while the X-ray structure of $\mathbf{1 - 5 6}$ gives angles of $134^{\circ}$ and $119^{\circ}$. Wender's trans,cis,cis,cis[5.5.5.5]fenestrane derivative (1-57) was not crystalline. ${ }^{66}$ No structure for $\mathbf{1 - 5 7}$ is available yet but derivatization allowed positive assignment of the stereochemistry of ring fusion.


1-54

$1-55$

$1-56$

$1-57$

Keese ${ }^{6 \mathrm{~b}}$ has considered the introduction of bridgehead $\mathrm{C}=\mathrm{C}$ double bonds in the [5.5.5.5]- and [4.5.5.5]fenestranes to give [5.5.5.5]- and [4.5.5.5]fenestrenes (e.g. 1-58 and 1-59). While the bridgehead double bond was found (from MNDO calculations) to

[^13]increase the planarizing distortion at $\mathrm{C}^{0}$ relative to an all-cis isomer, it was less effective than the introduction of a trans-fused bicyclo[x.y.0]alkane subunit. The resulting molecules, with highly distorted $\mathrm{C}=\mathrm{C}$ double bonds, are expected to suffer from significantly reduced kinetic stability.


1-58

$1-59$


1-60


1-61

Cook and coworkers ${ }^{62}$ have synthesized all-cis-[5.5.5.5]fenestratetraene ("staurane tetraene") (1-60). No crystal structure is available yet but 1-60 (which has no bridgehead double bonds) is not expected to have any greater distortion towards planarity at the central carbon atom than all-cis-[5.5.5.5]fenestrane (see Section 1.5.3 on page 30).

The smallest fenestrane that has been synthesized to date, which is also the fenestrane with the most distorted central carbon atom, is an all-cis-[4.4.4.5]fenestrane derivative (1-61). ${ }^{7,57}$ The angles across the central carbon atom are found from X-ray crystal structure analysis to be $128.3^{\circ}$ and $129.2^{\circ}$ (compared with the $180^{\circ}$ required for planarity at the central carbon).


1-62

The smallest possible fenestrane is [3.3.3.3]fenestrane which is better known as pyramidane (1-62). Pyramidane has not been synthesized but has been examined in great detail theoretically. ${ }^{61,67}$ Clearly, the bonding constraints placed on the four substituents to the central/apical carbon atom require a pyramidal-tetracoordinate arrangement. Pyramidane is the archetypal example of pyramidal-tetracoordinate bonding at
carbon. ${ }^{\dagger}$

It would seem that the best hope of achieving planar-tetracoordinate carbon via the fenestrane route is in all-trans-[5.5.5.5]fenestrane. However, with a CCC angle of $162^{\circ}$ $\mathbf{1 - 5 3}$ is still far from the planar ideal of $180^{\circ}$, and it is expected that this molecule will be unstable with respect to isomerization through inversion at the central carbon atom.

### 1.5.3 Vesiprenes and Fenestrindan

Two groups of compounds that are worthy of a brief mention are the vesiprenes (163) and fenestrindan (1-64) derivatives. The vesiprenes ( $n=6$ or 7 ) (1-63), synthesized by Prelog and Haas in $1969,{ }^{68}$ are fenestrane-like. They may be considered as unsaturated [5.m.5.m]fenestrane derivatives (with bridgehead double bonds to the four $\mathrm{C}^{\alpha}$, s) where $m$ is large (13 or 14). Also referred to as spirobifluorenes, X-ray structures of these compounds showed some distortion from the tetrahedral ideal at the central carbon atom. ${ }^{6 a}$ This distortion is only minimal, and the importance of the vesiprenes is only in

$1-63$


1-64
that they were the first fenestrane-like compounds to be considered.
Fenestrindan (1-64) is so called because it consists of four indan subunits fused in a similar manner to the four, fused cyclopentane rings in [5.5.5.5]fenestrane. This compound, synthesized by Kuck and coworkers, ${ }^{69}$ has also been called tetrabenzo[5.5.5.5]fenestratetraene, tetrabenzocentrotetraquinene and centrotetraindan. The only stereoisomer of fenestrindan that has been synthesized is the all-cis isomer (1-64). The planarizing distortion at the central carbon is almost identical to that of the simple

[^14]all-cis-[5.5.5.5]fenestrane (1-52); X-ray crystal structure analysis gives the $\mathrm{C}^{\alpha} \mathrm{C}^{0} \mathrm{C}^{\alpha^{\prime}}$ angle as $116.5^{\circ}$. Kuck has explored substitution at the bridgehead carbons $\left(\mathrm{C}^{\alpha}\right)$ and finds some extra flattening at the central carbon atom in sterically crowded derivatives (e.g. tetramethyl-, tetrabromo-, tetracyanofenestrindan), ${ }^{69 \mathrm{~b}}$ but never by more than a few degrees beyond that seen in 1-64.

### 1.5.4 Paddlanes and Bowlane

The paddlanes (1-IV), a family of saturated hydrocarbons, have been suggested as potential candidates for achieving planar-tetracoordinate carbon. The basic paddlane structure, and the usefulness of such a structure in applying a planarizing strain to tetracoordinate carbon, was first suggested by Wiberg et al. ${ }^{70}$ in $1968 .^{\dagger}$ The trivial name ${ }^{\ddagger}$ came later and is attributed to J. J. Bloomfield (see Hahn, Böhm and Ginsburg ${ }^{71}$ ). When the paddlane rings are all relatively small ( $n, m, p, q=1-3$ ), it is expected that the structural constraints placed on the bridgehead carbons will lead to a highly distorted tetracoordinate environment.


Wiberg ${ }^{70}$ has calculated $a b$ initio geometries for the symmetric [n.n.n.n]paddlanes, [1.1.1.1]- and [2.2.2.2]paddlane. He determined high symmetry HF/6-31G(d) optimized structures of $D_{4}$ and $D_{4 \mathrm{~h}}$ symmetry for [1.1.1.1]paddlane (1-65) and [2.2.2.2]paddlane (1-66), respectively. Steric crowding in the equatorial plane (close $\mathrm{H}-\mathrm{H}$ contacts between the methylene hydrogens) make the more symmetric $D_{4 \mathrm{~h}}$ structure for $\mathbf{1 - 6 5}$ unfavorable. Both calculated structures suggested close approaches between the two bridgehead carbon atoms ( $1.575 \AA$ for $\mathbf{1 - 6 5}$ and $1.525 \AA$ for $\mathbf{1 - 6 6}$ ) which Wiberg took to

[^15]indicate bonding between the two opposite bridgehead carbon atoms. The $\mathrm{C}^{\text {bh }}-\mathrm{C}^{\alpha}$ bonds are extremely long ( 1.668 and $1.787 \AA$, respectively) indicating a low bond-order, which added evidence for the notion of a bond between the bridgehead carbon atoms $\left(\mathrm{C}^{\mathrm{bh}}\right)$. As a consequence of this likely $\mathrm{C}^{\mathrm{bh}}-\mathrm{C}^{\mathrm{bh}}$ bond, the $D_{4 \mathrm{~h}}$ symmetry structure for [2.2.2.2]paddlane can be seen as a set of four fused cyclobutane rings and has an almost exactly planar-tetracoordinate carbon atom ( $\angle \mathrm{C}^{\alpha} \mathrm{C}^{\text {bh }} \mathrm{C}^{\alpha}=178.8^{\circ}$ ). The bridgehead carbon atoms in [1.1.1.1]paddlane are clearly pyramidalized. Earlier semi-empirical calculations on [2.2.2.2]paddlane by Schleyer and coworkers ${ }^{64}$ gave similar results.


1-65 ( $D_{4}$ )

$1-66\left(D_{4 \mathrm{~h}}\right)$

Wiberg ${ }^{70}$ and Schleyer ${ }^{64}$ both indicated highly unfavorable thermodynamics for $\mathbf{1 -}$ 65 and 1-66. But neither calculated the second-derivative or force-constant matrix; the stationary points located were not examined to see if they were high-order saddle points, transition structures or minima. Our own calculations at the MP2/6-31G(d) level show that the high-symmetry structures reported by Wiberg and Schleyer are indeed highorder saddle points and not minima on the potential energy surface. Following the down-hill (negative) modes on the potential energy surface until a minimum is reached leads in all cases to disintegration of the paddlane structure through separation at one or more of the over-long $\mathrm{C}^{\mathrm{bh}}-\mathrm{C}^{\alpha}$ bonds (which we calculate to be even longer at the MP2/ 6-31G(d) level than at the HF/6-31G(d) level). It seems unlikely that any small-ring paddlanes can exist. ${ }^{\dagger}$

More recently, Dodziuk ${ }^{72}$ has considered an unsaturated, hypothetical, conjugated paddlane (1-68). Although this cannot be considered a small-ring paddlane, it aims to distort the bridgehead carbons by using the rigid enediyne 1-67 as the 'arms' of the pad-

[^16]dlane. The only minimum located for this $\mathrm{C}_{28} \mathrm{H}_{8}$ structure on the $\mathrm{HF} / 6-31 \mathrm{G}(\mathrm{d})$ and B3-LYP/6-31G(d) potential energy surfaces has $D_{4 \mathrm{~d}}$ symmetry with a slightly distorted but still tetrahedral-like bridgehead carbon. The angle across the bridgehead carbon ( $\mathrm{C}^{\mathrm{bh}}$ ) was found to be $117.6^{\circ}$ at the B3-LYP/6-31G(d) level.

1-67

1-68 ( $D_{2 \mathrm{~d}}$ )

Experimentally-isolated paddlanes ${ }^{6,7 \mathrm{~b}, 70,71,73,74}$ are mostly heteroatomic substitution derivatives of the parent paddlane systems (i.e. the skeleton is not purely carbon) and all have a [k.p.q.r]paddlane structure where $k \geq 8$ and $p, q, r \leq 3$ (1-X). In all of these compounds, there is little or no angle strain at the bridgehead carbons (see for example 1$\mathbf{6 9}^{74 \mathrm{~b}}$ and $\mathbf{1 - 7 0}{ }^{70 \mathrm{~b}}$ ).

1-X

1-69

1-70

The lack of experimental progress in making small-ring paddlanes and the calculated instability of the symmetric small-ring paddlanes suggest that this will not be a very fruitful approach to forming planar-, or even highly-distorted, tetracoordinate carbon. However, a related approach to planar-tetracoordinate carbon, in which only a single carbon atom is highly distorted, has been suggested.

Bowlane (1-4) is a saturated hydrocarbon in which a $\mathrm{C}\left(\mathrm{CH}_{2}\right)_{4}$ neopentane-like subunit has been attached to a cyclooctane cap. The result of this is that all four substitu-

$1-4\left(C_{2 v}\right)$


1-71


1-72
ents to carbon are drawn to one side of the molecule in a bowl-like structure. Semiempirical calculations by Dodziuk ${ }^{9 b}$ indicated that the apical carbon ( $\mathrm{C}^{0}$ ) would be pyramidal. Ab initio calculations by McGrath, Radom and Schaefer ${ }^{9 \mathrm{a}}$ at the HF/6-31G(d) level indicated that the apical carbon is tetrahedrally distorted but considerably planarized $\left(\mathrm{C}^{\alpha, 1} \mathrm{C}^{0} \mathrm{C}^{\alpha, 3}=170.8^{\circ}\right.$ and $\left.\mathrm{C}^{\alpha, 2} \mathrm{C}^{0} \mathrm{C}^{\alpha, 4}=148.1^{\circ}\right){ }^{\dagger}$

Dodziuk has suggested other, larger bowlane-like structures ${ }^{96,75}$ (e.g. 1-71) and a curious double-bowlane structure ${ }^{75}$ (1-72) in which two bowlane molecules are fused via the cyclooctane bowl to give a structure that suggests that bowlane might well be considered as a half-paddlane-like molecule (with only a single highly distorted bridgehead carbon). The bowlane-like hemialkaplanes (1-XI) will be examined in detail in


1-XI


1-XII

Chapter 3. We have also considered a similar family of molecules that we call the hemispiroalkaplanes (1-XII). These bowl-like molecules also contain a single, highly distorted apical carbon atom. The substituents at the apical carbon atom are constrained to one hemisphere through attachment to a cycloalkane subunit (in the same manner as in the hemialkaplanes). However, the apical subunit, $\mathrm{C}(\mathrm{CH})_{4}$, is based on spiropentane (rather than neopentane in the hemialkaplanes). The apical carbon in these molecules is

[^17]expected to be pyramidal, rather than planar-tetracoordinate. These molecules are also examined in detail in Chapter 3.

### 1.5.5 Bridged Spiropentanes

Recently, the desire to synthesize compounds with a highly distorted tetracoordinate carbon has led researchers to examine the simple bridged spiropentanes (1-XIII). This approach to forming highly distorted (though not planar) tetracoordinate carbon in purely organic molecules has proven to be remarkably successful. It appears that deformations from the preferred tetrahedral-like geometry at a spiro[2.2] carbon (i.e. the spiro carbon in spiropentane) can be accomplished more readily than distortions at a tetracoordinate carbon atom like that in neopentane or the [k.l.m.n]fenestranes (where $k, l, m, n>$ 3)..$^{56,60 b}$ At the extreme, where the two three-membered rings approach planarity, it can be expected that steric repulsion, which results from the four methylene groups being packed into a plane, may be important. However, at the relatively small deformations that are typical in the systems that have been synthesized or where syntheses have been attempted, it seems that this effect should be small. It is likely that an electronic effect due to the peculiar bonding in the cyclopropane subunits is responsible.


1-XIII

$\mathrm{R}, \mathrm{R}^{\prime}=\mathrm{H}, \mathrm{CH}_{3}$
1-73 ( $C_{2}$ )


1-74 $\left(C_{2}\right)$


1-75 ( $C_{2}$ )

The first bridged spiropentanes (1-XIII) are due to Skattebøl, ${ }^{76}$ who, in 1966 synthesized tricyclo[4.1.0.0 ${ }^{1,3}$ ]heptane and a series of alkylated derivatives (1-73) through intramolecular cyclopropylidene insertion into a $\mathrm{C}=\mathrm{C}$ double bond (Scheme 1-1). Elec-tron-diffraction analysis ${ }^{77}$ of the structure of the unsubstituted tricyclo-[4.1.0.0 $0^{1,3}$ ]heptane (1-73) revealed a very highly distorted carbon atom $\left(\mathrm{C}^{0}\right)$. The angle across the apical carbon ( $\angle \mathrm{C}^{\alpha, 1} \mathrm{C}^{0} \mathrm{C}^{\alpha, 2}$ ) was found to be $162.4^{\circ}$ from the electron-diffraction analysis and $158.2^{\circ}$ from X-ray crystal structure analysis ${ }^{78}$ (compared with $137.2^{\circ}$ is spiropen-
tane). The apical carbon atom is, however, not particularly flattened; the angles around the five-membered ring average $105^{\circ}$, although the ring-angle at the apical carbon is somewhat widened $\left(110.1^{\circ}\right)$. Further, the two three-membered rings are twisted at an angle of $80.0^{\circ}$ (compared with the $90^{\circ}$ twist in spiropentane and $0^{\circ}$ twist in a planartetracoordinate structure). A number of workers ${ }^{60 \mathrm{~b}, 78}$ have considered the relative difficulty of bending versus twisting at the spiro carbon in spiropentane and find that bending should be favoured over twisting. Tricyclo[4.1.0.0 ${ }^{1,3}$ ]heptane (1-73) shows this effect quite distinctly.


Scheme 1-1

Brinker and coworkers ${ }^{79}$ have synthesized a benzo derivative of tricyclo[4.1.0.0 $0^{1,3}$ ]heptane ( $\mathbf{1 - 7 4}$ ) which is found to have a slightly larger angle at the apical carbon $\left(\angle \mathrm{C}^{\alpha, 1} \mathrm{C}^{0} \mathrm{C}^{\alpha, 2}=164.0^{\circ}\right)$. This represents increased bending at $\mathrm{C}^{0}$ but the angle between the three-membered rings is also increased to $85.2^{\circ}$ (from $80.0^{\circ}$ for $\mathbf{1 - 7 3}$ ), indicating less twist. Interestingly, this molecule is found to be somewhat thermally labile with a half-life at $25^{\circ} \mathrm{C}$ of approximately 52 hours. ${ }^{79,80}$ This is not the case for the saturated parent (1-73). ${ }^{80}$ However, the importance of this low barrier to thermal isomerization, and its implications regarding the hemispiroalkaplanes, is explored in Chapter 3.

Brinker has tried to extend the use of the cyclopropylidene insertion reaction (Scheme 1-1) to make other bridged spiropentanes. Synthesis of tricyclo[5.1.0.0 ${ }^{1,3}$ ]octane $(\mathbf{1 - 7 5})^{81}$ via this process was reported by Skattebø1 ${ }^{76 \mathrm{~b}}$ but proved problematic. ${ }^{81}$ Both Brinker ${ }^{81}$ and Wiberg ${ }^{82}$ have synthesized this bridged spiropentane via an alternate route. No structure has been reported yet. However, it is expected that the larger bridge $\left(-\left(\mathrm{CH}_{2}\right)_{3}-\right)$ will lead to less deformation at $\mathrm{C}^{\text {ap }}$ than for 1-73.

A number of other large-ring bridged spiropentanes (1-XIII, $n>2$ ) have been

1-76

$1-77$

1-78

1-79
reported. A dichloropentamethyl derivative of 1-75 (1-76) has been reported by Köbrich and Baumann ${ }^{83}$ and an $n=5$ bridged spiropentane (1-77) was synthesized by Kuznetsova and coworkers. ${ }^{84}$ The most unusual bridged spiropentane that has been synthesized is tetracyclo[3.3.1. $\left.0^{2,4} .0^{2,8}\right]$ nonane (1-78). ${ }^{85}$ This bridged spiropentane was made by treating 1-79 with MeLi (Skattebøl's carbene cyclization). This molecule's tridendate spiropentane bridge is unique. No structure is available yet but our calculations at the MP2/6-311+G(2d,p) level indicate that the angle across the apical carbon is almost linear $\left(174^{\circ}\right)$ although the degree of twist between the planes of the two three-membered rings is still high $\left(82^{\circ}\right)$. This compound is only one step away from the hemispiroalkaplanes (1-XII) (which might be viewed as spiropentanes bound with a tetradentate bridge).


Bridged spiropentanes (1-XIII) with small bridges ( $n<2$ ) have been explored in detail by Wiberg. ${ }^{82,86}$ Wiberg has had considerable success in synthesizing these [3.m.3]fenestranes (1-IX) (where $3<m<5$ ). Evidence for a one-carbon bridged species, presumably the small-ring ketene, tricyclo[3.1.0.0 ${ }^{1,3}$ ]hexane-4-ketene (1-80), was seen in a matrix at 15 K . This molecule (1-80) and its parent hydrocarbon (1-81) are expected to have a butterfly or half-planar geometry at the apical carbon; the angle across the apical carbon for both $\mathbf{1 - 8 0}$ and $\mathbf{1 - 8 1}$ is calculated to be very close to $180^{\circ}$ but
the twist between the two three-membered rings is found to be about $82^{\circ}$ (similar to the twist in 1-73). Wiberg has also found evidence for tricyclo[2.1.0.0 $\left.{ }^{1,3}\right]$ pentane (1-82) as the intermediate in the reaction of 1-bromo-2-chloromethylbicyclo[1.1.0]butane with phenylthiol. Calculated structures for $\mathbf{1 - 8 2}$ indicate that it will have $C_{1}$ symmetry, bondlengths of $1.49 \AA$ (for the $\mathrm{C}^{0}-\mathrm{C}^{\alpha}$ bonds) and $1.54 \AA$ (for the single bridge bond), and a pyramidal tetracoordinate carbon atom.


It is our belief that spiropentane represents the best opportunity for distortion at a quaternary tetracoordinate carbon atom in a neutral saturated hydrocarbon. However, the bridged spiropentanes show considerable bending but little twisting of the cyclopropane subunits. This twisting is necessary to give planar-tetracoordinate carbon. Incorporation of a spiropentane subunit into our designs is likely to be of great assistance but a means of establishing (and maintaining) the necessary twist must be devised. Our approach to solving this problem has been to use a pair of tetradentate bridges ( $c f$. the alkaplanes (1-V), spiroalkaplanes (1-VI) and dimethanospiroalkaplanes (1-VII)) (details are given in Chapter 4).

### 1.6 Concluding Remarks

A number of the various electronic approaches to forming planar-tetracoordinate carbon have clearly had great success. This is in part a tribute to the ingenuity of the workers and expeditious use of van't Hoff's "imaginative faculty", and in part serendipity. ${ }^{\dagger}$ However, as has been pointed out by Siebert and Gunale, ${ }^{25}$ the planar-tetracoordin-

[^18]ate carbon compounds that result from most of these approaches have an electronic structure that differs markedly from the electronic structure proposed originally by Hoffmann for square-planar methane. ${ }^{\dagger}$ As a result, these compounds, none of which are organic molecules, will not have properties consistent with having a $p$-type lone pair and four electron-deficient $\sigma$-bonds. In fact, rather than stabilizing the unusual electronic structure expected for planar-tetracoordinate carbon, which has been described as a $\sigma^{2} \pi^{2}$ configuration at the planar carbon (cf. the normal $\sigma^{4}$ configuration seen in tetrahedrallybonded carbon), most of these compounds alter the electronic structure to one that is more stable. This is generally done by removing one of the $\pi$-electrons, making it available for $\sigma$-bonding, and then stabilizing the remaining $\pi$-electron by involving it in a $\pi$ bonding system. The resulting electronic configuration at the planar-tetracoordinate carbon is usually $\sigma^{4} \pi^{1}$.

We think that the greater challenge involves taking a structural approach to forming planar-tetracoordinate carbon. Because such an approach relies on using covalent bonding in an organic framework, it is also more in the spirit of defying the van't Hoff/le Bel principle of tetrahedral tetracoordinate carbon, which was formulated for organic systems. Further, a structural approach should preserve the unusual electronic structure at the planar-tetracoordinate carbon. Because the electronic structure is not being disturbed by strongly electron-accepting or -withdrawing species, it is expected that a $p$ type lone pair of electrons will result. This unique feature should confer quite extraordi-

nary properties on the resulting molecule. In choosing to restrict our search for planartetracoordinate carbon to saturated hydrocarbons, we hope to design molecules that will have unique bonding at the target carbon and remarkable properties for a purely organic system.

[^19]Our search for planar-tetracoordinate carbon in saturated hydrocarbon cage systems has indeed involved considerable use of van't Hoff's "imaginative faculty". Novel structures, in the form of the hemialkaplanes (1-XI) and hemispiroalkaplanes (1-XII), and their properties are detailed in Chapter 3. Chapter 4 then explores the three alka-plane-like families, the alkaplanes (1-V), the spiroalkaplanes (1-VI) and the dimethanospiroalkaplanes (1-VII) in detail.

## References

(1) van’t Hoff, J. H. "Sur les formules de structure dans l'espace," Arch. Neerl. Sci. Exactes Nat. 1874, 9, 445-454. For a translation see, van’t Hoff, J. H. "A suggestion looking into the extension into space of the structural formulas at present used in chemistry. And a note upon the relation between the optical activity and the chemical constitution of organic compounds" in Classics in the Theory of Chemical Combinations; Benfey, O. T., Ed.; Dover: New York, 1963; Vol. I, pp 151-160.
(2) le Bel, J. A. "Sur les relations qui existent entre les formules atomiques des corps organiques, et le pouvoir rotatoire de leurs dissolutions," Bull. Chim. Soc. Fr. 1874, 22, 337-347. For a translation see, le Bel, J. A. "On the relations which exist between the atomic formulas of organic compounds and the rotatory power of their solutions" in Classics in the Theory of Chemical Combinations; Benfey, O. T., Ed.; Dover: New York, 1963; Vol. I, pp 161-171.
(3) (a) Kolbe, H. J. prakt. Chem. 1877, 15, 473. (b) A translation of Kolbe's comments appears in Wheland, G. W. Advanced Organic Chemistry, 2nd ed., Wiley: New York, 1949, p. 132.
(4) (a) Hoffmann, R.; Alder, R.; Wilcox Jr, C. F. "Planar tetracoordinate carbon," J. Am. Chem. Soc. 1970, 92, 4992-4993; (b) Hoffmann, R. "The theoretical design of novel stabilized systems," Pure Appl. Chem. 1971, 28, 181-194.
(5) Collins, J. B.; Dill, J. D.; Jemmis, E. D.; Apeloig, Y.; Schleyer, P. v. R.; Seeger, R.; Pople, J. A. "Stabilization of planar tetracoordinate carbon," J. Am. Chem. Soc. 1976, 98, 5419-5427.
(6) (a) Keese, R.; Pfenninger, A.; Roesle, A. "35. Planarization of tetracoordinate carbon atom. Synthesis of 13-oxa-14-oxo-pentacyclo[5.5.2.1.0 $\left.0^{4,15} .0^{10,15}\right]$ pentadecane, a bridged 'tetraquinacane'," Helv. Chim. Acta 1979, 62, 326-334. (b) For a recent review see: Thommen, M.; Keese, R. "Fenestranes in recent synthetic developments," Synlett 1997, 231-240.
(7) (a) Rao, V. B.; George, C. F.; Wolff, S.; Agosta, W. C. "Synthetic and structural studies in the [4.4.4.5]fenestrane series," J. Am. Chem. Soc. 1985, 107, 5732-5739; (b) Agosta, W. C. "Inverted and planar carbon" in The Chemistry of the Alkanes and Cycloalkanes; Patai, S. and Rappoport, Z., Ed.; Wiley: New York, 1992, pp 927-962.
(8) Röttger, D.; Erker, G. "Compounds containing planar-tetracoordinate carbon," Angew. Chem., Int. Ed. 1997, 36, 813-827; Angew. Chem. 1997, 109, 840-856.
(9) (a) McGrath, M. P.; Radom, L.; Schaefer, H. F. "Bowlane: toward planar tetracoordinate carbon," J. Org. Chem. 1992, 57, 4847-4850. (b) An earlier report of the molecule bowlane (1-4) calculated, using semi-empirical methods, that the apical carbon atom would be pyramidal: Dodziuk, H. "Bowlane (tetracyclo[3.3.3. $\left.1^{3,10} .1^{7,10}\right]$ tridecane): a new hypothetical molecule possessing a pyramidal tetracoordinated carbon atom in the ground state," $J$. Mol. Struct., Theochem. 1990, 239, 167-172.
(10) (a) McGrath, M. P.; Radom, L. "Alkaplanes: a class of neutral hydrocarbons containing a potentially planar tetracoordinate carbon," J. Am. Chem. Soc. 1993, 115, 3320-3321; (b) Lyons, J. E.; Rasmussen, D. R.; McGrath, M. P.; Nobes, R. H.; Radom, L. "Octaplane: a saturated hydrocarbon with a remarkably low ionization energy leading to a cation with a planar tetracoordinate carbon atom," Angew. Chem., Int. Ed. 1994, 33, 1667-1668; Angew. Chem. 1994, 106, 1722.
(11) Radom, L.; Rasmussen, D. R. "Planar Carbon Story," Pure Appl. Chem. 1998, 1977-1984.
(12) Rasmussen, D. R.; Radom, L. "Planar-tetracoordinate carbon in a neutral saturated hydrocarbon. Theoretical design and characterization," Angew. Chem., Int. Ed. 1999, 38, 2876-2878; Angew. Chem. 1999, 111, 3051-3054.
(13) Monkhorst, H. J. "Activation energy for interconversion of enantiomers containing an asymmetric carbon atom without breaking bonds," J. Chem. Soc., Chem. Commun. 1968, 1111-1112.
(14) (a) Saturno, A. F. "Walsh's rules for $\mathrm{AH}_{4}$ systems derived from united atom molecular orbitals," Theoret. Chim. Acta 1967, 7, 273-276. (b) See also, Gimarc, B. M. "The shapes of simple polyatomic molecules and ions. II. The series $\mathrm{AH}_{2}, \mathrm{AH}_{3}$, and $\mathrm{AH}_{4}$, J. Am. Chem. Soc. 1971, 93, 593-599.
(15) Firestone, R. "Linnett planar methane," J. Chem. Soc., Chem. Commun. 1973, 163.
(a) Wiberg, K. B.; Ellison, G. B. "Distorted geometries at carbon," Tetrahedron 1974, 30, 1573-1578; (b) Wiberg, K. B.; Ellison, G. B.; Wendoloski, J. J. "Electronic states of organic molecules. I. Potential functions for the deformation of methane," J. Am. Chem. Soc. 1976, 98, 1212.
(17) (a) Durmaz, S.; Murrell, J. N.; Pedley, J. B. "Calculation of the lowest energy state of planar methane," J. Chem. Soc., Chem. Commun. 1972, 933-934; (b) Murrell, J. N.; Pedley, J. B.; Durmaz, S. "Potential energy surfaces for the reaction $\mathrm{CH}_{2}+\mathrm{H}_{2} \rightarrow \mathrm{CH}_{4}$ " J. Chem. Soc., Faraday Trans. 2 1973, 69, 1370-1380.
(18) Minkin, V. I.; Minyaev, R. M.; Zacharov, I. I. "Semiempirical and ab initio calculations on the automerization of methane," J. Chem. Soc., Chem. Commun. 1977, 213-214.
(19) (a) Lathan, W. A.; Hehre, W. J.; Curtiss, L. A.; Pople, J. A. "Molecular orbital theory of the electronic structure of organic compounds. X. A systematic study of geometries and energies of $\mathrm{AH}_{4}$ molecules and cations," J. Am. Chem. Soc. 1971, 93, 6377-6387; (b) Crans, D. C.; Snyder, J. P. "Tetracoordinate planar carbon: a disinglet radical," J. Am. Chem. Soc. 1980, 102, 7152-7154; (c) Krogh-Jesperson, M.-B.; Chandrasekhar, J.; Würthwein, E.-U.; Collins, J. B.; Schleyer, P. v. R. "Molecular orbital study of tetrahedral, planar, and pyramidal structures of the isoelectronic series $\mathrm{BH}_{4}^{-}, \mathrm{CH}_{4}, \mathrm{NH}_{4}^{+}, \mathrm{SiH}_{4}$, and $\mathrm{PH}_{4}{ }^{+}$, J. Am. Chem. Soc. 1980, 102, 2263-2268.
(20) Gordon, M. S.; Schmidt, M. W. "Does methane invert through square planar?" J. Am. Chem. Soc. 1993, 115, 7486-7492.
(21) Pepper, M. J. M.; Shavitt, I.; Schleyer, P. v. R.; Glukhovtsev, M. N.; Janoschek, R.; Quack, M. "Is stereomutation of methane possible?" J. Comput. Chem. 1995, 16, 207-225.
(22) Wong, M. W.; Radom, L. "Methane dication: planar but not square," J. Am. Chem. Soc. 1989, 111, 1155-1156.
(23) Benson, S. W. Thermochemical kinetics: Methods for the estimation of thermochemical data and rate parameters; 2nd ed.; Wiley: New York, 1976, p. 309.
(24) (a) Yoshizawa, K.; Ohta, T.; Yamabe, T.; Hoffmann, R. "Dioxygen cleavage and methane activation on diiron enzyme models - A theoretical study," J. Am. Chem. Soc. 1997, 119, 12311-12321; (b) Yoshizawa, K.; Suzuki, A.; Yamabe, T. "Inversion of methane on transi-tion-metal complexes: A possible mechanism for inversion of stereochemistry," J. Am. Chem. Soc. 1999, 121, 5266-5273.
(25) Siebert, W.; Gunale, A. "Compounds containing a planar-tetracoordinate carbon atom as analogues of planar methane," Chem. Soc. Rev. 1999, 28, 367-371.
(26) For calculations on the electronic configuration of these and related compounds see: (a) Gleiter, R.; Hyla-Kryspin, I.; Niu, S.; Erker, G. "An ab initio study on stabilizing interactions in dinuclear $\mathrm{Zr} / \mathrm{Al}$ complexes with a planar tetracoordinate carbon center," Angew. Chem., Int. Ed. 1993, 32, 754-756; Angew. Chem. 1993, 105, 753; (b) Gleiter, R.; HylaKryspin, I.; Niu, S. Q.; Erker, G. "Stabilizing interactions and coordination in cationic zirconocene complexes - $\mathrm{Cp}_{2} \mathrm{ZrL}^{+}$- a MO theoretical study," Organometallics 1993, 12, 3828-3836; Gleiter, R.; Hyla-Kryspin, I.; Niu, S. Q.; Erker, G. "Stabilizing interactions and coordination in cationic zirconocene complexes - $\mathrm{Cp}_{2} \mathrm{ZrL}^{+}-$a MO theoretical study, (Vol 12, 3831, 1993)," Organometallics 1994, 13, 744; (c) Poumbga, C. N.; Bénard, M.; Hyla-Kryspin, I. "Planar tetracoordinate carbons in dimetallic complexes - Quantum chemical investigations,"J. Am. Chem. Soc. 1994, 116, 8259-8265; Poumbga, C. N.; Bénard, M.; Hyla-Kryspin, I. "Planar tetracoordinate carbons in dimetallic complexes Quantum chemical investigations (Vol 116, 8259, 1994)," J. Am. Chem. Soc. 1994, 116, 12135; (d) Hyla-Kryspin, I.; Gleiter, R.; Rohmer, M. M.; Devemy, J.; Gunale, A.; Pritzkow, H.; Siebert, W. "Quantum-chemical investigations of stabilizing interactions in $\mu$-diborylcarbene dicobalt complexes with a planar tetracoordinate carbon atom," Chem.-Eur. J. 1997, 3, 294-299.
(27) (a) Streitwieser Jr., A.; Williams Jr., J. E.; Alexandratos, S.; McKelvey, J. M. "Ab initio SCF-MO calculations of the methyllithium and related systems. Absence of covalent character in the C-Li bond,"J. Am. Chem. Soc. 1976, 98, 4778-4784; (b) Laidig, W. D.; Schaefer III, H. F. "Structures and energetics of planar tetrahedral dilithiomethane. A near degeneracy of singlet and triplet states," J. Am. Chem. Soc. 1978, 100, 5972-5973; (c) Bachrach, S. M.; Streitwieser Jr., A. "Structure and bonding in dilithiomethane," J. Am. Chem. Soc. 1984, 106, 5818-5824.
(28) See also, (a) Maerker, A.; Theis, M.; Kos, A. J.; Schleyer, P. v. R. "1,1-Dilithioethane," Angew. Chem., Int. Ed. 1983, 22, 733-734; (b) Ritchie, J. P.; Bachrach, S. M. "Bond paths and bond properties of carbon-lithium bonds," J. Am. Chem. Soc. 1987, 109, 5909-5916; (c) van Eikema Hommes, N. J. R.; Schleyer, P. v. R.; Wu, Y.-D. "Mechanism of the Zei-
gler dilithiomethane synthesis. An ab initio study of methyllithium pyrolysis," J. Am. Chem. Soc. 1992, 114, 1146-1151; (d) Ong, C. M.; Stephen, D. W. "Lithiations of bis-diphenyl-N-trimethylsilylphosphiniminomethane: An X-ray structure of a 1,1-dilithiomethane derivative," J. Am. Chem. Soc. 1999, 121, 2939-2940.
(a) Krogh-Jesperson, K.; Cremer, D.; Poppinger, D.; Pople, J. A.; Schleyer, P. v. R.; Chandrasekhar, J. "Molecular orbital theory of the electronic structure of molecules. 39. Highly unusual structures of electron-deficient carbon compounds. Reversal of van't Hoff stereochemistry in BBC ring systems," J. Am. Chem. Soc. 1979, 101, 4843-4851; (b) Jemmis, E. D.; Subramanian, G.; Srinivas, G. N. "Boron analogs of cyclopropenium cation: $\mathrm{B}_{3} \mathrm{H}_{6}{ }^{+}$, the first three membered nonplanar $2 \pi$ aromatic," J. Am. Chem. Soc. 1992, 114, 7939-7941; (c) Minyaev, R. M.; Quapp, W.; Subramanian, G.; Schleyer, P. v. R.; Mo, Y. R. "Internal conrotation and disrotation in $\mathrm{H}_{2} \mathrm{BCH}_{2} \mathrm{BH}_{2}$ and diborylmethane $1,3 \mathrm{H}$ exchange," J. Comput. Chem. 1997, 18, 1792-1803.
(a) Watts, J. D.; Stamper, J. G. "A molecular orbital study of $\mathrm{CLi}_{2} \mathrm{~F}_{2}$ : planar 3-coordinate and pyramidal 4-co-ordinate carbon," J. Chem. Soc., Chem. Commun. 1985, 5-6; (b) Watts, J. D.; Stamper, J. G. "On the computational realization of planar tetracoordinate carbon," Tetrahedron 1987, 43, 1019-1026.
(31) Sorger, K.; Schleyer, P. v. R. "Planar and inherently non-tetrahedral tetracoordinate carbon: a status report," J. Mol. Struct., Theochem. 1995, 338, 317-346.
(a) Bolton, E. E.; Laidig, W. D.; Schleyer, P. V.; Schaefer, H. F. "Singlet $\mathrm{C}_{2} \mathrm{H}_{2} \mathrm{Li}_{2}$ - Acetylenic and 1,2 -dilithioethene isomers - A remarkably congested potential energy hypersurface for a simple organometallic system," J. Am. Chem. Soc. 1994, 116, 9602-9612; (b) Bolton, E. E.; Laidig, W. D.; Schleyer, P. v. R.; Schaefer, H. F. "Does singlet 1,1-dilithioethene really prefer a perpendicular structure," J. Phys. Chem. 1995, 99, 17551-17557.
(33) Gribanova, T. N.; Minyaev, R. M.; Minkin, V. I. "Planar tetracoordinate carbon in organoboron compounds: ab initio computational study," Coll. Czech. Chem. Commun. 1999, 64, 1780-1789.
(a) Sorger, K.; Schleyer, P. v. R.; Stalke, D. "Towards planar tetracoordinate carbon in the puckered ladder structure of dilithiated 1-di-tert-butylhydroxymethyl-3,3-dimethycyclopropene," J. Chem. Soc., Chem. Commun. 1995, 2279-2280; (b) Sorger, K.; Schleyer, P. v. R.; Stalke, D. "Dimeric [3,3-dimethyl-2-(trimethylsilyl)cyclopropenyl]lithium-tetramethylenediamine: distortion of the cyclopropenyl geometry due to strong rehybridization at the lithiated carbon," J. Am. Chem. Soc. 1996, 118, 1086-1091; (c) Sorger, K.; Schleyer, P. v. R.; Fleischer, R.; Stalke, D. "Toward planar tetracoordinate carbon in the puckered ladder structures of chelated cyclopropenyllithium aggregates," J. Am. Chem. Soc. 1996, 118, 6924-6933.
(a) Chandrasekhar, J.; Schleyer, P. v. R. "Planar tetracoordinate carbon candidates. MNDO calculations on substituted phenyllithium dimers," J. Chem. Soc., Chem. Commun. 1981, 6, 260-261; (b) Dietrich, H.; Mahdi, W.; Storck, W. "Kristall- und Molekülstruktur von 2,6-Dimethoxyphenyllithium," J. Organomet. Chem. 1988, 349, 1-10; (c) Harder, S.; Boersma, J.; Brandsma, L.; van Heteren, A.; Kanters, J. A.; Bauer, W.; Schleyer, P. v. R. "Planar tetracoordinate carbon atoms hidden in the tetrameric aggregate of (2,6-dimethoxyphenyl)lithium," J. Am. Chem. Soc. 1988, 110, 7802-7806; (d) Harder, S.; Ekhart, P. F.; Brandsma, L.; Kanters, J. A.; Duisenberg, A. J. M.; Schleyer, P. v. R.
"Crystal structure of [2-(dimethylamino)-6-(tert-butoxy)phenyl]lithium," Organometallics 1992, 11, 2623-2627.
(36) Cotton, F. A.; Millar, M. "The probable existence of a triple bond between two vanadium atoms," J. Am. Chem. Soc. 1977, 99, 7886-7891.
(37) Buchwald, S. L.; Lucas, E. A.; Davies, W. M. "A bimetallic zirconium complex containing an in-plane bridging aromatic ring," J. Am. Chem. Soc. 1989, 111, 397-398.
(a) Erker, G.; Zwettler, R.; Krüger, C.; Noe, R.; Werner, S. "Planar tetracoordinate carbon in $\mathrm{Cp}_{2} \mathrm{Zr}\left(\mu-\eta^{1}, \eta^{2}-\mathrm{Me}_{3} \mathrm{SiCCPh}\right)(\mu-\mathrm{Cl}) \mathrm{AlMe}_{2}$," J. Am. Chem. Soc. 1990, 112, 9620-9621; (b) Erker, G.; Albrecht, M.; Werner, S.; Nolte, M.; Krüger, C. "Eine einfache Synthese van dimetallischen Zirconium/Aluminim-Verbindungen mit planar-tetrakoordiniertem Kohlenstoff," Chem. Ber. 1992, 125, 1953-1956; (c) Erker, G.; Albrecht, M.; Krüger, C.; Werner, S.; Binger, P.; Langhauser, F. "(Aryne)metallocene- and (Alkyne)metallocene-derived dimetallic zirconium/aluminium complexes containing planar-tetracoordinate carbon," Organometallics 1992, 11, 3517-3525; (d) Erker, G. "Planar-tetrakoordinierter Kohlenstoff," Nach. Chem. Tech. Lab. 1992, 40, 1099-1104; (e) Erker, G. "Planar-tetracoordinate carbon: making stable anti-van't Hoff/le Bel compounds," Comments Inorg. Chem. 1992, 13, 111-131; (f) Erker, G.; Röttger, D. "The energetic stabilization caused by a planar-tetracoordinate carbon atom: a dynamic NMR spectroscopic study of the dimetallabicycle $\left[\left(\mathrm{Cp}_{2} \mathrm{Zr}\right)_{2}\left(\mu-\mathrm{CCCH}_{3}\right)\left(\mu-\mathrm{H}_{3} \mathrm{CCCCH}_{3}\right)\right] \mathrm{BPH}_{4}$," Angew. Chem., Int. Ed. 1993, 32, 1623-1625; (g) Albrecht, M.; Erker, G.; Krüger, C. "The synthesis of stable, isolable planar-tetracoordinate carbon compounds," Synlett 1993, 441-448; (h) Röttger, D.; Erker, G.; Fröhlich, R.; Grehl, M.; Silverio, S. J.; Hyla-Kryspin, I.; Gleiter, R. "Determination of the stabilization energy of planar-tetracoordinate carbon in dynamic dinuclear ( $\mu$-hydrocarbyl)bis(zirconocene) cation complexes and detection of an organometallic memory effect in their formation," J. Am. Chem. Soc. 1995, 117, 10503-10512; (i) Röttger, D.; Erker, G.; Fröhlich, R. "Formation of a $\left[\mu-\left(\eta^{1}-N-\eta^{2}-C, N\right)\right.$-aryl cyanide biszirconocene cation by ligand exchange reaction," Chem. Ber. 1995, 128, 1045-1046; (j) Röttger, D.; Pflug, J.; Erker, G.; Kotila, S.; Fröhlich, R. "Reaction of the organometallic planar tetracoordinate carbon compound $\left[\left(\mathrm{Cp}_{2} \mathrm{Zr}\right)_{2}\left(\mu-\mathrm{C}-\mathrm{CCH}_{3}\right)\left(\mu-\left(\eta^{1}-\mathrm{C}-\eta^{2}-\mathrm{C}, \mathrm{C}\right)-\mathrm{CH}_{3} \mathrm{CCCH}_{3}\right)\right]^{+}$ $\left[\mathrm{BPh}_{4}\right]^{-}$with alkyl isocyanides," Organometallics 1996, 15, 1265-1267; (k) Röttger, D.; Erker, G.; Fröhlich, R.; Kotila, S. "Stabilization of a planar-tetracoordinate carbon center in an organometallic complex containing both a zirconocene and a hafnocene moiety," Chem. Ber. 1996, 129, 1-3; (l) Röttger, D.; Erker, G.; Fröhlich, R. "Formation of stable organometallic planar-tetracoordinate carbon compounds containing a cationic ( $\mu$ $\left.\mathrm{R}^{1} \mathrm{CCR}^{2}\right)\left[\mu-\mathrm{Cl}\left(\mathrm{ZrCp}_{2}\right)_{2}\right]$ framework," J. Org. Chem. 1996, 518, 221-225; (m) Ahlers, W.; Erker, G.; Fröhlich, R.; Peuchert, U. "Synthesis, structure, and dynamic behavior of ( $\mu$-aldimido) $\left(\mu-\eta^{1}, \eta^{2}\right.$-alkyne)-biszirconocene cation complexes that contain planar-tetracoordinate carbon," Chem. Ber. -Recueil 1997, 130, 1069-1077; (n) Schottek, J.; Erker, G.; Fröhlich, R. "Formation of metallocene-stabilized planar-tetracoordinate carbon compounds by a protonation route," Eur. J. Inorg. Chem. 1998, 551-558; (o) Schottek, J.; Röttger, D.; Erker, G.; Fröhlich, R. "Formation of hypercoordinated carbon inside a ( $\mu$-hydrocarbyl)bis(group 4 metallocene) framework by a simple protonation route," J. Am. Chem. Soc. 1998, 120, 5264-5273; (p) Erker, G. "Using bent metallocenes for stabilizing unusual coordination geometries at carbon," Chem. Soc. Rev. 1999, 28, 307-314.
(a) Binger, P.; Sandmeyer, F.; Krüger, C.; Kuhnigk, J. R.; Goddard, R.; Erker, G. "New ti-tanium-boron complexes with a planar tetracoordinate carbon or a planar tricoordinate phosphorus center," Angew. Chem., Int. Ed. 1994, 33, 197-198; (b) Binger, P.; Sandmeyer, F.; Krüger, C.; Erker, G. "New bimetallic complexes ( $\mathrm{M}^{1}-\mathrm{Ti}$; $\mathrm{M}^{2}-\mathrm{B}$ ) containing planar tetracoordinate carbon," Tetrahedron 1995, 51, 4277-4290; (c) Binger, P.; Sandmeyer, F.; Krüger, C. "Reactivity of bimetallic compounds containing planar tetracoordinate carbon toward unsaturated organic substrates," Organometalics 1995, 14, 2969-2976.
(40) Choukroun, R.; Cassoux, P. "Planar tetracoordination of carbon in groups 4 and 5 organometallic chemistry," Acc. Chem. Res. 1999, 32, 494-502.
(41) The first cation of type 1-28, where $\mathrm{M}^{1}=\mathrm{M}^{2}=\mathrm{Zr}, \mathrm{L}=\mathrm{CC}-t-\mathrm{Bu}, \mathrm{R}^{1}=t-\mathrm{Bu}, \mathrm{R}^{2}=\mathrm{Me}$, was reported by Horton and Orpen: Horton, A. D.; Orpen, A. G. "A structurally distorted ligand in an electron-deficient dizirconocene cation: unusual 1,2- and 1,1-dimetallioalkenes," Angew. Chem., Int. Ed. 1992, 31, 876-878; Angew. Chem. 1992, 104, 912.
(42) (a) Cayton, R. H.; Chacon, S. T.; Chisholm, M. H.; Hampden-Smith, M. J.; Huffman, J. C.; Folting, K.; Ellis, P. D.; Huggins, B. A. "Versatile modes of allene bonding in the structures of $\left.\left.\left[\mathrm{W}_{2} \mathrm{O} t \mathrm{Bu}\right)_{6}\left(\mathrm{C}_{3} \mathrm{H}_{4}\right)\right],\left[\mathrm{W}_{2} \mathrm{OtBu}\right)_{6}\left(\mathrm{C}_{3} \mathrm{H}_{4}\right)(\mathrm{CO})_{2}\right]$ and $\left[\mathrm{W}_{2}(\mathrm{O}-t \mathrm{Bu})_{6}\left(\mathrm{C}_{3} \mathrm{H}_{4}\right)_{2}\right]$," Angew. Chem., Int. Ed. 1989, 28, 1523-1525; (b) Chacon, S. T.; Chisholm, M. H.; Folting, K.; Huffman, J. C.; Hampden-Smith, M. J. "Allene adducts of ditungsten hexaalkoxides. Three modes of allene coordination to dinuclear centers as seen in the structures of $\mathrm{W}_{2}(\mathrm{O}-t \mathrm{Bu})_{6}\left(\mathrm{C}_{3} \mathrm{H}_{4}\right), \mathrm{W}_{2}(\mathrm{O}-t \mathrm{Bu})_{6}\left(\mathrm{C}_{3} \mathrm{H}_{4}\right)_{2}$, and $\mathrm{W}_{2}(\mathrm{O}-t \mathrm{Bu})_{6}\left(\mathrm{C}_{3} \mathrm{H}_{4}\right)(\mathrm{CO})_{2}$, Organometallics 1991, 10, 3722-3735.
(43) (a) Cotton, F. A.; Shamshoum, E. S. "Mechanistic insight into the reaction of phenyl isocyanate with ditungsten hexa-tert-butoxide: isolation and characterization of early intermediates," J. Am. Chem. Soc. 1985, 107, 4662-7; (b) Cotton, F. A.; Schwotzer, W.; Shamshoum, E. S. "Addition of di- $p$-tolylcarbodiimide to ditungsten hexa-tert-butoxide. Preparation and structure of $\left[\mathrm{W}\left(\mathrm{OCMe}_{3}\right)_{3}\right]_{2}\left(\mu-\mathrm{C}_{7} \mathrm{H}_{7} \mathrm{NCNC}_{7} \mathrm{H}_{7}\right)$," Organometallics 1985, 4, 461-465.
(44) Ogoshi, S.; Tsutsumi, K.; Ooi, M.; Kurosawa, H. "Synthesis, Structure and Reactivity of $\eta^{3}$-Allenyl/Propargyl Dinuclear Palladium Complexes," J. Am. Chem. Soc. 1995, 117, 10415-10416.
(a) Leoni, P.; Pasquali, M.; Pieri, G.; Albinati, A.; Pregosin, P. S.; Rüegger, H. "A stable palladium(I) dimer with one 14 e palladium center and its reversible reaction with $\mathrm{CS}_{2}$, affording a new complex with a planar four-coordinate carbon," Organometallics 1995, 14, 3143-3145. (b) For a related hexacoordinate carbon species see: Leoni, P.; Pasquali, M.; Fadini, L.; Albinati, A.; Hofmann, P.; Metz, M. "Synthesis and structure of $\mathrm{Pd}_{4}(\mu-$ $\left(\mathrm{P}_{\mathrm{B}} \mathrm{Bu}_{2}\right)_{2}\left(\mu-\mathrm{CS}_{2}\right)\left(\mathrm{PPh}_{3}\right)_{2} \mathrm{I}_{2}$, a neutral palladium(I) derivative with a hexacoordinate carbon and a $\mathrm{CS}_{2}$ molecule bridging four palladium centers," J. Am. Chem. Soc. 1997, 119, 8625-8629. For similar platinum based complexes see: (c) Farrar, D. H.; Gukathasan, R. R.; Morris, S. A. "Reaction of $\mathrm{CS}_{2}$ with trinuclear Pd and Pt clusters. Crystal structure of $\mathrm{Pt}_{2}\left(\mu-\mathrm{CS}_{2}\right)_{2}\left(\mathrm{P}(t \mathrm{Bu})_{2} \mathrm{Ph}\right)_{2}$," Inorg. Chem. 1984, 23, 3258-3261; (d) Farrar, D. H.; Gukathasan, R. R.; Won, K. "Reactions of carbon disulphide with palladium(0) complexes," J. Organomet. Chem. 1984, 275, 263-271.
(46) Chi, Y.; Cheng, P.-S.; Wu, H.-L.; Hwang, D.-K.; Su, P.-C.; Peng, S.-M.; Lee, G.-H. "Heterometallic carbonyl cluster oxide. Formation, structure and reactivity of $\mathrm{WRe}_{2}$ oxoacetylide cluster compounds," J. Chem. Soc., Chem. Commun. 1994, 1839-1840.
(47) Beringhelli, T.; Ciani, G.; D'Alfonso, G.; Sironi, A.; Freni, M. "A new metallic environment for carbon in a carbido metal cluster," J. Chem. Soc., Chem. Commun. 1985, 978-979.
(48) (a) Gunale, A.; Pritzkow, H.; Siebert, W.; Steiner, D.; Berndt, A. "Dicobalt and diplatinum complexes of diborylcarbenes," Angew. Chem., Int. Ed. 1995, 34, 1111-1113; (b) Gunale, A.; Steiner, D.; Schweikart, D.; Pritzkow, H.; Berndt, A.; Siebert, W. "Unusual mono- and dinuclear cobalt and platinum complexes of rearranged boriranylideneborane and diboretanylideneborane ligands - Dicobalt- $\mu$-diborylcarbene complexes as derivatives of planar methane," Chem. Eur. J. 1998, 4, 44-52.
(49) Böhm, M. C.; Gleiter, R.; Schang, P. "On the planarity of tetracyclo[5.5.1.0 $\left.{ }^{4,13} .0^{10,13}\right]$ tridecahexaene," Tetrahedron Lett. 1979, 28, 2575-2578.
(50) Chandrasekhar, J.; Würthwein, E.-U.; Schleyer, P. v. R. "On the planarity of tetracoordinate carbon enclosed by annulene perimeter," Tetrahedron 1981, 37, 921-927.
(51) Schoeller, W. W. "On the question of a planar tetravalent carbon centre in the ethyleneand acetylene-benzenium ion - a semi-empirical SCF-LCAO-study," J. Chem. Soc., Chem. Commun. 1974, 872.
(52) For more recent studies that have considered these phenonium ions, see for 1-40: (a) Sieber, S.; Schleyer, P. v. R.; Gauss, J. "The accurate $C_{2 v}$ phenonium and benzenonium ion structures confirmed by correlated GIAO-MP2 NMR chemical shift calculations," J. Am. Chem. Soc. 1993, 115, 6987-6988; (b) Rappoport, Z.; Kobayashi, S.; Stanger, A.; Boese, R. "Crystal structure of 1,2-diphenyl-5,7-di-tert-butylspiro[2.5]octa-1,4,7-trien-6-one, a possible model for diphenylvinylidenephenonium ions," J. Org. Chem. 1999, 64, 4370-4375. (c) For 1-41 see: Wang, H.; Weiner, B.; Frenklach, M. "Theoretical study of reaction between phenylvinyleum ion and acetylene," J. Phys. Chem. 1993, 97, 1036410371. (d) For 1-42 see: Olah, G. A.; Head, N. J.; Rasul, G.; Prakash, G. K. S. "Protonation of benzocyclobutene with superacid: Cram's phenonium ion (spiro[5.2]octa-5,7-dien-4-yl cation) revisited," J. Am. Chem. Soc. 1995, 117, 875-82.
(53) Georgian, V. "Synthesis directed toward saturated "flat" carbon," Tetrahedron Lett. 1972, 42, 4315-4317.
(54) (a) Keese, R. "Tetrakoordinierter Kohlenstoff mit planoider Konfiguration," Nach. Chem. Tech. Lab. 1982, 30, 844-849; (b) Keese, R. Planarization of tetracoordinate carbon. Synthesis and structure of [5.5.5.5]fenestranes; Chizhov, O. S., Ed.; Blackwell: Oxford, 1986, pp 43-52; (c) Luef, W.; Keese, R. "62. Angular distortions at tetracoordinate carbon. Planoid distortions in $\alpha, \alpha^{\prime}$-bridged spiro[4.4]nonanes and [5.5.5.5]fenestranes," Helv. Chim. Acta 1987, 70, 543-553; (d) van der Waals, A.; Keese, R. "Synthesis of a [5.5.5.5]fenestrenedione via tandem Pauson-Khand tetracyclization," J. Chem. Soc., Chem. Commun. 1992, 570-571; (e) Keese, R.; Guidetti-Grept, R.; Herzog, B. "Synthesis of [5.5.5.5]fenestranes by Pd-catalyzed carbonylation-cyclization," Tetrahedron Lett. 1992, 33, 1207-1210; (f) Brunvoll, J.; Guidetti-Grept, R.; Hargittai, I.; Keese, R. "204. Synthesis and electron-diffraction structure of all-cis-[5.5.5.5]fenestrane," Helv. Chim. Acta 1993, 76, 2838-2846; (g) Guidetti-Grept, R. G.; Herzog, B.; Debrunner, B.; Silje-
govic, V.; Keese, R.; Frey, H.-M.; Hauser, A.; König, O.; Lüthi, S.; Birrer, J.; Nyffeler, D.; Förster, M.; Bürgi, H.-B. "A [5.5.5.5]fenestrane derivative," Acta Crystallogr., Sect. C: Cryst. Struct. Commun. 1995, C51, 495-497.
(a) Keese, R. "Two stereoisomeric [4.5.5.5]fenestranes formed by intramolecular [2 + 2] cycloaddition," Angew. Chem., Int. Ed. 1992, 31, 344-345; (b) Hirschi, D.; Luef, W.; Gerber, P.; Keese, R. "147. Synthesis and structure of [4.5.5.5]fenestranes (= tetracyclo[5.4.1.0 $0^{4,12} .0^{9,12}$ ]dodecanes)," Helv. Chim. Acta 1992, 75, 1897-1908.
(a) Luef, W.; Keese, R. "Angular distortions at tetracoordinate carbon: planoid distortions in small spiroalkanes," J. Mol. Struct., Theochem. 1992, 257, 353-368; (b) Luef, W.; Keese, R. "Planarizing distortions in carbon compounds," Adv. Strain Org. Chem. 1993, 3, 229-267.
(57) (a) Venepalli, B. R.; Agosta, W. C. "Fenestranes and the flattening of tetrahedral carbon," Chem. Rev. 1987, 87, 399-410; (b) Venugopal, D.; Agosta, W. C. "Cation, carbene, and radical centers in a [4.4.4.5]fenestrane," Tetrahedron 1992, 48, 6757-6762.
(58) (a) Hoeve, W. T.; Wynberg, H. "Synthetic approaches to planar carbon. 1," J. Org. Chem. 1980, 45, 2925-2930; (b) Hoeve, W. T.; Wynberg, H. "Synthetic approaches to planar carbon. 2," J. Org. Chem. 1980, 45, 2930-2937.
(59) Smit, W. A.; Buhanjuk, S. M.; Simonyan, S. O.; Shashkov, A. S.; Struchkov, Y. T.; Yanovsky, A. I.; Caple, R.; Gybin, A. S.; Anderson, L. G.; Whiteford, J. A. "An efficient protocol for the synthesis of fenestrane derivatives," Tetrahedron Lett. 1991, 32, 2105-2108.
(60) (a) Wiberg, K. B.; Olli, L. K.; Golombeski, N.; Adams, R. D. "Tricyclo[4.2.0.0 ${ }^{1,4}$ ]octane," J. Am. Chem. Soc. 1980, 102, 7467-7475; (b) Wiberg, K. B.; Wendoloski, J. J. "Enthalpies of formation of fused cyclobutane derivatives," J. Am. Chem. Soc. 1982, 104, 5679-5686; (c) Wiberg, K. B. "Structures and energies of the tricyclo[4.1.0.0 ${ }^{1,3}$ ]heptanes and the tetracyclo[4.2.1. $\left.0^{2,9} .0^{5,9}\right]$ nonanes. Extended group equivalents for converting $a b$ initio energies to heats of formation," J. Org. Chem. 1985, 50, 5285-5291.
(61) For work by Minkin and coworkers relating to pyramidane (1-62) and other fenestranes see: (a) Minyaev, R. M.; Minkin, V. I. "Pyramidal tetracoordinate carbon," J. Org. Chem. USSR (Engl. Transl.) 1978, 14, 1-12; Zh. Org. Khim. 1978, 14, 3-15; (b) Minyaev, R. M.; Minkin, V. I.; Zefirov, N. S.; Zhdanov, Y. A. "An approach to the synthesis of pyramidane," J. Org. Chem. USSR (Engl. Transl.) 1979, 15, 1815-1821; Zh. Org. Khim. 1979, 15, 2009-2016; (c) Minkin, V. I.; Minyaev, R. M. "Stabilization of pyramidal tetracoordinated carbon in organic molecules," J. Org. Chem. USSR (Engl. Transl.) 1979, 15, 197-204; Zh. Org. Khim. 1979, 15, 225-234; (d) Minkin, V. I.; Minyaev, R. M.; Natanzon, V. I. "Structure of fenestranes and the eight-electron rule," J. Org. Chem. USSR (Engl. Transl.) 1980, 16, 589-596; (e) Natanzon, V. I.; Minyaev, R. M. "Stabilization of the carbon atom by two collinear double bonds," Theor. Exp. Chem. 1981, 17, 207-209; Teor. Éksp. Khim. 1981, 17, 264-268; (f) Minkin, V. I.; Minyaev, R. M. "The nonclassical polyhedral organic molecules and ions" in Progress in Theoretical Organic Chemistry; Csizmadia, I. G., Ed.; Elsevier: Amsterdam, 1982; Vol. 3, pp 121-155; (g) Minkin, V. I.; Minyaev, R. M.; Orlova, G. V. "Pyramidane and isoelectronic cations," J. Mol. Struct., Theochem. 1984, 110, 241-253; (h) Minyaev, R. M.; Minkin, V. I. "Structure of hetero derivatives and of the pentacoordinated anion of [4.4.4.4]fenestrane," J. Org. Chem. USSR
(Engl. Transl.) 1985, 21, 1239-1248; (i) Minkin, V. I.; Minyaev, R. M.; Zhdanov, Y. A. "Nontetrahedral tetracoordinate carbon atom in organic compounds" in Nonclassical Structures of Organic Compounds; Mir: Moscow, 1987, pp 248-306 (translated by B. V. Rassadin); (j) Minkin, V. I.; Ya Simkin, B.; Glukhovtsev, M. N. "Quantum-chemical studies of the structure and reactivity of carbenes," Russ. Chem. Rev. 1989, 58, 622-635.
(62) (a) Gupta, A. K.; Fu, X.; Snyder, J. P.; Cook, J. M. "General approach for the synthesis of polyquinenes via the Weiss reaction," Tetrahedron 1991, 47, 3665-3710; (b) Fu, X.; Kubiak, G.; Zhang, W.; Han, W.; Gupta, A. K.; Cook, J. M. "General approach for the synthesis of polyquinenes via the Weiss reaction XV. Synthesis of the [5.5.5.5]fenestrane system via the aldol approach and the studies directed toward the [5.5.6.6]fenestranes," Tetrahedron 1993, 49, 1511-1524.
(63) (a) Liebman, J. F.; Greenberg, A. "A survey of strained organic molecules," Chem. Rev. 1975, 76, 311-365; (b) Greenberg, A.; Liebman, J. F. "A potpourri of pathologies" in Strained Organic Molecules; Academic Press: New York, 1978; Vol. 38, pp 342-385.
(64) Würthwein, E.-U.; Chandrasekhar, J.; Jemmis, E. D.; Schleyer, P. v. R. "The [4.4.4.4]fenestranes and [2.2.2.2]paddlane. Prospects for the realization of planar tetracoordinate carbon?" Tetrahedron Lett. 1981, 22, 843-846.
(65) Schulman, J. M.; Sabio, M. L.; Disch, R. L. "Structure and energetics of [4.4.4.4]fenestrane," J. Am. Chem. Soc. 1983, 105, 743-744.
(66) (a) Wender, P. A.; Dore, T. M.; deLong, M. A. "An arene-alkene photocycloaddition-radical cyclization cascade: the first syntheses of cis,cis,cis,trans-[5.5.5.5]-fenestranes," Tetrahedron Lett. 1996, 37, 7687-7690; (b) Wender, P. A.; DeLong, M. A.; Wireko, F. C. "Novel oxidative rearrangement product of the first trans, cis,cis,cis-[5.5.5.5]fenestrane derivative," Acta Crystallogr., Sect. C: Cryst. Struct. Commun. 1997, C53, 954-956.
(67) Lewars, E. "Pyramidane - an ab initio study of the $\mathrm{C}_{5} \mathrm{H}_{4}$ potential energy surface," J. Mol. Struct., Theochem. 1998, 423, 173-188.
(68) (a) Haas, G.; Prelog, V. "Optically active $9,9^{\prime}$-spirobifluorene derivatives," Helv. Chim. Acta 1969, 52, 1202-1218; (b) Prelog, V.; Bedekovic, D. "Chiral 2,2'-polyoxaalkano-9,9'spirobifluorenes," Helv. Chim. Acta 1979, 62, 2285-2302.
(69) (a) Kuck, D.; Boegge, H. "Benzoannelated centropolyquinanes. 2. (all-cis)-tetrabenzotetracyclo[5.5.1.0 $\left.0^{4,13} .0^{10,13}\right]$ tridecane, 'fenestrindan'," J. Am. Chem. Soc. 1986, 108, 81078109; (b) Kuck, D.; Schuster, A.; Krause, R. A. "Benzoannelated centropolyquinanes. Part IX. Synthesis and conformational behavior of fenestrindans (tetrabenzo[5.5.5.5]fenestranes) with four bridgehead substituents," J. Org. Chem. 1991, 56, 3472-3475; (c) Kuck, D. "Benzoannelated fenestranes with [5.5.5], [5.5.5.6], and [5.5.5.5] frameworks: the route from 1,3-indandione to fenestrindan," Chem. Ber. 1994, 127, 409-25; (d) Kuck, D.; Schuster, a.; Gestmann, D.; Posteher, F.; Pritzkow, H. "Benzoannelated centropolyquinanes. Part 20. Centropentaindan, a fenestrane bearing five mutually fused indan units: syntheses, molecular structure, and bridgehead substitution," Chem. Eur. J. 1996, 2, 58-67; (e) Seifert, M.; Kuck, D. "Naphtho-annulated [5.6.5]- and [6.5.5.5]fenestranes," Tetrahedron 1996, 52, 13167-13180; (f) Kuck, D. "Benzoannelated fenestranes," Adv. Theor. Interesting Mol. 1998, 4, 81-155; (g) Kuck, D. "The centropolyindans and related centro-fused polycyclic organic compounds. Polycycles between neopentane $\mathrm{C}\left(\mathrm{CH}_{3}\right)_{4}$ and the carbon nucleus $\mathrm{C}\left(\mathrm{CC}_{3}\right)_{4}$," Top. Curr. Chem. 1998, 196, 167-220; (h)

Bredenkotter, B.; Barth, D.; Kuck, D. "Synthesis and base-induced epimerization of cis,cis,cis, trans-tribenzo[5.5.5.6]fenestranes," Chem. Commun. (Cambridge) 1999, 847848.
(a) Wiberg, K. B.; Hiatt, J. E.; Burgmaier, G. J. "Distorted geometries about bridgehead carbons," Tetrahedron Lett. 1968, 5855-5857; (b) Wiberg, K. B.; O'Donnell, M. J. "Preparation and Diels-Alder reactions of the $[n](1,4)$ naphthalenophanes. Isolation of a paddlane derivative containing the tricyclo[14.2.2.2 $\left.{ }^{1,6}\right]$ docosane ring system," J. Am. Chem. Soc. 1979, 101, 6660-6666; (c) Wiberg, K. B. "Bonding in small ring paddlanes," Tetrahedron Lett. 1985, 26, 5967-5970.
(71) Hahn, E. H.; Bohm, H.; Ginsburg, D. "The synthesis of paddlanes: compounds in which quaternary bridgehead carbons are joined by four chains," Tetrahedron Lett. 1973, 507-510.
(72) Dodziuk, H.; Leszczynski, J.; Nowinski, K. S. "The quest for a planar and pyramidal carbon atom. 4. An unsuccessful search for pyramidal carbon atoms in hypothetical unsaturated conjugated paddlane," J. Mol. Struct., Theochem. 1997, 391, 201-205.

Lee, W. B.; Oh, D. W. "The reaction of [1.1.1]propellane with methylene," Bull. Korean Chem. Soc. 1999, 20, 629-630.
(74) (a) Wynberg, H.; Helder, R. "The synthesis of [2.2](9,10)anthraceno(2,5)furanophane and its reaction with dimethyl acetylenedicarboxylate," Tetrahedron Lett. 1971, 45, 4317-4320; (b) Helder, R.; Wynberg, H. "Diels-Alder addition of dicyanocetylene to [8](2,5)furanophane. Synthesis of a paddlane," Tetrahedron Lett. 1973, 4321-4; (c) Wynberg, H.; Hulshof, L. A. "Optical activity of hydrocarbons," Tetrahedron 1974, 30, 177582; (d) Vögtle, F.; Koo Tze Mew, P. "Triptycenophanes - Synthesis via ‘double nonbenzylic sulfone pyrolysis'," Angew. Chem., Int. Ed. 1978, 17, 60-61; (e) Warner, P.; Chem, B.-L.; Bronski, C. A.; Karcher, B. A.; Jacobson, R. A. "Synthesis of some [n.1.3.1]- and [n.1.2.1]paddlanes," Tetrahedron Lett. 1981, 22, 375-6; (f) Eaton, P. E.; Leipzig, B. D. "Toward tricyclo[2.2.2.2]decane. 1. [n.2.2.2]Paddlane systems, n = 10-14," J. Am. Chem. Soc. 1983, 105, 1656-1658; (g) Tobe, Y.; Fujita, H.; Wakaki, I.; Terashima, K.; Kobiro, K.; Kakiuchi, K.; Odaira, Y. "Water-soluble macrocyclic paddlanes and propellane as a new class of host molecules," J. Chem. Soc., Perkin Trans. 1 1984, 2681-4; (h) Schwartz, M. H.; Rosenfeld, S. M.; Lee, C. I.; Jasinski, J. P.; Dardon, E. H. "The structure of 9,10-dihydro-9,10-bis(hydroxymethyl)-9,10-ethanoanthracene-11,12-anhydride," Tetrahedron Lett. 1992, 33, 6275-8.
(75) Dodziuk, H. "Unusual saturated hydrocarbons: Interaction between theoretical and synthetic chemistry," Top. Stereochem. 1994, 21, 351-380.
(a) Skattebøl, L. "Chemistry of gem-dihalocyclopropanes. II. The reaction of dienes with dibromocarbene," J. Org. Chem. 1964, 29, 2951-2956; (b) Skattebøl, L. "Chemistry of gem-dihalocyclopropanes. V. Formation of tricyclo[4.1.0.04,6]heptane and derivatives," J. Org. Chem. 1966, 31, 2789-2794; (c) Frey, H. M.; Hopkins, R. G.; Skattebøl, L. "Thermal unimolecular isomerization of tricyclo[4.1.0.0 ${ }^{1,3}$ ]heptane," J. Chem. Soc. B 1971, 539-541; (d) Becher, G.; Skattebø1, L. "Thermal reactions of meso- and racemic deca-2,3,7,8-tetraene," Tetrahedron Lett. 1979, 14, 1261-1264.
(77) Smith, Z.; Andersen, B.; Bunce, S. "Electron-diffraction study of gaseous tricyclo[4.1.0.0 ${ }^{1,3}$ heptane," Acta Chem. Scand. A 1977, 31, 557-562.
(78) Boese, R.; Bläser, D.; Gomann, K.; Brinker, U. H. "Spiropentane as a tensile spring," J. Am. Chem. Soc. 1989, 111, 1501-1503.
(79) (a) Brinker, U. H.; Streu, J. "4,5-Benzotricyclo[4.1.0.0 $0^{1,3}$ hept-4-ene," Angew. Chem., Int. Ed. 1980, 19, 631-632; Angew. Chem. 1980, 92, 641. See also: (b) Brinker, U. H.; Wilk, G.; Gomann, K. "Thermolysis and reactions of 4,5-benzotricyclo[4.1.0.0 ${ }^{1,3}$ ]hept-4-ene and o-(propadienyl)styrene," Angew. Chem., Int. Ed. 1983, 22, 868-869; Angew. Chem. 1983, 95, 892; (c) Brinker, U. H.; Gomann, K.; Zorn, R. "Tricyclo[4.1.0.0 ${ }^{1,3}$ ]hept-4-enes as intermediates," Angew. Chem., Int. Ed. 1983, 22, 869-870; Angew. Chem. 1983, 95, 893; (d) Gleiter, R.; Krennrich, G.; Brinker, U. H. "Electronic structure of spiropentane and some derivatives," J. Org. Chem. 1986, 51, 2899-2901.
(80) (a) Flowers, M. C.; Frey, H. M. "The thermal isomerization of spirobicyclopropane," 1961, J. Chem. Soc., 5550-5551; (b) Roth, W. R.; Wollweber, D.; Offerhaus, R.; Rekowski, V.; Lennartz, H.-W.; Sustmann, R.; Müller, W. "Zur Energiedelle von Diradikalen. IV. 2-Methylen-1,4-cyclohexadiyl," Chem. Ber. 1993, 126, 2701-2715.
(81) (a) Miebach, T.; Wuster, H.; Brinker, U. H. "Carbene rearrangements. 42. Intramolecular addition versus novel carbon hydrogen bond insertion reactions of N -alkenyl-substituted cyclopropylidenes," J. Org. Chem. 1993, 58, 6520-6523; (b) Miebach, T.; Brinker, U. H. "trans-Tricyclo[5.1.0.0 ${ }^{1,3}$ ]octane,"J. Org. Chem. 1993, 58, 6524-6525.
(82) (a) Wiberg, K. B.; McClusky, J. V.; Schulte, G. K. "The reaction of a bridged spiropentane with Zeise's dimer," Tetrahedron Lett. 1986, 27, 3083-3086; (b) Wiberg, K. B.; McClusky, J. V. "Tricyclo[2.1.0.0 ${ }^{1,3}$ ]pentane," Tetrahedron Lett. 1987, 28, 5411-5414; (c) Wiberg, K. B.; Chaves, A. "Predominant inversion of configuration in an intramolecular carbene addition to an alkene," J. Am. Chem. Soc. 1989, 111, 8052-8053; (d) Wiberg, K. B.; McMurdie, N.; McClusky, J. V.; Hadad, C. M. "Tricyclo[2.1.0.0 ${ }^{1,3}$ ]pentane," J. Am. Chem. Soc. 1993, 115, 10653-10657; (e) Wiberg, K. B.; Snoonian, J. R. "Bridged spiropentanes - ring expansion," Tetrahedron Lett. 1995, 36, 1171-1174; (f) Wiberg, K. B.; Snoonian, J. R.; Lahti, P. M. "Ring contraction of a two-carbon bridged spiropentane," Tetrahedron Lett. 1996, 37, 8285-8288; (g) Wiberg, K. B.; Snoonian, J. R. "Synthesis, reactions, and structural studies of two-carbon bridged spiropentanes," J. Org. Chem. 1998, 63, 1402-1407; (h) Wiberg, K. B.; Snoonian, J. R. "Ring expansion and contraction of a two-carbon bridged spiropentane," J. Org. Chem. 1998, 63, 1390-1401.
(83) Köbrich, G.; Baumann, M. "Bridged methylenecyclopropanes as test cases for Brett's rule: 2,5,5,7,7-pentamethylbicyclo[4.1.0]hept-1-ene," Angew. Chem., Int. Ed. 1972, 11, 52-53; Angew. Chem. 1972, 84, 62-63.
(84) Kuznetsova, T. S.; Eremenko, O. V.; Kokoreva, O. V.; Zatonsky, G. V.; Zefirov, N. S. "Synthesis of alicyclic derivatives of spiropentane based on 1,5-cyclooctadiene," Russ. Chem. Bull. 1996, 45, 1662-1666.
(85) Baird, M. S. "Tetracyclo[3.3.1.0 $\left.0^{2,4} \cdot 0^{2,8}\right]$ nonane. A strained spiro-compound," J. Chem. Soc., Chem. Commun. 1974, 197-198.
(86) See also: (a) Dodziuk, H.; Nowinski, K. S. "In quest for planar and pyramidal carbon atom. Part 2. AM1 study of small bridged spiropentanes," J. Mol. Struct., Theochem. 1994, 311, 97-100; (b) Dodziuk, H.; Leszczynski, J.; Nowinski, K. S. "The quest for a planar and pyramidal carbon atom. 3. Can a tetrahedrally coordinated carbon form a nearly linear C-C-C bond angle," J. Org. Chem. 1995, 60, 6860-6863.

## Chapter 2 Theoretical Methods

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### 2.1 Introduction

Computational quantum chemistry has become an invaluable tool for the elucidation of the structure and energy of chemical systems. The basic premise involves con-
sidering individual molecules as a group of particles that can be treated using the equations of quantum mechanics (which treat particles like waves). Its value was given the ultimate accolade in 1998 when the Nobel Prize in Chemistry was awarded to "John A. Pople for his development of computational methods for use in quantum chemistry" and "Walter Kohn for his development of the density functional theory".

In practice, any natural system interacts with its environment to some extent and so any complete solution is effectively infinite and clearly intractable. Fortunately, it is possible to simplify most systems by limiting them to some natural boundary. For the chemist, and in particular the organic chemist, this boundary falls naturally at the molecular level. The natural boundary in this case is a consequence of the large difference between the strength of covalent bonds and intermolecular forces. ${ }^{\dagger}$ As a result, chemical systems which involve either individual molecules or a small number of interacting molecules (a chemical reaction) can be readily treated using quantum mechanical techniques. The systems that have been examined in this work (saturated hydrocarbon cage compounds) all fall into the category of well-bounded covalent molecules and are thus well-suited to study by the computational techniques outlined in this chapter.

However, it turns out that the resulting equations are insoluble for all but the very simplest systems, i.e. exact solutions are available for systems of only one or two particles. ${ }^{1}$ To solve the resulting equations for all other systems requires the use of various approximations, and in most cases the use of computers to calculate the solution. The so-called $a b$ initio methods ${ }^{\ddagger}$ achieve this using only the laws of quantum mechanics, along with the fundamental constants of nature, e.g. the speed of light and Planck's constant, and various rigorously defined mathematical approximations. ${ }^{8}$ The methods known as semi-empirical use a number of empirically derived parameters for each of the atoms, which are determined by fitting calculated results to experimental data. This

[^20]enables more drastic simplification of the quantum mechanical equations but in doing so introduces both some degree of prejudice towards the systems used in the parametrization, and an incompleteness or inflexibility in the treatment that has been found in practise to sometimes lead to poor results outside the 'test set' used for the parametrization.

Because the complexity and the size of the problem, and as a result, the time to compute a solution, increases rapidly with the size of the system, increasing levels of approximation are required to treat ever larger systems. However, the steady advance in computer technology, which is well described by Moore's Law, ${ }^{\dagger}$ has meant that ever larger molecules can be investigated by the methods described hereafter.

This chapter presents a brief overview of the theoretical methods used in this thesis. More detailed discussions of these and other methods can be found elsewhere. ${ }^{1-4}$

### 2.2 Basic Concepts

### 2.2.1 The Schrödinger Equation

The state of almost any system can be described by the time-independent Schrödinger equation, ${ }^{5}$ which is most simply written as,

$$
\begin{equation*}
\boldsymbol{H} \Psi=E \Psi \tag{2-1}
\end{equation*}
$$

where $\boldsymbol{H}$ is the Hamiltonian, a differential operator representing the total energy (described below), $\Psi$ is the wavefunction and $E$ is the total energy of the system. The Hamiltonian operator $(\boldsymbol{H})$ can be divided into two components, corresponding to the kinetic and potential energy, i.e.

$$
\begin{equation*}
H=T+V \tag{2-2}
\end{equation*}
$$

where $\boldsymbol{T}$ and $\boldsymbol{V}$ are the kinetic and potential energy operators, respectively.

For a molecular system, the Hamiltonian operator can be written in atomic units as

[^21]follows, ${ }^{3}$
\[

$$
\begin{equation*}
H=-\sum_{i=1}^{N_{e}} \frac{\nabla_{i}^{2}}{2}-\sum_{a=1}^{N_{n}} \frac{\nabla_{a}^{2}}{2 M_{a}}-\sum_{i=1}^{N_{e}} \sum_{a=1}^{N_{n}} \frac{Z_{a}}{r_{i a}}+\sum_{i=1}^{N_{e}} \sum_{j>i}^{N_{e}} \frac{1}{r_{i j}}+\sum_{a=1 b>a}^{N_{n}} \sum_{n}^{N_{n}} \frac{Z_{a} Z_{b}}{r_{a b}} \tag{2-3}
\end{equation*}
$$

\]

where $i$ and $j$ represent the $i$ th and $j$ th electrons, $a$ and $b$ are the $a$ th and $b$ th nuclei, $M_{a}$ is the mass of the $a$ th nucleus relative to that of an electron, $Z_{a}$ is the charge on nucleus $a$, and $r_{x y}$ is the distance between the particles $x$ and $y$. The first two terms represent the kinetic energy of the electrons and nuclei, respectively, while the remainder represent the potential energy.

### 2.2.2 The Born-Oppenheimer Approximation

The complexity of Equation 2-3, and hence the difficulty of determining a solution, can be reduced somewhat by employing a simple approximation, known as the Born-Oppenheimer (or adiabatic) approximation. ${ }^{7}$ Since the nuclei are much heavier than the electrons, it is reasonable to suggest that the electrons can adjust rapidly to any change of the nuclear configuration, i.e. we assume that the electronic distribution depends on the instantaneous positions of the nuclei and not on their velocities. This allows separation of the Hamiltonian (Equation 2-3) into nuclear and electronic components, which allows calculation of the energy (an effective electronic energy) at fixed nuclear configurations. The electronic Hamiltonian is shown in Equation 2-4 below,

$$
\begin{equation*}
H=-\sum_{i=1}^{N_{e}} \frac{\nabla_{i}^{2}}{2}-\sum_{i=1}^{N_{e}} \sum_{a=1}^{N_{n}} \frac{Z_{a}}{r_{i a}}+\sum_{i=1}^{N_{e}} \sum_{j>i}^{N_{e}} \frac{1}{r_{i j}} \tag{2-4}
\end{equation*}
$$

The hypersurface describing the variation of energy with nuclear position for a given electronic state is known as the potential energy surface (PES).

Although the Born-Oppenheimer approximation allows for considerable simplification, the resulting equations still have no analytic solutions except for one-electron systems (e.g. $\mathrm{H}_{2}{ }^{+}$). In order to make these methods applicable to systems of chemical interest, approximations for treating the electron many-body problem must also be included.

### 2.2.3 Orbitals and the Basis Set Expansion

### 2.2.3.1 The Molecular Orbital Approximation

The essence of the molecular orbital approach is to further simplify the Schrödinger equation (Equation 2-1) by assuming that the motion of each electron is independent. Although this does not give an accurate description of the electron it serves as a useful approximation and the correlation of motions between electrons can be dealt with in other ways (as will be seen later). The wavefunction of the system can then be expressed as a product of one-electron wavefunctions, referred to as spin-orbitals. Each spin-orbital $\chi$, is the product of a spatial function $(\psi)$, which is dependent on the position of the electron (and whose square gives the probability distribution of the electron in space), and a spin function, indicating the spin state of the electron.

Because electrons are fermions the total electronic wavefunction must be antisymmetric (change sign) with respect to interchange of any two electron coordinates. A simple product of spin-orbitals is not adequate. The Pauli exclusion principle, which states that no two electrons can have all quantum numbers equal, is a direct consequence of the antisymmetry requirement. A wavefunction that does have the antisymmetry requirement and which obeys the Pauli principle can be formed from the determinant of the $n$-electron spin-orbital matrix,

$$
\Psi=\frac{1}{\sqrt{n!}}\left|\begin{array}{cccc}
\chi_{1}(1) & \chi_{2}(1) & \cdots & \chi_{n}(1)  \tag{2-5}\\
\chi_{1}(2) & \chi_{2}(2) & \cdots & \chi_{n}(2) \\
\vdots & \vdots & & \vdots \\
\chi_{1}(n) & \chi_{2}(n) & \cdots & \chi_{n}(n)
\end{array}\right|
$$

where $\chi_{i}(j)$ indicates electron $j$ occupying the spin orbital $\chi_{i}$ and the prefactor is a normalization constant. Expansion leads to a sum of products of spin orbitals. This expression is commonly referred to as a Slater determinant. ${ }^{8}$

### 2.2.3.2 Basis Set Expansions

In practice, the spatial component of a spin-orbital is expanded in terms of a finite set of one-electron basis functions $\left(\phi_{\mu}\right)$ which are usually atom centered. The molecular
orbitals can now be written as,

$$
\begin{equation*}
\psi_{i}=\sum_{\mu=1}^{N} c_{\mu i} \phi_{\mu} \tag{2-6}
\end{equation*}
$$

where $c_{\mu i}$ are the molecular orbital expansion coefficients, which represent the contributions from each of the basis functions to the molecular orbital. When the atomic orbitals of the substituent atoms are used as basis functions, the method is known as a linear combination of atomic orbitals (LCAO).

### 2.2.4 The Variational Theorem

The variational theorem ${ }^{1-4}$ states that the energy ( $\mathrm{E}_{\text {approx }}$ ) of an approximate wavefunction ( $\Psi_{\text {approx }}$ ) is an upper bound to the exact energy ( $\mathrm{E}_{\text {exact }}$ ), i.e.

$$
\begin{equation*}
E_{\text {approx }}=\frac{\int \Psi_{\text {approx }}^{*} \mathbf{H} \Psi_{\text {approx }} d \tau}{\int \Psi_{\text {approx }}^{*} \Psi_{\text {approx }} d \tau} \geq E_{\text {exact }} \tag{2-7}
\end{equation*}
$$

This allows an iterative approach to optimizing the molecular orbital coefficients $\left(c_{\mu i}\right)$ in order to obtain the minimum total energy. This will give the best wavefunction possible within the constraints of the approximations used. Methods that calculate the energy utilizing Equation 2-7 are said to be variational.

### 2.3 Single-Determinant Methods

### 2.3.1 Hartree-Fock (HF) Theory

Applying the variational theorem (Equation 2-7) to an approximate N -electron wavefunction formed by the methods described above gives the Roothaan-Hall equations, ${ }^{9}$

$$
\begin{equation*}
\sum_{\mu=1}^{N} c_{\mu i}\left(F_{\mu \nu}-\varepsilon_{i} S_{\mu \nu}\right)=0 \tag{2-8}
\end{equation*}
$$

where $F_{\mu \nu}$ is the Fock matrix, $\varepsilon_{i}$ is the energy of the molecular orbital $\psi_{i}$ and $S_{\mu \nu}$ is the overlap matrix. Since the Fock matrix $F_{\mu \nu}$ is itself dependent on the orbital coefficients $c_{\mu}$, these equations are not linear and must be solved iteratively until convergence of the energy and the orbital coefficients is achieved.

This approach was first proposed by Hartree ${ }^{10}$ and Fock ${ }^{11}$ and is referred to as Har-tree-Fock (HF) theory. Because the molecular orbitals are derived from their own effective potential, this technique is also often referred to as self-consistent-field (SCF) theory (although it is one of many procedures that make use of such an iterative approach to achieving self-consistency in the electronic probability distribution).

If the Roothaan-Hall equations are formulated in such a way that each spatial molecular orbital should contain two electrons, one of $\alpha$ and one of $\beta$ spin, the resulting wavefunction is known as a restricted Hartree-Fock (RHF) solution. This procedure works well for most ground-state molecules where the electronic configuration is welldescribed as a closed-shell singlet state. The majority of the calculations conducted in this work fall into this category. It has been necessary to consider open-shell states in a number of cases. ${ }^{\dagger}$ The Roothaan-Hall equations can be reformulated to remove the restriction that all spatial molecular orbitals be doubly-occupied. The most direct way of doing this, known as the unrestricted Hartree-Fock (UHF) method, defines two sets of Roothaan-Hall equations (the Pople-Nesbet equations ${ }^{12}$ ), one describing the $\alpha$-electrons and one for the $\beta$-electrons. Allowing the spatial components of the spin-orbitals to vary, including those that are doubly-occupied, makes it possible for unpaired spins to interact differently with the $\alpha$ - and $\beta$-electrons in the 'doubly-occupied' orbitals, even though this is 'unphysical'. When this occurs, the resulting wavefunction is no longer an eigenfunction of $\left\langle S^{2}\right\rangle$ (the expectation value of the spin-squared operator) because it is effectively including contributions from other high-lying spin states of the molecule. The added flexibility in the density distribution of the electron can also be seen as a weak form of electron correlation (see Section 2.3.2 on page 58). There is another formulation known as restricted open-shell Hartree-Fock (ROHF) which we have not used in this work but which is well described elsewhere. ${ }^{1-4}$

There are two fundamental limitations to the Hartree-Fock method. In the first place, it ignores relativistic effects, but since these effects are only important for heavier atoms (e.g transition metals), they need not concern us here. The second, more serious limitation, is its neglect of electron correlation. Methods for including electron correla-

[^22]tion are discussed below.

### 2.3.2 Electron Correlation

As has been seen, the HF equations replace the real electron-electron interaction with an average interaction in which each electron 'sees' only the 'field' generated by the other electrons. This does not account for direct interactions between pairs of electrons. This pair-wise electron interaction is termed electron correlation and is often separated into Coulomb and Fermi correlation terms, which correspond to opposite-spin and like-spin correlating terms, respectively. Although the contribution of electron correlation to the total energy is relatively small, it often plays an important part in chemical processes. There are many ways of dealing with electron correlation and a number of these will be described below.

### 2.3.2.1 Full Configuration Interaction (FCI)

The solution to the Hartree-Fock equations for an $N$-basis function system is a set of $N$ spin orbitals ( $\chi_{i}$ ). For an $n$-electron molecule/system only the lowest $n$ of these orbitals are occupied, the remainder being referred to as virtual orbitals. This occupation scheme, or configuration, is only one of a set of $N!/((N-n)!n!)$ possible configurations. Other configurations can be obtained by exciting electrons from occupied to virtual orbitals. If a single electron is promoted, a singly-excited configuration results, if two electrons are promoted this gives rise to a doubly-excited configuration. These excitations are usually abbreviated as singles (S), doubles (D), triples (T) etc.

In order to improve the Hartree-Fock wavefunction, the full configuration interaction (FCI) method adds variationally determined amounts of all possible configurations to the Hartree-Fock wavefunction,

$$
\begin{equation*}
\Psi_{\mathrm{FCI}}=\Psi_{0}+\sum_{i>0} a_{i} \Psi_{i} \tag{2-9}
\end{equation*}
$$

where $\Psi_{0}$ represents the Hartree-Fock wavefunction, $\Psi_{i}(i>0)$ represent the various other configurations of this wavefunction and $a_{i}$ is the amplitude of the configuration. This wavefunction represents the most accurate that is possible within the limits of the basis set used. The FCI wavefunction is variational and size-consistent. In the limit of
an infinite basis set, the FCI method gives the exact solution to the time-independent Schrödinger equation. However, in practice, the computational cost of this method makes it practical for treatment of only relatively small systems and even then with only modest basis sets. ${ }^{13}$ The limitation on basis set size is perhaps the most critical factor here because an adequate treatment of electron correlation requires considerable flexibility in the electron density distribution that can only be gained from employing a reasonably large basis set (this is certainly the case when the gaussian-type ${ }^{\dagger}$ functions generally employed in calculations today are used (see Section 2.5 on page 66 )).

### 2.3.2.2 Truncated Cl Methods (CI and QCI)

The main contribution to the cost of computing an FCI solution is the immense number of configurations involved (this number rises factorially with the number of electrons and the number of basis functions). One obvious method of reducing the cost of including electron correlation this way is not to include all possible configurations. This results in methods such as CIS (single excitations) (which only gives improvement to the wavefunctions for excited states because all matrix elements between the HF wavefunction and singly-excited determinants are zero), CID (double excitations), CISD (single and double excitations), etc. These methods are, however, not size consistent (nor size extensive). ${ }^{\ddagger}$

The quadratic configuration interaction (QCI) family of methods was introduced to overcome the problem of size consistency. ${ }^{14}$ These methods achieve size consistency by adding various terms to the CISD wavefunction. The resulting QCISD wavefunction contains contributions from single and double, as well as some quadruple excitations. Although this method is size consistent, it is not variational.

The QCISD wavefunction does not consider triple excitations, which can be important in some systems. The direct inclusion of triples (QCISDT) would make the calcula-

[^23]tion prohibitively expensive for larger systems. Hence, in the $\mathrm{QCISD}(\mathrm{T})$ method, the triple excitations are included in an approximate, and much cheaper, perturbative treatment.

### 2.3.2.3 Couple Cluster Methods (CC)

The methods known as couple-cluster (CC) methods ${ }^{15}$ take an approach to treating electron correlation which does not explicitly deal with configuration interaction. In these methods, the HF wavefunction is corrected using a coupled cluster scheme (or cluster operator, $\mathbf{T}$ ) which in practise needs to be truncated. ${ }^{1-4}$ The couple-cluster methods are based on an exponential wavefunction ansatz; the exact, non-relativistic groundstate molecular wavefunction, $\Psi_{\text {exact }}$, is written as,

$$
\begin{equation*}
\Psi_{\text {exact }}=\exp (\mathbf{T}) \Psi_{\mathrm{HF}} \tag{2-10}
\end{equation*}
$$

where $\Psi_{\mathrm{HF}}$ is the normalized Hartree-Fock wavefunction, and $\exp (\mathbf{T})$ is written as a Taylor-series expansion,

$$
\begin{equation*}
\exp (\mathbf{T})=1+\mathbf{T}+\frac{\mathbf{T}^{2}}{2!}+\frac{\mathbf{T}^{3}}{3!}+\ldots=\sum_{k=0}^{\infty} \frac{\mathbf{T}^{k}}{k!} \tag{2-11}
\end{equation*}
$$

and the cluster operator ( $\mathbf{T}$ ) is the sum of the $n$-particle excitation operators $\left(\mathbf{T}_{n}\right)$,

$$
\begin{equation*}
\mathbf{T}=\mathbf{T}_{1}+\mathbf{T}_{2}+\ldots+\mathbf{T}_{n} \tag{2-12}
\end{equation*}
$$

where $n=1,2,3 \ldots N$ (and $N$ is the total number of electrons in the system). These excitation operators (T) act on the HF reference wavefunction $\left(\Psi_{\mathrm{HF}}\right)$ to generate all $n$th excited Slater determinants ( $\Phi$ ). For example,

$$
\begin{align*}
& \mathbf{T}_{1} \Psi_{\mathrm{HF}}=\sum_{i}^{\mathrm{occ}} \sum_{a}^{\mathrm{vir}} t_{i}^{a} \Phi_{i}^{a}  \tag{2-13}\\
& \mathbf{T}_{2} \Psi_{\mathrm{HF}}=\sum_{i<j}^{\mathrm{occ}} \sum_{a<b}^{\mathrm{vir}} t_{i j}^{a b} \Phi_{i j}^{a b} \tag{2-14}
\end{align*}
$$

where the expansion coefficients $t$ are referred to as amplitudes, $i$ and $j$ are indices for the occupied orbitals and $a$ and $b$ are indices for the virtual orbitals.

The resulting methods, like both the QCI and MP methods (see Section 2.3.2.4 on page 61), are size extensive. The truncations in most common usage are couple-cluster doubles (CCD), where $\mathbf{T}=\mathbf{T}_{2}$, and couple-cluster singles doubles (CCSD), where $\mathbf{T}=$ $\mathbf{T}_{1}+\mathbf{T}_{2}$. Larger expansions can only be used on relatively small systems. Accurate treatment of electron correlation has been found to require the inclusion of triple excitations. CCSD includes some contribution for triples but a full treatment of the triples (CCSDT) is found to be too computationally time consuming on most systems of chemical interest and so a perturbative correction is generally employed. This method, referred to as $\operatorname{CCSD}(\mathrm{T})$, is found to be an excellent approximation to the full CI wavefunction.

CCSD and $\operatorname{CCSD}(\mathrm{T})$ methods include a few extra terms over the corresponding QCI methods, QCISD and QCISD(T), and are therefore more complete. They require comparable amounts of computer time to generate solutions, and give similar results (except for a few cases where QCI is found to give an inferior result). For this reason, the CC methods should generally be preferred over QCI calculations.

### 2.3.2.4 Many Body Perturbation Theory (MBPT)

Perturbation theory provides another method of accounting for electron correlation, the most common form in use being Møller-Plesset (MP) perturbation theory. ${ }^{16,17}$ The notion employed in many-body perturbation theory is that the correct solution should be in some sense close to a known solution. As its name implies, perturbation theory is concerned with finding the change in the energy that occurs as the result of a slight perturbation of the system. In Møller-Plesset (MP) perturbation theory, this is achieved by writing the Hamiltonian as a sum of the Hartree-Fock Hamiltonian $\left(\boldsymbol{H}_{0}\right)$ and a perturbation $\left(\boldsymbol{H}^{\prime}\right)$,

$$
\begin{equation*}
\boldsymbol{H}(\lambda)=\boldsymbol{H}_{0}+\lambda \boldsymbol{H}^{\prime} \tag{2-15}
\end{equation*}
$$

where $\lambda$ is a dimensionless expansion parameter. The perturbed Schrödinger equation is then written,

$$
\begin{equation*}
\boldsymbol{H}(\lambda) \Psi=E(\lambda) \Psi \tag{2-16}
\end{equation*}
$$

According to Rayleigh-Schrödinger perturbation theory, ${ }^{1-4}$ the wavefunction and
energy can be expanded as a Taylor series,

$$
\begin{align*}
& \Psi(\lambda)=\Psi^{(0)}+\lambda \Psi^{(1)}+\lambda^{2} \Psi^{(2)}+\ldots  \tag{2-17}\\
& E(\lambda)=\Psi^{(0)}+\lambda E^{(1)}+\lambda^{2} E^{(2)}+\ldots \tag{2-18}
\end{align*}
$$

With $\lambda$ set to one, these expressions are truncated to various levels (e.g. second-order truncation in the energy expression includes terms to $\lambda^{2} E^{(2)}$, giving the MPn series.

The expression for the second-order energy correction, which is the first contribution to the correlation energy, involves a sum over doubly-excited determinants and can be written explicitly as,

$$
\begin{equation*}
E(\mathrm{MP} 2)=\sum_{i<j}^{\text {occ }} \sum_{a<b}^{\text {vir }} \frac{\left[\left\langle\psi_{i} \psi_{j} \mid \psi_{a} \psi_{b}\right\rangle-\left\langle\psi_{i} \psi_{j} \mid \psi_{b} \psi_{a}\right\rangle\right]^{2}}{\varepsilon_{i}+\varepsilon_{\mathrm{j}}-\varepsilon_{\mathrm{a}}-\varepsilon_{\mathrm{b}}} \tag{2-19}
\end{equation*}
$$

where $i$ and $j$ are indices for the occupied molecular orbitals, $a$ and $b$ are indices for the virtual molecular orbitals, $\psi_{n}$ are the molecular orbitals, and $\varepsilon_{n}$ are the expectation values of the Fock operator $(\boldsymbol{F})$ in the MO basis.

$$
\begin{equation*}
\varepsilon_{n}=\left\langle\psi_{n}\right| \boldsymbol{F}_{n}\left|\psi_{n}\right\rangle \tag{2-20}
\end{equation*}
$$

The MP2 energy typically includes about $80-90 \%$ of the correlation energy and is the most economical way of computing electron correlation. The third order term in the energy also only contains terms from doubly-excited determinants. Qualitatively, the MP2 contribution can be taken to describe the correlation between electron pairs while the MP3 contribution describes the interaction between pairs. ${ }^{1}$

The main problem with the MP methods is the assumption that the perturbation is small. If the underlying HF solution is poor then the correction terms are large. This in turn requires the inclusion of a greater number of terms to achieve the desired level of accuracy. Further, convergence (through inclusion of further terms in the expansion) is generally found to oscillate somewhat, such that the MP2 energy slightly overestimates the correction, MP3 leads to an underestimate of the correction and so on (Figure 2-1).


Figure 2-1. MP convergence on the energy typically oscillates to some degree.

MP methods have also been extended to apply to UHF and ROHF wavefunctions and are called UMP $n$ and ROMP $n$ (or simply RMP $n$ ). UMP $n$ is generally expected to give a higher energy than the corresponding ROMP $n$ result. However, which of the two is more accurate depends on the system being considered. Also, for various reasons UMP methods are simpler to implement than ROMP and the availability of ROMP gradients is limited to very few packages. In this work we have only used the UMP2 method.

In considering the MPn methods as a way of treating the problem of including electron correlation, the MPn methods have an advantage over CI methods in that they are size consistent. However, they are not variational.

### 2.3.2.5 The Frozen-Core Approximation (FC)

The frozen-core approximation is a specific case of a more general treatment based on the idea of forming a correlation window. In such treatments orbitals that are not expected to have a large effect on electron correlation are removed from the correlation treatment. Although the chemical core orbitals contribute significantly to the total energy, they rarely have much effect on chemical processes, which generally involve effects in the valence orbitals. The frozen-core approximation removes from the correlation treatment, the chemical core orbitals (none for hydrogen, $1 s$ for the first-row
atoms, $2 s$ and $2 p$ for the second-row atoms, etc.). This has proven to save significant time in computations without greatly affecting the accuracy of results such as relative energy calculations and is applicable to all electron correlation treatments.

### 2.4 Multireference Methods

Multireference or multiconfigurational self-consistent-field (MCSCF) methods are especially well-suited to problems like the dissociation of a bond. ${ }^{1,18,19}$ In these methods, a CI window is defined which leads to a list of determinants or configuration state functions (CSFs). As in the case of CI, the coefficients of the determinants are optimized. However, the MOs used in constructing the determinants are also included in the optimization. Allowing this orbital relaxation does not recover much of the electron correlation and it is normal to use a relatively small number of determinants in the window or active space (Figure 2-2). ${ }^{\dagger}$ The energy lowering introduced by adding this extra flexibility to the wavefunction so that a better qualitative description is possible is usually referred to as non-dynamic (or sometimes static) electron correlation. This type of correlation is the result of allowing for near-degeneracy or partial occupancy of the MOs. The rest of the correlation energy is termed dynamic. An MCSCF wavefunction that includes the minimal number of determinants to allow for the correct qualitative description recovers only the static correlation. In the extreme case, where the active space includes all MOs, the MCSCF wavefunction is equivalent to full CI and all the dynamic correlation is also recovered.

### 2.4.1 Active Space Considerations

The major problem involved in using MCSCF techniques is defining the active space. This problem has a number of facets. Firstly, a decision needs to be made about which configurations to include in the MCSCF procedure. The most common MCSCF technique in use at present is known as the complete-active-space self-consistent-field (CASSCF) method. Unlike restricted active space (RAS) methods, CASSCF includes in the SCF procedure all the proper symmetry-adapted configurations resulting from all

[^24]

Figure 2-2. MCSCF techniques define an active space and determinants resulting from excitations within this space are then included in the SCF procedure.
excitations within the active space. Secondly, based on the problem at hand, one needs to decide which MOs (both doubly-occupied and empty) are to be included in the active space. ${ }^{18}$ Deciding how many orbitals, and which orbitals, to include is not always straightforward. In order to reduce the time required to compute solutions the active space is generally chosen to be as small as possible and still give a qualitatively correct description of the region of a molecule that is being considered. For example, a simple C-C bond cleavage may be well-described by a [2,2]-CASSCF (which includes two electrons in two orbitals). However, an inappropriate selection of active space can lead to an unbalanced description and caution must be used to select the appropriate active space. One solution is to include all valence electrons (and the corresponding set of orbitals) in the active space. However, the factorial rise in the number of configurations generated from the full CI within the active space limits $[n, m]$-CASSCF to about 12 or 14 electrons/orbitals.

### 2.4.2 Including Dynamic Correlation

Because MCSCF only recovers a small proportion of the electron correlation, it is usually necessary to account for the dynamic electron correlation through either multireference configuration interaction (MRCI), which includes all single and double excitations from all reference configurations (i.e. MRCISD), or a perturbative treatment such
as second-order complete active space perturbation theory (CASPT2), which is one of a number of implementations of many-body perturbation theory as applied to MCSCF. MRCI calculations are often corrected for a contribution from the quadruples using a multireference equivalent of the Davidson correction. ${ }^{20}$ This Davidson-corrected MRCI is usually written $\mathrm{MRCI}+\mathrm{Q}$ and has the advantage of size extensivity.

### 2.5 Basis Sets

As described earlier, molecular orbitals are usually described as a linear combination of known atomic-centered functions. This approach of breaking an unknown function into a set of known functions is an approximation because the basis set is inevitably incomplete. Increasing the size and/or scope of a basis set until it approaches complete ness allows for a systematic improvement in the resulting solution (which may however be incorrect due to other approximations made in the method).

Typically, basis functions are atom-centered although this need not be true. Two types of atom-centered functions are commonly used. Slater-type orbitals ${ }^{21}$ (STOs) are characterized by an $\exp (-\zeta r)$ radial dependence. STOs are the exact solutions to the hydrogen atom problem and therefore provide a good description of atomic wavefunctions, and importantly, they reproduce the correct behavior at the nucleus, where a cusp should exist. However, gaussian-type orbitals (GTOs), which are characterized by an $\exp \left(-\zeta r^{2}\right)$ radial dependence, ${ }^{22}$ are by far the most commonly used basis functions. This is a consequence of the cost of calculating the two-electron integrals, which is much less for GTOs than for STOs. It is expected that more GTOs than STOs will be needed to properly describe a given wavefunction, both because of the incorrect behavior at the nucleus and because GTOs are expected to fall-off too rapidly at long distances from the nucleus. However, the greater efficiency of integral evaluation makes them the basis functions of choice. In order to improve the properties of an individual basis function, gaussian-type basis functions are often expressed as a linear combination of primitive gaussian functions,

$$
\begin{equation*}
\phi_{\mu}=\sum_{i} d_{\mu i} g_{i} \tag{2-21}
\end{equation*}
$$

where the coefficients $\left(d_{\mu \nu}\right)$ and the exponents $(\zeta)$ for each of the primitive gaussians $\left(g_{i}\right)$
are chosen so as to better represent a true atomic orbital. This type of basis function $\left(\phi_{\mu}\right)$, known as a contracted gaussian, is used exclusively in this work and represents a mechanism for improving the form of the basis functions without increasing the number of basis functions. Keeping the total number of basis functions to a minimum is crucial because the time to compute a given system usually rises rapidly (in some cases to the seventh power) with the number of basis functions.

### 2.5.1 Split-Valence and Mixed Basis Sets

Selecting a set of basis functions for use in describing the molecular orbitals (Equation 2-6) generally involves some degree of chemical intuition. To start with, it is recognized that hydrogen and helium have no core electrons while atoms in the first row have clearly defined core and valence electrons.

Split-valence basis sets make use of a contraction scheme like that described in Equation 2-21, and the notion of core and valence electrons, to divide up the primitives into two components. By reducing the number of basis functions used to describe the core (by grouping primitives as a single function), this scheme allows more basis functions, and therefore flexibility, to be given to the chemically important valence orbitals while keeping the total number of basis functions to a minimum. Double-split-valence or valence-double-zeta (VDZ) basis sets have one basis function per core orbital and two basis functions per valence orbital, while triple-split-valence or valence-triple-zeta (VTZ) basis sets have one basis function for each core orbital and three basis functions per valence orbital. Increasing the number of functions used to describe the valence electron distribution allows, to some extent, for radial electron correlation. Common examples of VDZ basis sets are $6-31 \mathrm{G}^{23}$ and $\mathrm{cc}-\mathrm{pVDZ}{ }^{24}$ while $6-311 \mathrm{G}^{25}$ is a wellknown example of a VTZ basis set.

Another method for reducing the total number of basis functions required in a particular calculation relies on using more basis functions per atom in the chemically important or difficult-to-describe region of the system. In these so-called mixed basis sets one might use a $6-311 \mathrm{G}$ type basis for atoms in the important region while a $6-31 \mathrm{G}$ basis is used for atoms in less important regions of the molecule. For large systems this can lead to a significant reduction in the number of basis functions for a given calcula-
tion. ${ }^{\dagger}$ Mixed basis sets must be used with caution because they may, if not properly used, bias a calculation and/or create artefacts.

### 2.5.2 Polarization and Diffuse Functions

The basic VDZ and VTZ basis sets discussed above (6-31G and 6-311G) do not allow for polarization of the electron distribution around the nucleus. The electron distribution can be polarized by interactions with other atoms. In order that the basis set is flexible enough to accurately describe any charge polarization, so-called polarization functions are employed. Polarization functions are higher angular momentum functions, which can combine with other functions in the basis set to allow charge polarization. These functions also have the effect of allowing for angular electron correlation (i.e. they allow for non-spherical distributions of the electrons about a nucleus). Basis functions of high angular momentum are very important in correlation treatments.

Diffuse functions are used to properly describe the outlying regions of the molecule. These functions are low angular momentum functions ( $s$ and $p$ ) with low exponents ( $\zeta$ ), i.e. they extend further away from the nucleus. Diffuse functions are generally needed to properly describe species with loosely bound electrons such as anions or species containing lone pairs.

### 2.5.3 Pople Basis Sets

The Pople basis sets used in this work have a straightforward nomenclature scheme. The notation $6-31 \mathrm{G}$ means that 6 primitive gaussians are used for each core orbital and two functions containing three and one primitives are used for each of the valence orbitals. In similar fashion 6-311G means that 6 primitive gaussians are used for each core orbital and three functions containing three, one and one primitives are used for each of the valence orbitals. Most Pople basis sets start with 6-31G or 6-311G and then extend them by adding diffuse (+) and/or polarization functions. Details of the nomenclature

[^25]are best explained through a number of examples:
\[

$$
\begin{array}{ll}
6-31 \mathrm{G}(\mathrm{~d})^{23} & \begin{array}{l}
\text { As for 6-31G described above with the addition of } d \text {-func- } \\
\text { tions on heavy atoms (i.e. non-hydrogen atoms). }
\end{array} \\
6-311 \mathrm{G}(\mathrm{~d}, \mathrm{p})^{25} & \begin{array}{l}
\text { The } 6-311 \mathrm{G} \text { basis with addition of } d \text {-functions on heavy } \\
\text { atoms and } p \text {-functions on hydrogen. }
\end{array} \\
6-311+\mathrm{G}(2 \mathrm{~d}, \mathrm{p})^{25,26} & \begin{array}{l}
\text { As above with the addition of diffuse ( } s \text { - and } p \text {-) functions } \\
\text { on heavy atoms and replacing the single set of } d \text {-functions } \\
\text { with two well-spaced sets of } d \text {-functions (one set closer in }
\end{array} \\
\text { and the other further out from the nucleus than the single set } \\
6-311++\mathrm{G}(3 \mathrm{df}, 2 \mathrm{p})^{25,26} \begin{array}{l}
\text { The 6-311G basis with the addition of diffuse ( } s \text { - and } p \text {-) } \\
\text { functions on all atoms, three sets of } d \text {-functions and one set } \\
\text { of } f \text {-functions on heavy atoms, and two sets of } p \text {-functions }
\end{array} \\
\begin{array}{ll}
\text { on hydrogen. }
\end{array}
\end{array}
$$
\]

These basis sets are relatively small (compared with the correlation-consistent basis sets described below) and provide considerable flexibility in the choice of basis set size. They have also been used extensively so their performance in a wide variety of molecular situations is well-known. For these reasons, we have used these basis sets almost exclusively.

### 2.5.4 Correlation-Consistent Basis Sets

The correlation-consistent basis sets ${ }^{24}$ were designed with the aim of recovering the correlation energy of the valence electrons. In essence, a step up in quality, for example, from double-zeta (DZ) to triple-zeta (TZ), involves adding one set of functions to each of the types already represented plus one set of the next higher orbital angular momentum. The smallest correlation-consistent basis set is referred to as correlation-consistent polarized valence-double-zeta (cc-pVDZ), the next is cc-pVTZ and so on. The number of contracted functions for first row atoms/hydrogen used in each of these basis sets is $[3 \mathrm{~s}, 2 \mathrm{p}, 1 \mathrm{~d} / 2 \mathrm{~s}, 1 \mathrm{p}]$ and $[4 \mathrm{~s}, 3 \mathrm{p}, 2 \mathrm{~d}, 1 \mathrm{f} / 3 \mathrm{~s}, 2 \mathrm{p}, 1 \mathrm{~d}]$. These basis sets can also be augmented by the addition of diffuse functions (aug-). In this case, one extra set of functions with the same angular momentum as those functions already represented is added but a small value is used for the exponent ( $\zeta$ ). For example, the aug-cc-pVQZ (or sim-
ply AVQZ) basis represents a [6s,5p, $4 \mathrm{~d}, 3 \mathrm{f}, 2 \mathrm{~g} / 5 \mathrm{~s}, 4 \mathrm{p}, 3 \mathrm{~d}, 2 \mathrm{f}]$ basis. Similarly, the aug-ccpV5Z (or simply AV5Z) basis represents a $[7 \mathrm{~s}, 6 \mathrm{p}, 5 \mathrm{~d}, 4 \mathrm{f}, 3 \mathrm{~g}, 2 \mathrm{~h} / 6 \mathrm{~s}, 5 \mathrm{p}, 4 \mathrm{~d}, 3 \mathrm{f}, 2 \mathrm{~g}]$ basis. We have used these basis sets where very large basis sets which approached the basis set limit were desired.

### 2.6 Hierarchy of $\boldsymbol{A b}$ Initio Methods

The relationship between basis set and electron correlation level is summarized in the Pople diagram ${ }^{3}$ shown in Figure 2-3.


Figure 2-3. Pople diagram illustrating the progression of ab initio methods to the exact solution to the time-independent Schrödinger equation (under the Born-Oppenheimer approximation).

At the top of Figure 2-3 are various treatments of electron correlation, with Har-tree-Fock, which includes no electron correlation, at the far left. Successively more accurate treatments of electron correlation are shown from left to right until FCI, which takes into account all the electron correlation within the limits of the basis set used, is reached. Going downwards, the basis sets become successively larger until an infinite basis set is reached. As we go down the diagonal of the figure, the calculations become more accurate until the exact solution to the non-relativistic Schrödinger equation is reached at the bottom right-hand corner. Since the increased accuracy also results in a
greater computational cost (often increasing in dramatic fashion), a balance must be struck between the desired accuracy and computational cost.

### 2.7 Density Functional Theory

### 2.7.1 Kohn-Sham Theory

The density functional theory (DFT) approach to solving the time-independent electronic Schrödinger equation rests on the proof by Hohenberg and Kohn ${ }^{27}$ which showed that the ground-state electronic energy is determined completely by the electron density ( $\rho$ ) with a one-to-one correspondence. Unfortunately this proof does not give any clues as to the functional form of this correspondence between energy and density.

By comparing with the equations of wave mechanics (and assuming the BornOppenheimer approximation), it is clear that the functional can be divided into three parts, a term for kinetic energy ( $E^{\mathrm{T}}[\rho]$ ), one for the Coulombic attraction between nuclei and electrons $\left(E^{\mathrm{V}}[\rho]\right)$, and one for interactions between electrons, which in turn can be readily divided (with reference to HF theory) into Coulomb ( $E^{\mathrm{J}}[\rho]$ ) and exchange ( $\mathrm{E}^{\mathrm{K}}[\rho]$ ) terms (with correlation implicitly assumed in all terms).

$$
\begin{equation*}
E[\rho]=E^{\mathrm{T}}[\rho]+E^{\mathrm{V}}[\rho]+E^{\mathrm{J}}[\rho]+E^{\mathrm{K}}[\rho] \tag{2-22}
\end{equation*}
$$

The use of DFT theory in computational quantum chemistry has been facilitated by a reformulation (by Kohn and $\mathrm{Sham}^{28}$ ) of the problem of determining the functional form of the relationship between the energy and density. In this reformulation, Kohn and Sham introduced an orbital approach by writing the approximate density $(\rho(r))$ in terms of a set of auxiliary one-electron functions (Equation 2-23).

$$
\rho(\mathbf{r})=\sum_{i=1}^{N}\left|\psi_{i}(\mathbf{r})\right|^{2}
$$

Further, the kinetic energy is calculated under the assumption of non-interacting electrons ( $E^{\mathrm{Ts}}[\rho]$ ) (a similar approach to that used in HF theory). Equation 2-22 can
then be rewritten in the more customary form,

$$
\begin{equation*}
E[\rho]=E^{\mathrm{Ts}}[\rho]+E^{\mathrm{V}}[\rho]+E^{\mathrm{J}}[\rho]+E^{\mathrm{XC}}[\rho] \tag{2-24}
\end{equation*}
$$

where $E^{\mathrm{xC}}[\rho]$ is called the exchange-correlation term and by definition includes all contributions not accounted for in the first three terms. If the density is expressed as in Equation 2-23 (and in practice the one-electron functions are rewritten as a linear combination of atomic-centered orbitals), then the functional connection between the density and the energy for the first three terms of Equation 2-24 is known and the problem is reduced to finding the functional form for $E^{\mathrm{XC}}[\rho]$. If the exact form for this term could be deduced, then an exact solution to the energy would result. Unfortunately, the exact form is not known, and what is worse, no means for systematically improving the functional is evident. As a result, all trial functionals must be compared with experimental results in order to determine their accuracy. It is in this sense that many people do not consider DFT implementations truly ab initio.

### 2.7.2 Functionals

The exchange-correlation term $\left(E^{\mathrm{XC}}[\rho]\right)$ is usually divided into separate exchange ( $E^{\mathrm{X}}[\rho]$ ) and correlation $\left(E^{\mathrm{C}}[\rho]\right)$ terms, although there is no requirement to proceed in this manner. As a first approximation, it has then been assumed that the density can be treated locally as a uniform electron gas. This leads to what is called the local density (LDA) or local spin density (LSDA) approximation. The resulting expressions for $E^{X}$ and $E^{\mathrm{C}}$ are usually referred to as Slater or simply S (because of the similarity of the expression for the exchange term with that proposed by Slater ${ }^{29}$ in his $\mathrm{X} \alpha$ method) and VWN (after Vosko, Wilks and Nusair ${ }^{30}$ for their analytic interpolation formula for the correlation energy of a uniform electron gas), respectively. The LSDA approximation, although quite simple, performs remarkably well (even though it gives relatively large errors in the exchange and correlation energies) and is generally considered to do as well as HF theory.

Improvements over the LSDA approach have come from including dependency on not only the density but also the gradient of the density in the exchange and correlation terms. Becke ${ }^{31}$ has proposed such a correction to the LSDA exchange term. The corrected exchange term is usually referred to as Becke or simply B . One of the most pop-
ular gradient-corrected functionals for the correlation term is that proposed by Lee, Yang and Parr ${ }^{32}$ and is referred to as LYP. This functional is derived from fitting four parameters to data for the helium atom. The resulting gradient-corrected DFT method (B-LYP) has proven very popular.

Further improvements in the functional result from application of what is called the adiabatic connection formula (ACF). ${ }^{1}$ This leads to methods that are termed hybrid methods because they use a suitable combination of both the exact exchange (of a system of non-interacting electrons, i.e. the HF exchange) and a functional exchange term. The most widely used hybrid method is a three-parameter method ${ }^{33}$ and is referred to as B3-LYP,

$$
\begin{equation*}
E_{\mathrm{B} 3-\mathrm{LYP}}^{\mathrm{XC}}=\left[(1-a) E_{\mathrm{S}}^{\mathrm{X}}+a E_{\mathrm{HF}}^{\mathrm{X}}\right]+b E_{\Delta \mathrm{B}}^{\mathrm{X}}+c E_{\mathrm{LYP}}^{\mathrm{C}} \tag{2-25}
\end{equation*}
$$

where $\Delta \mathrm{B}$ refers to Becke's gradient correction to the LSDA exchange and the other terms are as detailed above. The three parameters $a, b$ and $c$ are fitted to experimental data. ${ }^{\dagger}$ This method has been found to give remarkably good results in many situations (often in good agreement with $\operatorname{CCSD}(\mathrm{T})$ ) and is the DFT method used exclusively in this work. However, like all functionals, its performance is only really known for systems similar to those for which it has been tested thoroughly. As a method for exploring the structure and energies of novel molecular systems (where no experimental data are available), it is clearly inferior to methods which can be systematically improved, or at the very least it needs to be tested in such cases against high-level calculations on model systems.

If confidence can be gained in the performance of a particular functional, DFT can be a very powerful technique because the computational cost (in terms of compute time) of even the hybrid methods is considerably less than any other method that allows for electron correlation.

[^26]
### 2.8 Semi-empirical Procedures

Unlike molecular mechanics ${ }^{1}$ (MM) or force-field methods, which treat molecules as a classical system of particles whose interaction is described by a parametric force field equation, the so-called semi-empirical methods ${ }^{1}$ are based on a quantum mechanical description of the molecule. The central assumption taken in the semi-empirical methods ${ }^{34}$ is the zero differential overlap (ZDO) approximation. This approximation sets to zero all products of basis functions which depend on the same electron coordinates when located on different atoms. ${ }^{\dagger}$ The result of this is that the overlap matrix becomes a unit matrix, one-electron integrals involving three centers are set to zero, and the most numerous two-electron integrals, i.e. all three- and four-center two-electron integrals, are neglected. The remaining integrals are then replaced with parameters. It is this parametrization (usually done by comparing with experimental results) which leads to the name semi-empirical. The various semi-empirical methods differ as to how many integrals are neglected and how the parametrization is done. To further simplify the problem, all core electrons are accounted for by reducing the nuclear charge, so only valence electrons are considered. And finally, a minimum basis set (of $s$ and $p$ Slatertype functions) is employed.

The most common semi-empirical methods in use at present (and used in this work) are the methods referred to as Austin model $1^{35}$ (AM1), and modified neglect of diatomic overlap, parametric method $3^{36}$ (PM3). ${ }^{\ddagger}$

For our purposes, these methods have been used in place of MM methods to find starting geometries for novel saturated hydrocarbon cage compounds because they were found to give superior geometries at the central quaternary carbon atom; MM methods were found to predict pyramidalization and loss of symmetry at the central carbon atom while AM1 and PM3 gave geometries of correct symmetry (for closed-shell species) with errors in the bond angles within the accepted limits for these methods $\left(3.5^{\circ}\right.$ and $4.0^{\circ}$, respectively). ${ }^{1}$ Energies from these calculations have not been considered.

[^27]
### 2.9 Potential Energy Surfaces

As a consequence of the Born-Oppenheimer approximation, a chemical system is viewed as a set of nuclei moving on a potential energy surface which is (at each point in space) a solution to the electronic Schrödinger equation.

### 2.9.1 Geometry Optimization

For almost all computational problems, it is impractical to calculate the entire potential energy surface (PES). It is often more convenient to locate points of interest on the surface, which are usually stationary points. These points are characterized by all the derivatives with respect to the $3 N-6$ (for a non-linear molecule) internal coordinates being equal to zero, i.e.

$$
\begin{equation*}
\frac{\partial E}{\partial r_{i}}=0 \quad \text { where } i=1,2,3 \ldots 3 N-6 . \tag{2-26}
\end{equation*}
$$

There are two types of stationary points that of most interest to chemists. The first are local minima, corresponding to equilibrium structures. The second are first-order saddle points, which correspond to transition structures. The two types of stationary points can be distinguished by examining the eigenvalues of the Hessian, or force-constant matrix, formed by the second derivatives of the energy with respect to the coordinates,

$$
\begin{equation*}
\frac{\partial^{2} E}{\partial r_{i} \partial r_{j}} \quad \text { where } i, j=1,2,3 \ldots 3 N-6 . \tag{2-27}
\end{equation*}
$$

Equilibrium structures are characterized by having no negative eigenvalues of the Hessian, while first-order saddle points have one negative eigenvalue.

Efficient geometry optimization techniques, ${ }^{1,37,38}$ for both minima and saddle points, are implemented into the GAUSSIAN 98 system of programs. ${ }^{39}$ These allow stationary points to be located in a relatively straightforward manner for methods that have readily available analytic first derivatives (HF, B3-LYP, MP2, QCISD, etc.). These techniques employ either an approximate second-derivative matrix (which is updated using information from the first derivatives and nuclear displacements) or no second-derivative matrix. As a consequence, true minima must be verified by calculation of the second
derivatives at the optimized geometry, i.e. where the first derivatives are all zero (to some level of accuracy). The HF, B3-LYP and MP2 methods are among those implemented in GaUSSIAN 98 which allow ready optimization and characterization of the resulting stationary points.

### 2.9.2 Normal Mode Analysis

Vibrational frequencies can be calculated by diagonalization of the force constant matrix (Equation 2-27), calculated by analytic or numerical second derivatives. The resulting values are known as normal-mode frequencies. An equilibrium structure is characterized by all frequencies being real while a first-order saddle point or transition structure has one imaginary frequency.

The harmonic approximation used in the calculation of normal mode frequencies leads to systematic errors; the calculated frequencies are usually larger than experimentally determined frequencies because of anharmonic contributions to the observed frequencies and inadequacies in the calculations. ${ }^{40,41}$ Consequently, the calculated frequencies are often scaled to take into account the effects of the neglect of anharmonicity, incomplete electron correlation and basis set deficiencies. Scaling factors for many methods and basis sets (which have been determined by comparison with a wide range of experimental data) are available. ${ }^{40}$

### 2.9.3 Zero-Point Energies

Because nuclei are not a set of classical particles but form a quantum system, the true energies of a system of nuclei at any given point on the PES require a correction which takes into account the zero-point vibrational energy associated with that geometry. When determining or comparing results from MO calculations with experiment (for example heats of formation), it is necessary to add to the calculated energies a correction for this zero-point energy. The zero-point vibrational energy (ZPVE) is given by

$$
\begin{equation*}
\mathrm{ZPVE}=\frac{1}{2} h \sum_{i} v_{i} \tag{2-28}
\end{equation*}
$$

where $v_{\mathrm{i}}$ are the scaled vibrational frequencies in appropriate units. It should be noted
that the optimum scaling factors for frequencies and zero-point energies often differ. ${ }^{40}$

### 2.10 Molecular Properties

### 2.10.1 Symmetry

Although symmetry is not strictly a molecular property it is indeed a geometric property of many molecular systems. We have found in this work that the use of molecular symmetry wherever possible has been of tremendous advantage. Because many computational algorithms are able to make use of molecular symmetry (for example this leads to block diagonalization of the overlap matrix), this can significantly reduce the time needed for calculations on a system. In principle, compute time is reduced by a factor of two for each order of symmetry (so $D_{2}$ symmetry reduces the computational cost by a factor of eight). In practice, sparse matrix techniques and other algorithmic improvements give better savings in compute time for molecules with little or no symmetry so the gain from making use of symmetry is somewhat less but it can still be quite considerable for high symmetry structures like dimethanospiro[2.2]octaplane (2-1). ${ }^{\dagger}$

### 2.10.2 Strain Energies

The concept of strain is inexact. However, it is extremely useful conceptually. ${ }^{42}$ It generally refers to the increase in energy of a molecule that results from structural deviations from the 'norm'. The effects of strain are generally discussed in terms of bond angle and bond length distortions, torsional effects, non-bonded interactions and so on. All of these effects refer to structural variation that can be seen to raise the energy of a molecule. The main problem with a rigorous definition of strain is that a reference point must be chosen. The usual definition of strain in hydrocarbon systems takes the molecules methane, ethane, propane, isobutane and neopentane to be strain-free. Essentially this defines the reference energy for methane and primary through to quaternary carbon centers. This definition can be extended to include further compounds (for example ole-

[^28]fins) by defining further reference compounds (in the case of simple olefins one would need to include propene and 2-methylpropene).

Such a definition of strain for saturated hydrocarbons, in which the strain energy is given relative to the simple hydrocarbons (listed above), leads to a direct method for the calculation of strain energies (SE). ${ }^{43}$ This involves writing a homodesmic reaction in which the target molecule is broken down into the unstrained hydrocarbons. For example,

$$
\begin{equation*}
\text { spiropentane }+6 \text { ethane } \longrightarrow \text { neopentane }+4 \text { propane } \tag{2-29}
\end{equation*}
$$

The associated total strain energy ( $S E$ ) of spiropentane is the negative of the enthalpy $\left(-\Delta H^{\text {homod }}\right)$ of the resulting reaction (Equation 2-29). Such a reaction is termed homodesmic because the number of primary, secondary, tertiary and quaternary carbon atoms and the number of bonds between atoms of the same hybridization on each side of the reaction are balanced. The aim in such a scheme is to maximize the cancellation of errors in the calculation of the enthalpy change. In order to obtain a true reaction enthalpy, the calculated energies are corrected for the ZPVE (as described above). The resulting entropies at 0 K are corrected to 298 K using the formula,

$$
\begin{array}{cl}
\Delta H(T)= & H_{\text {trans }}(T)+H_{\text {rot }}(T)+\Delta H_{\mathrm{vib}}(T)+R T \\
\text { where, } \quad & H_{\text {trans }}(T)=\frac{3}{2} R T \\
H_{\mathrm{rot}}(T)=\frac{3}{2} R T \text { (RT for linear molecules) } \\
\Delta H_{\mathrm{vib}}(T)=N h \sum_{i} \frac{v_{i}}{\left(e^{h v_{i} / k T}-1\right)} \tag{2-33}
\end{array}
$$

assuming ideal gas behavior ( $N$ is Avogadro's number and $h$ is Planck's constant). As with calculation of the ZPVE, scaled, calculated frequencies are used to calculate $\Delta H_{\text {vib }}(T)$, but a scale factor appropriate for reproducing temperature corrections is used.

Strain energies calculated in this way represent the total strain energy (SE) of a molecule. In this work we have found it useful in some cases to calculate strain energies
that are more localized to a certain region of a molecule by deducting the strain energy inherent in the remainder of the molecule. Such schemes are explained in detail where used.

### 2.10.3 Heats of Formation

Heats of formation allow for the relative energies of molecules to be compared in an absolute sense. They also allow for comparison between calculation and experiment. The method used for the calculation of heats of formation in this work is based on that of Schulman and Disch. ${ }^{43}$ The heat of formation is determined from the calculated enthalpy of the same homodesmic reactions used to calculate the total strain energy (e.g. Equation 2-29) together with the experimental heats of formation of the unstrained hydrocarbons used to balance the homodesmic reactions. Again using the example of spiropentane, the expression for the calculated heat of formation (at 298 K ) can be written,

$$
\begin{equation*}
\Delta H_{\mathrm{f}}^{\text {calc }}(\text { spiro })=S E^{\text {calc }}+\Delta H_{\mathrm{f}}^{\exp }(\text { neo })+4 \Delta H_{\mathrm{f}}^{\text {exp }}(\text { pro })-6 \Delta H_{\mathrm{f}}^{\exp }(\text { eth }) \tag{2-34}
\end{equation*}
$$

where $S E^{\text {calc }}$, the total strain energy, is calculated as described above, and the labels neo, pro and eth refer to neopentane, propane and ethane, respectively.

### 2.10.4 Proton Affinities

Knowledge of the energetics of the reaction in which a molecule attracts a proton has many applications in chemistry. Very strong bases can be used in reactions as proton sinks or to remove a proton from a molecule to enable further reactivity. One way of expressing this property is as a gas-phase proton affinity (PA). Gas-phase proton affinities $(P A)$ can be determined as the negative of the enthalpy of the protonation reaction, ${ }^{44}$

$$
\begin{equation*}
\mathrm{B}_{(\mathrm{g})}+\mathrm{H}_{(\mathrm{g})}^{+} \longrightarrow \mathrm{BH}_{(\mathrm{g})}^{+} \tag{2-35}
\end{equation*}
$$

where B is the target molecule. As with other calculations of enthalpy changes, the $a b$ initio total energies need to be corrected for ZPVE and to 298 K . The resulting calculated PAs can be compared with tabulations of experimentally determined gas-phase proton affinities.

### 2.10.5 Ionization Energies

The first adiabatic ionization energy (IE) indicates the ease or difficulty of removing a single electron from a molecule. Knowledge of the strength with which electrons are bound to a molecule is important in designing systems where electron transfer is facilitated. Adiabatic ionization energies are calculated as the negative of the enthalpy change in the following reaction,

$$
\begin{equation*}
\mathrm{B}_{(\mathrm{g})} \longrightarrow \mathrm{B}_{(\mathrm{g})}^{+} \tag{2-36}
\end{equation*}
$$

where $B$ is the molecule in question. If $B$ is a ground-state closed-shell system then $\mathrm{B}^{+}$ will be an open-shell doublet state and will need to be treated with a method suitable for dealing with open-shell systems. In our calculations of ionization energies we have used the UMP2 method. Correction of the energy difference for ZPVE and to 298 K allows for comparison against experimentally determined IEs.

### 2.11 Computational Resources

### 2.11.1 Software

The main software package used for the $a b$ initio calculations in this work was GAUSSIAN 98. ${ }^{39}$ The Spartan system of programs ${ }^{45}$ was used extensively for visualization purposes and for initial structure design studies. This initial design stage usually involved making use of SPARTAN's semi-empirical algorithms (in almost all cases AM1 was preferred). Calculations employing higher-level correlated techniques ( $\operatorname{CCSD}(\mathrm{T})$, MRCI, etc.) were carried out using the MoLPRO system of programs. ${ }^{46}$ One of the two numerical MP2 second derivatives reported here was calculated using GAMESS. ${ }^{47}$

### 2.11.2 Hardware

The majority of calculations in this work were performed using the Fujitsu VP2200, VPP-300, SUN E4500 and SGI PowerChallenge of the Australian National University Supercomputing Facility (ANUSF) and various IBM RS/6000 workstations situated at the Research School of Chemistry, Australian National University. A large proportion of the B3-LYP calculations were run on the IBM SP systems at the Maui High Performance Computing Center (MHPCC).

### 2.11.3 Resource Usage

In the discussion so far, we have alluded on occasion to the cost in terms of computer time required to generate solutions for the various methods. Generating solutions can become computationally very expensive either for very high-level correlated methods (like CCSDT), or when the number of basis functions employed becomes large, either through use of a large basis set or when large systems (with many atoms) are being examined. For large systems (like, for example, the spiroalkaplanes (2-2)) even methods which we have indicated as being relatively cheap, like MP2, can become computationally expensive. As a result, whether or not a method can be used, or a system can be studied, often depends on the efficient implementation of a method on a particular computer platform. The algorithms used, and the implementation of those algorithms, on each computer platform, can have a major effect on what problems can be attempted with any given hardware. To the pure theoretician the matter of implementation may seem a trivial matter of writing computer code. In practise this is anything but simple. The task of implementation is complicated in part because their may not be a unique way of defining a method (e.g. perturbation methods applied to MCSCF). Further complications arise from the need or desire to tune or optimize the code to get maximum performance from the available hardware. Thus the rapid pace of hardware development acts as both a boon and a bane; the increased performance of new generations of computer technology allow much larger problems to be examined but the introduction of new hardware designs makes carefully-tuned codes rapidly obsolete.

A further problem that becomes obvious as larger systems are considered is that Moore's Law (see Section 2.1 on page 51) only predicts a doubling of processing speed for each year or so, while the computational cost of most methods increases with a much higher power. For example, the compute time to solve MP2 gradients formally increases with the order $\mathrm{ON}^{4}$, where O is the number of occupied orbitals and N is the number of basis functions, while a $\operatorname{CCSD}(\mathrm{T})$ energy calculation scales as $\mathrm{O}^{3} \mathrm{~V}^{4}$, where V represents the number of virtual orbitals. ${ }^{48}$ This means that the size of systems being examined with these correlated techniques can only increase gradually from year-toyear.

The introduction of linear scaling techniques for HF and DFT methods, such as those based on the use of fast multipole methods (FMM), promises some relief from the
tyranny of exponential scaling in compute times. However, these methods all appear to introduce considerable up-front cost and the break-even point is usually somewhere beyond 50 atoms. ${ }^{\dagger}$ Further, DFT is the only method to date which includes electron correlation and which can be treated with these techniques. This suggests a bright future for DFT, especially if a means of systematically improving functionals can be derived.

Attempts to study relatively large systems (in this work molecules as large as 25 carbon atoms and 24 hydrogens have been considered in detail using correlated ab initio techniques) involve considerable effort in choosing the most efficient algorithms and maximizing usage of the available compute time. As an example, even the modest increase in molecular size from spiro[2.2]octaplane $\left(\mathrm{C}_{21} \mathrm{H}_{24}\right)$ (2-2) to dimethanospiro[2.2]binonaplane $\left(\mathrm{C}_{25} \mathrm{H}_{24}\right)(\mathbf{2 - 3})$, an increase of exactly four carbon atoms, leads to an increase in the compute time for an MP2/6-31G(d) gradient calculation (see Section 2.12 on page 84) in $C_{1}$ symmetry using GaUSSIAN $98^{39}$ (which we find to be the most efficient package for single-processor MP2 calculations) of about $100 \%$, i.e. a doubling of the compute time. This equates to an extra 5 days of compute time on an RS/ 6000 processor or 15 hours on a single VPP-300 processor.


2-1


2-2


2-3

The full ramifications of such large compute times can be seen when one considers the time required to compute the MP2 second derivatives for dimethanospiro[2.2]octaplane (2-1) and dimethanospiro[2.2]binonaplane (2-3). These calculations were done numerically (using a double differencing method) rather than analytically for two reasons. Firstly, the analytic second derivatives can not be restarted during the calculation

[^29]so a power failure or forced 'down-time' would mean restarting the computation from the beginning. Secondly, the amount of storage space required for integrals and to do the transformation would be on the order of 60 GB . Although most modern computer architectures (64-bit platforms) can handle files of this size, there are no packages that we know of that allow such large file storage (the limit in GAUSSIAN $98^{39}$ appears to be 20 GB which is a limitation in the algorithms for storing and retrieving data). The numerical second derivatives for dimethanospiro[2.2]binonaplane (2-3) took 1800 CPU hours ( 60 steps at 30 hours/step) on a single VPP-300 processor using Gaussian 98. This equates to 75 days of compute time and required 3 months to complete! The time to complete such a calculation on an RS/6000 is staggering (over 1 year). Clearly, such time-consuming calculations can only be accomplished in limited numbers. The second derivatives for dimethanospiro[2.2]octaplane (2-1) were computed in parallel over 128 nodes on a CRAY-T3E using the GAMESS package. ${ }^{47}$ This calculation required 30,000 node-hours to compute but because it was running over 128 nodes the total time to completion was around 10 days. The power of parallel execution becomes immediately obvious. Parallel computers represent a challenge to traditional software packages like GAUSSIAN $98^{39}$ which were originally designed and optimized for single-processor execution. Parallel computers, and the soon-to-be massively parallel systems, will offer further relief from the scaling problems inherent in treating electron correlation (other than by DFT). However, suitable algorithms for methods beyond MP2 are still in development.

Another aspect of performance that is critical is the algorithms used to implement a given method and how well this implementation is tuned to particular hardware. One example from the current study that illustrates this quite dramatically is a comparison between the times required to compute a B3-LYP/AV5Z energy for methane ( $T_{\mathrm{d}}$ symmetry) using GAUSSIAN $98^{39}$ and the $\operatorname{CCSD}(\mathrm{T}) /$ AV5Z energy for the same structure with Molpro. ${ }^{46}$ Considering that $\operatorname{CCSD}(\mathrm{T})$ is known to scale formally as $\mathrm{O}^{3} \mathrm{~V}^{4}$ (where O and V represent the number of occupieds and virtuals) ${ }^{48}$ while B3-LYP should only scale as $\mathrm{N}^{4}$ (in the worst case) (where N is the number of basis functions), it is surprising to find that the two calculations (which each use 447 basis functions) required roughly equal compute time of 4 hours on a single SGI PowerChallenge R10000 processor. Similarly, a $\operatorname{CCSD}(\mathrm{T}) / \mathrm{AVTZ}$ energy (total basis functions is reduced to 138) for
this same structure calculated using MoLPRO and GAUSSIAN $98^{39}$ required 2 and 44 minutes, respectively (GAUSSIAN 98 is not making good use of symmetry, but even allowing for this MOLPRO performs remarkably well). As systems get larger and total compute time becomes very large (as seen above) these differences in the implementation can have drastic effects on the type of calculations that can be accomplished. Welldesigned algorithms can allow calculations on today's computer hardware that otherwise could not be accomplished for years to come.

One final example of the CPU times required for calculations on molecules like the alkaplanes is in order. In this case we have chosen to examine the time to complete calculations of the cheapest method available to us which still includes the effects of correlation. A GAUSSIAN 98 UB3-LYP/6-31G(d) energy and gradient calculation (a single step in an optimization) with no symmetry on dimethanospiro[2.2]octaplane $\left(\mathrm{C}_{23} \mathrm{H}_{24}\right)$ (2-1) requires 3 node-days (or 18 hours over 4 nodes) on a SUN Enterprise 4500 (an SMP machine with 400 MHz UltraSPARC II processors). But for structures with high symmetry $\left(D_{2}\right)$, the time for this calculation is reduced to only 10 node-hours. Since typical optimizations to locate a local minimum will require at least six steps (and frequently more), it is clear that even the least-demanding calculations (in terms of compute time) are problematic when no symmetry is present. Further, optimizations to locate transition structures (which are frequently of low symmetry and often require the use of second derivatives to aid in the search) are clearly prohibitive for molecules of this size at this time.

The most extensively used code in this work has been the GAUSSIAN 98 package. ${ }^{39}$ GAUSSIAN has been developed over many years since the early days of its inception in the research laboratories of John Pople at Carnegie-Mellon University. This package has proven to have the most efficient implementations for all HF, DFT and MP2 calculations for systems of the type examined in this work and for use on the non-parallel hardware platforms, where we have had most compute time. In particular, the GaUSSIAN implementation of algorithms for MP2 energies and gradients on the Fujitsu VPP-300 is very efficient both in terms of I/O bandwidth usage and CPU time.

### 2.12 Notation and Abbreviations

Throughout this work standard notation for describing a particular method will be
used. There are two types of notation used to describe the details of a computational level. In general, this requires specification of the method and basis set used.

Method / Basis
This notation is used when geometries are being considered, or when the energy and geometry have been computed at the same level. When energies have been calculated at a geometry optimized at a different level of theory (generally a lower level), the following notation is used,

EnergyMethod / EnergyBasis // GeometryMethod / GeometryBasis
The abbreviations used for the various methods throughout this work are listed below.

| HF | Hartree-Fock theory |
| :--- | :--- |
| B3-LYP | Becke's three parameter density functional model (B3), <br> incorporating the Lee, Yang and Parr (LYP) correction to <br> the correlation energy |
| MP2 |  |
| second order Møller-Plesset perturbation theory |  |
| couple cluster singles doubles with a perturbative correc- |  |
| $[n, m]-C A S$ | tion for triples |
| $[n, m]-C A S P T 2$ | asing $n$ electrons in $m$ orbitals |
| the many-body perturbation algorithm as applied to a com- |  |

A prefix "U" indicates that the underlying wavefunction is of the UHF type for open-shell systems. All open-shell systems in this work treated with the HF, B3-LYP, MP2 and $\operatorname{CCSD}(\mathrm{T})$ methods fall into this category unless otherwise noted. The abbreviations "(fc)" or "(full)" written after a method (e.g. CCSD(T)(full)) indicates whether or not the frozen-core approximation has been used.

### 2.13 Units

All bond lengths are given in Ångstrom and all angles in degrees. All relative energies are in $\mathrm{kJ} \mathrm{mol}^{-1}$. Where quoted, total energies are reported in Hartree.

## References

(1) Jensen, F. Introduction to Computational Chemistry; John Wiley \& Sons: Chichester, 1998, and references therein.
(2) Szabo, A.; Ostlund, N. S. Modern Quantum Chemistry: Introduction to Advanced Electronic Structure Theory; Macmillan: New York, 1982.
(3) Hehre, W. J.; Radom, L.; Schleyer, P. v. R.; Pople, J. A. Ab Initio Molecular Orbital Theory; Wiley: New York, 1986.
(4) Levine, I. N. Quantum Chemistry, 4th ed.; Prentice-Hall: Englewood Cliffs, 1991.
(5) Schrödinger, E. Phys. Rev. 1926, 28, 1049.
(6) Schaefer, H. F. Craig Lecture Series; ANU, 1999.
(7) Born, M.; Oppenheimer, J. R. Ann. Physik 1927, 84, 457.
(8) Slater, J. C. Phys. Rev. 1929, 34, 1293.
(9) (a) Roothaan, C. C. J. Rev. Mod. Phys. 1951, 23, 161; (b) Hall, G. G. Proc. Roy. Soc. Lon$\operatorname{don} A$ 1951, 205, 541.
(10) (a) Hartree, D. R. Proc. Cam. Phil. Soc. 1928, 24, 89; (b) Hartree, D. R. Proc. Cam. Phil. Soc. 1928, 24, 111; (c) Hartree, D. R. Proc. Cam. Phil. Soc. 1928, 24, 246.
(11) Fock, V. Z. Z. Phys. 1930, 61, 126.
(12) Pople, J. A.; Nesbet, R. K. J. Chem. Phys. 1954, 22, 571.
(13) See for example, Evangelisti, S.; Bendazzoli, G. L.; Ansaloni, R.; Durì, F.; Rossi, E. "A one billion determinant full CI benchmark on the CRAY T3D" Chem. Phys. Lett. 1996, 252, 437.
(14) Pople, J. A.; Head-Gordon, M.; Raghavachari, K. "Quadratic configuration interaction. A general technique for determining electron correlation energies" J. Chem. Phys. 1987, 87, 5968.
(15) (a) Cizek, J. "Use of the cluster expansion and the technique of diagrams in calculations of correlation effects in atoms and molecules," Advan. Chem. Phys. 1969, 14, 35-89; (b) Cizek, J.; Paldus, J.; Sroubkova, L. "Cluster expansion analysis for delocalized systems," Int. J. Quantum Chem. 1969, 3, 149-67; (c) Cizek, J. "Correlation problem in atomic and molecular systems. Calculation of wave function components in Ursell-type expansion using quantum-field theoretical methods," J. Chem. Phys. 1966, 45, 4256-66.
(16) Møller, C.; Plesset, M. S. Phys. Rev. 1934, 46, 618.
(17) (a) Krishnan, R.; Pople, J. A. "Approximate fourth-order perturbation theory of the electron correlation energy" Int. J. Quantum Chem. 1978, 14, 91; (b) Krishnan, R.; Frisch, M.
J.; Pople, J. A. "Contribution of triple substitutions to the electron correlation energy in fourth order perturbation theory" J. Chem. Phys. 1980, 72, 4244.
(18) Schmidt, M. W.; Gordon, M. S. "The construction and interpretation of MCSCF wavefunctions," Ann. Rev. Phys. Chem. 1998, 49, 233-266.
(19) Bally, T.; Borden, W. T. "Calculations on open-shell molecules: A beginner's guide" in Reviews in Computational Chemistry; Lipkowitz, K. B. and Boyd, D. B., Ed.; WileyVCH: New York, 1999; Vol. 13, pp 1-97.
(20) (a) Langhoff, S. R.; Davidson, E. R. "Configuration interaction calculations on the nitrogen molecule," Int. J. Quantum Chem. 1974, 8, 61-72; (b) Bauschlicher, C. W., Jr.; Langhoff, S. R.; Taylor, P. R.; Handy, N. C.; Knowles, P. J. "Benchmark full configurationinteraction calculations on HF and $\mathrm{NH}_{2}$," J. Chem. Phys. 1986, 85, 1469-74.
(21) Slater, J. C. Phys. Rev. 1930, 36, 57.
(22) Boys, S. F. Proc. Roy. Soc. London A 1950, 26, 57.
(23) Ditchfield, R.; Hehre, W. J.; Pople, J. A. "Self-consistent molecular-orbital methods. IX. Extended gaussian-type basis for molecular-orbital studies of organic molecules," $J$. Chem. Phys. 1971, 54, 724-8.
(24) (a) Dunning, T. H. "Gaussian basis sets for use in correlated molecular calculations. I. The atoms boron through neon and hydrogen," J. Chem. Phys. 1989, 90, 1007-1023; (b) Kendall, R. A.; Dunning, T. H.; Harrison, R. J. "Electron affinities of the first-row atoms revisited. Systematic basis sets and wave functions," J. Chem. Phys. 1992, 96, 6796-6806; (c) Woon, D. E.; Dunning, T. H. "Gaussian basis sets for use in correlated molecular calculations. III. The atoms aluminum through argon," J. Chem. Phys. 1993, 98, 1358-1371.
(25) Krishnan, R.; Binkley, J. S.; Seeger, R.; Pople, J. A. "Self-consistent molecular orbital methods. XX. A basis set for correlated wave functions," J. Chem. Phys. 1980, 72, 650-4.
(26) Frisch, M. J.; Pople, J. A.; Binkley, J. S. "Self-consistent molecular orbital methods. 25. Supplementary functions for gaussian basis sets," J. Chem. Phys. 1984, 80, 3265-3269.
(27) Hohenberg, P.; Kohn, W. Phys. Rev. B 1964, 136, 864.
(28) Kohn, W.; Sham, L. J. Phys. Rev. A 1965, 140, 1133.
(29) Slater J. C. Phys. Rev. 1951, 81, 385.
(30) Vosko, S. H.; Wilk, L.; Nusair, M. "Accurate spin-dependent electron liquid correlation energies for local spin density calculations: a critical analysis," Can. J. Phys. 1980, 58, 1200-1211.
(31) Becke, A. D. "Density-functional exchange-energy approximation with correct asymptotic behavior," Phys. Rev. A: Gen. Phys. 1988, 38, 3098-3100.
(32) Lee, C.; Yang, W.; Parr, R. G. "Development of the Colle-Salvetti correlation-energy formula into a functional of the electron density," Phys. Rev. B 1988, 37, 785-789.
(33) The original three-parameter hybrid was suggested by Becke, (a) Becke, A. D. "Densityfunctional thermochemistry. III. The role of exact exchange," J. Chem. Phys. 1993, 98, 5648-5652. A modified version has been implemented in the GaUSSIAN programs, (b)

Stephens, P. J.; Devlin, F. J.; Chabalowski, C. F.; Frisch, M. J. "Ab initio calculation of vibrational absorption and circular dichroism spectra using density functional force fields," J. Phys. Chem. 1994, 98, 11623-11627.
(34) Zerner, M. C. "Semiempirical molecular orbital methods," Rev. Comput. Chem. 1991, 2, 313-365.
(35) Dewar, M. J. S.; Zoebisch, E. G.; Healy, E. F.; Stewart, J. J. P. "Development and use of quantum mechanical molecular models. 76. AM1: a new general purpose quantum mechanical molecular model," J. Am. Chem. Soc. 1985, 107, 3902-3909.
(36) (a) Stewart, J. J. P. "Optimization of parameters for semi-empirical methods. II. Applications," J. Comput. Chem. 1989, 10, 221-264; (b) Stewart, J. J. P. "Optimization of parameters for semi-empirical methods. I. Method," J. Comput. Chem. 1989, 10, 209-220.
(37) Schlegel, H. B. "Geometry optimization on potential energy surfaces" in Modern Electronic Structure Theory, Part I; D. R. Yarkony, Ed.; World Scientific Publishing: Singapore, 1995; Vol. 2, pp 459-500.
(38) Peng, C. Y.; Ayala, P. Y.; Schlegel, H. B.; Frisch, M. J. "Using redundant internal coordinates to optimize equilibrium geometries and transition states," J. Comp. Chem. 1996, 17, 49-56.
(39) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Zakrzewski, V. G.; Petersson, G. A.; Montgomery, J., J. A.; Stratmann, R. E.; Burant, J. C.; Dapprich, S.; Millam, J. M.; Daniels, A. D.; Kudin, K. N.; Strain, M. C.; Farkas, O.; Tomasi, J.; Barone, V.; Cossi, M.; Cammi, R.; Mennucci, B.; Pomelli, C.; Adamo, C.; Clifford, S.; Ochterski, J.; Petersson, G. A.; Ayala, P. Y.; Cui, Q.; Morokuma, K.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Cioslowski, J.; Ortiz, J. V.; Baboul, A. G.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Challacombe, M.; Gill, P. M. W.; Johnson, B. G.; Chen, W.; Wong, M. W.; Andres, J. L.; Gonzalez, C.; Head-Gordon, M.; Replogle, E. S.; Pople, J. A. GAUSSIAN 98, Revision A.7; Gaussian, Inc.: Pittsburgh PA, 1998.
(40) (a) Pople, J. A.; Scott, A. P.; Wong, M. W.; Radom, L. "Scaling factors for obtaining fundamental vibrational frequencies and zero-point energies from HF/6-31G* and MP2/631G* harmonic frequencies," Isr. J. Chem. 1993, 33, 345; (b) Scott, A. P.; Radom, L. "Harmonic vibrational frequencies: an evaluation of Hartree-Fock, Møller-Plesset, quadratic configuration interaction, density functional theory, and semi-empirical scale factors," J. Phys. Chem. 1996, 100, 16502-16513.
(41) Schaefer, H. F.; Thomas, J. R.; Yamaguchi, Y.; DeLeeuw, B. J.; Vacek, G. "The chemical applicability of standard methods in ab initio molecular quantum mechanics" in Modern Electronic Structure Theory, Part I; D. R. Yarkony, Ed.; World Scientific Publishing: Singapore, 1995; Vol. 2, pp 3-54.
(42) (a) Schleyer, P. v. R.; Williams, J. E.; Blanchard, K. R. "The evaluation of strain in hydrocarbons. The strain in adamantane and its origin," J. Am. Chem. Soc. 1970, 92, 23772386; (b) Liebman, J. F.; Greenberg, A. "A survey of strained organic molecules," Chem. Rev. 1975, 76, 311-365; (c) Greenberg, A.; Liebman, J. F. Strained Organic Molecules; Academic: New York, 1978; (d) Wiberg, K. B. "The concept of strain in organic chemis-
try," Angew. Chem., Int. Ed. 1986, 25, 312-322; (e) Wiberg, K. B.; Bader, R. F. W.; Lau, C. D. H. "Theoretical analysis of hydrocarbon properties. 2. Additivity of group properties and the origin of strain energy," J. Am. Chem. Soc. 1987, 109, 1001-1012; (f) Haufe, G.; Mann, G. Chemistry of alicyclic compounds. Structure and chemical transformations; Elsevier: Amsterdam, 1989; (g) Halton, B. "Strain in organic chemistry: a perspective," in Advances in strain in organic chemistry; Halton, B., Ed.; JAI Press: London, 1991; Vol. 1, pp 1-17.
(a) Schulman, J. M.; Sabio, M. L.; Disch, R. L. "Structure and energetics of [4.4.4.4]fenestrane," J. Am. Chem. Soc. 1983, 105, 743-744; (b) Schulman, J. M.; Disch, R. L. "Ab initio heats of formation of medium-sized hydrocarbons. The heat of formation of dodecahedrane," J. Am. Chem. Soc. 1984, 106, 1202-1204; (c) Disch, R. L.; Schulman, J. M.; Sabio, M. L. "Ab initio heats of formation of medium-sized hydrocarbons. 2. Use of second-order correlation energies," J. Am. Chem. Soc. 1985, 107, 1904-1906; (d) Disch, R. L.; Schulman, J. M. "Ab initio heats of formation of medium-sized hydrocarbons. 7. The [n]prismanes," J. Am. Chem. Soc. 1988, 110, 2102-2105; (e) Schulman, J. M.; Disch, R. L. "A theoretical study of pagodane and related systems," J. Mol. Struct., Theochem. 1995, 358, 51-54; (f) Disch, R. L.; Schulman, J. M. "Heat of formation of dodecahedrane," J. Phys. Chem. 1996, 100, 3504-3506.
(44) (a) Smith, B. J.; Radom, L. "Assigning absolute values to proton affinities - A differentiation between competing scales," J. Am. Chem. Soc. 1993, 115, 4885-4888; (b) Smith, B. J.; Radom, L. "An evaluation of the performance of density functional theory, MP2, MP4, F4, G2(MP2) and G2 procedures in predicting gas-phase proton affinities," Chem. Phys. Lett. 1994, 231, 345-351; (c) Smith, B. J.; Radom, L. "Calculation of proton affinities using the G2(MP2,SVP) procedure,"J. Phys. Chem. 1995, 99, 6468-6471.
(45) Spartan V5.1, Wavefunction Inc., 18401 Von Karman, Suite 370, Irvine, CA, 92715, 1998.
(46) MOLPRO is a package of ab initio programs written by H.-J. Werner and P. J. Knowles with contributions from J. Almlöf, R. D. Amos, A. Berning, D. L. Cooper, M. J. O. Deegan, A. J. Dobbyn, F. Eckert, S. T. Elbert, C. Hampel, R. Lindh, W. A. Lloyd, W. Meyer, A. Nicklass, K. Peterson, R. Pitzer, A. J. Stone, P. R. Taylor, M. E. Mura, P. Pulay, M. Schütz, H. Stoll and T. Thorsteinsson.
(47) Schmidt, M. W.; Baldridge, K. K.; Boatz, J. A.; Elbert, S. T.; Gordon, M. S.; Jensen, J. H.; Koseki, S.; Matsunaga, N.; Nguyen, K. A.; Su, S. J.; Windus, T. L.; Dupuis, M.; Montgomery, J. A."General atomic and molecular electronic structure system," J. Comput. Chem. 1993, 14, 1347-1363.
(48) Schlegel, H. B.; Frisch, M. J. "Computational bottlenecks in molecular orbital calculations" in Theoretical and Computational Models for Organic Chemistry, Formosinho, S. J. et al. Eds., Kluwer: Amsterdam, 1991, pp 5-33.

## Chapter 3 <br> Hemialkaplanes Pyramidal Carbon

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### 3.1 Introduction

Various schemes for applying considerable distortion at a tetracoordinate carbon atom through structural means alone were discussed in Chapter 1. An example is provided by the paddlanes (3-I), a group of hypothetical molecules which were designed with the aim of achieving a very high degree of distortion at a pair of tetracoordinate bridgehead-carbon atoms. Another example is bowlane (3-1) which, unlike the paddlanes, has only a single highly-distorted tetracoordinate carbon atom and might therefore be a more accessible target. Bowlane can be thought of as a kind of half-paddlane. It can also be thought of as half an alkaplane (3-II) or a hemialkaplane (3-III). Bowlane


3-I


3-1
(3-1) was found by McGrath, Radom and Schaefer ${ }^{1}$ to be a local minimum on the
$\mathrm{C}_{13} \mathrm{H}_{20}$ potential energy surface and to contain a highly-flattened tetracoordinate carbon atom.

In Chapter 4 we examine the alkaplane (3-II) and spiroalkaplane (3-IV) families of molecules as systems potentially containing a planar-tetracoordinate carbon atom. The alkaplanes (or spiroalkaplanes) may be regarded as neopentane-type (or spiropentanetype) units capped on both the top and bottom by cycloalkane moieties. These molecules are found ${ }^{2-4}$ to show remarkable flattening at the central tetracoordinate carbon atom (for details see Chapter 4). ${ }^{5}$ In this chapter we examine the situation in which there is capping on one side only. The resultant molecules are termed hemialkaplanes (3-III) and hemispiroalkaplanes (3-V). We present detailed results for three hemialkaplanes (see 3-III and 3-1-3-3), of which hemioctaplane (3-1) (which has also been called bowlane) has already been the subject of theoretical study, ${ }^{1}$ and three hemispiroalkaplanes (see 3-V and 3-4-3-6), members of a new class of saturated hydrocarbons. ${ }^{\dagger}$ All the hemispiroalkaplanes are predicted to have an apical, pyramidal-tetracoordinate carbon atom.


There has been much interest in pyramidal-tetracoordinate carbon since the pro-

[^30]

3-4 $\left(C_{2 v}\right)$


3-5 $\left(C_{2 v}\right)$


3-6 $\left(C_{2 v}\right)$
posal by Liebman and Greenberg ${ }^{6}$ that the tetracoordinate, central carbon of all-trans[4.4.4.4]fenestrane (3-7) should prefer a pyramidal over a planar arrangement, a contention supported by model calculations on methane (see Section 1.2 on page 4 and Section 1.3 on page 6). ${ }^{7}$ Keese, Agosta and others ${ }^{8}$ have had much success in synthesiz-


3-VI $(k, l, m, n \geq 4)$


3-VII ( $l, m, n \geq 3$ )
ing larger fenestranes (3-VI) - the archetypal molecule being the all-cis-[5.5.5.5]fenestrane (3-8) and the smallest, and most strained, example being a derivative of the all-cis isomer of [4.4.4.5]fenestrane (3-9) ${ }^{8}$ — but so far all isomers of [4.4.4.4]fenestrane have proven elusive (for more information regarding the larger fenestranes see Section 1.5.2 on page 24). More recently, Wiberg has had considerable success in synthesizing


3-7 $\left(C_{2 v}\right)$


3-8 ( $D_{2 d}$ )


3-9 $\left(\mathrm{R}=\mathrm{COOCH}_{3}\right.$
smaller molecules with highly-distorted geometries at a tetracoordinate carbon, that can be viewed as either bridged spiropentanes or [3.n.3]fenestranes (3-VII). ${ }^{9}$ He has found evidence for a number of the smallest bridged spiropentanes, including both a
[3.4.3]fenestrane derivative (3-10), ${ }^{9, \mathrm{~d}}$ which is expected to have a butterfly or halfplanar geometry, ${ }^{10}$ and [3.3.3]fenestrane (3-11), ${ }^{9 \mathrm{e}}$ which is expected to have a pyrami-dal-tetracoordinate carbon atom. ${ }^{9 h}$ Prior to Wiberg's work, considerable success had also been achieved by Brinker, Skattebøl and others, ${ }^{11}$ in the synthesis and study of larger, bridged spiropentanes (e.g. 3-12-3-14). Although these molecules do not have


3-10 $\left(C_{2}\right)$


3-11 ( $C_{1}$ )


3-12 $\left(C_{2}\right)$


3-13 $\left(C_{2}\right)$


3-14 $\left(C_{2}\right)$
a pyramidal-tetracoordinate carbon atom, they do show considerable distortion at the spiro carbon ${ }^{12}$ (for further details regarding the bridged spiropentanes see Section 1.5.5 on page 35 ).


Pyramidane (3-15) or [3.3.3.3]fenestrane, perhaps the archetypal hydrocarbon with a pyramidal-tetracoordinate carbon atom, has been identified through molecular orbital calculations as a true minimum on the $\mathrm{C}_{5} \mathrm{H}_{4}$ potential energy surface. ${ }^{13,14}$ Semi-empirical molecular orbital calculations had suggested that 3-1 and a number of larger, related molecules (3-16-3-18) (all of which can be seen as [k.l.m.n]fenestranes where $k, l, m$ and $n$ are each greater than four) will also have a pyramidal-tetracoordinate carbon atom. ${ }^{1 \mathrm{lbc}}$ However, ab initio calculations indicate that the apical carbon atom $\left(\mathrm{C}^{0}\right)$ in 3-1 is not pyramidal ${ }^{1 \mathrm{a}}$ and it seems unlikely that the other suggested molecules will have a pyramidal carbon atom either, as they all allow greater flexibility at the central, quaternary carbon atom.

Particularly striking have been recent discoveries in both iron-cluster and gold chemistry. Compounds with an $\mathrm{Fe}_{4} \mathrm{C}$ core ${ }^{10,15}$ are found to have a butterfly geometry (3-

3-1 $\left(C_{2 v}\right)$

3-16

3-17

3-18
19) in which the tetracoordinate carbon atom is bound to four Fe atoms in the one hemisphere. A number of unusual ruthenium cluster compounds have also been observed, in which carbon is bound on the face of the ruthenium core and is therefore 'exposed' or almost planar-tetracoordinate. ${ }^{15 \mathrm{c}, \mathrm{d}}$ Schmidbaur has found that the as-yet-unisolated compound $\left[\left(\mathrm{Ph}_{3} \mathrm{PAu}\right)_{4} \mathrm{C}\right]$ prefers to bind a fifth ligand and form $\left[\left(\mathrm{Ph}_{3} \mathrm{PAu}\right)_{5} \mathrm{C}\right]^{+},{ }^{16}$ suggesting that it has a largely unbound pair of electrons, and possibly a pyramidal geometry at the carbon atom. Further work by Schmidbaur and others on coordination of gold


3-19 ( $\mathrm{A}=\mathrm{H}$ or CO )


3-20 ( $C_{4 v}$ )
ligands to other main-group elements, ${ }^{17,18}$ suggests that pyramidal-tetracoordination of an atom with eight valence electrons can indeed lead to stable, isolable compounds.


3-21-H ${ }^{+}$


3-22-H ${ }^{+}$

$\mathbf{3 - 2 3 - H}{ }^{+}$

An examination of the molecular orbitals for a pyramidal-tetracoordinate carbon constructed from a carbon atom and two ethylene units (Figure 3-1) reveals that the apical carbon atom will indeed possess a lone pair of non-bonding electrons and will have four electron-deficient $\mathrm{C}-\mathrm{C} \sigma$-bonds (six bonding electrons spread over four bonds). As


Figure 3-1. Orbital interaction diagram showing the molecular orbitals in pyramidaltetracoordinate carbon formed from the interaction of a carbon atom with a pair of $\mathrm{C}=\mathrm{C}$ double bonds.
a result, molecules containing a pyramidal-tetracoordinate carbon should be very strong Lewis bases, as observed by Schmidbaur. ${ }^{16}$ And indeed, calculations by Pyykkö predict a remarkably high value of $1213 \mathrm{~kJ} \mathrm{~mol}^{-1}$ for the proton affinity ${ }^{18 \mathrm{c}}$ of the pyramidal isomer of $\left[\left(\mathrm{H}_{3} \mathrm{PAu}\right)_{4} \mathrm{C}\right] .{ }^{\dagger}$ Both Jemmis and Schleyer ${ }^{19}$ and Minkin, Minyaev and coworkers ${ }^{14 \mathrm{a}}$ have also noted the potentially very high proton affinity at the pyramidal-tetracoordinate carbon in pyramidane (3-15), a purely organic system. Jemmis and Schleyer

[^31]calculated the proton affinity of $\mathbf{3 - 1 5}$ to be $1060 \mathrm{~kJ} \mathrm{~mol}^{-1}$ at the HF/3-21G level. The resulting $\mathrm{C}_{5} \mathrm{H}_{5}{ }^{+}$species is typical of the group of non-classical carbocations known as pyramidal carbocations. Since their conception, pyramidal carbocations ${ }^{20-22}$ have been studied extensively and a number of systems, including $\mathbf{3 - 2 1}-\mathbf{H}^{+}, \mathbf{3 - 2 2}-\mathbf{H}^{+}$and $\mathbf{3 - 2 3 -} \mathbf{H}^{+}$, have been observed in superacid media. ${ }^{20,21 d, h, \mathrm{~h}, \mathrm{j}}$

Given the wealth of experimental support both for distorted spiropentanes and for pyramidal carbocations, we have embarked on an examination of the hemialkaplanes and hemispiroalkaplanes as attractive, prototypical hydrocarbon examples of such species, and as possible synthetic targets.

### 3.2 Methods

Standard ab initio molecular orbital calculations ${ }^{23}$ were carried out using the GAUSSIAN 98 system of programs. ${ }^{24}$ All structures ${ }^{\dagger}$ were optimized initially without symmetry constraints at the B3-LYP/6-31G(d) level. Structures of interest were then re-optimized with the preferred symmetry, and either analytic or numerical normal-mode analysis was used to characterize the nature of the resulting stationary points. A selection of the more interesting structures (3-1 - 3-3, 3-4 - 3-6, the tetramethyl derivative (3-24) of $\mathbf{3 - 5}$, and the protonated species $\mathbf{3 - 1}-\mathbf{H}^{+}, \mathbf{3}-\mathbf{4}-\mathrm{H}^{+}, \mathbf{3}-\mathbf{5}-\mathrm{H}^{+}, \mathbf{3 - 6}-\mathrm{H}^{+}$and $\mathbf{3 - 2 4}-\mathrm{H}^{+}$) were further optimized at the MP2/6-31G(d) level and improved energies were calculated at the MP2/6-311+G(2d,p)//MP2/6-31G(d) level, using the frozen-core approximation in all the MP2 calculations. All these MP2/6-31G(d) structures were characterized as local minima by numerical normal-mode analysis. Reaction enthalpies were computed ini-

tially using B3-LYP/6-31G(d) energies, corrected for zero-point energy (ZPVE) using B3-LYP/6-31G(d) analytic frequencies scaled by 0.9806 and corrected to 298 K using

[^32]standard statistical thermodynamics and the same frequencies scaled by $0.9989 .{ }^{25}$ For a


3-4 $\left(C_{2 v}\right)$


3-5 $\left(C_{2 v}\right)$


3-6 $\left(C_{2 v}\right)$
selection of molecules, reaction enthalpies were also computed at the MP2/6$311+\mathrm{G}(2 \mathrm{~d}, \mathrm{p}) / / \mathrm{MP} 2 / 6-31 \mathrm{G}(\mathrm{d})$ level using MP2/6-31G(d) frequencies scaled by 0.9670 for the ZPVE and corrected to 298 K using these same frequencies scaled by $1.0211 .^{25}$ In all cases, we used a set of five pure $d$-functions rather than the usual six cartesian functions for the $6-31 \mathrm{G}(\mathrm{d})$ basis set.

The strain associated with formally building the hemialkaplanes from a neopentane unit and the appropriate capping hydrocarbon can be estimated from the enthalpy change in the homodesmic reaction:

$$
\begin{equation*}
\text { 3-III }+8 \text { ethane } \rightarrow \text { cap }+ \text { neopentane }+4 \text { isobutane } \tag{3-1}
\end{equation*}
$$

We have defined the apical strain energy ( $A p S E$ ) for a hemialkaplane as $-\Delta H$ for Reaction 3-1. This strain energy includes contributions from the strain in the highly distorted apical $\mathrm{C}_{5} \mathrm{H}_{8}$ moiety, the strain involved in binding this unit to the capping hydrocarbon and the energy involved in deformation of the capping hydrocarbon to the geometry found in the corresponding hemialkaplane (this final contribution being by far the smallest). Results are given in Table 3-2 on page 103.

Similarly, the apical strain energy for the hemispiroalkaplanes, i.e. the strain associated with formally building the hemispiroalkaplanes from a capping hydrocarbon and unstrained hydrocarbons, is defined as the negative of the enthalpy change in the homodesmic reaction:

$$
\begin{equation*}
\text { 3- } \mathbf{V}+4 \text { propane }+10 \text { ethane } \rightarrow \text { cap }+ \text { neopentane }+8 \text { isobutane } \tag{3-2}
\end{equation*}
$$

Values of the $A p S E=-\Delta H$ (Reaction 3-2) are given in Table 3-4 on page 108. As a spe-
cial case, we considered tetramethylhemispirooctaplane (3-24). The apical strain energy for 3-24 is given as the negative of the enthalpy change in the homodesmic reaction:

$$
\begin{equation*}
\text { 3-24 }+4 \text { propane }+10 \text { ethane } \rightarrow \text { cyclooctane }+5 \text { neo }^{\dagger}+4 \text { isobutane } \tag{3-3}
\end{equation*}
$$

The calculated $A p S E$ for 3-24, $-\Delta H$ (Reaction 3-3), is also included in Table 3-4.
Conventional total strain energies ( $S E$ ) were calculated using a homodesmic reaction scheme ${ }^{26}$ in which the target hydrocarbon is broken down into the basic unstrained hydrocarbons: ethane, propane, isobutane and neopentane. ${ }^{26,27}$ For example, hemispirooctaplane (3-5) gives the following reaction:

$$
\begin{equation*}
\text { 3-5 }+16 \text { ethane } \rightarrow \text { neopentane }+4 \text { isobutane }+8 \text { propane } \tag{3-4}
\end{equation*}
$$

The total strain energy for hemispirooctaplane (3-5) is then defined as $-\Delta H$ (Reaction 34). The heat of formation $\left(\Delta H_{\mathrm{f}}\right)$ of the hydrocarbon in question (e.g. hemispirooctaplane (3-5)) is calculated using the computed enthalpy of the appropriate homodesmic reaction (e.g. $\Delta H$ (Reaction 3-4)) and the experimental values for the heats of formation of the small unstrained hydrocarbons: ethane ( $-83.9 \mathrm{~kJ} \mathrm{~mol}^{-1}$ ), propane ( $-104.7 \mathrm{~kJ} \mathrm{~mol}^{-1}$ ), isobutane $\left(-134.2 \mathrm{~kJ} \mathrm{~mol}^{-1}\right)$ and neopentane $\left(-167.9 \mathrm{~kJ} \mathrm{~mol}^{-1}\right){ }^{28}$ Calculated strain energies (SE) and heats of formation for a variety of hydrocarbons (including the novel systems described herein) are given in Table 3-5 on page 114.

We find that the B3-LYP/6-31G(d) procedure is not suitable for reliably predicting the enthalpy changes for homodesmic reactions such as Reaction 3-4 because of poor cancellation of errors. For example, the strain energy of spiropentane is given as the negative of the enthalpy change ( $-\Delta H$ (Reaction 3-5)) in the reaction:

$$
\begin{equation*}
\text { spiropentane }+6 \text { ethane } \rightarrow \text { neopentane }+4 \text { propane } \tag{3-5}
\end{equation*}
$$

Even with B3-LYP/6-311+G(3df,2p), the computed $S E$ differs from the experimental value by approximately $50 \mathrm{~kJ} \mathrm{~mol}^{-1}$. This can be traced to non-cancelling errors in the individual heats of formation calculated from atomization energies at this level of theory for spiropentane $\left(-22.8 \mathrm{~kJ} \mathrm{~mol}^{-1}\right)$, neopentane $\left(-38.1 \mathrm{~kJ} \mathrm{~mol}^{-1}\right)$, propane $(-5.5$

[^33]$\mathrm{kJ} \mathrm{mol}^{-1}$ ) and ethane $\left(+2.5 \mathrm{~kJ} \mathrm{~mol}^{-1}\right) .^{29}$ In contrast, although MP2/6-311+G(2d,p)// MP2/6-31G(d) gives much larger errors for the individual heats of formation calculated from atomization energies, there is considerably better cancellation of errors for the homodesmic reaction. The $S E$ for spiropentane (one of the worst cases) computed via a homodesmic scheme differs from experiment by approximately $15 \mathrm{~kJ} \mathrm{~mol}^{-1}$ (see Table 3-5 on page 114 for comparisons of this level of theory with experiment ${ }^{28}$ ). As a consequence, only MP2/6-311+G(2d,p)//MP2/6-31G(d) values are reported in Table 35.

Gas-phase proton affinities were determined as the negative of the enthalpy change
 MP2/ 6-31G(d) energies, corrected for $Z P V E$ and to 298 K using MP2/6-31G(d) analytic frequencies and the same scaling factors mentioned above. The ideal gas value of $2.5 R T$ was used as the temperature correction for the proton. To provide an indication of the approximate accuracy of this level of theory, ${ }^{30}$ we used it to determine the proton affinities of $\mathrm{CH}_{4}, \mathrm{NH}_{3}$, and $\mathrm{H}_{2} \mathrm{O}$, giving values of 530 , 852 and $687 \mathrm{~kJ} \mathrm{~mol}^{-1}$, respectively, which may be compared with experimental values ${ }^{31}$ of 552,854 and 697 $\mathrm{kJ} \mathrm{mol}^{-1}$, respectively.

The total energies, scaled ZPVEs, and corrections for $H^{298}-H^{0}$ are given in Tables C-2 - C-4 of Appendix C. GAUSSIAN archive files (which include geometries) for all B3-LYP/6-31G(d) and MP2/6-31G(d) optimized structures are given in Tables C18 - C-20 of Appendix C.

### 3.3 Results and Discussion

### 3.3.1 Structures of Hemialkaplanes

The hemialkaplanes (3-III) are constructed formally by capping a neopentane-type unit with a cycloalkane. We examined structures which result from using the following eight cyclic hydrocarbons as the basis for the capping unit: cyclobutane, cyclopentane, bicyclo[2.2.0]hexane, cyclohexane, norbornane (bicyclo[2.2.1]heptane), cyclooctane, bicyclo[3.3.0]octane, and bicyclo[3.3.1]nonane. The resulting molecules, named hemibutaplane, hemipentaplane, hemibihexaplane (3-25), hemihexaplane (3-2), hemibiheptaplane (3-3), hemibioctaplane (3-26), hemioctaplane (3-1) and hemibinonaplane (3-27),

respectively, were surveyed initially at the B3-LYP/6-31G(d) level. Structures of particular interest were then re-optimized at the MP2/6-31G(d) level. General structural features for the hemialkaplanes, 3-1-3-3 and 3-25-3-27 are presented in Table 3-1 on page 102. Some important structural parameters for 3-1-3-3 and 3-25-3-27 are presented in Table 3-2 on page 103, while more complete structures for hemihexaplane (32), hemibiheptaplane (3-3) and hemioctaplane (3-1) are displayed in Figure 3-2.


Figure 3-2. Structural parameters (MP2/6-31G(d) values in bold type, B3-LYP/6$31 \mathrm{G}(\mathrm{d})$ values in plain text, all values in $\AA$ or degrees) for hemihexaplane (3-2), hemibiheptaplane (3-3) and hemioctaplane (3-1). The apical angle is $\theta_{\alpha 0 \alpha}$, i.e. $\angle \mathrm{C}^{\alpha} \mathrm{C}^{0} \mathrm{C}^{\alpha}$; the other angle indicated is $\theta_{0 \alpha \beta}$ i.e. $\angle \mathrm{C}^{0} \mathrm{C}^{\alpha} \mathrm{C}^{\beta}$.

Table 3-1. General structural features of the hemialkaplanes. ${ }^{\text {a }}$

| Molecule |  | Sym. ${ }^{\text {b }}$ | Cap <br> Formula | Cap <br> Structure ${ }^{\text {c }}$ | Apical $\mathrm{C}_{5} \mathrm{H}_{8}$ <br> Subunit ${ }^{\text {c }}$ | Molecular Formula |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| hemibihexaplane | 3-25 | $C_{2}$ | bicyclo- $\mathrm{C}_{6} \mathrm{H}_{6}$ |  |  | $\mathrm{C}_{11} \mathrm{H}_{14}$ |
| hemihexaplane | 3-2 | $C_{2}$ | cyclo- $\mathrm{C}_{6} \mathrm{H}_{8}$ |  |  | $\mathrm{C}_{11} \mathrm{H}_{16}$ |
| hemibiheptaplane | 3-3 | $C_{2}$ | bicyclo- $\mathrm{C}_{7} \mathrm{H}_{8}$ |  |  | $\mathrm{C}_{12} \mathrm{H}_{16}$ |
| hemibioctaplane | 3-26 | $C_{2}$ | bicyclo- $\mathrm{C}_{8} \mathrm{H}_{10}$ |  |  | $\mathrm{C}_{13} \mathrm{H}_{18}$ |
| hemioctaplane | 3-1 | $C_{2 \mathrm{v}}$ | cyclo- $\mathrm{C}_{8} \mathrm{H}_{12}$ |  |  | $\mathrm{C}_{13} \mathrm{H}_{20}$ |
| hemibinonaplane | 3-27 | $C_{2}$ | bicyclo- $\mathrm{C}_{9} \mathrm{H}_{12}$ |  |  | $\mathrm{C}_{14} \mathrm{H}_{20}$ |

[^34]Cyclobutane- and cyclopentane-type caps do not lead to stable bound structures; high-symmetry structures were located but these are found from analytic frequency analysis to be high-order saddle points. Hemialkaplanes with capping units containing a primary eight-membered ring (3-1, 3-26 and 3-27) are found to be stable, but the apical carbon atom in these structures is not pyramidal. Indeed, of all the hemialkaplanes examined, only those with capping units which have a primary ring of six carbon atoms are found both to be stable and to have a pyramidal-tetracoordinate carbon atom. In particular, we find that 3-2 and 3-3 have a pyramidal-tetracoordinate carbon atom. However, as can be seen from Table 3-2 and Figure 3-2, the degree of pyramidalization at the

Table 3-2. Calculated apical strain energies $(A p S E)$ and apical structural parameters for the hemialkaplanes. ${ }^{\text {a,b }}$

| Molecule |  | $A p S E^{\text {d }}$ | Apical Parameters ${ }^{\text {c }}$ |  |  |  |  |  |  |  |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
|  |  |  | lengths |  |  |  | angles |  |  |  |
|  |  |  | $r_{0 \alpha}$ | $r_{\alpha \beta}$ | $r_{0 \alpha^{\prime}}$ | $r_{\alpha^{\prime} \beta^{\prime}}$ | $\theta_{\alpha 0 \alpha}{ }^{\text {e }}$ | $\theta_{\alpha^{\prime} 0 \alpha^{\prime}}$ | $\theta_{0 \alpha \beta}$ | $\theta_{0 \alpha^{\prime} \beta^{\prime}}$ |
| hemibihexaplane | 3-25 | 687 | 1.585 | 1.586 | 1.730 | 1.469 | 185.7 | 141.1 | 91.3 | 101.2 |
| hemihexa- <br> plane | 3-2 | $\begin{aligned} & 726 \\ & 716 \end{aligned}$ | $\begin{aligned} & 1.601 \\ & \mathbf{1 . 6 0 4} \end{aligned}$ | $\begin{aligned} & 1.656 \\ & \mathbf{1 . 6 4 0} \end{aligned}$ | $\begin{aligned} & 1.708 \\ & \mathbf{1 . 6 7 4} \end{aligned}$ | $\begin{aligned} & 1.481 \\ & \mathbf{1 . 4 7 7} \end{aligned}$ | $\begin{aligned} & 189.2 \\ & \mathbf{1 8 7 . 8} \end{aligned}$ | $\begin{aligned} & 139.9 \\ & \mathbf{1 4 0 . 2} \end{aligned}$ | $\begin{aligned} & 91.8 \\ & \mathbf{9 0 . 8} \end{aligned}$ | $\begin{aligned} & 100.9 \\ & \mathbf{1 0 1 . 0} \end{aligned}$ |
| hemibiheptaplane | 3-3 | $\begin{aligned} & 717 \\ & 706 \end{aligned}$ | $\begin{aligned} & 1.598 \\ & \mathbf{1 . 6 0 2} \end{aligned}$ | $\begin{aligned} & 1.653 \\ & \mathbf{1 . 6 3 9} \end{aligned}$ | $\begin{aligned} & 1.713 \\ & \mathbf{1 . 6 7 8} \end{aligned}$ | $\begin{aligned} & 1.470 \\ & \mathbf{1 . 4 6 7} \end{aligned}$ | $\begin{aligned} & 191.3 \\ & \mathbf{1 8 9 . 8} \end{aligned}$ | $\begin{aligned} & 140.7 \\ & \mathbf{1 4 1 . 2} \end{aligned}$ | $\begin{aligned} & 92.3 \\ & \mathbf{9 1 . 3} \end{aligned}$ | $\begin{aligned} & 101.2 \\ & \mathbf{1 0 1 . 3} \end{aligned}$ |
| hemibioctaplane | 3-26 | 673 | 1.578 | 1.653 | 1.728 | 1.489 | 174.2 | 145.8 | 93.8 | 111.6 |
| hemiocta- <br> plane | 3-1 | $\begin{aligned} & 642 \\ & \mathbf{6 2 3} \end{aligned}$ | $\begin{aligned} & 1.606 \\ & \mathbf{1 . 6 0 4} \end{aligned}$ | $\begin{aligned} & 1.645 \\ & \mathbf{1 . 6 2 8} \end{aligned}$ | $\begin{aligned} & 1.686 \\ & \mathbf{1 . 6 6 1} \end{aligned}$ | $\begin{aligned} & 1.480 \\ & \mathbf{1 . 4 7 5} \end{aligned}$ | $\begin{aligned} & 172.3 \\ & \mathbf{1 7 1 . 2} \end{aligned}$ | $\begin{aligned} & 148.7 \\ & \mathbf{1 4 8 . 8} \end{aligned}$ | $\begin{aligned} & 96.3 \\ & \mathbf{9 5 . 5} \end{aligned}$ | $\begin{aligned} & 112.8 \\ & \mathbf{1 1 3 . 1} \end{aligned}$ |
| hemibinonaplane | 3-27 | 696 | 1.581 | 1.659 | 1.704 | 1.477 | 172.9 | 148.7 | 95.0 | 112.7 |

${ }^{\text {a }}$ B3-LYP/6-31G(d) values are given in plain text. MP2/6-311+G(2d,p)//MP2/6-31G(d) and MP2/6$31 \mathrm{G}(\mathrm{d})$ values are given in bold type. ${ }^{\mathrm{b}}$ Bond lengths are given in $\AA$, bond angles in degrees, and energies in $\mathrm{kJ} \mathrm{mol}^{-1}$. ${ }^{\mathrm{c}}$ See structure 3-VIII for a description of the geometrical parameters. ${ }^{\mathrm{d}} \mathrm{ApSE}$ is the apical strain energy, the negative of the enthalpy change at 298 K for Reaction 3-1 on page $98 .{ }^{\mathrm{e}}$ Values for $\theta_{\alpha 0 \alpha}$ greater than $180.0^{\circ}$ indicate a pyramidal carbon.
apical carbon even in these cases is not great. In fact, all the stable hemialkaplanes show quite similar geometrical features at the apical $\mathrm{C}\left(\mathrm{CH}_{2}\right)_{4}$ moiety: (i) there is a pair of elongated $\mathrm{C}-\mathrm{C}$ bonds to the apical carbon atom, $\mathrm{C}^{0}$, i.e. with lengths $r_{0 \alpha}$ in the range 1.58-1.60 $\AA$; (ii) these two elongated C-C bonds are attached to the apical carbon in an almost linear arrangement $\left(\theta_{\alpha 0 \alpha}=170-190^{\circ}\right)$; (iii) associated with this pair of elongated $\mathrm{C}-\mathrm{C}$ bonds is another long $\mathrm{C}-\mathrm{C}$ bond between $\mathrm{C}^{\alpha}$ and $\mathrm{C}^{\beta}$ whose length, $r_{\alpha \beta}$, is considerably greater than $1.60 \AA$ in all but 3-25; (iv) in all cases these two elongated bonds form a tight angle, $\theta_{0 \alpha \beta}=\angle \mathrm{C}^{0} \mathrm{C}^{\alpha} \mathrm{C}^{\beta}$, which is close to $90.0^{\circ}$; (v) there is a second pair of very long $\mathrm{C}-\mathrm{C}$ bonds to $\mathrm{C}^{0}$ which have a bond length, $r_{0 \alpha^{\prime}}$, around $1.70 \AA$ at B 3 -LYP/6$31 \mathrm{G}(\mathrm{d})$ and greater than $1.65 \AA$ at $\mathrm{MP} 2 / 6-31 \mathrm{G}(\mathrm{d})$; and (vi) associated with this pair of very long $\mathrm{C}-\mathrm{C}$ bonds is a pair of compressed $\mathrm{C}-\mathrm{C}$ bonds between $\mathrm{C}^{\alpha^{\prime}}$ and $\mathrm{C}^{\beta^{\prime}}$ which are in the range $1.47-1.49 \AA$ at both levels of theory. We suspect that the presence of four

C-C bonds with lengths greater than $1.65 \AA$, found in all the hemialkaplanes except 3 25, will make the hemialkaplanes somewhat susceptible to internal rearrangement/ isomerization to lower energy species.

### 3.3.2 Structures of Hemispiroalkaplanes

The hemispiroalkaplanes (3-V) are constructed formally by capping a spiropentanetype unit with a cycloalkane. We examined structures which result from using the following seven cyclic hydrocarbons as the basis for the capping unit: cyclobutane, bicyclo[2.2.0]hexane, cyclohexane, norbornane (bicyclo[2.2.1]heptane), cyclooctane, bicyclo[3.3.0]octane, and bicyclo[3.3.1]nonane. The resulting molecules, named hemispirobutaplane (3-28), hemispirobihexaplane (3-29 and 3-30), hemispirohexaplane (3-31 and 3-32), hemispirobiheptaplane (3-33 and 3-34), hemispirobioctaplane (3-4 and 3-35), hemispirooctaplane (3-5) and hemispirobinonaplane (3-6 and 3-36), respectively, were surveyed at the $\mathrm{B} 3-\mathrm{LYP} / 6-31 \mathrm{G}(\mathrm{d})$ level. A tetramethyl derivative of 3-5 in which the $\mathrm{C}^{\alpha}$


3-IX ${ }^{32}$


3-4 $\left(C_{2 v}\right)$


3-5 ( $C_{2 \mathrm{v}}$ )


3-6 ( $C_{2 v}$ )
hydrogens are replaced with methyl groups, tetramethylhemispirooctaplane (3-24), was also examined. Structures of particular interest were then re-optimized at the MP2/631G(d) level. General structural features for 3-4-3-6, 3-24 and 3-28-3-36 are given in Table 3-3 on page 105 and important structural parameters for these molecules are given in Table 3-4 on page 108. Structures for hemispirobioctaplane (3-4), hemispirooctaplane (3-5), hemispirobinonaplane (3-6) and tetramethylhemispirooctaplane (3-24) are displayed in Figure 3-3 on page 107.

The spiropentane-type $\mathrm{C}_{5} \mathrm{H}_{4}$ apical subunit (in hemispiroalkaplanes) lacks the fourfold symmetry of the neopentane-type $\mathrm{C}_{5} \mathrm{H}_{8}$ apical subunit (in hemialkaplanes). As a consequence, there are two possible structural isomers for each of the hemispiroalkapl-
anes constructed from the capping hydrocarbons that do not have four-fold symmetry. In cases where these structural isomers exist, and well-bound minima could be located, they have been designated as parallel or perpendicular, referring to the relative orientations of the longest axes of the two subunits (see Table 3-4). We note that the perpendic-

Table 3-3. General structural features for the hemispiroalkaplanes.

| Molecule |  | Sym. $^{a}$ | Cap Formula |
| :--- | :--- | :--- | :--- |
| Lemispirobutaplane | $\mathbf{3 - 2 8}$ | $C_{2 \mathrm{v}}$ | cyclo $-\mathrm{C}_{4} \mathrm{H}_{4}$ |
| Structure |  |  |  |

Table 3-3. (Continued) General structural features for the hemispiroalkaplanes.

| Molecule |  | Sym. ${ }^{\text {a }}$ | Cap Formula | Cap <br> Structure ${ }^{\text {b }}$ | Apical $\mathrm{C}_{5} \mathrm{H}_{4}$ Subunit ${ }^{\text {b }}$ | Molecular Formula |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| hemispirooctaplane | 3-5 | $C_{2 v}$ | cyclo- $\mathrm{C}_{8} \mathrm{H}_{12}$ |  |  | $\mathrm{C}_{13} \mathrm{H}_{16}$ |
| hemispirobinonaplane (perpendicular) | 3-6 | $C_{2 \mathrm{v}}$ | bicyclo- $\mathrm{C}_{9} \mathrm{H}_{12}$ |  |  | $\mathrm{C}_{14} \mathrm{H}_{16}$ |
| hemispirobinonaplane (parallel) | 3-36 | $C_{2 \mathrm{v}}{ }^{\text {c }}$ | bicyclo- $\mathrm{C}_{9} \mathrm{H}_{12}$ |  |  | $\mathrm{C}_{14} \mathrm{H}_{16}$ |
| tetramethylhemispirooctaplane | 3-24 | $C_{2 \mathrm{v}}$ | cyclo- $\mathrm{C}_{8} \mathrm{H}_{12}$ |  |  | $\mathrm{C}_{17} \mathrm{H}_{24}$ |

[^35]ular isomer is favoured in all cases (see below).

An examination of the structures of the hemispiroalkaplanes that we have considered reveals that they all prefer a pyramidal arrangement at the apical, tetracoordinate carbon atom. There is one relatively long $\mathrm{C}-\mathrm{C}$ bond ( $r_{0 \alpha}=1.61-1.67 \AA$ ) from $\mathrm{C}^{0}$ to $\mathrm{C}^{\alpha}$ while all other $\mathrm{C}-\mathrm{C}$ bonds are unremarkable. A more detailed examination requires a division of the hemispiroalkaplanes on the basis of the size of the primary-ring cap. The molecules with a primary-ring cap of six carbon atoms can be divided into two groups, those with a steep angle at the apical carbon (3-29, 3-31, 3-33) $\left(\theta_{x 0 x}=107-108^{\circ}\right)^{32}$ and those with a wider angle (3-30, 3-32, 3-34) $\left(\theta_{x 0 x}=121-124^{\circ}\right)$ at the apical carbon. The latter are all parallel-type hemispiroalkaplanes and are typified by the existence of two cyclobutane rings fused between the apical $\mathrm{C}_{5} \mathrm{H}_{4}$ unit and the cap. Interestingly, it is these structures with the wider value for $\theta_{\mathrm{x} 0 \mathrm{x}}$ that have shorter $\mathrm{C}^{0}-\mathrm{C}^{\alpha}$ bonds $\left(r_{0 \alpha}=\right.$


Figure 3-3. Structural parameters (MP2/6-31G(d) values in bold type, B3-LYP/6$31 \mathrm{G}(\mathrm{d})$ values in plain text, all values in $\AA$ or degrees) for hemispirobioctaplane (3-4), hemispirooctaplane (3-5), hemispirobinonaplane (3-6), and tetramethylhemispirooctaplane (3-24). The apical angle shown is $360-\theta_{x 0 x}$, i.e. the outer angle made by $x, C^{0}$ and x . ${ }^{32}$
$1.62 \AA$ for $\mathbf{3 - 3 2}$ and 3-34, $r_{0 \alpha}=1.65 \AA$ and $1.59 \AA$ for $\mathbf{3 - 3 0}^{\dagger}$ ). Hemispirobutaplane (328) is a special case as it is the only hemispiroalkaplane with a four-membered primary-

[^36]Table 3-4. Calculated apical strain energies $(A p S E)$ and structural parameters for the hemispiroalkaplanes. ${ }^{\text {a,b }}$

| Molecule |  | $A p S E^{\text {d }}$ | Apical Parameters ${ }^{\text {c }}$ |  |  |  |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: |
|  |  |  | lengths |  | angles |  |
|  |  |  | $\begin{gathered} r_{0 \alpha} \\ r_{0 \alpha}{ }^{\prime \mathrm{e}} \end{gathered}$ | $\begin{gathered} r_{\alpha \beta} \\ r_{\alpha \beta}{ }^{\prime \mathrm{e}} \end{gathered}$ | $\theta_{\mathrm{x} 0 \mathrm{x}}{ }^{\text {f }}$ | $\begin{gathered} \theta_{0 \alpha \beta} \\ \theta_{0 \alpha \beta}{ }^{\prime} \end{gathered}$ |
| hemispirobutaplane | 3-28 | 736 | 1.644 | 1.549 | 109.7 | 108.1 |
| hemispirobihexaplane (perpendicular) | 3-29 | 537 | 1.665 | 1.531 | 107.8 | 114.6 |
| hemispirobihexaplane (parallel) | 3-30 | 756 | $\begin{aligned} & 1.646 \\ & 1.586^{\text {e }} \end{aligned}$ | $\begin{aligned} & 1.563 \\ & 1.531^{\mathrm{e}} \end{aligned}$ | 124.3 | $\begin{aligned} & 117.2 \\ & 117.7^{\complement} \end{aligned}$ |
| hemispirohexaplane (perpendicular) | 3-31 | 582 | 1.644 | 1.549 | 106.9 | 115.7 |
| hemispirohexaplane (parallel) | 3-32 | 679 | 1.619 | 1.541 | 121.1 | 115.8 |
| hemispirobiheptaplane (perpendicular) | 3-33 | 542 | 1.651 | 1.538 | 107.4 | 114.9 |
| hemispirobiheptaplane (parallel) | 3-34 | 715 | 1.616 | 1.543 | 121.8 | 116.8 |
| hemispirobioctaplane | 3-4 | $504$ | $1.650$ | $1.524$ | $120.1$ | $121.1$ |
| (perpendicular) |  | 547 | 1.633 | 1.516 | 120.6 | 121.2 |
| hemispirobioctaplane (parallel) | 3-35 | 618 | 1.631 | 1.542 | 120.6 | 125.2 |
| hemispirooctaplane | 3-5 | 527 | 1.632 | 1.532 | 123.2 | 123.5 |
|  |  | 572 | 1.622 | 1.523 | 123.1 | 123.6 |
| hemispirobinonaplane (perpendicular) | 3-6 | 499 | 1.642 | 1.524 | 122.2 | 122.3 |
|  |  | 550 | 1.628 | 1.515 | 122.3 | 122.4 |
| hemispirobinonaplane (parallel) | 3-36 | 662 | 1.609 | 1.546 | 120.0 | 127.4 |
| tetramethylhemispirooctaplane | 3-24 | $\begin{aligned} & 480 \\ & 516 \end{aligned}$ | $\begin{aligned} & 1.636 \\ & \mathbf{1 . 6 2 4} \end{aligned}$ |  |  |  |
|  |  |  | $1.515^{\text {g }}$ | 1.528 | 127.2 | $120.9$ |
|  |  |  | 1.508 ${ }^{\text {g }}$ |  |  |  |

[^37]ring cap. Hemispirobutaplane has both a steep angle at the pyramidal carbon $\left(\theta_{\mathrm{x} 0 \mathrm{x}}=\right.$ $109.7^{\circ}$ ) and a pair of fused cyclobutanes between the apical unit and the cap. The rest of the hemispiroalkaplanes have an eight-membered primary-ring cap (3-4-3-6, 3-35 and 3-36). Unlike the case for the hemispiroalkaplanes with a six-membered primary-ring cap (3-29-3-34), these molecules all have a comparatively less steep, pyramidal-tetracoordinate carbon ( $\theta_{\mathrm{x} 0 \mathrm{x}}=120-123^{\circ}$ ) and intermediate values for the $\mathrm{C}^{0}-\mathrm{C}^{\alpha}$ bond length $\left(r_{0 \alpha}=1.61-1.65 \AA\right.$ ). Although these $\mathrm{C}-\mathrm{C}$ bonds are longer than normal $\mathrm{C}-\mathrm{C}$ single bonds, they are not without precedent. ${ }^{33}$

One further geometrical aspect of the hemispiroalkaplanes worth noting is that the capping hydrocarbons are usually forced into higher symmetry when bound into the cage than in the free form. For example, whereas the appropriately oriented conformer of bicyclo[3.3.1]nonane prefers a $C_{2}$ structure with the expected twistboat conformation of the two fused cyclohexane rings, hemispirobinonaplane (3-6) prefers $C_{2 v}$ symmetry with regular boat conformations of the fused cyclohexane rings and no twisting in the cap. This is expected to worsen the situation with respect to a number of possible $\mathrm{H}-\mathrm{H}$ close contacts. The shortest $\mathrm{H}-\mathrm{H}$ contact is found in the $C_{2 \mathrm{v}}$ structure for the paralleltype hemispirobinonaplane (3-36) where the $\mathrm{H}-\mathrm{H}$ distance is calculated at the B3-LYP/ $6-31 G(d)$ level to be $1.864 \AA$. Perhaps as a consequence, this structure is found not to be a local minimum but a first-order saddle point, leading to ring-opening at the apical carbon. After ring-opening, this $\mathrm{H}-\mathrm{H}$ distance is increased to $1.954 \AA$. All other $\mathrm{H}-\mathrm{H}$ close approaches, in all structures, are greater than $2.0 \AA$.

The tetramethyl derivative of 3-5 (i.e. 3-24), shows slightly greater widening of the $\theta_{\mathrm{x} 0 \mathrm{x}}$ angle at the pyramidal carbon than in 3-5 $\left(\theta_{\mathrm{x} 0 \mathrm{x}}=127^{\circ}\right)$. The only other notable feature is that the $\mathrm{C}^{\alpha}-\mathrm{CH}_{3}$ bond $(1.51 \AA)$ is somewhat shorter than a standard $\mathrm{C}-\mathrm{C}$ bond.

### 3.3.3 Strain Energies

Although strain energies do not necessarily reflect kinetic stability, they can still be used profitably to assess possible targets for synthesis. The quantity that we have labelled as the apical strain energy ( $A p S E$ ) is effectively the total strain energy ( $S E$ ) less the strain inherent in the capping hydrocarbon. We find this quantity useful for two reasons. Firstly, we recognize that the capping hydrocarbon may be considerably strained in its own right and yet this strain may have little effect on the stability at the apical car-
bon atom. Secondly, although the ApSEs calculated by B3-LYP may have considerable error, this error is expected to be systematic when we are comparing similar systems (see Reactions 3-1-3-3). Thus, relative values for the $A p S E$, calculated at the B3-LYP level, should be fairly reliable within each of the hemialkaplane and hemispiroalkaplanes families but not for comparisons between the two families. Values for the ApSEs of the hemialkaplanes and the hemispiroalkaplanes are included in Table 3-2 on page 103 and Table 3-4 on page 108, respectively. Total strain energies (SE) and heats of formation $\left(\Delta H_{\mathrm{f}}\right)$ for systems for which we have calculated MP2/6-311+G(2d,p)// MP2/6-31G(d) energies are given in Table 3-5.

The calculated ApSEs for the hemialkaplanes range from about $620-730 \mathrm{~kJ} \mathrm{~mol}^{-1}$ (Table 3-2 on page 103). A comparison of the B3-LYP/6-31G(d) and MP2/6$311+\mathrm{G}(2 \mathrm{~d}, \mathrm{p}) / / \mathrm{MP} 2 / 6-31 \mathrm{G}(\mathrm{d})$ values shows that the B3-LYP values tend to be higher by about $10-20 \mathrm{~kJ} \mathrm{~mol}^{-1}$. Strain in the smaller systems with a six-membered primary-ring cap (3-2, 3-3, 3-25) is generally higher than in the larger systems which have an eightmembered primary-ring cap (3-1, 3-26, 3-27). This is also reflected in the total strain energies (SE) given in Table 3-5 for 3-2 (743 $\mathrm{kJ} \mathrm{mol}^{-1}$ ), 3-3 ( $768 \mathrm{~kJ} \mathrm{~mol}^{-1}$ ) and 3-1 ( 674 $\mathrm{kJ} \mathrm{mol}{ }^{-1}$ ). Hemioctaplane (3-1) stands out clearly as the least-strained hemialkaplane, being the only system to have an $A p S E$ lower than $650 \mathrm{~kJ} \mathrm{~mol}^{-1}$ and an $S E$ less than 700 $\mathrm{kJ} \mathrm{mol}^{-1}$.

The hemispiroalkaplanes give directly-calculated ApSEs that lie between 480 and $760 \mathrm{~kJ} \mathrm{~mol}^{-1}$ (see Table 3-4 on page 108). A comparison of the B3-LYP and MP2 values indicates that the former are systematically too low by about $40 \mathrm{~kJ} \mathrm{~mol}^{-1} .^{\dagger}$ In the discussion that follows, the APSEs have consequently been adjusted by $40 \mathrm{~kJ} \mathrm{~mol}^{-1}$. Once again, it is useful to split the hemispiroalkaplanes into groups based on the size of the primary-ring cap. The structures with a six- membered primary-ring cap (3-29-334) clearly form two groups: the parallel-type isomers (3-30, 3-32, 3-34) which all have very high ApSEs (around $720-800 \mathrm{~kJ} \mathrm{~mol}^{-1}$ after correction) and their perpendiculartype counterparts (3-29, 3-31, 3-33) which have more modest ApSEs (580-620

[^38]$\mathrm{kJ} \mathrm{mol}^{-1}$ ). Part of the cause of the much higher strain in the parallel-type structures is the existence of a pair of cyclobutane rings fused between the apical subunit and the capping hydrocarbon. The fact that this introduces considerably more strain at the $\mathrm{C}^{\alpha}$ atoms suggests that the parallel-type isomers would not make good targets for synthesis. Hemispirobutaplane (3-28) is the only system with a four-membered primary-ring cap. Like the parallel-type systems with a six-membered primary-ring cap, it also has a pair of fused cyclobutane rings but this is in addition to the cyclobutane ring of the capping hydrocarbon. The $A p S E$ for $\mathbf{3 - 2 8}\left(776 \mathrm{~kJ} \mathrm{~mol}^{-1}\right.$ after correction) is similar to that of the parallel-type systems with a six-membered primary-ring cap, and 3-28 is also unlikely to be a good target for synthesis.

The hemispiroalkaplanes with an eight-membered primary-ring cap also form two groups. The parallel-type isomers (3-35 and 3-36) are considerably more strained (ApSEs greater than $650 \mathrm{~kJ} \mathrm{~mol}^{-1}$ ) than the other four structures in this group (3-4-3-6, 3-24) (ApSEs in the range $515-575 \mathrm{~kJ} \mathrm{~mol}^{-1}$ ). Unlike the smaller parallel-type systems (3-30, 3-32, 3-34), there are no additional fused, small rings (e.g. cyclobutanes) in these molecules. Instead, these systems appear to derive extra strain, compared with their per-pendicular-type counterparts (3-4 and 3-6), from an unfavorable placement of the $\mathrm{C}^{\alpha}$ atoms. The hemispiroalkaplanes can also be thought of as a carbon atom stabilized over


3-38 ( $C_{2 \mathrm{v}}$ )


3-37 $\left(C_{\mathrm{s}}\right)$
a polycyclic diene (e.g. hemispirobutaplane 3-28 has been suggested previously as a species in which a carbon atom is stabilized over syn-tricyclo[4.2.0.0 ${ }^{2,5}$ ]octa-3,7-diene (3-37)). ${ }^{14 \mathrm{~d}}$ The underlying polycyclic dienes for the parallel-/perpendicular-type hemispiroalkaplane pairs 3-4/3-35 and 3-6/3-36 reveal that in the parallel-type isomers, 3-35 and 3-36, the $\mathrm{C}^{\alpha}$ atoms are forced by the 'half-cage' framework into a close-contact situation (see Figure 3-4 on page 112). This situation appears to provide a strongly adverse effect on the thermodynamic stability of the corresponding hemispiroalkaplanes. In the
parallel-type hemispirobinonaplane (3-36), the $\mathrm{H}-\mathrm{H}$ close contacts mentioned earlier also contribute to the $A p S E$. As a result, the $C_{2 v}$ structure for $\mathbf{3 - 3 6}$ is a saddle point and not a minimum. Optimization with reduced symmetry constraints leads to asymmetric ring-opening at the apical carbon to give a cyclopentylidene ring (3-38), thereby forming a bond between one pair of opposing $\mathrm{C}^{\alpha}$ atoms and relieving much of the strain associated with keeping the opposing $\mathrm{C}^{\alpha}$ atoms at a non-bonding distance.
a

b


C

d


Figure 3-4. The polycyclic diene 'half-cage' frameworks for 3-4 (a), 3-6 (b), 3-35 (c) and 3-36 (d). The olefinic carbon atoms in (c) and (d) (which correspond to $\mathrm{C}^{\alpha}$ in 335 and 3-36) are forced into a close-contact situation. MP2/6-31G(d) optimized lengths are given in $\AA$.

The non-parallel-type hemispiroalkaplanes (3-4-3-6, 3-24) have the lowest ApSEs of the hemispiroalkaplanes studied. Further, both their ApSEs and SEs are 50-100
$\mathrm{kJ} \mathrm{mol}^{-1}$ lower than the $A p S E$ and $S E$ of hemioctaplane. Tetramethylhemispirooctaplane (3-24) is of particular interest. It appears that methylation at $\mathrm{C}^{\alpha}$ helps to reduce the strain in the hemispiroalkaplanes considerably. The total strain energy of tetramethylhemispirooctaplane (3-24) ( $S E=567 \mathrm{~kJ} \mathrm{~mol}^{-1}$ ) is almost $50 \mathrm{~kJ} \mathrm{~mol}^{-1}$ lower than the strain in hemispirooctaplane (3-5) $\left(S E=623 \mathrm{~kJ} \mathrm{~mol}^{-1}\right)$.

In order to probe more widely the effect of alkylation on strain, we have also calculated the strain energies for tetrahedrane (3-40) $\left(S E=601 \mathrm{~kJ} \mathrm{~mol}^{-1}\right)$ and tetrakis $($ tertbutyl)tetrahedrane (3-45) (SE = $535 \mathrm{~kJ} \mathrm{~mol}^{-1}$ ) (see Table 3-5 on page 114). We find a similar effect to that observed for hemispirooctaplane, namely, that alkylation reduces considerably the strain in the system. This may well be one of the factors that has enabled the synthesis of tetrakis (tert-butyl)tetrahedrane (3-45) while tetrahedrane (3-40) remains experimentally unknown. ${ }^{34}$ Further, in similar fashion to that seen in $\mathbf{3 - 4 5}$, it is likely that alkylation of the $\mathrm{C}^{\alpha}$ atoms with bulky alkyl groups like tert-butyl, or perhaps isopropyl, would have a beneficial effect on kinetic stability by protecting the 'sensitive' $\mathrm{C}-\mathrm{C}$ bonds. Semi-empirical modelling suggests that tetrakis(tert-butyl)hemispirooctaplane is somewhat crowded but might be feasible.

It is useful to compare the properties of our novel hydrocarbon structures with those of related species (Table 3-5). The total strain energy (SE) of hemioctaplane (3-1) (674 $\mathrm{kJ} \mathrm{mol}^{-1}$ ) is quite large but comparable to the $S E$ of cubane (3-44) $\left(708 \mathrm{~kJ} \mathrm{~mol}^{-1}\right)$ or prismane (3-43) ( $639 \mathrm{~kJ} \mathrm{~mol}^{-1}$ ), both of which are known experimentally. However, in cubane and prismane this strain is evenly distributed over eight (or six) carbon atoms and twelve (or nine) $\mathrm{C}-\mathrm{C}$ bonds. The situation in the hemialkaplanes is a little more complex as the strain is clearly not evenly distributed throughout the molecule. A useful comparison would consider the $\operatorname{ApSE}\left(623 \mathrm{~kJ} \mathrm{~mol}^{-1}\right.$ in 3-1), which in the hemialkaplanes is mainly distributed over the five apical carbon atoms and approximately eight $\mathrm{C}-\mathrm{C}$ bonds (the four $\mathrm{C}^{0}-\mathrm{C}^{\alpha}$ and four $\mathrm{C}^{\alpha}-\mathrm{C}^{\beta}$ bonds), suggesting a greater strain per carbon or per $\mathrm{C}-\mathrm{C}$ bond in 3-1 than in cubane (3-44) or prismane (3-43). The strain energy of pyramidane (3-15), the archetypal pyramidal-tetracoordinate carbon species, is found to be $645 \mathrm{~kJ} \mathrm{~mol}^{-1}$. This is close to the ApSE of 3-1 and this strain is likely to be distributed in a similar fashion, i.e. spread over five carbon atoms and eight $\mathrm{C}-\mathrm{C}$ bonds with one carbon atom more strained than the others. But synthesis of pyramidane (3-15) has not yet been accomplished. The hemialkaplanes may prove equally challenging.

Table 3-5. Calculated strain energies $(S E)^{\text {a }}$ and calculated and experimental heats of formation $\left(\Delta H_{\mathrm{f}}\right)$ at $298 \mathrm{~K}^{\left(\mathrm{kJ} \mathrm{mol}^{-1}\right)}$.

| Molecule | Homodesmic reaction ${ }^{\text {b }}$ | $\begin{gathered} S E \\ (\mathrm{calc})^{\mathrm{c}} \end{gathered}$ | $\begin{gathered} \Delta H_{\mathrm{f}} \\ (\mathrm{calc}) \end{gathered}$ | $\Delta H_{\mathrm{f}}(\exp )^{\mathrm{d}}$ |
| :---: | :---: | :---: | :---: | :---: |
| cyclopropane | 3-39 + 3 ethane $\rightarrow 3$ propane | 125 | 62 | $53.3 \pm 0.6$ |
| tetrahedrane | 3-40 + 6 ethane $\rightarrow 4$ isobutane | 601 | 567 | $(535 \pm 4)^{e}$ |
| pyramidane | $\mathbf{3 - 1 5}+8$ ethane $\rightarrow$ neopentane +4 isobutane | 645 | 611 |  |
| spiropentane | $3-41+6$ ethane $\rightarrow$ neopentane +4 propane | 284 | 200 | $185.1 \pm 0.8$ |
| [1.1.1]propellane | 3-42 +7 ethane $\rightarrow 2$ neopentane +3 propane | 432 | 369 | $351 \pm 4^{\text {f }}$ |
| prismane | 3-43 + 9 ethane $\rightarrow 6$ isobutane | 639 | 589 |  |
| cubane | $\mathbf{3 - 4 4}+12$ ethane $\rightarrow 8$ isobutane | 708 | 641 | $622.2 \pm 3.7$ |
| tetra-tert-butyltetrahedrane | 3-45 + 10 ethane $\rightarrow 8$ neopentane | 535 | 30 | $25.9 \pm 8.8^{\text {g }}$ |
| cyclobutane | $\mathbf{3 - 4 6}+4$ ethane $\rightarrow 4$ propane | 115 | 32 | $28.5 \pm 0.6$ |
| bicyclo[2.2.0]- <br> hexane | 3-47 +7 ethane $\rightarrow 2$ isobutane +4 propane | 238 | 138 | $125^{\text {f }}$ |
| cyclohexane (twistboat) | TB-3-48 + 6 ethane $\rightarrow 6$ propane | 27 | -98 |  |
| cyclohexane (chair) | $\mathbf{C - 3 - 4 8}+6$ ethane $\rightarrow 6$ propane | 1 | -124 | $-123.1 \pm 0.8$ |
| norbornane | $3-49+8$ ethane $\rightarrow 2$ isobutane +5 propane | 62 | -59 | $-54.9 \pm 4.7$ |
| cis-bicyclo[3.3.0]octane (cis-octahydropentalene) | $\mathbf{3 - 5 0}+9$ ethane $\rightarrow 2$ isobutane +6 propane | 49 | -93 | $-93.3 \pm 1.5$ |
| cyclooctane (boat-chair) | BC-3-51 +8 ethane $\rightarrow 8$ propane | 41 | -125 | $-124.4 \pm 1.0$ |
| cyclooctane (crown) | Crown-3-51 +8 ethane $\rightarrow 8$ propane | 51 | -116 |  |
| bicyclo[3.3.1]nonane (chair-chair) | CC-3-52 +10 ethane $\rightarrow 2$ iso +7 propane | 27 | -135 | $-127.5 \pm 2.3$ |
| bicyclo[3.3.1]nonane (twistboat-twistboat) | TBTB-3-52 +10 ethane $\rightarrow 2$ iso +7 propane | 63 | -100 |  |

Table 3-5. (Continued) Calculated strain energies $(S E)^{\mathrm{a}}$ and calculated and experimental heats of formation $\left(\Delta H_{\mathrm{f}}\right)$ at $298 \mathrm{~K}\left(\mathrm{~kJ} \mathrm{~mol}^{-1}\right)$.

| Molecule | Homodesmic reaction ${ }^{\text {b }}$ | $\begin{gathered} S E \\ (\mathrm{calc})^{\mathrm{c}} \end{gathered}$ | $\begin{gathered} \Delta H_{\mathrm{f}} \\ \text { (calc) } \end{gathered}$ | $\Delta H_{\mathrm{f}}(\exp )^{\text {d }}$ |
| :---: | :---: | :---: | :---: | :---: |
| [3.3.3]fenestrane | $\mathbf{3 - 1 1}+7$ ethane $\rightarrow$ neo +2 iso +2 propane | 586 | 528 |  |
| [3.4.3]fenestrane | $\mathbf{3 - 5 3}+8$ ethane $\rightarrow$ neo +2 iso +3 propane | 499 | 420 |  |
| [3.5.3]fenestrane | $\mathbf{3 - 1 2}+9$ ethane $\rightarrow$ neo +2 iso +4 propane | 355 | 255 |  |
| tetracyclo- <br> [3.3.1. $0^{2,4} .0^{2,8}$ ]nonane | 3-54 +12 ethane $\rightarrow$ neo +4 iso +4 propane | 426 | 309 |  |
| hemihexaplane | $\mathbf{3 - 2}+14$ ethane $\rightarrow$ neo +4 iso +6 propane | 743 | 584 |  |
| hemibiheptaplane | 3-3 +16 ethane $\rightarrow$ neo +6 iso +5 propane | 768 | 613 |  |
| hemioctaplane | $\mathbf{3 - 1}+16$ ethane $\rightarrow$ neo +4 iso +8 propane | 674 | 473 |  |
| hemispirobioctaplane (perpendicular) | 3-4 + 19 ethane $\rightarrow$ neo +10 iso +2 propane | 595 | 469 |  |
| hemispirooctaplane | $\mathbf{3 - 5}+18$ ethane $\rightarrow$ neo +8 iso +4 propane | 623 | 472 |  |
| hemispirobinonaplane (perpendicular) | 3-6 +20 ethane $\rightarrow$ neo +10 iso +3 propane | 613 | 466 |  |
| tetramethylhemispirooctaplane | 3-24 +18 ethane $\rightarrow 5$ neo +4 iso +4 propane | 567 | 281 |  |

${ }^{\text {a }}$ MP2/6-311+G(2d,p)//MP2/6-31G(d) values corrected to $298 \mathrm{~K}^{\left(\mathrm{kJ} \mathrm{mol}^{-1}\right)}$. ${ }^{\mathrm{b}}$ The abbreviations "neo" and "iso" indicate neopentane and isobutane, respectively. ${ }^{\mathrm{c}}$ The strain energy $(S E)$ is determined as the negative of the enthalpy change for the given homodesmic reaction. ${ }^{\mathrm{d}}$ Taken from Ref. 28 b unless otherwise noted. ${ }^{\mathrm{e}} \mathrm{G} 2$ calculated value from Ref. 28d. ${ }^{\mathrm{f}}$ From Ref. 28c. ${ }^{\text {g }}$ From Ref. 28a.

The situation for the hemispiroalkaplanes is more promising. In the first place, ApSEs for the hemispiroalkaplanes are generally lower than for the hemialkaplanes. Again, strain is concentrated mainly in the apical unit and is distributed mostly over these five carbon atoms and the ten associated $\mathrm{C}-\mathrm{C}$ bonds (four $\mathrm{C}^{\alpha}-\mathrm{C}^{0}$, two $\mathrm{C}^{\alpha}-\mathrm{C}^{\alpha}$ and four $\mathrm{C}^{\alpha}-\mathrm{C}^{\beta}$ bonds). We find that the ApSEs for the least-strained hemispiroalkaplanes (3-4 - 3-6) (550-570 $\mathrm{kJ} \mathrm{mol}^{-1}$ ) are considerably lower than the strain energy for pyramidane (3-15). In fact, the ApSEs for 3-4-3-6 are comparable to, or slightly less than, the $S E$ for the experimentally observed species, [3.3.3]fenestrane (3-11) ( $586 \mathrm{~kJ} \mathrm{~mol}^{-1}$ ). We have also determined the strain energies of a number of other distorted spiropentanes


3-53


3-12


3-54
(3-53, 3-12 and 3-54) (499, 355 and $426 \mathrm{~kJ} \mathrm{~mol}^{-1}$, respectively) that have been observed experimentally. ${ }^{11}$ Although these strains are somewhat lower than the ApSEs for the hemispiroalkaplanes 3-4-3-6, the strain in 3-53 is comparable to the $A p S E$ for the tetramethyl derivative of $\mathbf{3 - 5}$ (i.e. 3-24) $\left(516 \mathrm{~kJ} \mathrm{~mol}^{-1}\right)$. We also expect that the tetramethyl derivatives of 3-4 and 3-6 will have ApSEs around $500 \mathrm{~kJ} \mathrm{~mol}^{-1}$. These alkylated derivatives would appear to be the most attractive synthetic targets.

### 3.3.4 Synthetic Considerations

We will not attempt here to design a synthetic strategy, but simply to make a few observations. Firstly, synthesis of a number of strained spiropentanes has been achieved through cyclization reactions that involve the insertion of a cyclopropylidene moiety into a $\mathrm{C}=\mathrm{C}$ double bond. ${ }^{11}$ For example, both the tricycloheptane 3-12 ${ }^{11 \mathrm{a}}$ and the tetracyclononane $\mathbf{3 - 5 4}{ }^{11 \mathrm{c}}$ have been synthesized in this manner (see Scheme 1 ). ${ }^{\dagger}$ An analo-


Scheme 1
gous reaction pathway for the synthesis of the hemispiroalkaplanes would involve, as principle reactant, a polycyclic diene ${ }^{\ddagger}$ such as 3-55 (the hydrocarbon parent of the wellknown insecticide isodrin) or 3-56 (the tetraquinane isomer of 3-55, which is thermally

[^39]accessible ${ }^{36}$ from birdcage hydrocarbon). An initial insertion of one equivalent of dihalocarbene at one of the $\mathrm{C}=\mathrm{C}$ double bonds might then allow for ring closure via generation of a cyclopropylidene intermediate (Scheme 2). ${ }^{\dagger}$


3-55


3-56

For cases where this type of cyclization reaction was found to be successful, Skattebøl observed that methylation at the $\mathrm{C}=\mathrm{C}$ double bond aided ring-closure and improved yields. ${ }^{11}$ This suggests that attempts at synthesis of the methylated hemispiroalkaplanes via such a route may prove to be more successful than attempts to make the unsubstituted parent molecules.


Scheme 2

### 3.3.5 Proton Affinities

One clear consequence of the binding arrangement at the apical carbon atom in both the hemialkaplanes and the hemispiroalkaplanes is that the highest occupied molecular orbital (HOMO) is a lone pair of electrons located at the apical carbon atom (see Figure 3-1). An examination of the HOMO of hemispirooctaplane 3-5 (Figure 3-5) shows this very clearly. This situation leads us to expect ready protonation. The structures resulting from protonation at the apical carbon atoms of 3-1, 3-4-3-6 and 3-24 (Figure 3-6) have $C_{2 v}$ symmetry and are found to be minima on their respective potential

[^40]

Figure 3-5. The highest occupied molecular orbital (HOMO) for hemispirooctaplane $(3-5)$ is a lone pair orbital located at the apical carbon atom. The iso-surface is drawn at $0.080 e \AA^{-3}$.
energy surfaces. Once again, the longest bonds are found to be the $\mathrm{C}^{0}-\mathrm{C}^{\alpha}$ bonds ( $r_{0 \alpha}=$ $1.73 \AA$ for $\mathbf{3 - 1}-\mathbf{H}^{+}, r_{0 \alpha}=1.61-1.62 \AA$ for $\mathbf{3 - 4}-\mathbf{H}^{+}, \mathbf{3 - 5}-\mathbf{H}^{+}, \mathbf{3 - 6}-\mathbf{H}^{+}$and $\mathbf{3 - 2 4}-\mathbf{H}^{+}$). These structures appear to be typical pyramidal carbocations, although the angle at the apex $\left(\theta_{\mathrm{x} 0 \mathrm{x}}=131-138^{\circ}\right)^{32}$ is somewhat flatter than in known pyramidal carbocations like 3-21$\mathbf{H}^{+}, \mathbf{3 - 2 2 - H} \mathbf{H}^{+}$and $\mathbf{3 - 2 3 - H} \mathbf{H}^{+}\left(\theta_{\mathrm{x} 0 \mathrm{x}}=93-94^{\circ}\right)$ (see Table 3-6 on page 119). ${ }^{20-22}$

The predicted gas-phase proton affinities (PA) of these molecules (3-1, 3-4-3-6 and 3-24) are all greater than $1100 \mathrm{~kJ} \mathrm{~mol}^{-1}$ (Table 3-6)! The non-pyramidal hemialkaplane 3-1, as would be expected, has the lowest $P A\left(1119 \mathrm{~kJ} \mathrm{~mol}^{-1}\right)$ while 3-24 has a slightly greater proton affinity ( $1193 \mathrm{~kJ} \mathrm{~mol}^{-1}$ ) than the non-alkylated hemispiroalkaplanes 3-4-3-6 (1172-1179 $\mathrm{kJ} \mathrm{mol}^{-1}$ ). These values are considerably larger than the PAs of any of the organic systems listed in a recent compendium, ${ }^{31}$ including the renowned superbase, 'proton sponge' (1,8-bis(dimethylamino)naphthalene) (1028 $\mathrm{kJ} \mathrm{mol}^{-1}$ ). It is truly remarkable for saturated hydrocarbons to have such high proton affinities.

Other evidence for very high basicity at carbon has been seen in the incredibly strong preference for $\left[\left(\mathrm{Ph}_{3} \mathrm{PAu}\right)_{4} \mathrm{C}\right]$ (which does not, however, adopt a pyramidal structure) to attract a fifth ligand and form $\left[\left(\mathrm{Ph}_{3} \mathrm{PAu}\right)_{5} \mathrm{C}\right]^{+} .{ }^{16}$ In addition, calculations by

Table 3-6. Calculated gas-phase proton affinities (PA) at $298 \mathrm{~K}\left(\mathrm{~kJ} \mathrm{~mol}^{-1}\right)$ for selected molecules ${ }^{\mathrm{a}}$ and selected geometrical parameters ( $\AA$ or degrees) for the protonated species. ${ }^{\text {b }}$

| Molecule | $P A^{\mathrm{c}}$ | $r_{0 \alpha}$ | $\theta_{\mathrm{x} 0 \mathrm{x}}{ }^{\mathrm{d}}$ |
| :--- | :---: | :---: | :---: |
| pyramidane (3-15) | 965 | 1.646 | 58.6 |
| $\mathbf{3 - 2 1}^{\mathrm{e}}$ | 1094 | 1.623 | 92.9 |
| $\mathbf{3 - 2 2}^{\mathrm{e}}$ | 1096 | 1.619 | 94.1 |
| $\mathbf{3 - 2 3}^{\mathrm{e}}$ | 1102 | 1.620 | 93.1 |
| hemioctaplane (3-1) $^{\text {hemispirobioctaplane (3-4) }}$ | 1119 | 1.732 | 138.1 |
| hemispirooctaplane (3-5) | 1172 | 1.620 | 131.4 |
| hemispirobinonaplane (3-6) | 1175 | 1.613 | 133.5 |
| tetramethylhemispirooctaplane (3-24) | 1193 | 1.620 | 132.7 |

${ }^{\text {a }}$ MP2/6-311+G(2d,p)//MP2/6-31G(d) values corrected to 298 K as described in the text.
${ }^{\mathrm{b}}$ MP2/6-31G(d) values. ${ }^{\mathrm{c}}$ PA is determined as the negative of the enthalpy change for reaction (6). ${ }^{\mathrm{d}}$ See Ref $32 .{ }^{\mathrm{e}}$ The conjugate bases of $\mathbf{3} \mathbf{- 2 1}-\mathbf{H}^{+}, \mathbf{3} \mathbf{- 2 2}-\mathbf{H}^{+}$and $\mathbf{3} \mathbf{- 2 3}-\mathbf{H}^{+}$.

Pyykkö indicate that both the pyramidal and tetrahedral-like isomers of $\left[\left(\mathrm{H}_{3} \mathrm{PAu}\right)_{4} \mathrm{C}\right]$ have proton affinities comparable to those of the hemispiroalkaplanes. ${ }^{18 \mathrm{c}}$ We have recalculated the proton affinity of pyramidane (3-15) ( $965 \mathrm{~kJ} \mathrm{~mol}^{-1}$ ), and find it to be somewhat less than that predicted by Jemmis and Schleyer ${ }^{19}$ ( $1060 \mathrm{~kJ} \mathrm{~mol}^{-1}$ ) and considerably less than the PAs of the hemispiroalkaplanes 3-4-3-6 and 3-24.

Once again, the effects of methylation appear to be beneficial. Thus the greater $P A$ for 3-24 over 3-5 indicates that methylation, as well as reducing the strain in the unprotonated species (see above), also reduces the relative energy of the protonated molecule. This advantageous effect of 'basal' methylation has been suggested previously from calculations. ${ }^{20}$

### 3.3.6 Stabilities

Determining the kinetic stability of prospective synthetic targets is not a simple task, yet the absence of low-lying transition states, leading to potential decomposition pathways, is essential to their eventual isolation. An exhaustive search of all the possi-


Figure 3-6. Structural parameters (MP2/6-31G(d) values in bold type, B3-LYP/6$31 \mathrm{G}(\mathrm{d})$ values in plain text, all values in $\AA$ or degrees) for protonated hemioctaplane $\left(\mathbf{3 - 1}-\mathbf{H}^{+}\right)$, hemispirobioctaplane $\left(\mathbf{3}-4-\mathbf{H}^{+}\right)$, hemispirooctaplane ( $\left.\mathbf{3}-\mathbf{5}-\mathbf{H}^{+}\right)$, hemispirobinonaplane $\left(\mathbf{3}-6-\mathbf{H}^{+}\right)$, and tetramethylhemispirooctaplane $\left(\mathbf{3}-\mathbf{2 4}-\mathbf{H}^{+}\right)$. The apical angle shown is $360-\theta_{\mathrm{x} 0 \mathrm{x}}$, i.e. the outer angle made by $\mathrm{x}, \mathrm{C}^{0}$ and $\mathrm{x} .{ }^{32}$
ble modes of decomposition, at a correlated level of theory, which deals adequately with bond separations, in systems with more than 20 atoms, is clearly not feasible at the present time. It is therefore necessary that we be guided to some extent by comparing with similar systems for which there are experimental data. Although, as Luef and Keese ${ }^{8 c}$ have remarked, there are few experimental studies on the kinetic stability of saturated, strained hydrocarbon systems with respect to mechanism, ${ }^{37}$ the systems that have been studied do provide some useful clues. Rearrangement or decomposition often appears to occur via a homolytic C-C bond cleavage. ${ }^{37,38}$ Results for the bridged spiropentanes suggest that the rearrangement in these cases might alternatively occur via a retro-Diels-Alder mechanism. ${ }^{11}$ A third possibility is decomposition via a carbene intermediate; a possibility that might be considered for very highly-strained systems. Finally, Luef and Keese have also found that the rigid geometries and the highly strained, fused structures of the fenestranes (3-VI) lead to fragmentation via unusual reaction channels. ${ }^{8 c}$ In considerations of these decomposition pathways, the hemialkaplanes are probably best considered as extremely strained, saturated [k.l.m.n]fenestranes (3-VI) (where $k(=m)$ and $l(=n)$ are both greater than or equal to 5), while the hemispiroalkaplanes might be best compared with bridged spiropentanes because they also contain a pair of spiro-linked cyclopropane rings.

An examination of the structural parameters (in particular $\mathrm{C}-\mathrm{C}$ bond lengths) should give an indication of any particularly weak bonds that may have low dissociation barriers. The pair of elongated $\mathrm{C}^{0}-\mathrm{C}^{\alpha}$ bonds in the hemialkaplanes (3-III), that are approximately $1.67 \AA$ at MP2/6-31G(d) (Table 3-2 on page 103), suggest the possibility of a low-barrier rearrangement pathway via cleavage at one of these bonds. This, in combination with a number of other fairly long C-C bonds (e.g. $r_{\alpha \beta}=1.64 \AA$ at the MP2/6-31G(d) level), suggests that, although these molecules are true minima on their respective potential energy surfaces, they may not be isolable. The barrier to rearrangement via $\mathrm{C}-\mathrm{C}$ cleavage at these extended bonds might reasonably be expected to be relatively small, and fragmentation via cleavage at a number of these longer bonds is likely to be facile.

The situation in the hemispiroalkaplanes (3-V) appears to be more encouraging in that the $\mathrm{C}^{0}-\mathrm{C}^{\alpha}$ bonds are, in general, considerably shorter (approximately $1.63 \AA$ at MP2/6-31G(d)) (Table 3-4 on page 108). However, studies by Frey, Brinker, Skattebøl
and Roth, ${ }^{11,38}$ have shown that distorted spiropentanes with even quite short $\mathrm{C}^{0}-\mathrm{C}^{\alpha}$ bonds (1.49-1.52 $\AA$ ) can readily rearrange via what is thought to be either initial $\mathrm{C}-\mathrm{C}$ cleavage at one of the $\mathrm{C}^{0}-\mathrm{C}^{\alpha}$ bonds or a retro-Diels-Alder reaction. We have modelled the rearrangements of spiropentane, tricyclo[4.1.0.0 ${ }^{1,3}$ ]heptane (3-12) and 4,5-benzotri-cyclo-[4.1.0.0 $0^{1,3}$ ]hept-4-ene (3-14) and find a good correlation between the energy of homolytic dissociation at the inner $\mathrm{C}^{0}-\mathrm{C}^{\alpha}$ bond and the rate of thermal rearrangement. Initial calculations on the cleavage at one of the $\mathrm{C}^{0}-\mathrm{C}^{\alpha}$ bonds in hemispirooctaplane (35) indicate that this process is exothermic (rather than endothermic, as is customary for $\mathrm{C}-\mathrm{C}$ bond cleavage). However, we do find a barrier to $\mathrm{C}-\mathrm{C}$ bond cleavage which varies from approximately $20 \mathrm{~kJ} \mathrm{~mol}^{-1}$, as calculated with UB3-LYP/6-31G(d), to $60 \mathrm{~kJ} \mathrm{~mol}^{-1}$, when calculated using (2/2)CASPT2. ${ }^{39}$ Unfortunately, an accurate description of the potential energy surface for this reaction would require an (8/8)CASPT2 or better calculation (because of the unusual bonding arrangement at the pyramidal-tetracoordinate carbon). ${ }^{40}$ Use of this method on a system of this size is prohibitive with our current computational resources because of the immense number of configuration state functions (CSFs) involved in such a treatment of a $\mathrm{C}_{13}$ hydrocarbon.

Examination of the normal vibrational modes gives some further insights into possible mechanisms for rearrangement. The hemialkaplanes (3-III) have generally similar vibrational profiles. The three lowest-frequency modes, with values of around $300-350 \mathrm{~cm}^{-1}$, correspond to a symmetric and an anti-symmetric $\mathrm{C}-\mathrm{C}$ stretch of the $\mathrm{C}^{0}-\mathrm{C}^{\alpha}$ bonds and a scissor-like motion which causes inversion at the apical carbon atom, $\mathrm{C}^{0}$. Hemioctaplane (3-1) is unusual because of its $C_{2 v}$ symmetry. In this case, there are a few low frequencies that correspond to twisting motions, especially of the cap. The scissor-like motion at $\mathrm{C}^{0}$ appears at about $250 \mathrm{~cm}^{-1}$, the lowest $\mathrm{C}^{0}-\mathrm{C}^{\alpha}$ stretching motion (antisymmetric) appears at about $350 \mathrm{~cm}^{-1}$, and the symmetric $\mathrm{C}^{0}-\mathrm{C}^{\alpha}$ stretch is found at about $550 \mathrm{~cm}^{-1}$. It appears from the relatively low frequencies for $\mathrm{C}^{0}-\mathrm{C}^{\alpha}$ stretching, coupled with the rather long $\mathrm{C}^{0}-\mathrm{C}^{\alpha}$ bonds, that initial cleavage of the $\mathrm{C}^{0}-\mathrm{C}^{\alpha}$ bond would be the most likely mechanism of isomerization/rearrangement in the hemialkaplanes.

The normal vibrational modes of the hemispiroalkaplanes (3-V) are characterized by two relatively low-frequency modes associated with vibration along the $\mathrm{C}^{0}-\mathrm{C}^{\alpha}$ bonds (see Figure 3-7). One of these modes (A) leads to ring opening at $\mathrm{C}^{0}$ (with $\mathrm{C}-\mathrm{C}$ bond formation between $\mathrm{C}^{\alpha, 2}$ and $\mathrm{C}^{\alpha, 3}$ ) to give a cyclopentylidene structure, while the other
mode (B) represents a symmetric stretching of the opposing $\mathrm{C}^{0}-\mathrm{C}^{\alpha}$ bonds and is likely to lead to homolytic $\mathrm{C}^{0}-\mathrm{C}^{\alpha}$ bond cleavage. The ring opening mode $(\mathbf{A})$ is generally the lowest-frequency mode in the hemispiroalkaplanes, but it is particularly low in the parallel-type hemispiroalkaplanes (3-30, 3-32, 3-34, 3-35 and 3-36). In fact, in the $C_{2 v}$ structure for hemispirobinonaplane (3-36) this mode becomes a down-hill mode and as a result 3-36 is a saddle point, as noted above. In both 3-30 and 3-35, the frequency associated with this mode is below $100 \mathrm{~cm}^{-1}$. It is only in the perpendicular-type hemispiroalkaplane isomers 3-4, 3-6, 3-29, 3-31 and 3-33, and in hemispirobutaplane (3-28), that the frequency associated with this mode lies above $200 \mathrm{~cm}^{-1}$. Even in the hemispirooc-

A



B



or


Figure 3-7. The two lowest vibrational modes, $\mathbf{A}$ and $\mathbf{B}$, which may lead to ring opening at the apical carbon atom in the hemispiroalkaplanes. The apical carbon atom, $\mathrm{C}^{0}$, is above the plane of the $\mathrm{C}^{\alpha}$ atoms.
taplanes 3-5 and 3-24, the frequency associated with this mode is quite small (100 and $200 \mathrm{~cm}^{-1}$, respectively). This vibration might provide a facile route to rearrangement. However, we note that the vibrational profile of the hemispiroalkaplanes and their pyramidal carbocation counterparts are similar in this low-frequency region, and further, the
vibrational profiles of the protonated hemispiroalkaplanes in this low-frequency region are similar to those we calculate for the experimentally-observed pyramidal carbocations $\mathbf{3 - 2 1}-\mathbf{H}^{+}, \mathbf{3 - 2 2}-\mathbf{H}^{+}$and $\mathbf{3 - 2 4}-\mathbf{H}^{+}$. These observations suggest that this particular vibration, despite being quite facile, may not lead to a favorable rearrangement pathway. ${ }^{41}$

The other low-frequency vibrational mode (B) probably corresponds to the mode which leads to thermal rearrangement in distorted spiropentane systems such as 3-12 and 3-14, i.e. this mode corresponds to cleavage at one of the $\mathrm{C}^{0}-\mathrm{C}^{\alpha}$ bonds, and the resulting diradical then rearranges to lower energy products. The value of the frequency associated with this mode is similar in the distorted spiropentanes (3-11, 3-12 and 3-53) (250-290 $\mathrm{cm}^{-1}$ ) and the perpendicular-type hemispiroalkaplanes with an eight-membered primary-ring cap (3-4-3-6) (190-240 $\mathrm{cm}^{-1}$ ). The value of the corresponding frequency in the parallel-type hemispiroalkaplanes (3-30, 3-32 and 3-34-336) is somewhat lower ( $100-200 \mathrm{~cm}^{-1}$ ). However, this same mode corresponds to a much larger frequency (approximately $300-400 \mathrm{~cm}^{-1}$ ) in the perpendicular-type hemispiroalkaplanes with a six-membered primary-ring cap (3-29, 3-31 and 3-33) and in hemispirobutaplane (3-28). In any case, it seems likely that $\mathrm{C}^{0}-\mathrm{C}^{\alpha}$ bond cleavage will be one of the preferred modes of rearrangement in the hemispiroalkaplanes, and an accurate determination of the barrier to this $\mathrm{C}-\mathrm{C}$ bond cleavage is required if we are to establish the stability of these molecules with respect to unimolecular rearrangement.

### 3.4 Concluding Remarks

The hemialkaplanes (3-III) and the hemispiroalkaplanes (3-V) represent two new families of saturated hydrocarbons with remarkable properties. A key feature of these molecules is that they exhibit a pyramidal, or near-pyramidal, arrangement of bonds at the apical carbon atom. The highest occupied molecular orbital is essentially a lone pair localized at this carbon and this leads to a very high basicity for the hemialkaplanes and hemispiroalkaplanes, even greater than that of the so-called proton sponges.

Of the hemialkaplanes, hemioctaplane (or bowlane) (3-1) appears to be the best synthetic target; it has the lowest apical strain energy $(A p S E)$, the shortest $\mathrm{C}^{0}-\mathrm{C}^{\alpha}$ bonds, and probably the greatest (albeit small) barrier to $\mathrm{C}^{0}-\mathrm{C}^{\alpha}$ bond cleavage (and subsequent rearrangement). We expect, however, that the hemispiroalkaplanes will generally have

better prospects of synthesis. Alkylated derivatives of hemispirobioctaplane (3-4), hemispirooctaplane (3-5) and hemispirobinonaplane (3-6) are predicted to be the best target molecules. These molecules are the least strained hemispiroalkaplanes, and the amount of strain associated with the highly distorted regions of these molecules is of a similar magnitude to that found for experimentally observed compounds of a similar nature. Only the $\mathrm{C}^{0}-\mathrm{C}^{\alpha}$ bonds (1.61-1.63 $\AA$ ) are found to be significantly longer than standard $\mathrm{C}-\mathrm{C}$ bonds, and bonds of this length are not without experimental precedent amongst molecules with a partially flattened tetracoordinate carbon center.


3-1


3-4 $\left(C_{2 v}\right)$


3-5 $\left(C_{2 v}\right)$


3-6 $\left(C_{2 v}\right)$

We find that methylation (or perhaps alkylation with larger groups like isopropyl or tert-butyl) at the $\mathrm{C}^{\alpha}$ atoms reduces the total strain and the $A p S E$ in the hemispiroalkaplanes. Such groups are also likely to have some effect in protecting the apical carbon atom, and may facilitate the ring-closure reaction (a carbene insertion reaction) that forms the last step in a potential route to hemispiroalkaplanes. Clearly, alkylation at $\mathrm{C}^{\alpha}$ should be considered in any synthetic strategy.

We hope that the remarkable features of the hemispiroalkaplanes - a new class of saturated hydrocarbons with a pyramidal-tetracoordinate carbon atom and basicity higher than that measured to date for any known organic compound - will fuel attempts at synthesis of these molecules.

## References

(1) (a) McGrath, M. P.; Radom, L.; Schaefer, H. F. "Bowlane: toward planar tetracoordinate carbon," J. Org. Chem. 1992, 57, 4847-4850. See also: (b) Dodziuk, H. "Bowlane (tetracyclo[3.3.3.1 $\left.{ }^{3,10} .1^{7,10}\right]$ tridecane): a new hypothetical molecule possessing a pyramidal tetracoordinated carbon atom in the ground state," J. Mol. Struct., Theochem. 1990, 239, 167-172; (c) Dodziuk, H. "Unusual saturated hydrocarbons: Interaction between theoretical and synthetic chemistry," Top. Stereochem. 1994, 21, 351-380.
(2) McGrath, M. P.; Radom, L. "Alkaplanes: a class of neutral hydrocarbons containing a potentially planar tetracoordinate carbon," J. Am. Chem. Soc. 1993, 115, 3320-3321.
(3) Lyons, J. E.; Rasmussen, D. R.; McGrath, M. P.; Nobes, R. H.; Radom, L. "Octaplane: a saturated hydrocarbon with a remarkably low ionization energy leading to a cation with a planar tetracoordinate carbon atom," Angew. Chem., Int. Ed. 1994, 33, 1667-1668; Angew. Chem. 1994, 106, 1722.
(4) (a) Radom, L.; Rasmussen, D. R. "Planar Carbon Story," Pure Appl. Chem. 1998, 1977-1984; (b) Rasmussen, D. R.; Radom, L. "Planar-tetracoordinate carbon in a neutral saturated hydrocarbon. Theoretical design and characterization," Angew. Chem., Int. Ed. 1999, 38, 2876-2878; Angew. Chem. 1999, 111, 3051-3054.
(5) For recent reviews of work in the design and synthesis of planar-tetracoordinate carbon containing molecules, see: (a) Sorger, K.; Schleyer, P. v. R. "Planar and inherently nontetrahedral tetracoordinate carbon: a status report," J. Mol. Struct., Theochem. 1995, 338, 317-346; (b) Röttger, D.; Erker, G. "Compounds containing planar-tetracoordinate carbon," Angew. Chem., Int. Ed. 1997, 36, 813-827; Angew. Chem. 1997, 109, 840-856; (c) Siebert, W.; Gunale, A. "Compounds containing a planar-tetracoordinate carbon atom as analogues of planar methane," Chem. Soc. Rev. 1999, 28, 367-371.
(6) (a) Liebman, J. F.; Greenberg, A. "A survey of strained organic molecules," Chem. Rev. 1975, 76, 311-365; (b) Greenberg, A.; Liebman, J. F. "A potpourri of pathologies" in Strained Organic Molecules; Academic Press: New York, 1978; Vol. 38, pp 342-385.
(7) (a) Minkin, V. I.; Minyaev, R. M.; Zacharov, I. I. "Semiempirical and ab initio calculations on the automerization of methane," J. Chem. Soc., Chem. Commun. 1977, 213-214; (b) Gordon, M. S.; Schmidt, M. W. "Does methane invert through square planar?" J. Am. Chem. Soc. 1993, 115, 7486-7492; (c) Pepper, M. J. M.; Shavitt, I.; Schleyer, P. v. R.; Glukhovtsev, M. N.; Janoschek, R.; Quack, M. "Is stereomutation of methane possible?" J. Comput. Chem. 1995, 16, 207-225.
(8) (a) Venepalli, B. R.; Agosta, W. C. "Fenestranes and the flattening of tetrahedral carbon," Chem. Rev. 1987, 87, 399-410; (b) Agosta, W. C. "Inverted and planar carbon" in The Chemistry of the Alkanes and Cycloalkanes; Patai, S. and Rappoport, Z., Ed.; Wiley: New York, 1992, pp 927-962, and references therein; (c) Luef, W.; Keese, R. "Planarizing distortions in carbon compounds," Adv. Strain Org. Chem. 1993, 3, 229-267, and references therein; (d) Brunvoll, J.; Guidetti-Grept, R.; Hargittai, I.; Keese, R. "204. Synthesis and electron-diffraction structure of all-cis-[5.5.5.5]fenestrane," Helv. Chim. Acta 1993, 76, 2838-2846; (e) Guidetti-Grept, R. G.; Herzog, B.; Debrunner, B.; Siljegovic, V.; Keese, R.; Frey, H.-M.; Hauser, A.; König, O.; Lüthi, S.; Birrer, J.; Nyffeler, D.; Förster, M.; Bürgi, H.-B. "A [5.5.5.5]fenestrane derivative," Acta Crystallogr., Sect. C: Cryst. Struct.

Commun. 1995, C51, 495-497; (f) Thommen, M.; Keese, R. "Fenestranes in recent synthetic developments," Synlett 1997, 231-240; and references therein.
(a) Wiberg, K. B.; McClusky, J. V. "Tricyclo[2.1.0.0 ${ }^{1,3}$ ]pentane," Tetrahedron Lett. 1987, 28, 5411-5414; (b) Wiberg, K. B.; Chaves, A. "Predominant inversion of configuration in an intramolecular carbene addition to an alkene," J. Am. Chem. Soc. 1989, 111, 8052-8053; (c) Wiberg, K. B.; McMurdie, N.; McClusky, J. V.; Hadad, C. M. "Tricyclo[2.1.0.0 ${ }^{1,3}$ ]pentane," J. Am. Chem. Soc. 1993, 115, 10653-10657; (d) Wiberg, K. B.; Snoonian, J. R. "Bridged spiropentanes - ring expansion," Tetrahedron Lett. 1995, 36, 1171-1174; (e) Wiberg, K. B.; Snoonian, J. R.; Lahti, P. M. "Ring contraction of a twocarbon bridged spiropentane," Tetrahedron Lett. 1996, 37, 8285-8288; (f) Wiberg, K. B.; Snoonian, J. R. "Synthesis, reactions, and structural studies of two-carbon bridged spiropentanes," J. Org. Chem. 1998, 63, 1402-1407; (g) Wiberg, K. B.; Snoonian, J. R. "Ring expansion and contraction of a two-carbon bridged spiropentane," J. Org. Chem. 1998, 63, 1390-1401; (h) Our MP2/6-31G(d) calculations predict the preferred symmetry of 3-11 to be $C_{1}$ and not $C_{2}$ as might be expected, but all four bonds to the tetracoordinate carbon do lie in the same hemisphere.
(10) The term half-planar methane has been suggested to describe a 'see-saw' geometry at tetracoordinate, pentavalent carbon (e.g. 3-19): Radius, U.; Silverio, S. J.; Hoffmann, R.; Gleiter, R. "A five-coordinate carbon center and Zr to $\mathrm{H}, \mathrm{B}$, and C bonding in $\mathrm{Cp}_{2} \mathrm{Zr}\left[\mathrm{CH}_{2}\left(\mathrm{BH}\left(\mathrm{C}_{6} \mathrm{~F}_{5}\right)_{2}\right)_{2}\right]$," Organometallics 1996, 15, 3737-3745.
(11) (a) Skattebøl, L. "Chemistry of gem-dihalocyclopropanes. II. The reaction of dienes with dibromocarbene," J. Org. Chem. 1964, 29, 2951-2956; (b) Skattebøl, L. "Chemistry of gem-dihalocyclopropanes. V. Formation of tricyclo[4.1.0.04,6]heptane and derivatives," J. Org. Chem. 1966, 31, 2789-2794; (c) Köbrich, G.; Baumann, M. "Bridged methylenecyclopropanes as test cases for Brett's rule: 2,5,5,7,7-pentamethylbicyclo[4.1.0]hept-1-ene," Angew. Chem., Int. Ed. 1972, 11, 52-53; Angew. Chem. 1972, 84, 62-63; (d) Baird, M. S. "Tetracyclo[3.3.1. $0^{2,4} .0^{2,8}$ ]nonane. A strained spiro-compound," J. Chem. Soc., Chem. Commun. 1974, 197-198; (e) Becher, G.; Skattebøl, L. "Thermal reactions of meso- and racemic deca-2,3,7,8-tetraene," Tetrahedron Lett. 1979, 14, 1261-1264; (f) Brinker, U. H.; Streu, J. "4,5-Benzotricyclo[4.1.0.0., ${ }^{1,3}$ ]hept-4-ene," Angew. Chem., Int. Ed. 1980, 19, 631-632; Angew. Chem. 1980, 92, 641; (g) Brinker, U. H.; Wilk, G.; Gomann, K. "Thermolysis and reactions of 4,5-benzotricyclo[4.1.0.0 ${ }^{1,3}$ ]hept-4-ene and $o$-(propadienyl)styrene," Angew. Chem., Int. Ed. 1983, 22, 868-869; Angew. Chem. 1983, 95, 892; (h) Brinker, U. H.; Gomann, K.; Zorn, R. "Tricyclo[4.1.0.0 ${ }^{1,3}$ hept-4-enes as intermediates," Angew. Chem., Int. Ed. 1983, 22, 869-870; Angew. Chem. 1983, 95, 893; (i) Wiberg, K. B.; Chaves, A. "Predominant inversion of configuration in an intramolecular carbene addition to an alkene," J. Am. Chem. Soc. 1989, 111, 8052-8053; (j) Miebach, T.; Wuster, H.; Brinker, U. H. "Carbene rearrangements. 42. Intramolecular addition versus novel carbon hydrogen bond insertion reactions of N -alkenyl-substituted cyclopropylidenes," $J$. Org. Chem. 1993, 58, 6520-6523; (k) Miebach, T.; Brinker, U. H. "trans-Tricyclo[5.1.0.0 ${ }^{1,3}$ ]octane," J. Org. Chem. 1993, 58, 6524-6525.
(12) (a) Smith, Z.; Andersen, B.; Bunce, S. "Electron-diffraction study of gaseous tricyclo[4.1.0.0 ${ }^{1,3}$ ]heptane," Acta Chem. Scand. A 1977, 31, 557-562; (b) Wiberg, K. B. "Structures and energies of the tricyclo[4.1.0.0 $0^{1,3}$ heptanes and the tetracyclo[4.2.1.0 ${ }^{2,9}$ $\left..0^{5,9}\right]$ nonanes. Extended group equivalents for converting $a b$ initio energies to heats of for-
mation," J. Org. Chem. 1985, 50, 5285-5291; (c) Gleiter, R.; Krennrich, G.; Brinker, U. H. "Electronic structure of spiropentane and some derivatives," J. Org. Chem. 1986, 51, 2899-2901; (d) Boese, R.; Bläser, D.; Gomann, K.; Brinker, U. H. "Spiropentane as a tensile spring," J. Am. Chem. Soc. 1989, 111, 1501-1503; (e) Luef, W.; Keese, R. "Angular distortions at tetracoordinate carbon: planoid distortions in small spiroalkanes," J. Mol. Struct., Theochem. 1992, 257, 353-368.
(13) For reviews, see: (a) Minkin, V. I.; Minyaev, R. M. "The nonclassical polyhedral organic molecules and ions" in Progress in Theoretical Organic Chemistry; Csizmadia, I. G., Ed.; Elsevier: Amsterdam, 1982; Vol. 3, pp 121-155; (b) Minkin, V. I.; Minyaev, R. M.; Zhdanov, Y. A. "Nontetrahedral tetracoordinate carbon atom in organic compounds" in Nonclassical Structures of Organic Compounds; Mir: Moscow, 1987, pp 248-306 (translated by B. V. Rassadin).
(14) See also: (a) Minyaev, R. M.; Minkin, V. I. "Pyramidal tetracoordinate carbon," J. Org. Chem. USSR (Engl. Transl.) 1978, 14, 1-12; Zh. Org. Khim. 1978, 14, 3-15; (b) Minyaev, R. M.; Minkin, V. I.; Zefirov, N. S.; Zhdanov, Y. A. "An approach to the synthesis of pyramidane," J. Org. Chem. USSR (Engl. Transl.) 1979, 15, 1815-1821; Zh. Org. Khim. 1979, 15, 2009-2016; (c) Minkin, V. I.; Minyaev, R. M. "Stabilization of pyramidal tetracoordinated carbon in organic molecules," J. Org. Chem. USSR (Engl. Transl.) 1979, 15, 197-204; Zh. Org. Khim. 1979, 15, 225-234; (d) Natanzon, V. I.; Minyaev, R. M. "Stabilization of the carbon atom by two collinear double bonds," Theor. Exp. Chem. 1981, 17, 207-209; Teor. Éksp. Khim. 1981, 17, 264-268; (e) Minkin, V. I.; Minyaev, R. M.; Orlova, G. V. "Pyramidane and isoelectronic cations," J. Mol. Struct., Theochem. 1984, 110, 241-253; (f) Lewars, E. "Pyramidane - an ab initio study of the $\mathrm{C}_{5} \mathrm{H}_{4}$ potential energy surface," J. Mol. Struct., Theochem. 1998, 423, 173-188.
(15) (a) Rossell, O.; Seco, M.; Segales, G.; Alvarez, S.; Pellinghelli, M. A.; Tiripicchio, A.; Demontauzon, D. "Iron-gold (or -mercury) carbide clusters derived from $\left[\mathrm{Fe}_{6} \mathrm{C}(\mathrm{CO})_{16}\right]^{2-}$ -X-ray crystal structures of $\mathrm{NEt}_{4}\left[\mathrm{Fe}_{6} \mathrm{C}\left(\mathrm{AuPPh}_{3}\right) \mathrm{CO}_{16}\right]$ and $\left[\mathrm{Fe}_{4} \mathrm{C}\left(\mathrm{AuPPh}_{3}\right) \mathrm{CO}_{11} \mathrm{NO}\right]$," Organometallics 1997, 16, 236-245. For other examples of exposed carbon atoms stabilized by coordination to a metal cluster see: (b) Bradley, J. S.; Ansell, G. B.; Leonowicz, M. E.; Hill, E. W. "Synthesis and molecular structure of $\mu^{4}$-carbido- $\mu^{2}$-carbonyl-dodecacarbonyltetrairon, a neutral iron butterfly cluster bearing an exposed carbon atom," J. Am. Chem. Soc. 1981, 103, 4968-4970; (c) Adams, C. J.; Bruce, M. I.; Skelton, B. W.; White, A. H. "Synthesis and X-ray structures of two complexes containing dicarbon $\left(\mathrm{C}_{2}\right)$ attached to $\mathrm{Ru}_{5}$ clusters with unusual core geometries," J. Chem. Soc., Chem. Commun. 1992, 26-29; (d) Adams, C. J.; Bruce, M. I.; Skelton, B. W.; White, A. H. "Planar tetracoordinate carbon - a novel environment in a pentaruthenium cluster," J. Chem. Soc., Chem. Commun. 1996, 975-976.
(16) (a) Scherbaum, F.; Huber, B.; Müller, G.; Schmidbaur, H. "Use of the CH acidity of 2,4,4-trimethyl-4,5-dihydroxyazole to synthesize triauriomethanes and novel gold clusters," Angew. Chem., Int. Ed. 1988, 27, 1542-1544; Angew. Chem. 1988, 100, 1600; (b) Scherbaum, F.; Grohmann, A.; Müller, G.; Schmidbaur, H. "Synthesis, structure and bonding of the cation $\left[\left\{\left(\mathrm{C}_{6} \mathrm{H}_{5}\right) \mathrm{PAu}\right\}_{5} \mathrm{C}^{+}, "\right.$ Angew. Chem., Int. Ed. 1989, 28, 463-465; Angew. Chem. 1989, 101, 464; (c) Schmidbaur, H.; Gabbaï, F. P.; Schier, A.; Riede, J. "Hypercoordinate carbon in protonated tetraauriomethane molecules," Organometallics 1995, 14, 4969-4971.
(17) (a) For pyramidal $\left[\left(\mathrm{Ph}_{3} \mathrm{PAu}\right)_{4} \mathrm{As}\right]^{+}$, see: Zeller, E.; Beruda, H.; Kolb, A.; Bissinger, P.; Riede, J.; Schmidbaur, H. "Change of coordination from tetrahedral gold-ammonium to square-pyramidal gold-arsonium cations," Nature 1991, 352, 141-143; (b) For pyramidal $\left[\left(\mathrm{Ph}_{3} \mathrm{PAu}\right)_{4} \mathrm{~S}^{2+}\right.$ see: Canales, F.; Gimeno, M. C.; Jones, P. G.; Laguna, A. "Aurophilicity at sulfur centers - synthesis and structure of the tetragold(I) species $\left[\left(\mathrm{Ph}_{3} \mathrm{PAu}\right)_{4} \mathrm{~S}\right]\left(\mathrm{Cf}_{3} \mathrm{SO}_{3}\right)_{2}$. $2 \mathrm{CH}_{2} \mathrm{Cl}_{2}$," Angew. Chem., Int. Ed. 1994, 33, 769-770; Angew. Chem. 1994, 106, 811.
(18) For ab initio calculations on $\left[\left(\mathrm{H}_{3} \mathrm{PAu}\right)_{4} \mathrm{C}\right]$ and isoelectronically-related systems (including a prediction that $\left[\left(\mathrm{H}_{3} \mathrm{PAu}\right)_{4} \mathrm{P}\right]^{+}$will prefer to be pyramidal), see: (a) Li, J.; Pyykkö, P. "Structure of $\mathrm{E}\left(\mathrm{AuPH}_{3}\right)^{4+}, \mathrm{E}=\mathrm{N}, \mathrm{P}, \mathrm{As}-T_{\mathrm{d}}$ or $C_{4 \mathrm{v}}$ ?" Inorg. Chem. 1993, 32, 2630-2634; (b) Haberlen, O. D.; Schmidbaur, H.; Rösch, N. "Stability of main-group element-centered gold cluster cations," J. Am. Chem. Soc. 1994, 116, 8241-8248; (c) Pyykkö, P.; Tamm, T. "Theory of the $\mathrm{d}^{10}-\mathrm{d}^{10}$ closed-shell attraction - $4-\left(\mathrm{XAu}^{1}\right)_{\mathrm{n}} \mathrm{M}^{+}$centered systems," Organometallics 1998, 17, 4842-4852.
(19) Jemmis, E. D.; Schleyer, P. v. R. "Aromaticity in three dimensions. 4. Influence of orbital compatibility on the geometry and stability of capped annulene with six interstitial electrons," J. Am. Chem. Soc. 1982, 104, 4781-4788.
(20) For a review, see: Schwarz, H. "Pyramidal carbocations," Angew. Chem., Int. Ed. 1981, 20, 991-1066; Angew. Chem. 1981, 93, 1046.
(21) (a) Stohrer, W.-D.; Hoffmann, R. "Bond-stretch isomerism and polytopal rearrangements in $(\mathrm{CH})_{5}{ }^{+}$, $(\mathrm{CH})_{4} \mathrm{CO}$," J. Am. Chem. Soc. 1972, 94, 1661-1668; (b) Masamune, S.; Sakai, M.; Ona, H. "Nature of the (CH) ${ }_{5}{ }^{+}$species. I. Solvolysis of 1,5-dimethyltricyclo[2.1.0.0 ${ }^{2,5}$ ]pent-3-yl benzoate," J. Am. Chem. Soc. 1972, 94, 8955-8956; (c) Masamune, S.; Sakai, M.; Ona, H.; Jones, A. J. "Nature of the (CH) ${ }_{5}{ }^{+}$species.II. Direct observation of the carbonium ion of 3-hydroxyhomotetrahedrane derivatives," J. Am. Chem. Soc. 1972, 94, 8956-8958; (d) Hart, H.; Kuzuya, M. "Evidence concerning the structure of (CH) ${ }_{5}{ }^{+}$ type carbonium ions," J. Am. Chem. Soc. 1972, 94, 8958-8959; (e) Saunders, M.; Berger, R.; Jaffe, A.; McBride, J. M.; O’Neill, J.; Breslow, R.; Hoffman Jr., J. M.; Perchonock, C.; Wasserman, E.; Hutton, R. S.; Kuck, V. J. "Unsubstituted cyclopentadienyl cation, a ground state triplet," J. Am. Chem. Soc. 1973, 95, 3017-3018; (f) Kollmar, H.; Smith, H. O.; Schleyer, P. v. R. "CNDO calculations on isomeric (CH) ${ }_{5}{ }^{+}$cations," J. Am. Chem. Soc. 1973, 95, 5834-5836; (g) Hehre, W. J.; Schleyer, P. v. R. "Cyclopentadienyl and related $(\mathrm{CH})_{5}{ }^{+}$cations," J. Am. Chem. Soc. 1973, 95, 5837-5839; (h) Masamune, S.; Sakai, M.; Kemp-Jones, A. V.; Ona, H.; Venot, A.; Nakashima, T. "The nature of carbocations derived from tricyclo[3.1.1.0 $0^{2,4}$ ]hept-6-yl and tricyclo[3.2.0.0 $0^{2,7}$ ]hept-4-yl systems," Angew. Chem., Int. Ed. 1973, 12, 769-771; Angew. Chem. 1973, 85, 829; (i) Dewar, M. J. S.; Haddon, R. C. "MINDO/3 study of (CH) ${ }_{5}{ }^{+}$and (CH) ${ }_{5}{ }^{-}$," J. Am. Chem. Soc. 1973, 95, 5836-5837; (j) Kemp-Jones, A. V.; Nakamura, N.; Masamune, S. "A bishomo square-pyramidal carbonium ion," J. Chem. Soc., Chem. Commun. 1974, 109-110; (k) Hogeveen, H.; Kwant, P. "Pyramidal mono- and dications: bridge between organic and organometallic chemistry," Acc. Chem. Res. 1975, 8, 413-420; (1) Köhler, H.-J.; Lischka, H. "Theoretical investigations on carbocations. Structure and stability of $\mathrm{C}_{3} \mathrm{H}_{5}{ }^{+}, \mathrm{C}_{4} \mathrm{H}_{9}{ }^{+}$(2-butyl cation), $\mathrm{C}_{5} \mathrm{H}_{5}^{+}, \mathrm{C}_{6} \mathrm{H}_{7}{ }^{+}$(protonated benzene), and $\mathrm{C}_{7} \mathrm{H}_{11}{ }^{+}$(2-norbornyl cation)," J. Am. Chem. Soc. 1979, 101, 3479-3486; (m) Olah, G. A.; Surya Prakash, G. K.; Liang, G.; Westerman, P. W.; Kunde, K.; Chandrasekhar, J.; Schleyer, P. v. R. "1 ${ }^{H}$ and ${ }^{13}$ C NMR spectroscopic study of 9-fluorenyl cations," J. Am. Chem. Soc. 1980, 102, 4485-4492.
(22) (a) Feng, J.; Leszczynski, J.; Weiner, B.; Zerner, M. "The reaction $\mathrm{C}_{3} \mathrm{H}_{3}{ }^{+}+\mathrm{C}_{2} \mathrm{H}_{2}$ and the structural isomers of $\mathrm{C}_{5} \mathrm{H}_{5}{ }^{+}$, , J. Am. Chem. Soc. 1989, 111, 4648-4655; (b) Glukhovtsev, M. N.; Reindl, B.; Schleyer, P. V. R. "What is the preferred structure of the singlet cyclopentadienyl cation," Mendeleev Commun. 1993, 100-102; (c) Glukhovtsev, M. N.; Bach, R. D.; Laiter, S. "Computational study of the thermochemistry of $\mathrm{C}_{5} \mathrm{H}_{5}{ }^{+}$isomers - Which $\mathrm{C}_{5} \mathrm{H}_{5}{ }^{+}$isomer is the most stable," J. Phys. Chem. 1996, 100, 10952-10955.
(23) Hehre, W. J.; Radom, L.; Schleyer, P. v. R.; Pople, J. A. Ab Initio Molecular Orbital Theory; Wiley: New York, 1986.
(24) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Zakrzewski, V. G.; Petersson, G. A.; Montgomery, J., J. A.; Stratmann, R. E.; Burant, J. C.; Dapprich, S.; Millam, J. M.; Daniels, A. D.; Kudin, K. N.; Strain, M. C.; Farkas, O.; Tomasi, J.; Barone, V.; Cossi, M.; Cammi, R.; Mennucci, B.; Pomelli, C.; Adamo, C.; Clifford, S.; Ochterski, J.; Petersson, G. A.; Ayala, P. Y.; Cui, Q.; Morokuma, K.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Cioslowski, J.; Ortiz, J. V.; Baboul, A. G.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Challacombe, M.; Gill, P. M. W.; Johnson, B. G.; Chen, W.; Wong, M. W.; Andres, J. L.; Gonzalez, C.; Head-Gordon, M.; Replogle, E. S.; Pople, J. A. GaUSSIAN 98, Revision A.7; Gaussian, Inc.: Pittsburgh PA, 1998.
(25) (a) Pople, J. A.; Scott, A. P.; Wong, M. W.; Radom, L. "Scaling factors for obtaining fundamental vibrational frequencies and zero-point energies from HF/6-31G* and MP2/6$31 G^{*}$ harmonic frequencies," Isr. J. Chem. 1993, 33, 345; (b) Scott, A. P.; Radom, L. "Harmonic vibrational frequencies: an evaluation of Hartree-Fock, Møller-Plesset, quadratic configuration interaction, density functional theory, and semi-empirical scale factors," J. Phys. Chem. 1996, 100, 16502-16513.
(26) (a) Schulman, J. M.; Sabio, M. L.; Disch, R. L. "Structure and energetics of [4.4.4.4]fenestrane," J. Am. Chem. Soc. 1983, 105, 743-744; (b) Schulman, J. M.; Disch, R. L. "Ab initio heats of formation of medium-sized hydrocarbons. The heat of formation of dodecahedrane," J. Am. Chem. Soc. 1984, 106, 1202-1204; (c) Disch, R. L.; Schulman, J. M.; Sabio, M. L. "Ab initio heats of formation of medium-sized hydrocarbons. 2. Use of second-order correlation energies," J. Am. Chem. Soc. 1985, 107, 1904-1906; (d) Disch, R. L.; Schulman, J. M. "Ab initio heats of formation of medium-sized hydrocarbons. 7. The [n]prismanes," J. Am. Chem. Soc. 1988, 110, 2102-2105; (e) Schulman, J. M.; Disch, R. L. "A theoretical study of pagodane and related systems," J. Mol. Struct., Theochem. 1995, 358, 51-54; (f) Disch, R. L.; Schulman, J. M. "Heat of formation of dodecahedrane," J. Phys. Chem. 1996, 100, 3504-3506.
(27) For general aspects of the treatment of strain in hydrocarbons, see: (a) Schleyer, P. v. R.; Williams, J. E.; Blanchard, K. R. "The evaluation of strain in hydrocarbons. The strain in adamantane and its origin," J. Am. Chem. Soc. 1970, 92, 2377-2386; (b) Greenberg, A.; Liebman, J. F. Strained Organic Molecules; Academic: New York, 1978; Ch. 1, pp 1-24; (c) Wiberg, K. B. "The concept of strain in organic chemistry," Angew. Chem., Int. Ed. 1986, 25, 312-322; (d) Wiberg, K. B.; Bader, R. F. W.; Lau, C. D. H. "Theoretical analysis of hydrocarbon properties. 2. Additivity of group properties and the origin of strain energy," J. Am. Chem. Soc. 1987, 109, 1001-1012; (e) Haufe, G.; Mann, G. Chemistry of alicyclic compounds. Structure and chemical transformations; Elsevier: Amsterdam, 1989,
pp 79-158; (f) Halton, B. "Strain in organic chemistry: a perspective," in Advances in strain in organic chemistry; Halton, B., Ed.; JAI Press: London, 1991; Vol. 1, pp 1-17; (g) Grimme, S. "Theoretical bond and strain energies of molecules derived from properties of the charge density at bond critical points," J. Am. Chem. Soc. 1996, 118, 1529-1534; (h) Wiberg, K. B.; Ochterski, J. W. "Comparison of different ab initio theoretical models for calculating isodesmic reaction energies for small-ring and related compounds," $J$. Comput. Chem. 1997, 18, 108-114.
(a) The experimental heats of formation of the small unstrained hydrocarbons (ethane propane, isobutane and neopentane) were taken from: Afeefy, H. Y.; Liebman, J. F.; Stein, S. E. "Neutral Thermochemical Data" in NIST Chemistry WebBook, NIST Standard Reference Database Number 69; Mallard, W. G. and Linstrom, P. J., Ed.; National Institute of Standards and Technology: Gaithersburg MD, May 1999, (http://webbook.nist.gov); (b) Most other experimental values for the heats of formation were taken from: Pedley, J. B.; Naylor, R. D.; Kirby, S. P. Thermochemical Data of Organic Compounds; 2nd ed.; Chapman and Hall: London, 1986; (c) The heat of formation of [1.1.1]propellane (3-42) is quoted from: Wiberg, K. B.; Ochterski, J. W. "Comparison of different ab initio theoretical models for calculating isodesmic reaction energies for small-ring and related compounds," J. Comput. Chem. 1997, 18, 108-114; (d) The G2 value for the heat of formation of tetrahedrane (3-40) is given in the absence of an experimental value: Glukhovtsev, M. N.; Laiter, S.; Pross, A. "Thermochemistry of cyclobutadiene and tetrahedrane: A highlevel computational study," J. Phys. Chem. 1995, 99, 6828-6831.
(29) (a) Curtiss, L. A.; Raghavachari, K.; Redfern, P. C.; Pople, J. A. "Assessment of Gaussian2 and density functional theories for the computation of enthalpies of formation," $J$. Chem. Phys. 1997, 106, 1063-1079; (b) Petersson, G. A.; Malick, D. K.; Wilson, W. G.; Ochterski, J. W.; Montgomery, J. A.; Frisch, M. J. "Calibration and comparison of the Gaussian-2, complete basis set, and density functional methods for computational thermochemistry," J. Chem. Phys. 1998, 109, 10570-10579.
(30) For assessments of various $a b$ initio methods in predicting gas-phase proton affinities, see: (a) Smith, B. J.; Radom, L. "Assigning absolute values to proton affinities - A differentiation between competing scales," J. Am. Chem. Soc. 1993, 115, 4885-4888; (b) Smith, B. J.; Radom, L. "An evaluation of the performance of density functional theory, MP2, MP4, F4, G2(MP2) and G2 procedures in predicting gas-phase proton affinities," Chem. Phys. Lett. 1994, 231, 345-351; (c) Smith, B. J.; Radom, L. "Calculation of proton affinities using the G2(MP2,SVP) procedure," J. Phys. Chem. 1995, 99, 6468-6471.
(31) (a) Lias, S. G.; Liebman, J. F.; Levin, R. D. "Evaluated gas phase basicities and proton affinities of molecules; heats of formation of protonated molecules," J. Phys. Chem. Ref. Data 1984, 13, 695-808; (b) Hunter, E. P. L.; Lias, S. G. "Evaluated gas phase basicities and proton affinities of molecules - an update," J. Phys. Chem. Ref. Data 1998, 27, 413-656.
(32) The points x referred to in $\theta_{\mathrm{x} 0 \mathrm{x}}$ are the midpoints of the $\mathrm{C}^{\alpha, 1}-\mathrm{C}^{\alpha, 2}$ and $\mathrm{C}^{\alpha, 3}-\mathrm{C}^{\alpha, 4}$ bonds (see 3-V and Figure 3-7 on page 123).
(33) $\mathrm{C}-\mathrm{C}$ single bonds in stable, isolable molecules can be greater than $1.7 \AA$ but such long $\mathrm{C}-\mathrm{C}$ single bonds are normally only found in perphenylated compounds. Bond lengths
up to $1.62 \AA$ are known in saturated hydrocarbons: Kaupp, G.; Boy, J. "Overlong C-C single bonds," Angew. Chem., Int. Ed. 1997, 36, 48-49, and references therein.
(34) The primary factor in the successful isolation of the tetra-tert-butyl derivative of tetrahedrane but not the parent has been shown to be the improved thermodynamic and kinetic stability of tetrahedrane relative to cyclobutadiene as a result of tetra-tert-butyl-substitution: (a) Schweig, A.; Thiel, W. "MNDO study of tetra-tert-butyltetrahedrane and tetra-tert-butylcyclobutadiene and of their thermal interconversion," J. Am. Chem. Soc. 1979, 101, 4742-3; (b) Kollmar, H. "An MO theoretical study on the stability of tetrahedrane," J. Am. Chem. Soc. 1980, 102, 2617-21; (c) Kollmar, H.; Carrion, F.; Dewar, M. J. S.; Bingham, R. C. "Ground states of molecules. 58. The $\mathrm{C}_{4} \mathrm{H}_{4}$ potential surface," J. Am. Chem. Soc. 1981, 103, 5292-303; (d) Maier, G. "Tetrahedrane and cyclobutadiene," Angew. Chem., Int. Ed. 1988, 27, 309-332; (e) Balci, M.; McKee, M. L.; Schleyer, P. v. R. "Theoretical study of tetramethyl- and tetra-tert-butyl-substituted cyclobutadiene and tetrahedrane," J. Phys. Chem. A 2000, 104, 1246-1255.
(a) Sedelmeier, G.; Fessner, W.-D.; Pinkos, R.; Grund, C.; Murty, B. A. R. C.; Hunkler, D.; Rihs, G.; Fritz, H.; Krüger, C.; Prinzbach, H. "Studien im Umfeld funktioalisierter/ anellierter acs-Tetracyclo[7.2.1.0 ${ }^{4,11} .0^{6,10}$ ]dodeca-2,7-dien-Gerüste - Röntgenstrukturanalysen einer 'face-to-face'-Dibenzoverbindung und eines Tetraoxadihydro-pagodans," Chem. Ber. 1986, 119, 3442-3472; (b) Prinzbach, H.; Fessner, W.-D. "Novel organic polycycles - An adventure in molecular architecture" in Organic Synthesis: Modern Trends; Chizhov, O., Ed.; Blackwell: Oxford, 1987, pp 23-42; (c) Fessner, W.-D.; Prinzbach, H. "The pagodane route to dodecahedrane" in Cage Hydrocarbons; Olah, G., Ed.; Wiley: New York, 1990, pp 353-405; (d) Prinzbach, H.; Weber, K. "From an insecticide to Plato's universe - The pagodane route to dodecahedranes - New pathways and new perspectives," Angew. Chem., Int. Ed. 1994, 33, 2239-2257; Angew. Chem. 1994, 106, 2329; (e) Pinkos, R.; Weiler, A.; Voss, T.; Weber, K.; Wahl, F.; Melder, J. P.; Fritz, H.; Hunkler, D.; Prinzbach, H. "From pagodanes to homologous, non-pentagonal dodecahedranes," Liebigs Ann./Recueil 1997, 2069-2088; (f) Sharma, V.; Keller, M.; Weiler, A.; Hunkler, D.; Prinzbach, H. "From pagodanes to nonpentagonal (homo)dodecahedranes - the undecacyclo[10.10.0.0 $\left.0^{2,20} .0^{3,10} .0^{4,19} .0^{5,9} .0^{6,18} .0^{7,15} .0^{8,13} .0^{19,22} .0^{16,21}\right]$ docosane cage," Angew. Chem., Int. Ed. 1997, 35, 2858-2861; Angew. Chem. 1997, 108, 3029-3031; (g) Prakash, G. K. S.; Weber, K.; Olah, G. A.; Prinzbach, H.; Wollenweber, M.; Etzkorn, M.; Voss, T.; Herges, R. "Long-lived [1.1.1.1]- and [2.2.1.1]-'isopagodane' dications: novel 4c/2e $\sigma$ bishomoaromatic dications," J. Chem. Soc., Chem. Commun. 1999, 1029-1030.
(36) Fukunaga, T.; Clement, R. A. "Thermal and base-catalyzed isomerization of birdcage and half-cage compounds," J. Org. Chem. 1977, 42, 270-275.
(37) Gajewski, J. J. Hydrocarbon thermal isomerizations; Academic Press: New York, 1981.
(38) (a) Flowers, M. C.; Frey, H. M. "The thermal isomerization of spirobicyclopropane," 1961, J. Chem. Soc., 5550-5551; (b) Frey, H. M.; Hopkins, R. G.; Skattebøl, L. "Thermal unimolecular isomerization of tricyclo[4.1.0.0 ${ }^{1,3}$ ]heptane," J. Chem. Soc. B 1971, 539-541; (c) Roth, W. R.; Wollweber, D.; Offerhaus, R.; Rekowski, V.; Lennartz, H.-W.; Sustmann, R.; Müller, W. "Zur Energiedelle von Diradikalen. IV. 2-Methylen-1,4-cyclohexadiyl," Chem. Ber. 1993, 126, 2701-2715.
(39) For the use of (2/2)CASPT2 in examining the stereomutation of spiropentane, see: Johnson, W. T. G.; Hrovat, D. A.; Borden, W. T. "Ab initio calculations on spiropentane stereomutations lead to a reinterpretation of the experimental results," J. Am. Chem. Soc. 1999, 121, 7766-777.
(40) For a description of CASPT2 and other MCSCF methods, and for leading references, see: (a) Schmidt, M. W.; Gordon, M. S. "The construction and interpretation of MCSCF wavefunctions," Annu. Rev. Phys. Chem. 1998, 49, 233-266; (b) Bally, T.; Borden, W. T. "Calculations on open-shell molecules: a beginner's guide" in Reviews in computational chemistry; Liptowitz, K. B. and Boyd, D. B., Ed.; Wiley-VCH: New York, 1999; Vol. 13, pp 1-97.
(41) A detailed examination of the potential energy surface of the hemispiroalkaplane-related pyramidal carbocation, tricyclo[4.1.0.0 ${ }^{1,3}$ heptyl cation (an ethano-bridged derivative of center-protonated spiropentane), found relatively high barriers for all dissociation routes: Szabo, K. J.; Cremer, D. "Route to a kinetically stabilized protonated spirocyclopentane with a pentacoordinated carbon atom - the missing link between bicyclo[3.2.0]hept-3-yl and 7-norbornyl cation," J. Org. Chem. 1995, 60, 2257-2259.

## Chapter 4 <br> Alkaplanes - Planar Carbon

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### 4.1 Introduction

In Chapter 1 we discussed in detail the contributions made to date in the search for planar-tetracoordinate carbon through both structural and electronic means. We also explained how this work led to our present approach to planar-tetracoordinate carbon. We present in this section highlights of the most important elements of that discussion which relate to attempts to design and synthesize systems containing a planar-tetracoordinate carbon.

The possibility of the existence of planar-tetracoordinate carbon has aroused much interest since the seminal work by Hoffmann, Alder and Wilcox in 1970. ${ }^{1}$ In this work Hoffmann et al. challenged the long-standing tenet of organic chemistry, established by van't Hoff and le Bel in 1870, ${ }^{2}$ which supposes that tetracoordinate carbon will have a tetrahedral geometry. However, Hoffmann suggested that because molecules with a simple chiral center at carbon do not racemize we should expect that an achiral geometry, such as a planar one, will lie at least $250 \mathrm{~kJ} \mathrm{~mol}^{-1}$ above the tetrahedral form. Model calculations on methane ${ }^{3}$ showed that the preference for a tetrahedral over a square-
planar bonding arrangement, at least in methane, was much greater than this proposed lower limit; computed estimates went as high as $1000 \mathrm{~kJ} \mathrm{~mol}^{-1}$. This preference for the tetrahedral geometry appeared so strong that it was considered unlikely that a simple carbon compound could be found that actually prefers a planar arrangement.



Figure 4-1. The electronic structure of square-planar methane ( $D_{4 \mathrm{~h}}$ symmetry) showing the $p$-type lone pair (HOMO) and six $\mathrm{C}-\mathrm{H}$ bonding electrons.

It has since been shown by both Gordon et al. ${ }^{4 \mathrm{a}}$ and Pepper et al. ${ }^{4 \mathrm{~b}}$ that the lowestenergy path for the hypothetical classical inversion of methane is not via a planar structure but via a pyramidal-type structure (with $C_{\mathrm{s}}$ or possibly $C_{4 \mathrm{v}}$ symmetry). ${ }^{4}$ Both groups also found that the lowest-energy planar structure for methane does not have four equivalent hydrogen atoms, as had been supposed, but has $C_{2 \mathrm{v}}$ symmetry and a structure that resembles a complex between $\mathrm{CH}_{2}$ and $\mathrm{H}_{2}$ (reminiscent of the structure for $\mathrm{CH}_{4}{ }^{2+}$ ). ${ }^{5}$ Further, the energy of the $C_{2 \mathrm{v}}\left(D_{4 \mathrm{~h}}\right)$ symmetry planar structure relative to the tetrahedral geometry is about $500(600) \mathrm{kJ} \mathrm{mol}^{-1}$. This is significantly higher than the homolytic dissociation energy of the $\mathrm{C}-\mathrm{H}$ bond in methane $\left(435 \mathrm{~kJ} \mathrm{~mol}^{-1}\right)^{6}$ and suggests that pla-
nar methane will not be achievable.
The problem of overcoming this strong preference for the tetrahedral geometry at a tetracoordinate carbon can be approached in one of two ways. The method that has received most attention and success to date is best described as electronic. ${ }^{\dagger}$ This approach tries to reduce the destabilization of the planar arrangement relative to the tetrahedral arrangement by replacing hydrogen with substituents that afford relative electronic stabilization to a planar or near-planar arrangement. An examination of the electronic structure of $D_{4 \mathrm{~h}}$ methane (Figure 4-1) shows a lone-pair $p$-type HOMO and four electron-deficient $\sigma$-bonds. ${ }^{\ddagger}$ It would thus be expected that substitution of hydrogen by groups with $\sigma$-donor $/ \pi$-acceptor characteristics (e.g. $\mathrm{Li}, \mathrm{BH}_{2}$ or $\mathrm{SiH}_{3}$ ) should favor a planar bonding arrangement at carbon. Such ligands afford electronic stabilization to the planar geometry (relative to the tetrahedral geometry) by delocalizing the electrons in the lone pair $p$-type orbital and increasing the electron density in the $\sigma$-bonds to carbon. It has also been found that placing the target carbon atom in small rings (particularly three-membered rings) also greatly helps in stabilizing the planar geometry over the tetrahedral-like geometry (see Section 1.5 .1 on page 23 ).


4-1


4-2


4-3

The electronic approach to planar carbon has been examined extensively using computational techniques. ${ }^{7}$ In 1976, Schleyer, Pople and co-workers ${ }^{7 \mathrm{a}}$ found a number of molecules (including 4-1-4-3) that were predicted by minimal basis set ab initio calculations to prefer a planar-tetracoordinate geometry over a tetrahedral-type geometry. ${ }^{\S}$

[^41]Much of their ground-breaking work has been subsequently re-examined at higher levels of theory and extended to include other similar, small polarorganometallic molecules. More recently, Sorger and Schleyer $^{7 b}$ have examined a range of small, lithium- and

4-4

4-5

4-6

4-7
boron-containing compounds with up to ten heavy atoms. They found seven molecules that are predicted to have a planar-tetracoordinate carbon atom (4-1-4-7). Most recently, Gribanova, Minyaev and Minkin ${ }^{7 c}$ have identified three isomers of $\mathrm{C}_{2} \mathrm{~B}_{2} \mathrm{H}_{4}(4$ $\mathbf{8 - 4 - 1 0}$ ) as preferring a planar geometry at the central tetracoordinate carbon atom.


4-8


4-9


4-10

None of these molecules (4-1-4-10) has yet been synthesized. Further, synthesis of the lithium-containing species may be complicated both by the tendency for lithium compounds to aggregate and by the tendency of donor solvent molecules to coordinate to the lithium centers and disrupt planar-tetracoordination at carbon. ${ }^{8}$ There is, however,

$)_{3} \mathrm{~W}=\mathrm{W}(\mathrm{O}-t-\mathrm{Bu})_{3}$
Dur (2,3,5,6-tetramethylpheny)
b $\mathrm{Ar}=$ Mes (2,4,6-trimethylphenyl)
a growing list of compounds that have been synthesized which have one or more planartetracoordinate carbon atoms. ${ }^{9,12}$ These compounds can be broadly classified into two groups. The first ${ }^{9}$ (e.g. 4-11 and 4-12) are polarorganometallics which owe the stability of the planar-tetracoordinate carbon solely to strong electronic stabilization afforded by one or more metal centers. The others ${ }^{12}$ are also polarorganometallics which rely on strong electronic stabilization from one or more metal centers, but also depend on the planar-tetracoordinate carbon atom being included in a $\pi$-bonding system (e.g. 4-13, 414 and $\mathbf{4 - 1 5}) .^{\dagger}$ Including the carbon atom of interest in a $\pi$-system is clearly a very

effective way of reducing the energy of the otherwise lone-pair p-type HOMO. In fact, in these compounds, the $\sigma^{2} \pi^{2}$ electronic configuration of square-planar methane becomes $\sigma^{n} \pi^{1}$, where $n \approx 3-4$ (a drastic reduction of $\pi$-electron density). However, this


$$
\begin{gather*}
\mathrm{M}^{1}=\mathrm{Ti}, \mathrm{Zr}, \mathrm{Hf} ; \mathrm{R}^{1}, \mathrm{R}^{2}=\mathrm{Alkyl}, \mathrm{Aryl}, \mathrm{SiMe}_{3} \\
\mathrm{M}^{2} \mathrm{R}^{3}{ }_{2}=\mathrm{BEt}_{2}, \mathrm{AlBBu}_{2}, \mathrm{AlMe}_{2}, \mathrm{AlEt}_{2}, \mathrm{GaMM}_{2} \\
\mathrm{~L}=\mathrm{Me}, \mathrm{Et}, \mathrm{CCMe}, \mathrm{CCPh}, \mathrm{CC} H e x, \mathrm{Cl}
\end{gather*}
$$

[^42]leaves some ambiguity as to the nature of the planar-tetracoordinate carbon atom which, although tetracoordinate, is clearly not derived from a saturated carbon atom. ${ }^{\dagger}$

The alternative approach to forming planar-tetracoordinate carbon may be described as structural. This method tries to flatten tetracoordinate carbon by constraining the positions of the four coordinating atoms to be in a plane. This is done by building a covalent molecular framework that benefits a planar arrangement at carbon. Although this approach to making planar-tetracoordinate carbon has been pursued actively, there has been only limited success to date. ${ }^{13}$


4-I


4-II

The simplest scheme which involves some planarizing distortion requires binding the four coordinating substituents to one another so as to form a fused, cyclic structure that is at least tricyclic but preferably tetracyclic (see Section 1.5 on page 19 for a detailed discussion). Saturated hydrocarbons of this form are commonly referred to as fenestranes (4-I and 4-II). Previous work, ${ }^{14-18}$ both theoretical and experimental,


4-16

$\mathrm{R}=\underset{\mathbf{4 - 1 7}}{\mathrm{CONHC}_{6} \mathrm{H}_{4} \mathrm{Br}}$
directed towards finding molecules with structurally imposed planarizing distortions at a tetracoordinate carbon atom, has centered mostly on this very broad class of hydrocarbons (e.g. tetracyclo[4.2.1.0 $0^{2,9} .0^{5,9}$ ]nonane or [3.5.3.5]fenestrane (4-16), ${ }^{16}$ an all-cis[4.4.4.5]fenestrane derivative (4-17), ${ }^{15}$ all-trans-[4.4.4.4]-fenestrane (all-trans-4-18), ${ }^{13,18}$

[^43]and $[5.5 .5 .5]$ fenestrane $\left.(\mathbf{4 - 1 9})^{13,14}\right)$. However, these molecules at best show only moderate distortions from the tetrahedral ideal. The most flattened tetracoordinate carbon reported to date for an isolable molecule can be found in the all-cis-[4.4.4.5]fenestrane derivative 4-17, ${ }^{13 \mathrm{~d}, 15 \mathrm{e}}$ which has opposing CCC angles ( $\angle \mathrm{C}^{\alpha, 1} \mathrm{C}^{0} \mathrm{C}^{\alpha, 3}$ and $\angle \mathrm{C}^{\alpha, 2} \mathrm{C}^{0} \mathrm{C}^{\alpha, 4}$ ) (see 4-II) of approximately $130^{\circ}$ (which is not greatly disturbed from the tetrahedral ideal of $109.5^{\circ}$ ).

all-trans-4-18

all-cis-4-19

all-trans-4-19

The all-trans isomer of [5.5.5.5]fenestrane (all-trans-4-19) is exceptional amongst the fenestranes. It is found through semi-empirical calculations to have an almost planar-tetracoordinate geometry at the central carbon atom. This isomer has not been synthesized but the lower-energy all-cis isomer (all-cis-4-19) has been synthesized. Our best calculations (at the MP2/6-31G(d) level) indicate that while all-trans-4-19 appears to be the most highly distorted (from tetrahedral) fenestrane examined to date, it still shows considerable deviation from planarity with a $\mathrm{C}^{\alpha, 1} \mathrm{C}^{0} \mathrm{C}^{\alpha, 3}$ angle of $164.1^{\circ}$. The alltrans isomer of [5.5.5.5]fenestrane also suffers from a low-energy barrier for conversion to the much lower energy all-cis isomer (all-cis-4-19), in which the central carbon atom is only slightly distorted from the tetrahedral ideal $\left(\angle \mathrm{C}^{\alpha, 1} \mathrm{C}^{0} \mathrm{C}^{\alpha, 3}=116.1^{\circ}\right)$.


4-20


4-21

Unsaturated fenestranes in which the central carbon atom is surrounded by an annu-
lene perimeter (e.g. 4-20 and 4-21), have also been proposed by Hoffman ${ }^{1}$ as candidates for containing a planar-tetracoordinated carbon atom. The intention here is clearly to gain some help in flattening the central carbon from delocalization of the lone pair on the central carbon into the $\pi$-system of the annulene perimeter. However, it appears that this is unlikely to be of much assistance. Böhm et al. and Chandrasekhar et al. have performed semi-empirical calculations ${ }^{19}$ on a number of Hoffmann's more promising systems and did not find any significant distortion beyond that imposed by the $\sigma$-framework. These calculations and other theoretical considerations led them to state emphatically that enclosure in an annulene perimeter does not confer any significant electronic stabilization on the planar form.


4-III


4-22

$4-23^{21 b}$

Some years ago, Wiberg proposed the paddlanes (4-III), ${ }^{20}$ which use structural constraints to effect strong deformation at a pair of quaternary bridgehead carbon atoms. In particular, Wiberg ${ }^{20 \mathrm{~d}}$ and Schleyer ${ }^{18 \mathrm{a}}$ have both suggested that the two bridgehead atoms of the symmetric paddlane 4-22 might be highly flattened. Our calculations indicate that the proposed, highly-symmetric $\left(D_{4 h}\right)$ structure for $\mathbf{4 - 2 2}$ is not stable but represents a high-order saddle point; resolution of all down-hill modes leads to disintegration of the basic paddlane structure. Although larger paddlanes are found to be stable, they no longer impose sufficient structural constraints at the bridgehead atoms to effect significant flattening. Consequently, the stable and known paddlanes ${ }^{21}$ all exhibit a relatively undistorted tetrahedral geometry at the two bridgehead atoms (e.g. 4-23 ${ }^{21 b}$ ). ${ }^{\dagger}$

As was discussed in Chapter 3, the hemialkaplanes (4-IV) can be seen as half-paddlane-like structures. Like the hemispiroalkaplanes (4-V), these molecules show considerable distortion from the tetrahedral ideal at a tetracoordinate carbon atom.

[^44]

4-IV


4-V


4-24

However, while the hemispiroalkaplanes (4-V) are all found to have a highly pyramidalized, tetracoordinate carbon, the larger hemialkaplanes, e.g. hemioctaplane or bowlane (4-24), are found to have a tetrahedral-like, but considerably flattened, apical carbon atom. For example, hemioctaplane is found to have CCC angles across the apical carbon atom $\left(\mathrm{C}^{0}\right)$ of $171.0^{\circ}$ and $148.8^{\circ}$.

Recently, Wiberg has had good success in achieving large distortions at a tetracoordinate carbon center through binding spiropentane with very short bridges (e.g. 4-25ketene and 4-26). ${ }^{22,23}$ These experimentally observed compounds have a CCC angle



across $\mathrm{C}^{0}$ of close to $180^{\circ}$. Although this work is not directed explicitly towards the synthesis of a planar-tetracoordinated carbon, it gives an indication of just how much distortion is possible at a $\mathrm{C}(\mathrm{C})_{4}$ center. However, although these compounds exhibit very large distortions at the quaternary carbon they are not particularly flattened. The angle between the two cyclopropane rings which are spiro-bound at $\mathrm{C}^{0}$ is around $80^{\circ}$ for 4-25 and $50^{\circ}$ for 4-26 (for a planar-tetracoordinate geometry this angle needs to be $0^{\circ}$ ).

Clearly, it is very difficult to significantly flatten tetracoordinate carbon in purely organic systems. Unusual bonding arrangements are possible, like the well-known 'inverted' carbon bonding in [1.1.1]propellane and the 'see-saw'-like bonding seen in the small, bridged spiropentanes (see above), but significant distortion toward a planartetracoordinate carbon geometry in a saturated hydrocarbon is not known. Can this incredible preference to distort from a planar bonding arrangement in saturated hydro-
carbons be overcome? With the aid of molecular orbital techniques it is possible to design and test a much larger number of molecules than could be readily examined in a laboratory. In this way, it is possible to pin-point which molecules are expected to have the desired property, in this case a planar-tetracoordinate carbon atom. This would then provide invaluable direction for attempts at synthesis.

In the following sections of this chapter, we will begin by accurately determining the energy required to flatten the central, tetracoordinate carbon atom in a number of small, prototypical saturated hydrocarbon systems - methane, neopentane and spiropentane. A complete examination of the lower-lying states of planar methane with a


4-VI


4-VII


4-VIII
range of methods (up to the most advanced techniques available) will provide us with valuable information on the accuracy of these methods in describing the unusual bonding situation found in a planar-tetracoordinate carbon atom. Neopentane and spiropentane serve as good model quaternary systems (they are two of the simplest systems which posses a $\mathrm{C}(\mathrm{C})_{4}$ substructure), and will provide some insight into the level of theory necessary to adequately describe a planar $\mathrm{C}(\mathrm{C})_{4}$ moiety.


We will then investigate a number of novel, neutral, saturated hydrocarbon cage
systems - members of the alkaplane (4-VI), spiroalkaplane (4-VII) and dimethanospiroalkaplane (4-VIII) families (e.g. octaplane ${ }^{24}$ (4-27), spiro[2.2]octaplane (4-28) and dimethanospiro[2.2]octaplane (4-29)). ${ }^{\dagger}$ These saturated hydrocarbons are designed to have good potential of containing a quaternary carbon atom where the four $\mathrm{C}-\mathrm{C}$ bonds all lie in a plane of symmetry, i.e. planar-tetracoordinate carbon in a neutral saturated hydrocarbon.

### 4.2 Methods

$A b$ initio molecular orbital calculations ${ }^{25}$ were carried out using the GAUSSIAN $98^{26}$ and MOLPRO ${ }^{27,28}$ programs.

Methane was treated using B3-LYP, MP2, $\operatorname{CCSD}(\mathrm{T})$ and MRCI methods. ${ }^{29}$ The methane manifold was examined by geometry optimization at the MP2 level with basis sets ranging from $6-31 \mathrm{G}(\mathrm{d})$ to $6-311+\mathrm{G}(3 \mathrm{df}, 2 \mathrm{p})$. Our best optimized structures on the methane manifold were determined at the $\operatorname{CCSD}(\mathrm{T}) / 6-311+\mathrm{G}(3 \mathrm{df}, 2 \mathrm{p})$ level. For the open-shell systems, a UHF wavefunction was used for the reference state in the singledeterminant methods and the UMP2 and UCCSD(T) formalisms were used in the correlation treatment in geometry optimizations which were all performed using GAUSSIAN 98. All electrons were correlated in these calculations. The $\operatorname{CCSD}(\mathrm{T})$ optimizations were performed numerically. The nature of the stationary points on the MP2 surfaces (as deduced from the number of imaginary frequencies) was determined using analytic force constant analysis. Examination of the nature of the stationary points on the $\operatorname{CCSD}(\mathrm{T})$ surfaces was done numerically using the energy-only scheme of GAUSSIAN 98. $\operatorname{CCSD}(\mathrm{T}) /$ AVQZ single point energies were determined at our best, $\operatorname{CCSD}(\mathrm{T}) / 6-$ $311+G(3 \mathrm{df}, 2 \mathrm{p})$ optimized, structures. $\operatorname{CCSD}(\mathrm{T})$ single point energy calculations on all systems except the open-shell singlet, were performed using the URCCSD(T) method (which uses an RHF reference function) of MOLPRO ${ }^{28 a}$ and the frozen-core approximation. Our best single determinant energy for the open-shell singlet configuration was calculated using the $\operatorname{UCCSD}(\mathrm{T})$ method of GAUSSIAN 98. MRCI calculations ${ }^{28 b, c}$ employing a very large basis set (AV5Z), which were corrected with a multi-reference equivalent of the Davidson correction ${ }^{30}$ (MRCI+Q), were also determined for our best

[^45]$\operatorname{CCSD}(\mathrm{T})$ optimized structures. Optimized geometries are listed in Table 4-2. Relative energies are given in Table 4-3 and Figure 4-3. Total energies are given in Tables C-5 and C-6 of Appendix C.

Neopentane and spiropentane were treated using the B3-LYP, MP2 and CCSD(T) methods. Structures were optimized at either the MP2(full)/6-31G(d) level for closed shell systems or the UMP2(full)/6-31G(d) level for open-shell (triplet) systems. For these calculations, all electrons were correlated and the usual six cartesian $d$-functions were used with the $6-31 \mathrm{G}(\mathrm{d})$ basis. The nature of the stationary points located was then determined by analytic force constant evaluations. The geometries of the stationary points were improved by optimization at the MP2(full)/6-311+G(2d,p) level. Improved energies for these structures were then calculated using the $\operatorname{CCSD}(\mathrm{T})$ and $\operatorname{URCCSD}(\mathrm{T})$ methods in Molpro. Here the frozen-core approximation was employed. Relative energies are given in Table 4-5. Total energies are given in Tables C-7 - C-10 of Appendix C .

Geometries for the planar-carbon target molecules were first obtained by optimization with constrained symmetry using the AM1 semi-empirical method. ${ }^{31}$ This was followed by HF/6-31G(d) and/or B3-LYP/6-31G(d) geometry optimization. The nature of the resulting stationary points was then examined by analytic frequency analysis at the appropriate level. Improved relative energies were obtained from MP2/6-311+G(2d,p)// HF/6-31G(d) and B3-LYP/6-311+G(2d,p)//B3-LYP/6-31G(d) calculations. Except where otherwise noted, five pure $d$-functions (instead of the usual six cartesian functions) were used with the $6-31 \mathrm{G}(\mathrm{d})$ basis and the carbon $1 s^{2}$-like core molecular orbitals were excluded from the correlation treatment (the frozen-core approximation).

For molecules of particular interest, improved geometries were obtained by optimization at the MP2 level using a $6-31 \mathrm{G}(\mathrm{d})$ basis that was enhanced to $6-311+\mathrm{G}(2 \mathrm{~d})$ at the central carbon atom $\left(\mathrm{C}^{0}\right)$ and to $6-311+\mathrm{G}(\mathrm{d})$ at the four adjacent carbon atoms $\left(\mathrm{C}^{\alpha}\right) .{ }^{\dagger}$ Four of the resulting structures (4-39, 4-47, 4-29 and 4-48) were then examined by numerical frequency analysis using double differencing to determine the nature of the

[^46]stationary points we had located. Improved relative energies were then determined from MP2(fc)/6-311+G(2d,p) single point energy calculations on the resulting structures.

The enhanced $6-31 \mathrm{G}(\mathrm{d})$ basis, designated hereafter as $6-311+\mathrm{G}(2 \mathrm{~d}, \mathrm{p})(\mathrm{red})$, was designed to afford $6-311+\mathrm{G}(2 \mathrm{~d}, \mathrm{p})$ at the central carbon atom without the added computational cost of using such a large basis for the entire molecule. The suitability of such a method is examined in Figure 4-2 on page 147 by comparing results obtained using this basis set with MP2 energies calculated using the full $6-311+G(2 d, p)$ basis.


Figure 4-2. Potential energy surfaces for the lowest-energy vibrational mode of dimethanospiro[2.2]octaplane calculated at a number of levels: $\square$ - MP2/6$311+G(2 d, p)$, - MP2/6-311+G(2d,p)(red), and O - MP2/6-31G(d). Geometries at fixed angles of deviation from planarity were optimized at the MP2/6$311+G(2 d, p)(r e d)$ level.

Calculations on methane have shown ${ }^{4}$ that an accurate description of the planartetracoordinate carbon moiety requires at least a second set of $d$-functions and a set of
diffuse functions on carbon. Without these components in the basis set, energies for planar structures are overestimated relative to distorted geometries. We find a similar result (see Table 4-3 on page 153), although we also find that the need for very large basis sets is somewhat less important for $\mathrm{C}(\mathrm{C})_{4}$ planar carbon moieties (i.e. a quaternary carbon) and when the B3-LYP method is being used (see Table 4-5 on page 158). Choosing an adequate basis set to properly describe the planar carbon electronic structure becomes critical for alkaplanes where the structures being examined approach planarity at the central quaternary carbon. Essentially, as the barrier to inversion at the central carbon atom (which occurs via a 'planar' geometry) becomes small, the relative increase in energy around the 'planar' structure, which results from not including two sets of $d$ functions nor diffuse functions, becomes important. This effect can artificially raise the barrier to inversion and shift the equilibrium to a more distorted geometry when too small a basis set is employed. In extreme cases, it can even introduce a barrier where no barrier should exist. As an example, we find that MP2(fc)/6-31G(d) and B3-LYP/6$31 \mathrm{G}(\mathrm{d})$ optimized geometries for dimethanospiro[2.2]octaplane (4-29) prefer a slight distortion away from planar-tetracoordination at $\mathrm{C}^{0}$, giving a $D_{2}$ symmetry structure. However, when optimized at the MP2(fc)/6-311+G(2d,p)(red) level, dimethanospiro[2.2]octaplane (4-29) optimizes to a $D_{2 \mathrm{~h}}$ symmetry structure. An examination of the lowest-energy vibrational mode of 4-29 (see Figure 4-2), which normally corresponds to the pathway for inversion at $\mathrm{C}^{0}$ for the spiroalkaplanes (4-VII), shows no barrier to inversion at both the MP2(fc)/6-311+G(2d,p) and MP2(fc)/6-311+G(2d,p)(red) levels and a very small $\left(0.35 \mathrm{~kJ} \mathrm{~mol}^{-1}\right)$, probably artificial, barrier at the MP2(fc)/6$31 \mathrm{G}(\mathrm{d})$ level. Our $6-311+\mathrm{G}(2 \mathrm{~d}, \mathrm{p})($ red $)$ basis, which adds extra $d$-functions and diffuse functions to the central region only, gives good agreement with the full $6-311+G(2 d, p)$ basis.

In order to compare the degree of flattening at the central carbon atom of a variety of molecules with different symmetry and structural properties, we have found it necessary to define a general quantity, $\alpha_{\text {plan }}$, that measures how close the five central carbon atoms come to forming a plane. The quantity $\alpha_{\text {plan }}$ is defined as the average deviation of each of the $\mathrm{C}^{\alpha}$ atoms from a best-fit plane drawn through the central carbon atom $\left(\mathrm{C}^{0}\right)$. This deviation from the best-fit plane is calculated as an angle so that it is independent of the bond lengths to each of the $\mathrm{C}^{\alpha}$ atoms. The best-fit plane is defined so as to mini-
mize the sum of these angles. ${ }^{\dagger}$ The quantity $\alpha_{\text {plan }}$ is thus bounded on the one hand by absolute planarity, $\alpha_{\text {plan }}=0^{\circ}$, and on the other by an exact tetrahedral arrangement, $\alpha_{\text {plan }}$ $=35.3^{\circ}$. Thus, neopentane, which has exact $T_{\mathrm{d}}$ symmetry, has $\alpha_{\text {plan }}=35.3^{\circ}$, while the MP2/6-31G(d) optimized structure for spiropentane has $\alpha_{\text {plan }}=21.2^{\circ}$, which reflects the opening up of two of the CCC angles through the spiro carbon to $137.2^{\circ}$. Values of $\alpha_{\text {plan }}$ for the MP2/6-31G(d) optimized structures of distorted tetracoordinate systems like all-trans-[4.4.4.4]fenestrane (all-trans-4-18), a highly distorted system with $D_{2 \mathrm{~d}}$ symmetry, ${ }^{13,18}$ and the experimentally known lowest-energy isomer of [5.5.5.5]fenestrane (all-cis-4-19), ${ }^{13,14}$ a mildly distorted system, are $18.3^{\circ}$ and $32.0^{\circ}$, respectively. ${ }^{\ddagger}$

Conventional total strain energies ( $S E$ ) were calculated in much the same way as was done in Chapter 3, by using a homodesmic reaction scheme in which the target hydrocarbon is broken down into the basic unstrained hydrocarbons: ethane, propane, isobutane and neopentane. ${ }^{32}$ For example, spiro[2.2]octaplane (4-28) gives the following reaction:

$$
\begin{equation*}
\mathbf{4 - 2 8}+30 \text { ethane } \rightarrow 5 \text { neopentane }+8 \text { isobutane }+8 \text { propane } \tag{4-1}
\end{equation*}
$$

The strain energy (SE) for spiro[2.2]octaplane (4-28) is then defined as $-\Delta H$ (Reaction 41). The heat of formation $\left(\Delta H_{\mathrm{f}}\right)$ of the hydrocarbon in question (in this case spirooctaplane (4-28)) is calculated using the computed enthalpy of the appropriate homodesmic reaction (e.g. $\Delta H$ (Reaction 4-1) for 4-28) and the experimental values for the heats of formation of the small unstrained hydrocarbons: ethane $\left(-83.9 \mathrm{~kJ} \mathrm{~mol}^{-1}\right)$, propane $\left(-104.7 \mathrm{~kJ} \mathrm{~mol}^{-1}\right)$, isobutane $\left(-134.2 \mathrm{~kJ} \mathrm{~mol}^{-1}\right)$ and neopentane $\left(-167.9 \mathrm{~kJ} \mathrm{~mol}^{-1}\right)$. ${ }^{33}$ Total energies were calculated at the MP2(fc)/6-311+G(2d,p) level and geometries were determined at the MP2(fc)/6-311+G(2d,p)(red) level for the majority of the alkaplanes (4-VI, 4-VII and 4-VIII), except where otherwise noted. The geometries for other

[^47]hydrocarbons, whose geometries are not expected to show the same basis set dependency as the alkaplanes, were calculated at the MP2/6-31G(d) level. Zero-point vibrational energy ( $Z P V E$ ) corrections were determined using the B3-LYP/6-31G(d) calculated frequencies scaled by 0.9806 , and corrections to $298 \mathrm{~K}\left(H^{298}-H^{0}\right)$ for the resulting enthalpies were determined using the same frequencies but scaled by $0.9989 .{ }^{34}$ Calculated total strain energies $(S E)$ and heats of formation for a variety of hydrocarbons (including the novel systems described herein) are given in Tables 4-12 to 4-15. Total energies, ZPVEs and the values of the temperature corrections $\left(H^{298}-H^{0}\right)$ are given in Tables C-11-C-15 of Appendix C. Optimized geometries are given in Tables C22 - C-26 of Appendix C.

Table 4-1. Comparison of calculated and experimentally determined adiabatic ionization energies, $I E_{\mathrm{a}}\left(\mathrm{kJ} \mathrm{mol}^{-1}\right)$.

| molecule | $I E_{\mathrm{a}}($ calc $)$ | $I E_{\mathrm{a}}(\exp )^{\mathrm{a}}$ |
| :---: | :---: | :---: |
| $\mathrm{CH}_{4}$ | 12.47 | $12.61 \pm 0.01$ |
| $\mathrm{NH}_{3}$ | 10.03 | $10.07 \pm 0.02$ |
| ${ }^{3} \mathrm{CH}_{2}$ | 10.25 | $10.396 \pm 0.003$ |
| $\mathrm{H}_{2} \mathrm{O}$ | 12.52 | $12.621 \pm 0.001$ |
| neopentane | 10.14 | $\leq 10.30 \pm 0.08$ |
| spiropentane (4-58) | 9.36 | 9.26 |

${ }^{\text {a }}$ Experimental values are taken from Ref. 36.

The first adiabatic ionization energies have been determined at the MP2/ $6-311+\mathrm{G}(2 \mathrm{~d}, \mathrm{p}) / / \mathrm{MP} 2 / 6-311+\mathrm{G}(2 \mathrm{~d}, \mathrm{p})($ red $)$ level for a few representative molecules (4$\mathbf{2 7}^{+\boldsymbol{+}}, \mathbf{4 - 2 8}{ }^{+}$and $\mathbf{4 - 2 9 ^ { + + }}$ ), taken from each of the alkaplane classes (4-VI, 4-VII and $\mathbf{4 -}$ VIII, respectively). We have used the stationary electron (or ion) convention. ${ }^{35}$ Calculated values are determined at 0 K and zero-point vibrational energy (ZPVE) corrections were determined using B3-LYP/6-31G(d) calculated frequencies scaled by $0.9806 .{ }^{34}$ Thus, for the reaction, $\mathrm{A} \rightarrow \mathrm{A}^{++}+e^{-}$, the ionization energy is calculated as,

$$
\begin{equation*}
I E_{\mathrm{a}}[\mathrm{~A}]=\left(E\left[\mathrm{~A}^{\bullet+}\right]+Z P V E\left[\mathrm{~A}^{\bullet+}\right]\right)-(E[\mathrm{~A}]+Z P V E[\mathrm{~A}]) \tag{4-2}
\end{equation*}
$$

Calculations on a number of small molecules for which experimental values are
available ${ }^{36}$ indicate that this method is expected to give ionization energies which are underestimated by about $0.1-0.2 \mathrm{eV}$ (see Table 4-1). Total energies and ZPVEs are given in Table C -16 of Appendix C. Optimized geometries are given in Tables C 27 - C-29 of Appendix C.

Relative triplet energies for octaplane (4-27) and spirooctaplane (4-28) were examined with both the B3-LYP and MP2 methods. Geometries were optimized at both the UB3-LYP/6-31G(d) and UMP2(fc)/6-31G(d) levels. Improved B3-LYP energies were determined at the UB3-LYP/6-311+G(2d,p)//B3-LYP/6-31G(d) level. Optimized geometries are given in Tables C-30 and C-31 of Appendix C.

### 4.3 Results and Discussion

### 4.3.1 How hard is it to flatten methane?

Designing a molecule with a planar-tetracoordinate carbon imposed purely through structural means requires overcoming the very strong energetic preference for a tetrahedral bonding arrangement. Methane serves as a good first candidate in which to examine the size of this barrier because very accurate calculations are possible, allowing a detailed assessment of the performance of the less computationally expensive calculations, which can be applied to the larger systems. It has also been suggested that the preferred state of a planar-tetracoordinate carbon moiety may be an open-shell singlet or triplet and not the closed-shell singlet state. ${ }^{3}$ For these reasons we have chosen to investigate the three lowest-lying electronic states of planar methane.

Our best calculations were performed at the MRCI+Q/AV5Z//UCCSD(T)/ $6-311+G(3 \mathrm{df}, 2 \mathrm{p})$ level. Optimized structures, an indication of the nature of the stationary points located, and, for single-reference calculations, some indication of spin contamination (as reflected in $\left\langle S^{2}\right\rangle$ values) in the wavefunction, are given in Table 4-2. Energies relative to the tetrahedral ground state $\left(\Delta \mathrm{E}_{\mathrm{PT}}\right)$ for the three planar methane states, calculated at a variety of levels of theory, are given in Table 4-3 on page 153. The relative energies of the various states are summarized in Figure 4-3 on page 154.

Firstly, we examined relative energies for structures with the highest possible symmetry, i.e. $D_{4 \mathrm{~h}}$ symmetry. The three lowest-lying states of square-planar methane are ${ }^{1} \mathrm{~A}_{\mathrm{g}},{ }^{1} \mathrm{~B}_{2 \mathrm{u}}$ and ${ }^{3} \mathrm{~B}_{2 \mathrm{u}}$. Our best estimates, indicate clearly that the lowest of these three

Table 4-2. Geometries, ${ }^{a}\left\langle S^{2}\right\rangle$ values for UHF wavefunctions, and number of imaginary frequencies for the three lowest planar methane states.

| method | $\begin{gathered} \text { triplet }^{\mathrm{b}} \\ D_{4 h}(1+0)^{\mathrm{c}} \end{gathered}$ |  | open singlet ${ }^{\text {b }}$$D_{4 h}(1+1)^{\mathrm{c}}$ |  | closed-shell singlet |  |  |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
|  |  |  | $D_{4 h}(2+2)^{\text {c }}$ | $C_{2 v}(0+2)^{c, d}$ |  |
|  | $r(\mathrm{CH})$ | $\left\langle S^{2}\right\rangle$ |  |  | $r(\mathrm{CH})$ | $\left\langle S^{2}\right\rangle$ | $r(\mathrm{CH})$ | $\begin{aligned} & r_{\mathrm{a}}(\mathrm{CH}) \\ & r_{\mathrm{b}}(\mathrm{CH}) \end{aligned}$ | $\begin{aligned} & \theta_{\mathrm{a}}(\angle \mathrm{HCH}) \\ & \theta_{\mathrm{b}}(\angle \mathrm{HCH}) \end{aligned}$ |
| $\begin{aligned} & \text { UB3-LYP/ } \\ & 6-31 G(d) \end{aligned}$ | 1.177 | 2.003 | 1.181 | 1.020 | 1.090 | 1.075 1.159 | $\begin{array}{r} 92.7 \\ 128.8 \end{array}$ |
| $\begin{aligned} & \text { UB3-LYP/ } \\ & \text { 6-311+G(2d,p) } \end{aligned}$ | 1.175 | 2.003 | 1.178 | 1.019 | 1.090 | 1.073 1.164 | $\begin{array}{r} 92.4 \\ 129.8 \end{array}$ |
| $\begin{aligned} & \text { UB3-LYP/ } \\ & 6-311+G(3 \mathrm{df}, 2 \mathrm{p}) \end{aligned}$ | 1.173 | 2.003 | 1.176 | 1.019 | 1.089 | $\begin{aligned} & 1.071 \\ & 1.162 \end{aligned}$ | $\begin{array}{r} 92.4 \\ 129.9 \end{array}$ |
| $\begin{aligned} & \text { UMP2(full)/ } \\ & \text { 6-31G(d) } \end{aligned}$ | 1.170 | 2.013 | 1.175 | 1.077 | 1.085 | 1.070 1.160 | $\begin{array}{r} 93.0 \\ 129.6 \end{array}$ |
| $\begin{aligned} & \text { UMP2(full)/ } \\ & 6-311+G(2 d, p) \end{aligned}$ | 1.168 | 2.015 | 1.171 | 1.075 | 1.088 | 1.072 1.160 | $\begin{array}{r} 92.2 \\ 130.2 \end{array}$ |
| $\begin{aligned} & \text { UMP2(full)/ } \\ & \text { 6-311+G(3df,2p) } \end{aligned}$ | 1.164 | 2.016 | 1.167 | 1.073 | 1.086 | 1.068 1.154 | $\begin{array}{r} 92.0 \\ 130.3 \end{array}$ |
| UCCSD(T)(full)/ $6-311+G(3 \mathrm{df}, 2 \mathrm{p})^{\mathrm{c}}$ | 1.172 | 2.016 | 1.176 | 1.076 | 1.089 | $\begin{aligned} & 1.071 \\ & 1.166 \end{aligned}$ | $\begin{array}{r} 92.2 \\ 131.0 \end{array}$ |

${ }^{\text {a }}$ Bond lengths in Ångstrom ( $\AA$ ), angles in degrees $\left({ }^{\circ}\right)$. ${ }^{\mathrm{b}}$ A UHF reference wavefunction was used for single-determinant calculations on the open-shell systems. ${ }^{\mathrm{c}}(x+y)$ indicates the number of in-plane and out-of-plane imaginary frequencies, respectively. This was consistent across all methods. ${ }^{\mathrm{d}}$ The bond lengths $\left(r_{\mathrm{a}}(\mathrm{CH})\right.$ and $\left.r_{\mathrm{b}}(\mathrm{CH})\right)$ and angles $\left(\theta_{\mathrm{a}}(\angle \mathrm{HCH})\right.$ and $\left.\theta_{\mathrm{b}}(\angle \mathrm{HCH})\right)$ are defined in Figure 4-3 on page 154.
states is the closed-shell singlet $\left({ }^{1} \mathrm{~A}_{\mathrm{g}}\right)$, which is found to lie $573 \mathrm{~kJ} \mathrm{~mol}^{-1}$ above the tetrahedral ground-state. The $D_{4 \mathrm{~h}}$ triplet $\left({ }^{3} \mathrm{~B}_{2 \mathrm{u}}\right)$ lies considerably higher in energy than the $D_{4 \mathrm{~h}}$ closed-shell singlet $\left(\Delta \Delta \mathrm{E}_{\mathrm{PT}}\left[{ }^{3} \mathrm{~B}_{2 \mathrm{u}}-{ }^{1} \mathrm{~A}_{\mathrm{g}}\right]=+106 \mathrm{~kJ} \mathrm{~mol}^{-1}\right)$, while the open-shell singlet $\left({ }^{1} \mathrm{~B}_{2 \mathrm{u}}\right)$ is slightly lower in energy than the triplet $\left(\Delta \Delta \mathrm{E}_{\mathrm{PT}}\left[{ }^{1} \mathrm{~B}_{2 \mathrm{u}}-{ }^{1} \mathrm{~A}_{\mathrm{g}}\right]=+100\right.$ $\mathrm{kJ} \mathrm{mol}^{-1}$ ).

Optimizations in which a plane of symmetry through the five atoms is enforced, but where all other symmetry constraints are relaxed, lead to the lowest-energy structures for each of the three planar methane states. The closed-shell singlet relaxes to a $C_{2 v}$

Table 4-3. Energies relative to the methane tetrahedral ground state, $\Delta \mathrm{E}_{\mathrm{PT}}\left(\mathrm{kJ} \mathrm{mol}^{-1}\right)$, for the three lowest planar methane states.

|  |  | $\Delta \mathrm{E}_{\mathrm{PT}}$ |  |  |  |
| :--- | :---: | :---: | :---: | :---: | :---: |
| method |  | triplet $^{\mathrm{a}}$ | open singlet $^{\mathrm{a}}$ | closed-shell singlet |  |
|  | nbf $^{\mathrm{b}}$ | $D_{4 \mathrm{~h}}$ | $D_{4 \mathrm{~h}}$ | $D_{4 \mathrm{~h}}$ | $C_{2 \mathrm{v}}$ |
| UB3-LYP/6-31G(d) | 23 | 660.3 | 650.2 | 629.6 | 606.1 |
| UB3-LYP/6-311+G(2d,p) | 51 | 647.2 | 639.6 | 562.4 | 525.2 |
| UB3-LYP/6-311+G(3df,2p) | 75 | 647.2 | 639.8 | 555.7 | 517.0 |
| UMP2(full)/6-31G(d) | 23 | 707.6 | 694.6 | 668.6 | 630.9 |
| UMP2(full)/6-311+G(2d,p) | 51 | 691.1 | 689.3 | 582.4 | 536.6 |
| UMP2(full)/6-311+G(3df,2p) | 75 | 689.6 | 690.7 | 568.0 | 522.4 |
| UCCSD(T)(fc)/AVQZ |  |  |  |  |  |

${ }^{\text {a }}$ A UHF reference wavefunction was used for single-determinant calculations on the open-shell systems except as noted in footnote d. ${ }^{\text {b }}$ Number of basis functions. ${ }^{c}$ Calculated at UCCSD(T)(full)/6$311+G(3 d f, 2 p)$ optimized geometries. ${ }^{\text {d }}$ Calculated with MOLPRO's URCCSD(T) algorithm. ${ }^{\mathrm{e}}$ Calculated with GAUSSIAN 98 's $\operatorname{UCCSD}(\mathrm{T})$ algorithm.
geometry (reminiscent of the situation for $\mathrm{CH}_{4}{ }^{2+}$ which has a ' $\mathrm{CH}_{2}{ }^{2+}+\mathrm{H}_{2}$ '-like structure) which is a minimum with respect to in-plane distortion. This structure is considerably lower in energy (by $51 \mathrm{~kJ} \mathrm{~mol}^{-1}$ ) than the $D_{4 \mathrm{~h}}$ geometry $\left(\Delta \mathrm{E}_{\mathrm{PT}}\left[{ }^{1} \mathrm{~A}_{1}\left(C_{2 \mathrm{v}}\right)\right]=522\right.$ $\mathrm{kJ} \mathrm{mol}^{-1}$ ). The two planar open-shell states ( ${ }^{3} \mathrm{~B}_{2 \mathrm{u}}$ and ${ }^{1} \mathrm{~B}_{2 \mathrm{u}}$ ) are not well bound; relaxation in $C_{\mathrm{s}}$ symmetry leads to homolytic $\mathrm{C}-\mathrm{H}$ bond cleavage giving $\mathrm{CH}_{3}{ }^{-}+\mathrm{H}^{\bullet}$ which lies $469 \mathrm{~kJ} \mathrm{~mol}^{-1}$ above the tetrahedral ground state of methane. Clearly, planar methane prefers the $C_{2 \mathrm{v}}$ closed-shell singlet and single excitations to the $\mathrm{B}_{2 \mathrm{u}}$ states will lead to exothermic dissociation into $\mathrm{CH}_{3}{ }^{\circ}+\mathrm{H}^{+}$.

We have explored methane at a variety of levels in order to gain some information on how well lower level calculations perform relative to the most sophisticated, and accurate, methods available to us (in this case MRCI+Q/AV5Z//UCCSD(T)(full)/ $6-311+G-(3 d f, 2 p))$. We find that the $\operatorname{UCCSD}(T)(f c) / A V Q Z / / U C C S D(T)(f u l l) /$


Figure 4-3. The lowest-energy planar methane structure is found to have $C_{2 \mathrm{v}}$ symmetry. Open-shell $D_{4 \mathrm{~h}}$ structures have downhill in-plane modes that lead to dissociation into $\mathrm{CH}_{3}{ }^{-}+\mathrm{H}^{\bullet}$. MRCI $+\mathrm{Q} / \mathrm{AV} 5 \mathrm{Z} / / \mathrm{UCCSD}(\mathrm{T}) / 6-311+\mathrm{G}\left(3 \mathrm{df}, 2 \mathrm{p}\right.$ ) energies (in $\mathrm{kJ} \mathrm{mol}{ }^{-1}$ ) are relative to the tetrahedral ground-state singlet. Where appropriate, the number of imaginary frequencies ( $\mathrm{n} i$ ) is indicated.
$6-311+\mathrm{G}(3 \mathrm{df}, 2 \mathrm{p})$ level performs essentially as well as our best method. ${ }^{\dagger}$ We also find that small basis sets do not give an adequate description of the closed-shell singlet (both $D_{4 h}$ and $C_{2 v}$ ). The energy of the planar closed-shell singlet drops considerably relative to the ground-state as the basis set size is increased. This is most evident in the progression of the MP2 relative energies given in the final column of Table 4-3, but the same effect is also seen in the B3-LYP calculations. This effect has been noted by Gordon and Schmidt ${ }^{4 \mathrm{a}}$ with respect to MCSCF calculations and is also evident in the calculations of Pepper and co-workers. ${ }^{4 b}$ Our calculations indicate that diffuse functions at the central atom are very helpful in obtaining a good estimate of $\Delta \mathrm{E}_{\mathrm{PT}}$ and that the $6-311+G(2 d, p)$ basis appears to be the smallest basis set which adequately approaches the basis set limit for $\Delta \mathrm{E}_{\mathrm{PT}}$. We also note that both B3-LYP and MP2 perform quite well for the closed-shell singlet state provided an adequate basis set is used.

[^48]Methane provides some valuable insights into the electronic structure of a general planar-tetracoordinate carbon moiety. Accepting that in a hydrocarbon a hydrogen substituent is a special case, it would appear that even in molecules where all four substituents are identical, it may be necessary to consider geometries in which the four central bonding distances vary. Further, the use of three-membered rings or bonding between substituents may aid in reducing the energy of a planar-tetracoordinate carbon moiety by providing a more favorable interaction at the central carbon. ${ }^{\dagger}$ Essentially, distortions from a square geometry are expected to be advantageous to achieving planar-tetracoordinate carbon.

The predicted $522 \mathrm{~kJ} \mathrm{~mol}^{-1}$ preference for tetrahedral bonding in methane is about 1.2 times the energy required to break the $\mathrm{CH}_{3}-\mathrm{H}$ bond homolytically. ${ }^{6}$ Overcoming this huge penalty for distorting the bonding arrangement at a saturated carbon atom is clearly a formidable task and it seems likely that any successful attempt to design a molecule with a planar-tetracoordinate carbon atom will need to protect or enclose the sensitive central bonds to carbon, preventing the highly exothermic homolytic dissociation.

### 4.3.2 Flattening Neopentane and Spiropentane

Our strategy for achieving planar-tetracoordinate carbon through incorporation into a rigid hydrocarbon cage system relies on the ability to constrain the positioning of the four atoms attached to the central carbon atom. In general, this will require a quaternary central carbon because it is only through covalent bonds to the four coordinating atoms that we can restrict the positioning of these atoms (i.e. hydrogen positions cannot be constrained). For this reason we have examined the 'flattening' of both neopentane and spiropentane - two of the simplest saturated hydrocarbon systems containing the necessary $\mathrm{C}(\mathrm{C})_{4}$ central substructure. Information on the performance of our methods and the electronic structure of these species will serve as a guide for calculations on larger systems.

There are four geometries for neopentane that give a plane of symmetry through the five carbon atoms of the central $\mathrm{C}(\mathrm{C})_{4}$ substructure. These structures have $D_{2 \mathrm{~h}}, C_{4 \mathrm{~h}}, C_{2 \mathrm{v}}$ and $C_{\mathrm{s}}$ symmetry depending on the orientation of the four methyl groups (see Figure 4-

[^49]

Figure 4-4. The four possible orientations of the methyl groups in 'planar' neopentane $(\mathbf{A}, \mathbf{B}, \mathbf{C}$ and $\mathbf{D})$ which lead to a structure with a molecular plane of symmetry running through the five carbon atoms. Major symmetry elements are indicated, rotational axes ( $C_{4}$ or $C_{2}$ ) and mirror planes ( $\sigma$ ).
4). We have calculated optimized structures (some geometric parameters are given in Table 4-4) and energies (see Table 4-5) for the closed-shell singlet states relative to the ground-state tetrahedral geometry. Remarkably, we find that all these structures have similar energies (i.e. all lie within $3 \mathrm{~kJ} \mathrm{~mol}^{-1}$ of one another). It appears that the adverse energetics which result from the different types of H-H close contacts (such as the difference between the six very tight contacts in the $D_{2 \mathrm{~h}}$ structure versus the eight weaker contacts in the $C_{4 \mathrm{~h}}$ structure) are balanced by preferential electronic effects (see Table 44 for details of the $\mathrm{H}-\mathrm{H}$ close-contact distances). Alternatively, it may simply be that the energetic consequences of the difference between the various degrees of $\mathrm{H}-\mathrm{H}$ close contact in the four structures are relatively small and fall within this $3 \mathrm{~kJ} \mathrm{~mol}^{-1}$ difference.

At our best level of theory, $\operatorname{CCSD}(\mathrm{T})(\mathrm{fc}) / 6-311+\mathrm{G}(3 \mathrm{df}, 2 \mathrm{p}) / / \mathrm{MP} 2(\mathrm{full}) / 6-311+\mathrm{G}-$ ( $2 \mathrm{~d}, \mathrm{p}$ ), we determine the energy difference between the planar and tetrahedral-like structures for closed-shell singlet neopentane to be approximately $880 \mathrm{~kJ} \mathrm{~mol}^{-1}$ (see Table 4-

Table 4-4. Some geometrical parameters for 'planar' neopentane and 'planar' spiropentane closed-shell singlet species. ${ }^{\text {a }}$

| 'planar' neopentane | 'planar' <br> spiropentane |
| :---: | :---: | :---: |


| method | A ( $C_{4 \mathrm{~h}}$ ) | B $\left(D_{2 \mathrm{~h}}\right)$ | C ( $C_{2 \mathrm{v}}$ ) | D ( $\mathrm{C}_{\mathrm{s}}$ ) | $D_{2 \mathrm{~h}}$ |
| :---: | :---: | :---: | :---: | :---: | :---: |
| $\begin{aligned} & \text { B3-LYP/ } \\ & \text { 6-31G(d) } \end{aligned}$ | $\begin{aligned} & \mathrm{C}^{0}-\mathrm{C}^{\alpha}=1.639 \\ & \mathrm{H}^{\mathrm{i}}-\mathrm{H}^{\mathrm{o}}=2.053 \end{aligned}$ | $\begin{aligned} \mathrm{C}^{0}-\mathrm{C}^{\alpha} & =1.644 \\ \mathrm{H}^{\mathrm{o}}-\mathrm{H}^{\mathrm{o}} & =1.978 \\ \mathrm{H}^{\mathrm{i}}-\mathrm{H}^{\mathrm{i}} & =1.677 \end{aligned}$ | $\begin{aligned} \mathrm{C}^{0}-\mathrm{C}^{\alpha, 1} & =1.623 \\ \mathrm{C}^{0}-\mathrm{C}^{\alpha, 2} & =1.666 \\ \mathrm{H}^{\mathrm{o}}-\mathrm{H}^{\mathrm{o}} & =1.980 \\ \mathrm{H}^{\mathrm{i}}-\mathrm{H}^{\mathrm{i}} & =1.708 \\ \mathrm{H}^{\mathrm{i}}-\mathrm{H}^{\mathrm{o}} & =2.034 \end{aligned}$ | $\begin{aligned} & \mathrm{C}^{0}-\mathrm{C}^{\alpha, 1}=1.621 \\ & \mathrm{C}^{0}-\mathrm{C}^{\alpha, 2}=1.621 \\ & \mathrm{C}^{0}-\mathrm{C}^{\alpha, 3}=1.666 \\ & \mathrm{C}^{0}-\mathrm{C}^{\alpha, 4}=1.633 \\ & \mathrm{H}^{\mathrm{o}}-\mathrm{H}^{\mathrm{o}}=1.995 \\ & \mathrm{H}^{\mathrm{i}-\mathrm{H}^{\mathrm{i}}}=1.705 \\ & \mathrm{H}^{-}-\mathrm{H}^{\mathrm{o}}=2.037 \\ & \mathrm{H}^{\mathrm{i}}-\mathrm{H}^{\mathrm{o}}=2.022 \end{aligned}$ | $\begin{aligned} \mathrm{C}^{0}-\mathrm{C}^{\alpha} & =1.530 \\ \mathrm{C}^{\alpha, 1}-\mathrm{C}^{\alpha, 2} & =1.432 \end{aligned}$ |
| $\begin{aligned} & \text { B3-LYP/ } \\ & 6-311+G(2 \mathrm{~d}, \mathrm{p}) \end{aligned}$ | $\begin{aligned} & \mathrm{C}^{0}-\mathrm{C}^{\alpha}=1.649 \\ & \mathrm{H}^{\mathrm{i}}-\mathrm{H}^{\mathrm{o}}=2.049 \end{aligned}$ | $\begin{aligned} \mathrm{C}^{0}-\mathrm{C}^{\alpha} & =1.652 \\ \mathrm{H}^{\mathrm{o}}-\mathrm{H}^{\mathrm{o}} & =1.974 \\ \mathrm{H}^{\mathrm{i}}-\mathrm{H}^{\mathrm{i}} & =1.677 \end{aligned}$ | $\begin{aligned} \mathrm{C}^{0}-\mathrm{C}^{\alpha, 1} & =1.630 \\ \mathrm{C}^{0}-\mathrm{C}^{\alpha, 2} & =1.678 \\ \mathrm{H}^{\mathrm{o}}-\mathrm{H}^{\mathrm{o}} & =1.972 \\ \mathrm{H}^{\mathrm{i}}-\mathrm{H}^{\mathrm{i}} & =1.703 \\ \mathrm{H}^{\mathrm{i}}-\mathrm{H}^{\mathrm{o}} & =2.03 \end{aligned}$ | $\begin{aligned} & \mathrm{C}^{0}-\mathrm{C}^{\alpha, 1}=1.625 \\ & \mathrm{C}^{0}-\mathrm{C}^{\alpha, 2}=1.627 \\ & \mathrm{C}^{0}-\mathrm{C}^{\alpha, 3}=1.680 \\ & \mathrm{C}^{0}-\mathrm{C}^{\alpha, 4}=1.674 \\ & \mathrm{H}^{\mathrm{o}}-\mathrm{H}^{\mathrm{o}}=1.991 \\ & \mathrm{H}^{\mathrm{i}-\mathrm{H}^{\mathrm{i}}}=1.703 \\ & \mathrm{H}^{-}-\mathrm{H}^{\mathrm{o}}=2.033 \\ & \mathrm{H}^{\mathrm{i}}-\mathrm{H}^{\mathrm{o}}=2.015 \end{aligned}$ | $\begin{aligned} \mathrm{C}^{0}-\mathrm{C}^{\alpha} & =1.535 \\ \mathrm{C}^{\alpha, 1}-\mathrm{C}^{\alpha, 2} & =1.441 \end{aligned}$ |
| $\begin{aligned} & \text { MP2(full)/ } \\ & \text { 6-31G(d) } \end{aligned}$ | $\begin{gathered} \mathrm{C}^{0}-\mathrm{C}^{\alpha}=1.622 \\ \mathrm{H}^{\mathrm{i}}-\mathrm{H}^{\mathrm{o}}=2.036 \end{gathered}$ | $\begin{aligned} \mathrm{C}^{0}-\mathrm{C}^{\alpha} & =1.627 \\ \mathrm{H}^{\mathrm{o}}-\mathrm{H}^{\mathrm{o}} & =1.962 \\ \mathrm{H}^{\mathrm{i}}-\mathrm{H}^{\mathrm{i}} & =1.665 \end{aligned}$ | $\begin{aligned} \mathrm{C}^{0}-\mathrm{C}^{\alpha, 1} & =1.613 \\ \mathrm{C}^{0}-\mathrm{C}^{\alpha, 2} & =1.640 \\ \mathrm{H}^{\mathrm{o}}-\mathrm{H}^{\mathrm{o}} & =1.973 \\ \mathrm{H}^{\mathrm{i}}-\mathrm{H}^{\mathrm{i}} & =1.692 \\ \mathrm{H}^{\mathrm{i}}-\mathrm{H}^{\mathrm{o}} & =2.015 \end{aligned}$ | $\begin{aligned} \mathrm{C}^{0}-\mathrm{C}^{\alpha, 1} & =1.607 \\ \mathrm{C}^{0}-\mathrm{C}^{\alpha, 2} & =1.610 \\ \mathrm{C}^{0}-\mathrm{C}^{\alpha, 3} & =1.643 \\ \mathrm{C}^{0}-\mathrm{C}^{\alpha, 4} & =1.641 \\ \mathrm{H}^{\mathrm{o}}-\mathrm{H}^{\mathrm{o}} & =1.982 \\ \mathrm{H}^{\mathrm{i}}-\mathrm{H}^{\mathrm{i}} & =1.692 \\ \mathrm{H}^{-}-\mathrm{H}^{\mathrm{o}} & =2.014 \\ \mathrm{H}^{\mathrm{i}}-\mathrm{H}^{\mathrm{o}} & =2.005 \end{aligned}$ | $\begin{aligned} \mathrm{C}^{0}-\mathrm{C}^{\alpha} & =1.517 \\ \mathrm{C}^{\alpha, 1}-\mathrm{C}^{\alpha, 2} & =1.448 \end{aligned}$ |
| $\begin{aligned} & \text { MP2(full)/ } \\ & 6-311+G(2 \mathrm{~d}, \mathrm{p}) \end{aligned}$ | $\begin{aligned} \mathrm{C}^{0}-\mathrm{C}^{\alpha} & =1.637 \\ \mathrm{H}^{\mathrm{i}}-\mathrm{H}^{\mathrm{o}} & =2.031 \end{aligned}$ | $\begin{aligned} \mathrm{C}^{0}-\mathrm{C}^{\alpha} & =1.640 \\ \mathrm{H}^{\mathrm{o}}-\mathrm{H}^{0} & =1.953 \\ \mathrm{H}^{\mathrm{i}}-\mathrm{H}^{\mathrm{i}} & =1.660 \end{aligned}$ | $\begin{aligned} \mathrm{C}^{0}-\mathrm{C}^{\alpha, 1} & =1.626 \\ \mathrm{C}^{0}-\mathrm{C}^{\alpha, 2} & =1.656 \\ \mathrm{H}^{\mathrm{o}}-\mathrm{H}^{\mathrm{o}} & =1.961 \\ \mathrm{H}^{\mathrm{i}}-\mathrm{H}^{\mathrm{i}} & =1.685 \\ \mathrm{H}^{\mathrm{i}}-\mathrm{H}^{\mathrm{o}} & =2.014 \end{aligned}$ | $\begin{aligned} & \mathrm{C}^{0}-\mathrm{C}^{\alpha, 1}=1.622 \\ & \mathrm{C}^{0}-\mathrm{C}^{\alpha, 2}=1.622 \\ & \mathrm{C}^{0}-\mathrm{C}^{\alpha, 3}=1.657 \\ & \mathrm{C}^{0}-\mathrm{C}^{\alpha, 4}=1.654 \\ & \mathrm{H}^{\mathrm{o}}-\mathrm{H}^{\mathrm{o}}=1.971 \\ & \mathrm{H}^{\mathrm{i}-\mathrm{H}^{\mathrm{i}}}=1.687 \\ & \mathrm{H}^{-}-\mathrm{H}^{\mathrm{o}}=2.011 \\ & \mathrm{H}^{\mathrm{i}}-\mathrm{H}^{\mathrm{o}}=2.004 \end{aligned}$ | $\begin{aligned} \mathrm{C}^{0}-\mathrm{C}^{\alpha} & =1.531 \\ \mathrm{C}^{\alpha, 1}-\mathrm{C}^{\alpha, 2} & =1.448 \end{aligned}$ |

[^50]5). This is about 2.6 times the tert- $\mathrm{C}_{4} \mathrm{H}_{9}-\mathrm{CH}_{3}$ bond dissociation energy, ${ }^{6}$ and clearly rules out the existence of any neutral acyclic saturated hydrocarbon containing a planar carbon, however fleetingly.

The situation for flattening spiropentane appears to be quite different to that of neo-

Table 4-5. Energies, $\Delta \mathrm{E}_{\mathrm{PT}}\left(\mathrm{kJ} \mathrm{mol}^{-1}\right)$, for 'planar' neopentane and 'planar' spiropentane closed-shell singlet species relative to their respective tetrahedral-like ground states.

| method | 'planar' neopentane ${ }^{\text {a }}$ |  |  |  | 'planar' |
| :---: | :---: | :---: | :---: | :---: | :---: |
|  | A ( $C_{4 \mathrm{~h}}$ ) | B ( $D_{2 \mathrm{~h}}$ ) | $\mathrm{C}\left(C_{2 \mathrm{v}}\right)$ | D ( $\mathrm{C}_{\mathrm{s}}$ ) | $D_{2 \mathrm{~h}}$ |
| B3-LYP/6-31G(d) | 881.7 | 878.9 | 880.2 | 879.1 | 431.2 |
| B3-LYP/6-311+G(2d,p) | 858.1 | 858.8 | 858.3 | 857.5 | 421.5 |
| B3-LYP/6-311+G(3df,2p) | 854.7 | 855.9 | 855.1 | 854.3 | 419.5 |
| MP2(full)/6-31G(d) ${ }^{\text {c }}$ | 927.4 | 930.2 | 928.9 | 927.5 | 459.0 |
| MP2(full)/6-311+G(2d,p)(red) ${ }^{\text {c,d }}$ | 888.5 | 892.3 | 888.8 | 890.9 | 431.7 |
| MP2(full)/6-311+G(2d,p) ${ }^{\text {c }}$ | 869.8 | 872.5 | 871.9 | 870.6 | 430.2 |
| MP2(full)/6-311+G(3df, 2p) ${ }^{\text {c }}$ | 866.9 | 869.2 | 868.8 | 867.4 | 426.5 |
| $\operatorname{CCSD}(\mathrm{T})(\mathrm{fc}) / 6-311+\mathrm{G}(2 \mathrm{~d}, \mathrm{p})^{\mathrm{e}}$ | 879.8 | 883.0 | 881.2 | 880.4 | 443.3 |
| $\operatorname{CCSD}(\mathrm{T})(\mathrm{fc}) / 6-311+\mathrm{G}(3 \mathrm{df}, 2 \mathrm{p})^{\mathrm{e}}$ | 880.1 | 882.7 | 881.1 | 880.2 | 440.0 |
| $\operatorname{CCSD}(\mathrm{T})(\mathrm{fc}) / \mathrm{AVTZ}^{\text {e }}$ | - | - | - | - | 437.5 |

${ }^{\text {a }}$ Neopentane energies are calculated relative to the $T_{\mathrm{d}}$ closed-shell singlet state $\left({ }^{1} \mathrm{~A}_{1}\right)$.
${ }^{\mathrm{b}}$ Spiropentane energies are calculated relative to the $D_{2 \mathrm{~d}}$ closed-shell singlet state $\left({ }^{1} \mathrm{~A}_{1}\right)$. ${ }^{\mathrm{c}}$ Calculated at the MP2(full)/6-31G(d) optimized geometries. ${ }^{\text {d }}$ Our reduced 6$311+\mathrm{G}(2 \mathrm{~d}, \mathrm{p})($ red $)$ basis set is detailed in Section 4.2 on page $145 .{ }^{\mathrm{e}}$ Calculated at MP2(full)/ $6-311+G(2 d, p)$ optimized geometries.
pentane. Our best estimate indicates that the $\Delta \mathrm{E}_{\mathrm{PT}}$ is less than $440 \mathrm{~kJ} \mathrm{~mol}^{-1}$, which is half the size of $\Delta \mathrm{E}_{\mathrm{PT}}$ for neopentane. Incorporation of the central carbon atom into a pair of three-membered rings has reduced $\Delta \mathrm{E}_{\mathrm{PT}}$ by more than $80 \mathrm{~kJ} \mathrm{~mol}^{-1}$ compared with methane and by more than $440 \mathrm{~kJ} \mathrm{~mol}^{-1}$ compared with neopentane. However, $\Delta \mathrm{E}_{\mathrm{PT}}$ for spiropentane is still 1.9 times the expected bond strength for the weakest bond in the tetrahedral-like spiropentane (the central $\mathrm{C}-\mathrm{C}$ bonds are expected to have a dissociation energy ${ }^{37}$ less than $230 \mathrm{~kJ} \mathrm{~mol}^{-1}$ ).

Once again, we have repeated our calculations over a range of levels in order to assess the accuracy of the lower level methods to which we will be restricted when examining larger molecules (see Table 4-5). Of particular note, we find that the MP2/6$31 \mathrm{G}(\mathrm{d})$ level predicts much better values for $\Delta \mathrm{E}_{\mathrm{PT}}$ for spiropentane and neopentane than
was the case with methane; at worst, $\Delta \mathrm{E}_{\mathrm{PT}}$ values are over-estimated by $50 \mathrm{~kJ} \mathrm{~mol}^{-1}$. MP2/6-311+G(2d,p) gives consistently low values (compared with our best estimates) for the energy required to flatten the bonding to the central carbon atom, but the underestimation at both this level and MP2/6-311+G(2d,p)(red) $)^{38}$ is less than $10 \mathrm{~kJ} \mathrm{~mol}^{-1}$. B3-LYP calculations all under-estimate $\Delta \mathrm{E}_{\mathrm{PT}}$ For large basis sets this error becomes quite significant (up to $25 \mathrm{~kJ} \mathrm{~mol}^{-1}$ ).

Clearly, the preference for tetrahedral-like bonding in tetracoordinate carbon is very strong and overcoming this will not be an easy task. However, we believed that by careful design we should be able to devise a system that overcomes this barrier.

A simple examination of the problem at hand leads us to stipulate the following design parameters. Firstly, we desire a saturated hydrocarbon. This should remove any ambiguity as to the coordination of the planar-tetracoordinate carbon atom. Secondly, we only want a single planar-tetracoordinate carbon atom. All other carbons should have, as far as possible, tetrahedral-like bonding. Considering the energy required to flatten just a single carbon atom, this is the only approach that is likely to lead to viable molecules. Finally, we desire a structure that has an identical bonding arrangement both above and below the plane of the central $\mathrm{C}(\mathrm{C})_{4}$ substructure, a necessary requirement for exact planarity at the central carbon atom. Clearly, the only way to achieve planar-tetracoordination in a saturated hydrocarbon is to build a cage system. But any design without an implicit plane of symmetry which coincides with the central $\mathrm{C}(\mathrm{C})_{4}$ substructure can only hope to achieve near or coincidental planarity. With these design parameters in mind we set about designing novel saturated hydrocarbon cage systems that might afford planar-tetracoordinate carbon.

### 4.3.3 Alkaplane Structures

Our first attempt at designing a saturated hydrocarbon with a planar-tetracoordinate carbon involves molecules which are built up by bicapping planar $\mathrm{C}_{5} \mathrm{H}_{4}$ (a neopentane subunit) with identical cyclic hydrocarbon caps both above and below the plane, resulting in a family of molecules that we have labelled the alkaplanes (4-VI). Initial work on these molecules by McGrath and Radom, ${ }^{24}$ in which they obtained HF/6$31 \mathrm{G}(\mathrm{d})$ structures and HF/3-21G frequencies showed great promise. Unlike previous attempts, this design has the advantage that the environment around the central carbon
atom is such that a plane of symmetry through the central $\mathrm{C}(\mathrm{C})_{4}$ subunit is possible without requiring multiple planar-tetracoordinate carbon atoms (cf. [4.4.4.4]fenestrane (4-18)). We examined structures for molecules designed using the following cyclic hydrocarbon caps: bicyclo[3.3.1]nonane (bicyclo- $\mathrm{C}_{9} \mathrm{H}_{12}$ ), cyclooctane (cyclo- $\mathrm{C}_{8} \mathrm{H}_{12}$ ), bicyclo[3.3.0]octane (bicyclo- $\mathrm{C}_{8} \mathrm{H}_{10}$ ), bicyclo[2.2.1]heptane or norbornane (bicyclo$\mathrm{C}_{7} \mathrm{H}_{8}$ ), cyclohexane (cyclo- $\mathrm{C}_{6} \mathrm{H}_{8}$ ), and bicyclo[2.2.0]hexane (bicyclo- $\mathrm{C}_{6} \mathrm{H}_{6}$ ). Each pair of caps was combined with a neopentane subunit corresponding to one of the three neopentane structures, $\mathbf{A}\left(C_{4 \mathrm{~h}}\right), \mathbf{B}\left(D_{2 \mathrm{~h}}\right)$, or $\mathbf{C}\left(C_{2 \mathrm{v}}\right)$, of Figure 4-4 on page 156. The resulting structures were examined initially using the AM1 method for local minima. The molecules identified by this process as worthy of further examination, named bihexaplane (4-30), hexaplane (4-31), biheptaplane (4-32), heptaplane (4-33), bioctaplane (4-34), octaplane (4-27 and 4-35) and binonaplane (4-36), were re-optimized at the HF/6-31G(d), B3-LYP/6-31G(d) and, in the case of 4-27, 4-31 and 4-33, at the MP2/ $6-311+\mathrm{G}(2 \mathrm{~d}, \mathrm{p})(\mathrm{red})^{38}$ levels. ${ }^{\dagger}$ General structural features of these molecules are listed in


4-VI


4-31 $\left(D_{2}\right)$


4-33 $\left(C_{2}\right)$


4-27 $\left(S_{4}\right)$

Table 4-6 on page 161. The symmetry of the equilibrium structure, the degree of distortion from planarity at $C^{0}$, and the barrier to inversion at $C^{0}$ are listed in Table 4-7 on page 163. More complete structural information (all bond lengths and selected bond angles) for hexaplane (4-31), heptaplane (4-33) and the $S_{4}$ symmetry isomer of octaplane (4-27) are given in Figure 4-5 on page 165.

At first, we examined structures for the eight alkaplanes listed in Table 4-6 (4-27 and 4-30-4-36) which had been optimized with symmetry constraints (as mentioned

[^51]below) that were guaranteed to give an exactly planar-tetracoordinate central carbon atom. Alkaplanes constructed from neopentane subunits based on the neopentane struc-

Table 4-6. General structural features of the alkaplanes.

| Molecule |  | Sym. ${ }^{\text {a }}$ | Cap Formula | Cap <br> Structure ${ }^{\text {b }}$ | $\begin{gathered} \mathrm{C}_{5} \mathrm{H}_{4} \\ \text { Subunit } \end{gathered}$ | Molecular Formula |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| bihexaplane | 4-30 | $D_{2}$ | bicyclo- $\mathrm{C}_{6} \mathrm{H}_{6}$ |  |  | $\mathrm{C}_{17} \mathrm{H}_{16}$ |
| hexaplane | 4-31 | $D_{2}$ | cyclo- $\mathrm{C}_{6} \mathrm{H}_{8}$ |  |  | $\mathrm{C}_{17} \mathrm{H}_{20}$ |
| biheptaplane | 4-32 | $D_{2}$ | bicyclo- $\mathrm{C}_{7} \mathrm{H}_{8}$ |  | H | $\mathrm{C}_{19} \mathrm{H}_{20}$ |
| heptaplane | 4-33 | $C_{2}$ | cyclo- $\mathrm{C}_{7} \mathrm{H}_{10}$ |  |  | $\mathrm{C}_{19} \mathrm{H}_{24}$ |
| bioctaplane | 4-34 | $D_{2}$ | cyclo- $\mathrm{C}_{8} \mathrm{H}_{10}$ |  |  | $\mathrm{C}_{21} \mathrm{H}_{24}$ |
| octaplane (A-type) | 4-27 | $S_{4}$ | cyclo- $\mathrm{C}_{8} \mathrm{H}_{12}$ |  |  | $\mathrm{C}_{21} \mathrm{H}_{28}$ |
| octaplane (B-type) | 4-35 | $D_{2}$ | cyclo- $\mathrm{C}_{8} \mathrm{H}_{12}$ |  |  | $\mathrm{C}_{21} \mathrm{H}_{28}$ |
| binonaplane | 4-36 | $D_{2}$ | bicyclo- $\mathrm{C}_{9} \mathrm{H}_{12}$ |  |  | $\mathrm{C}_{23} \mathrm{H}_{28}$ |

${ }^{\text {a }}$ The symmetry of the equilibrium structure. ${ }^{\text {b }}$ The carbon atoms with unfilled valences, which form $\mathrm{C}-\mathrm{C}$ bonds to the planar unit, are marked $\bullet$. The caps and planar units are bound in the orientation given.
tures $\mathbf{A}, \mathbf{B}$ or $\mathbf{C}$ (which we refer to as $\mathbf{A}$-, $\mathbf{B}$ - and $\mathbf{C}$-type templates) were thus constrained to $C_{4 \mathrm{~h}}, D_{2 \mathrm{~h}}$ or $C_{2 \mathrm{v}}$ symmetry, respectively. In almost all cases we find that these
structures are second-order saddle points (see Table 4-7 on page 163). The only exception is the MP2/6-311+G(2d,p)(red) force constant analysis for 4-31. At this level of theory, the $D_{2 \mathrm{~h}}$ symmetry structure for $\mathbf{4 - 3 1}$ is found to be a first-order saddle point (and the transition structure for inversion at $\mathrm{C}^{0}$ ). Equilibrium geometries for the alkaplanes 4-27 and 4-30-4-36 result from a small distortion toward a tetrahedral-like arrangement of bonds at the central carbon atom $\left(\mathrm{C}^{0}\right)$, giving structures with $S_{4}, D_{2}$ and $C_{2}$ symmetry from molecules built on $\mathbf{A}$-, B- and $\mathbf{C}$-type neopentane subunits, respectively. We have determined $\alpha_{\text {plan }}$ values (an average of the distortions of each of the four $C^{\alpha}$ atoms from the best-fit plane) as a measure of the degree of distortion from planarity at the central quaternary carbon atom $\left(\mathrm{C}^{0}\right) .{ }^{\dagger}$ These values are listed in Table 4-7.

The alkaplanes with the most flattened central quaternary carbon atom are hexaplane (4-31), biheptaplane (4-32), heptaplane (4-33) and the $S_{4}$ symmetry isomer of octaplane (4-27), all of which have $\alpha_{\text {plan }}$ values of about $5^{\circ}$. Calculated values for $\alpha_{\text {plan }}$ vary between the methods we have used by at most $0.8^{\circ}$. The alkaplanes with the largest deviations from planar-tetracoordination at the central carbon atom are bioctaplane (4-34) and binonaplane (4-36) which have $\alpha_{\text {plan }}$ values around 8 or $9^{\circ}$. The other two alkaplanes we examined, bihexaplane ( $\mathbf{4 - 3 0}$ ) and the $D_{2}$ symmetry isomer of octaplane (4-35) fall in between with $\alpha_{\text {plan }}$ values of around $6^{\circ}$.

As a family of structures, the alkaplanes (4-VI) exhibit an impressive degree of flattening at a quaternary carbon atom ( $\alpha_{\text {plan }}=5-9^{\circ}$ ). Although the distortion from planarity at $\mathrm{C}^{0}$ is clearly non-negligible, the only saturated hydrocarbon previously predicted to show this degree of flattening at a tetracoordinate carbon atom is the all-trans isomer of $[5.5 .5 .5]$-fenestrane (all-trans-4-19) $\left(\alpha_{\text {plan }}[\mathrm{MP} 2 / 6-31 \mathrm{G}(\mathrm{d})]=7.9^{\circ}\right)$. The three hemi-

alkaplanes, hemibioctaplane (4-37), hemioctaplane (4-24) and hemibinonaplane (4-38),

[^52]Table 4-7. Structural information, the angle of deviation from planarity, $\alpha_{\text {plan }}\left({ }^{\circ}\right)$, and the inversion barrier at $\mathrm{C}^{0}, \Delta \mathrm{E}_{\text {plan }}\left(\mathrm{kJ} \mathrm{mol}^{-1}\right)$, for the alkaplanes.

| Molecule |  | Sym. ${ }^{\text {a }}$ | $\mathrm{n} i^{\text {b }}$ | $\alpha_{\text {plan }}{ }^{\text {c }}$ | $\Delta \mathrm{E}_{\text {plan }}{ }^{\text {d }}$ |
| :---: | :---: | :---: | :---: | :---: | :---: |
| bihexaplane | 4-30 | $D_{2}$ | 2/2 | $\left(7.0^{\circ}\right)$ | (63.3) |
|  |  |  |  | $6.2^{\circ}$ | 78.7 |
| hexaplane | 4-31 | $D_{2}$ | $1 / 2 /-^{\text {e }}$ | $\begin{gathered} 4.5^{\circ} \\ \left(5.7^{\circ}\right) \end{gathered}$ | $\begin{gathered} \mathbf{4 1 . 5} \\ (37.3) \end{gathered}$ |
|  |  |  |  | $5.1{ }^{\circ}$ | 58.6 |
| biheptaplane | 4-32 | $D_{2}$ | $2 / 2$ | $\left(5.7^{\circ}\right)$ | (34.8) |
|  |  |  |  | $5.0^{\circ}$ | 55.9 |
| heptaplane | 4-33 | $C_{2}$ | 1/1 | $\begin{gathered} \mathbf{5 . 0}^{\circ} \\ \left(5.8^{\circ}\right) \end{gathered}$ | $\begin{gathered} \mathbf{6 7 . 7} \\ (71.7) \end{gathered}$ |
|  |  |  |  | $5.8^{\circ}$ | 79.5 |
| bioctaplane | 4-34 | $D_{2}$ | $2 / 2$ | $\left(8.9^{\circ}\right)$ | (135.5) |
|  |  |  |  | $8.4^{\circ}$ | 137.5 |
| octaplane (A-type) | 4-27 | $S_{4}$ | 1/1 | $\begin{gathered} \mathbf{5 . 1}^{\circ} \\ \left(5.6^{\circ}\right) \end{gathered}$ | $\begin{gathered} \mathbf{5 8 . 6} \\ (57.9) \end{gathered}$ |
|  |  |  |  | $5.2^{\circ}$ | 72.5 |
| octaplane (B-type) | 4-35 | $D_{2}$ | 2/2 | $\left(7.1^{\circ}\right)$ | (59.7) |
|  |  |  |  | $6.3^{\circ}$ | 76.6 |
| binonaplane | 4-36 | $D_{2}$ | $2 / 2$ | $\begin{gathered} \left(8.0^{\circ}\right) \\ 7.5^{\circ} \end{gathered}$ | $\begin{gathered} - \\ (98.1) \\ 102.1 \end{gathered}$ |

${ }^{\mathrm{a}}$ The symmetry of the equilibrium structure. ${ }^{\mathrm{b}}$ The number of imaginary vibrational frequencies for the structure constrained to contain a planar-tetracoordinate carbon atom at HF/6-31G(d) and B3-LYP/6-31G(d) levels, respectively. ${ }^{c}$ Values given are calculated at MP2/6-311+G(2d,p)(red) ${ }^{38}$ (bold text), HF/6-31G(d) (in parentheses) and B3-LYP/ $6-31 \mathrm{G}(\mathrm{d})$ (plain text) optimized geometries. ${ }^{\mathrm{d}}$ Values given are calculated at MP2/ 6-311+G(2d,p)//MP2/6-311+G(2d,p)(red) (bold text), MP2/6-311+G(2d,p)//HF/6-31G(d) (in parentheses) and B3-LYP/6-311+G(2d,p)//B3-LYP/6-31G(d) (plain text). ${ }^{\mathrm{e}}$ MP2/ $6-311+G(2 d, p)($ red ) (bold text), HF/6-31G(d) and B3-LYP/6-31G(d) levels, respectively. The B3-LYP/6-31G(d) frequency was not obtainable because of an internal instability in the wavefunction.
(which have been examined in detail in Chapter 3), are the only other molecules which are predicted to have a similar degree of planarization at the central carbon atom (they have $\alpha_{\text {plan }}$ [B3-LYP/6-31G(d)] values of $10.0^{\circ}, 9.7^{\circ}$ and $9.6^{\circ}$, respectively). ${ }^{\dagger}$ However, as has been discussed in Chapter 3, certain features of the hemialkaplanes suggest that they are unlikely to be particularly stable structures (see Section 3.3.1 on page 100). Further, the stability of all-trans-4-19 is dependent on a large barrier to inversion at the central carbon atom because inversion at this atom leads to the energetically much more favorable all-cis-[5.5.5.5]fenestrane (all-cis-4-19). However, as the coordination at the central atom approaches planarity, the barrier to inversion at this carbon atom must approach zero. Problems relating to this inversion barrier approaching zero are overcome in the alkaplanes by the inherent symmetry. Inversion at the central carbon atom in the alkaplanes formally gives interconversion between two identical structures. ${ }^{\ddagger}$ This situation is essential to obtaining planar-tetracoordinate carbon.

However, the fact that all alkaplanes built on a $\mathbf{B}$-type neopentane subunit (4-30, 431, 4-32, 4-34, 4-35 and 4-36) give two imaginary frequencies when optimized in $D_{2 \mathrm{~h}}$ symmetry (see Table 4-6 on page 161), indicates that inversion for these molecules does not proceed via this highly symmetric structure. A closer examination of the imaginary frequencies reveals that in all cases one corresponds to an in-plane vibrational mode and the other to an out-of-plane mode. The out-of-plane, downhill mode leads to the $D_{2}$ symmetry equilibrium structure but the in-plane, downhill mode, in all cases, leads to a much lower-energy $C_{\mathrm{s}}$ symmetry equilibrium structure in which one of the $\mathrm{C}^{0}-\mathrm{C}^{\alpha}$ bonds is lengthened beyond $2.0 \AA$. This suggests that homolytic cleavage of one of the $\mathrm{C}^{0}-\mathrm{C}^{\alpha}$ bonds will result. The correct transition structure for inversion at $\mathrm{C}^{0}$ is expected to have either $C_{1}$ or $C_{2}$ symmetry and the barrier to inversion will necessarily be less than $\Delta \mathrm{E}_{\text {plan }}$, the difference in energy between the $D_{2}$ symmetry equilibrium structure and the $D_{2 \mathrm{~h}}$ structure, also referred to as the 'planar' structure (for $\Delta \mathrm{E}_{\text {plan }}$ values see Table 4-7 on page 163). The true barrier to inversion must be lower than $\Delta \mathrm{E}_{\text {plan }}$ for these alkaplanes because the $D_{2 \mathrm{~h}}$ symmetry structure is a second-order saddle point in which one of the downhill modes corresponds to the inversion mode. However, the presence of the sec-

[^53]
$\alpha_{\text {plan }}=4.5 / 5.1$
4-31 $\left(D_{2}\right)$

$$
\alpha_{\text {plan }}=5.0 / 5.8
$$
$$
4-33\left(C_{2}\right)
$$

Figure 4-5. Structural parameters (MP2/6-311+G(2d,p)(red) ${ }^{38}$ values in bold type, B3-LYP/6-31G(d) values in plain text) for hexaplane (4-31), heptaplane (4-33), and $S_{4}$ symmetry octaplane (4-27). All unique bond lengths and H-H close contacts ( $\AA$ ) are shown. The most highly distorted CCC angles and the distortion from planarity, $\alpha_{\text {plan }}$, $\left({ }^{\circ}\right)$ are also given.
ond downhill mode in the $D_{2 \mathrm{~h}}$ symmetry structure suggests that inversion may not be observed because of competition from a highly exothermic and irreversible channel that leads to bond cleavage. The barrier to this decomposition pathway is also expected to be lower than the $\Delta \mathrm{E}_{\text {plan }}$ values quoted in Table 4-7 on page 163.

We have examined two structures which are not based on a B-type neopentane subunit, heptaplane (4-33) and the A-type octaplane (4-27). The 'planar' structures for both $\mathbf{4 - 2 7}$ and 4-33 have only a single imaginary frequency. This frequency corresponds to the vibrational mode connecting the two identical equilibrium structures. The $C_{4 \mathrm{~h}}\left(C_{2 \mathrm{v}}\right)$ structure for 4-27 (4-33) is the transition structure for inversion at $\mathrm{C}^{0}$. This suggests that, for these molecules, the transition structure leading to $\mathrm{C}^{0}-\mathrm{C}^{\alpha}$ cleavage is higher-
lying than in the B-type alkaplanes (4-30, 4-31, 4-32, 4-34, 4-35 and 4-36). Although we have not explicitly searched for possible rearrangement or decomposition pathways, it is likely that 4-27 and $\mathbf{4 - 3 3}$ will have greater kinetic stability than the B-type alkaplanes.

A closer examination of the structures of hexaplane (4-31), heptaplane (4-33) and the $S_{4}$ symmetry octaplane (4-27) (Figure 4-5) reveals that the distortion at the central carbon atom is largely the result of alternation of bond lengths between pairs of $\mathrm{C}^{\alpha}-\mathrm{C}^{\beta}$ bonds, although some twisting of the cage is also evident. The MP2 optimized values for these bond pairs are 1.61/1.52 for hexaplane (4-31), 1.73/1.55 and 1.54/1.49 for heptaplane (4-33), and 1.60/1.51 for $S_{4}$ octaplane (4-27) (see Table 4-8 on page 167 for details and a comparison with B3-LYP/6-31G(d) values). We also note that the cyclohexane caps of hexaplane have considerable bond length strain as the MP2 calculated bond lengths of four of the $\mathrm{C}-\mathrm{C}$ bonds have increased to $1.60 \AA$ from $1.53 \AA$ in the boat conformer of cyclohexane. The bond lengths of the $\mathrm{C}-\mathrm{C}$ bonds in the heptaplane caps are all only slightly higher than the standard length of $1.54 \AA$, indicating little bondlength strain in the caps. However, the stability of heptaplane is likely to be affected adversely by the very long $\mathrm{C}^{\alpha}-\mathrm{C}^{\beta}$ bond $\left(r\left(\mathrm{C}^{\alpha}-\mathrm{C}^{\beta}\right)=1.73 \AA\right.$ at $\mathrm{MP} 2 / 6-$ $311+\mathrm{G}(2 \mathrm{~d}, \mathrm{p})($ red $)$ ). The accompanying $\mathrm{C}^{\beta} \mathrm{C}^{\alpha} \mathrm{C}^{\beta}$ angle of $158.4^{\circ}$, and the very short $\mathrm{H}-\mathrm{H}$ distance of $1.77 \AA$ also indicate that there is considerable strain associated with this region of the molecule (as well as with the central carbon atom). The $S_{4}$ symmetry octaplane structure (4-27) shows some bond lengthening in the cyclooctane cap (MP2 calculated C-C bonds lengths are in the range $1.54-1.58 \AA$ ) over the MP2 calculated bond lengths of crown cyclooctane $(1.53 \AA)$. Of all the alkaplanes we examined, $\mathbf{4 - 2 7}$ has the smallest $\mathrm{C}^{\beta} \mathrm{C}^{\alpha} \mathrm{C}^{\beta}$ angle (146.4 ${ }^{\circ}$ at MP2/6-311+G(2d,p)(red)) and, because of the orientation of the central methine $(\mathrm{CH})$ groups, no $\mathrm{H}-\mathrm{H}$ close contacts.

Octaplane (4-27) appears to be the best candidate for attempts at synthesis, of all the parent alkaplanes (4-VI) we have examined. However, the large degree of angle strain present at the relatively exposed $\mathrm{C}^{\alpha}$ atoms suggests that these centers will need to be protected. The orientation of the $\mathrm{C}^{\alpha}$ hydrogens in octaplane is well placed to allow substitution, and methylation at these positions may prove advantageous. A brief examination of possible alkyl protecting groups using the AM1 method indicated that tertbutyl groups will be too bulky but methyl groups fit well and form a complete protec-

Table 4-8. Selected structural parameters, $r\left(\mathrm{C}^{\alpha}-\mathrm{C}^{\beta}\right)(\AA)$ and $\angle \mathrm{C}^{\beta} \mathrm{C}^{\alpha} \mathrm{C}^{\beta}\left({ }^{\circ}\right)$, for the alkaplanes.

| Molecule | Sym. $^{\mathrm{a}}$ | $r\left(\mathrm{C}^{\alpha}-\mathrm{C}^{\beta}\right)^{\mathrm{b}}$ | $\angle \mathrm{C}^{\beta} \mathrm{C}^{\alpha} \mathrm{C}^{\beta \mathrm{b}}$ |  |
| :--- | :---: | :---: | :---: | :---: |
| bihexaplane | $\mathbf{4 - 3 0}$ | $D_{2}$ | - | - |
|  |  |  | $1.599 / 1.505$ | $142.9^{\circ}$ |
| hexaplane | $\mathbf{4 - 3 1}$ | $D_{2}$ | $\mathbf{1 . 6 0 9 / 1 . 5 1 9}$ | $\mathbf{1 4 8 . 5 ^ { \circ }}$ |
|  |  |  | $1.634 / 1.521$ | $148.8^{\circ}$ |
| biheptaplane | $\mathbf{4 - 3 2}$ | $D_{2}$ | - | - |
|  |  |  | $1.616 / 1.520$ | $153.9^{\circ}$ |
| heptaplane ${ }^{\mathrm{c}}$ | $\mathbf{4 - 3 3}$ | $C_{2}$ | $\mathbf{1 . 5 3 6 / 1 . 4 8 8} \mathbf{1 . 7 3 4 / 1 . 5 5 1}$ | $\mathbf{1 3 4 . 9}{ }^{\circ} \mathbf{1 5 8 . 4}^{\circ}$ |
|  |  |  | - | $134.9^{\circ} 158.3^{\circ}$ |
| bioctaplane | $\mathbf{4 - 3 4}$ | $D_{2}$ | $1.636 / 1.527$ | - |
|  |  |  | $\mathbf{1 . 6 0 4 / 1 . 5 1 2}$ | $153.0^{\circ}$ |
| octaplane (A-type) | $\mathbf{4 - 2 7}$ | $S_{4}$ | $1.624 / 1.519$ | $\mathbf{1 4 6 . 4}$ |
|  |  |  | - | $146.6^{\circ}$ |
| octaplane (B-type) | $\mathbf{4 - 3 5}$ | $D_{2}$ | $1.618 / 1.520$ | - |
|  |  |  | - | $153.9^{\circ}$ |
| binonaplane | $\mathbf{4 - 3 6}$ | $D_{2}$ | $1.627 / 1.513$ | - |

${ }^{\mathrm{a}}$ The symmetry of the equilibrium structure. ${ }^{\mathrm{b}}$ Values given are calculated at MP2/ $6-311+G(2 d, p)(r e d)$ (bold text) and B3-LYP/6-31G(d) (plain text) optimized geometries. ${ }^{\text {c }}$ Lower symmetry in this $C_{2}$ structure results in two long/short $C^{\alpha}-C^{\beta}$ bond pairs and two $C^{\beta} C^{\alpha} C^{\beta}$ angles.
tive ring about the $\mathrm{C}^{\alpha}$ carbons.

The energy difference between the equilibrium structure and the 'planar' structure, $\Delta \mathrm{E}_{\text {plan }}$, gives us an indication of how much more work is required to achieve planartetracoordination at carbon. We have obtained estimates for $\Delta \mathrm{E}_{\text {plan }}$ at the MP2/ $6-311+\mathrm{G}(2 \mathrm{~d}, \mathrm{p}) / / \mathrm{MP} 2 / 6-311+\mathrm{G}(2 \mathrm{~d}, \mathrm{p})(\mathrm{red}), \quad \mathrm{MP} 2 / 6-311+\mathrm{G}(2 \mathrm{~d}, \mathrm{p}) / / \mathrm{HF} / 6-31 \mathrm{G}(\mathrm{d}) \quad$ and B3-LYP/6-311+G(2d,p)//B3-LYP/6-31G(d) levels (see Table 4-7 on page 163 ).

As might be expected, the size of $\Delta \mathrm{E}_{\text {plan }}$ correlates fairly well with values for $\alpha_{\text {plan }}$. The alkaplanes, 4-27, 4-30-4-33 and 4-35, which have $\alpha_{\text {plan }}$ values in the range $5-6^{\circ}$, require the least work to achieve planarity $\left(\Delta \mathrm{E}_{\text {plan }}=35-80 \mathrm{~kJ} \mathrm{~mol}^{-1}\right)$, while the alkaplanes, 4-34 and 4-36, which exhibit the least flattening ( $\alpha_{\text {plan }} \geq 7^{\circ}$ ), have the largest values for $\Delta \mathrm{E}_{\text {plan }}\left(100-140 \mathrm{~kJ} \mathrm{~mol}^{-1}\right)$.

The values for $\Delta \mathrm{E}_{\text {plan }}$ for the alkaplanes are remarkably small (ca. $35-140 \mathrm{~kJ} \mathrm{~mol}^{-1}$ )
when compared with the barrier for inversion at the central carbon atom in neopentane (ca. $880 \mathrm{~kJ} \mathrm{~mol}^{-1}$ ) (see Section 4.3.2 on page 155). Clearly, the alkaplanes (4-VI) are a family of molecules that show remarkable flattening of the central tetracoordinate carbon atom (having overcome most of the $880 \mathrm{~kJ} \mathrm{~mol}^{-1}$ preference for tetrahedral bonding), achieved through purely structural means. However, our survey of many possible capping subunits suggests that such modifications alone will not lead to planar-tetracoordinate carbon and that further reduction of the degree of distortion at the central $\mathrm{C}(\mathrm{CH})_{4}$ subunit will probably require modification to the central $\mathrm{C}_{5}$ moiety. It seems likely that steric effects resulting from attempts to force four carbon atoms not bonded to each other into a plane ${ }^{\dagger}$ are such that they contribute strongly to the preferential, alternate lengthening and compression of the $\mathrm{C}^{\alpha}-\mathrm{C}^{\beta}$ bond pairs, which results in distortion from planar-tetracoordination at $\mathrm{C}^{0}$ despite the overall rigidity of the cage structure. One way to overcome this problem is to replace the four central methine $\left(\mathrm{C}^{\alpha} \mathrm{H}\right)$ groups with two $\mathrm{C}-\mathrm{C}$ bonded pairs, i.e. to form bonds between adjacent pairs of $\mathrm{C}^{\alpha}$ atoms. This leads to the spiroalkaplanes (4-VII), which are discussed in the next section.

### 4.3.4 Spiroalkaplane Structures

The spiro[2.2]alkaplanes (4-VII) are constructed in a similar fashion to the alkaplanes (4-VI), by bicapping a planar $\mathrm{C}(\mathrm{C})_{4}$ subunit with cyclic hydrocarbons from both above and below the plane. In the case of the spiroalkaplanes, the planar neopentane subunit used in the alkaplanes is replaced with a spiropentane subunit $\left(\mathrm{C}^{0}\left(\mathrm{C}^{\alpha}\right)_{4}\right)$. This effectively replaces the four in-plane methine groups $(\mathrm{CH})$ with two pair of bonded quaternary carbon atoms. By bonding adjacent pairs of $\mathrm{C}^{\alpha}$ atoms, a large degree of the repulsive non-bonding interaction is removed and we expect the in-plane crowding to be significantly relieved; the target, planar-tetracoordinate carbon atom has been incorporated into a pair of three-membered rings, a characteristic which is present in all planartetracoordinate carbon containing species synthesized to date (see Section 1.5.1 on page 23). Further, like the alkaplanes, the spiroalkaplanes are designed in a manner that allows (but does not require) a plane of symmetry through the central $\mathrm{C}(\mathrm{C})_{4}$ moiety.

We have completed a computational survey of likely spiro[2.2]alkaplane molecules.

[^54]

4-VII


4-39 $\left(D_{2}\right)$


4-40 $\left(D_{2}\right)$


4-41 $\left(C_{2}\right)$

Bicyclo[3.3.1]nonane (bicyclo- $\mathrm{C}_{9} \mathrm{H}_{12}$ ), cyclooctane (cyclo- $\mathrm{C}_{8} \mathrm{H}_{12}$ ), bicyclo[3.3.0]octane (bicyclo- $\mathrm{C}_{8} \mathrm{H}_{10}$ ), bicyclo[2.2.1]heptane or norbornane (bicyclo- $\mathrm{C}_{7} \mathrm{H}_{8}$ ), and cyclohexane (cyclo- $\mathrm{C}_{6} \mathrm{H}_{8}$ ) were used in identical pairs as capping hydrocarbons in an initial search, performed using the AM1 method, designed to locate promising spiroalkaplane structures. Seven spiro[2.2]alkaplanes were identified as worthy of further investigation ${ }^{\dagger}$ and

4-42 $\left(C_{2}\right)$

4-43 $\left(D_{2}\right)$

4-28 $\left(D_{2}\right)$

4-44 $\left(D_{2}\right)$
structures for these molecules, spiro[2.2]hexaplane (4-39), spiro[2.2]biheptaplane (440), two spiro[2.2]heptaplane isomers (4-41 and 4-42), spiro[2.2]bioctaplane (4-43), spiro[2.2]octaplane (4-28) and spiro[2.2]binonaplane (4-44), were determined by optimization at the B3-LYP/6-31G(d) and MP2/6-311+G(2d,p)(red) ${ }^{38}$ levels. General structural features of the seven spiroalkaplanes listed above are given in Table 4-9 on page 170. The symmetry of the equilibrium structure, the degree of distortion from planarity at $\mathrm{C}^{0}$, the number of imaginary frequencies for the structure constrained to have a

[^55]planar-tetracoordinate carbon atom, and the barrier to inversion at $\mathrm{C}^{0}\left(\Delta \mathrm{E}_{\text {plan }}\right)$ are also included in Table 4-9. More complete structural information (all bond lengths and

Table 4-9. General structural parameters, degree of non-planarity, $\alpha_{\text {plan }}\left({ }^{\circ}\right)$, and inversion barrier at $\mathrm{C}^{0}$, $\Delta \mathrm{E}_{\text {plan }}\left(\mathrm{kJ} \mathrm{mol}^{-1}\right)$, for the spiroalkaplanes.

\begin{tabular}{|c|c|c|c|c|c|c|c|c|}
\hline Molecule \& \& Sym. \({ }^{\text {a }}\) \& Cap Formula \& \begin{tabular}{l}
Cap \\
Structure \({ }^{\text {b }}\)
\end{tabular} \& Molecular Formula \& \(n i^{\text {c }}\) \& \(\alpha_{\text {plan }}{ }^{\text {d }}\) \& \(\Delta \mathrm{E}_{\text {plan }}{ }^{\text {e }}\) \\
\hline spiro[2.2]hexaplane \& 4-39 \& \(D_{2}\) \& cyclo-
\[
\mathrm{C}_{6} \mathrm{H}_{8}
\] \&  \& \(\mathrm{C}_{17} \mathrm{H}_{16}\) \& 1 \& \[
\begin{aligned}
\& 3.8^{\circ} \\
\& 4.1^{\circ}
\end{aligned}
\] \& \[
\begin{array}{r}
9.0 \\
18.9
\end{array}
\] \\
\hline spiro[2.2]biheptaplane \& 4-40 \& \(D_{2}\) \& bicyclo-
\[
\mathrm{C}_{7} \mathrm{H}_{8}
\] \&  \& \(\mathrm{C}_{19} \mathrm{H}_{16}\) \& 1 \& \[
\begin{aligned}
\& 3.5^{\circ} \\
\& 3.8^{\circ}
\end{aligned}
\] \& \[
\begin{array}{r}
4.7 \\
16.1
\end{array}
\] \\
\hline spiro[2.2]heptaplane \& 4-41 \& \(C_{2}\) \& \[
\begin{aligned}
\& \text { cyclo- } \\
\& \mathrm{C}_{7} \mathrm{H}_{10}
\end{aligned}
\] \&  \& \(\mathrm{C}_{19} \mathrm{H}_{20}\) \& 1 \& \[
\begin{aligned}
\& 3.6^{\circ} \\
\& 3.9^{\circ}
\end{aligned}
\] \& \[
\begin{aligned}
\& \mathbf{1 2 . 0} \\
\& 18.9
\end{aligned}
\] \\
\hline spiro[2.2]heptaplane \& 4-42 \& \(C_{2}\) \& \[
\begin{aligned}
\& \text { cyclo- } \\
\& \mathrm{C}_{7} \mathrm{H}_{10}
\end{aligned}
\] \&  \& \(\mathrm{C}_{19} \mathrm{H}_{20}\) \& 1 \& \[
\begin{aligned}
\& 3.0^{\circ} \\
\& 3.3^{\circ}
\end{aligned}
\] \& \[
\begin{aligned}
\& \mathbf{1 4 . 4} \\
\& 18.7
\end{aligned}
\] \\
\hline spiro[2.2]bioctaplane \& 4-43 \& \(D_{2}\) \& bicyclo-
\[
\mathrm{C}_{8} \mathrm{H}_{10}
\] \&  \& \(\mathrm{C}_{21} \mathrm{H}_{20}\) \& 1 \& \[
\begin{aligned}
\& 3.4^{\circ} \\
\& 3.7^{\circ}
\end{aligned}
\] \& \[
\begin{aligned}
\& 12.9 \\
\& 21.7
\end{aligned}
\] \\
\hline spiro[2.2]octaplane \& 4-28 \& \(D_{2}\) \& \[
\begin{aligned}
\& \text { cyclo- } \\
\& \mathrm{C}_{8} \mathrm{H}_{12}
\end{aligned}
\] \&  \& \(\mathrm{C}_{21} \mathrm{H}_{24}\) \& 1 \& \[
\begin{aligned}
\& \mathbf{3 . 1}^{\circ} \\
\& 3.5^{\circ}
\end{aligned}
\] \& \[
\begin{array}{r}
7.4 \\
15.0
\end{array}
\] \\
\hline spiro[2.2]binonaplane \& 4-44 \& \(D_{2}\) \& bicyclo-
\[
\mathrm{C}_{9} \mathrm{H}_{12}
\] \&  \& \(\mathrm{C}_{23} \mathrm{H}_{24}\) \& 1 \& 2.7

3.2 \& 4.4
11.7 <br>
\hline
\end{tabular}

[^56]selected bond angles) for spirohexaplane (4-39), spirobiheptaplane (4-40), and the two spiroheptaplane isomers (4-41 and 4-42) are given in Figure 4-6 on page 174, and for spirobioctaplane (4-43), spirooctaplane (4-28) and spirobinonaplane (4-44) are given in Figure 4-7 on page 175.

Initially, we examined structures for the spiroalkaplanes in which the bonding at the central, quaternary carbon atom was constrained to be exactly planar-tetracoordinate. For spiroalkaplanes 4-39, 4-40, 4-43 and 4-44, these 'planar' structures had $D_{2 \mathrm{~h}}$ symmetry, while for spiroalkaplanes 4-41 and 4-42 the 'planar' structures had $C_{2 \mathrm{v}}$ symmetry. In all cases, analysis of the analytic force constant matrix indicated that these 'planar' structures are transition structures, with a single imaginary frequency, and that the mode corresponding to this imaginary frequency leads to a distortion in the direction of tetra-hedral-like bonding at $\mathrm{C}^{0}$. This distortion leads to $D_{2}$ symmetry equilibrium structures for 4-39, 4-40, 4-43 and 4-44 (see Figure 4-6), and to $C_{2}$ symmetry equilibrium structures for the spiroheptaplane isomers, 4-41 and 4-42 (see Figure 4-7). Thus, the 'planar' structures are the transition structures for inversion at $\mathrm{C}^{0}$, a process which connects a pair of identical equilibrium structures. This suggests that the spiro[2.2]-alkaplanes (4VII) will be less susceptible than the alkaplanes (4-VI) (especially the $D_{2}$ symmetry alkaplanes) to potential kinetic instability from ring opening at the central carbon atom.

All the spiroalkaplanes that we have identified show a similar degree of flattening at the central tetracoordinate carbon atom (for $\alpha_{\text {plan }}$ values see Table 4-9 on page 170). This degree of flattening ( $\alpha_{\text {plan }}$ in the range $3-4^{\circ}$ ) is remarkable. The only saturated hydrocarbons predicted to have anywhere near this degree of flattening at a tetracoordinate carbon atom are the alkaplanes ( $\alpha_{\text {plan }}$ in the range $5-9^{\circ}$ ). We have calculated, using MP2/6-31G(d) optimized geometries, that experimentally observed compounds like [3.3.3]fenestrane (4-26) and [3.4.3]fenestrane-ketene (4-25-ketene) $)^{22}$ have $\alpha_{\text {plan }}$ values of $13.2^{\circ \dagger}$ and $18.9^{\circ}$, respectively, while experimentally isolable compounds like [3.5.3]fenestrane (4-45) ${ }^{16 c, 39,40}$ and tetracyclo[3.3.1.0 $\left.0^{2,4} .0^{2,8}\right]$ nonane (4-46) ${ }^{41}$ have values of $19.7^{\circ}$ and $20.4^{\circ}$, respectively. These distorted spiropentane-based compounds are

[^57]also considerably more flattened than the most flattened [k.l.m.n]fenestrane synthesized to date, an all-cis-[4.4.4.5]-fenestrane derivative (4-17), which we have determined to have $\alpha_{\text {plan }}=24.3^{\circ}$ (MP2/6-31G(d) optimized geometry). In fact, our measure for planar-


4-45 $\left(C_{2}\right)$


4-46 ${ }^{41}\left(C_{1}\right)$
ity suggests that spiropentane itself exhibits some flattening at the central carbon atom $\left(\alpha_{\text {plan }}=21.4^{\circ}\right)$. This is entirely consistent with what is observed. In the fenestrane derivative $\mathbf{4 - 1 7}{ }^{15}$ the opposite CCC angles ${ }^{\dagger}$ are $128.3^{\circ}$ and $129.2^{\circ}$ (see Section 1.5 .2 on page 24), while in spiropentane the opposite CCC angles are both $137.2^{\circ}$. These opposite CCC angles are $109.5^{\circ}$ in an ideal tetrahedral structure and $180.0^{\circ}$ for planar-tetracoordination. Clearly, spiropentane should be considered more flattened than 4-17. We also note that, 4-25-ketene, 4-26, 4-45 and 4-46, although considerably bent from the parent spiropentane structure, exhibit only slightly greater flattening at the central carbon atom over spiropentane (for a more detailed discussion of bending, which leads to pyramidal carbon, versus twisting, which leads to planar carbon, in these bridged spiropentanes, see Section 1.5.5 on page 35). Much of the considerable strain in spiropentane arises from angle strain, and some of this angle strain can be thought of as contributing to flattening at the central carbon atom.

This inherent flattening of the spiropentane moiety, combined with the relief of steric problems as a consequence of forming bonds between pairs of $\mathrm{C}^{\alpha}$ atoms, helps explain the improved planarization of the bonding at $\mathrm{C}^{0}$ in the spiroalkaplanes (4-VII) over the alkaplanes (4-VI).

Further examination of the structures of the spiroalkaplanes reveals a number of interesting features. Firstly, there are no extraordinarily long C-C bonds. ${ }^{\ddagger}$ The longest

[^58]$\mathrm{C}-\mathrm{C}$ bonds are found in the smallest spiroalkaplanes (4-39-4-42) (see Figure 4-6). Both 4-39 and 4-40 have six-membered primary-ring caps ${ }^{\dagger}$ and each of these molecules has a $C^{\alpha}-C^{\beta}$ bond of $1.64 \AA$ and a $C^{\beta}-C^{\beta}$ bond of $1.62 \AA$. ${ }^{\ddagger}$ The spiroheptaplane isomer 4-41 has an usually long $C^{\beta}-C^{\beta}$ bond in the seven-membered ring caps of $1.65 \AA$ and a $C^{\alpha}-C^{\beta}$ bond of $1.61 \AA$. The other spiroheptaplane isomer (4-42) also has an elongated $C^{\beta}-C^{\beta}$ bond of $1.60 \AA$. In the larger-ring spiroalkaplanes 4-28, 4-43 and 4-44, all the $\mathrm{C}-\mathrm{C}$ bonds are less than $1.60 \AA$. As a consequence, there are no obvious sources of kinetic instability in these molecules, due to overlong $\mathrm{C}-\mathrm{C}$ bonds. We also note that in all the spiroalkaplanes examined, the $\mathrm{C}^{0}-\mathrm{C}^{\alpha}$ bonds vary in length from 1.45 to $1.51 \AA$, and are thus generally similar in length to, or slightly shorter than, the equivalent bonds in spiropentane $(1.47 \AA)$.

One structural aspect that is of particular interest is the origin of the distortion from planar-tetracoordination at $\mathrm{C}^{0}$. When examining the alkaplanes (4-VI) (see Section 4.3.3), it was seen that a large proportion of the distortion of the $\mathrm{C}^{\alpha}$ atoms from the plane is a consequence of the alternate lengthening and compression of pairs of $\mathrm{C}^{\alpha}-\mathrm{C}^{\beta}$ bonds. ${ }^{\S}$ This bond alternation must be overcome if true planar-tetracoordination is to be achieved. The central spiropentane subunit of the spiroalkaplanes does appear to reduce this effect. However, the alternate lengthening and compression is still evident (see Table 4-10 on page 176 for details). Pairs of $\mathrm{C}^{\alpha}-\mathrm{C}^{\beta}$ bond lengths for spirohexaplane (4-39) (1.64/1.53 $\AA$ ), spirobiheptaplane (4-40) (1.64/1.53 $\AA$ ), the spiroheptaplane isomer 4-41 (1.58/1.53 and 1.61/1.52 $\AA$ ), the spiroheptaplane isomer 4-42 (1.58/ 1.52 and $1.58 / 1.52 \AA$ ), spirobioctaplane (4-43) (1.56/1.50 $\AA$ ), spirooctaplane (4-28) (1.55/1.50), and spirobinonaplane (4-44) (1.55/1.50) differ by at most $0.11 \AA$ in the case of the small spiroalkaplanes 4-39 and 4-40, and by $0.05-0.06 \AA$ for the larger spiroalkaplanes with an eight-membered primary-ring cap, 4-28, 4-43 and 4-44. The equivalent $\mathrm{C}^{\alpha}-\mathrm{C}^{\beta}$ bond-length differences for hexaplane (4-31) and $S_{4}$ octaplane (4-27) are 0.11

[^59]

Figure 4-6. Structural parameters (MP2/6-311+G(2d,p)(red) ${ }^{38}$ values in bold type, B3-LYP/6-31G(d) values in plain text, all values in $\AA$ or degrees) for spirohexaplane (4-39), spirobiheptaplane (4-40) and the two spiroheptaplane isomers (4-41 and 4-42). All unique bond lengths are shown. The most distorted CCC angles and the distortion from planarity at $\mathrm{C}^{0}, \alpha_{\text {plan }}$, are given. The angles and bond lengths around the central $\mathrm{C}(\mathrm{C})_{4}$ subunit for $\mathbf{4 - 4 2}$ are also shown.
and $0.09 \AA$, respectively. Clearly, for species based on cyclohexane there has been no reduction in the alternation effect while for the species based on cyclooctane the effect has been almost halved.


Figure 4-7. Structural parameters (MP2/6-311+G(2d,p)(red) values in bold type, B3-LYP/6-31G(d) values in plain text, all values in $\AA$ or degrees) for spirobioctaplane (443), spirooctaplane (4-28) and spirobinonaplane (4-44). All unique bond lengths, any $\mathrm{H}-\mathrm{H}$ close contacts, and the most distorted CCC angles are shown. The distortion from planarity at $\mathrm{C}^{0}, \alpha_{\text {plan }}\left({ }^{\circ}\right)$, is also given.

One possible cause for the alternate lengthening and compression of the $\mathrm{C}^{\alpha}-\mathrm{C}^{\beta}$ bonds may be that these bonds are weakened as a consequence of the significant angle strain introduced at $\mathrm{C}^{\alpha}$ by the geometric constraints which are the result of a bicapped structure. In fact, there is a reasonably good correlation between the size of the $\mathrm{C}^{\beta} \mathrm{C}^{\alpha} \mathrm{C}^{\beta}$ angles and the differences in length of the $\mathrm{C}^{\alpha}-\mathrm{C}^{\beta}$ bond-pairs (see Table 4-8 on page 167 and Table 4-10); the difference in length of the $\mathrm{C}^{\alpha}-\mathrm{C}^{\beta}$ bond-pairs is larger when $\angle C^{\beta} C^{\alpha} C^{\beta}$ is large. In the spiroalkaplanes in particular, very large $C^{\beta} C^{\alpha} C^{\beta}$ angles (greater than $170^{\circ}$ ) are present in the two smallest molecules, 4-39 and 4-40, and these

Table 4-10. Selected geometric parameters, $r\left(\mathrm{C}^{\alpha}-\mathrm{C}^{\beta}\right)(\AA)$ and $\angle \mathrm{C}^{\beta} \mathrm{C}^{\alpha} \mathrm{C}^{\beta}\left({ }^{\circ}\right)$, for the spiroalkaplanes.

| Molecule |  | Sym. $^{\mathrm{a}}$ | $r\left(\mathrm{C}^{\alpha}-\mathrm{C}^{\beta}\right)^{\mathrm{b}}$ | $\angle \mathrm{C}^{\beta} \mathrm{C}^{\alpha} \mathrm{C}^{\beta \mathrm{b}}$ |
| :--- | :---: | :---: | :---: | :---: |
| spiro[2.2]hexaplane | $\mathbf{4 - 3 9}$ | $D_{2}$ | $\mathbf{1 . 6 3 5 / 1 . 5 3 2}$ | $\mathbf{1 7 4 . 1}^{\circ}$ |
|  |  |  | $1.650 / 1.532$ | $172.7^{\circ}$ |
| spiro[2.2]biheptaplane | $\mathbf{4 - 4 0}$ | $D_{2}$ | $\mathbf{1 . 6 4 0 / 1 . 5 3 1}$ | $\mathbf{1 7 3 . 2}^{\circ}$ |
|  |  |  | $1.653 / 1.529$ | $171.9^{\circ}$ |
| spiro[2.2]heptaplane ${ }^{\text {c }}$ | $\mathbf{4 - 4 1}$ | $C_{2}$ | $\mathbf{1 . 5 7 5 / 1 . 5 2 5 ~ 1 . 6 1 4 / 1 . 5 2 0}$ | $\mathbf{1 4 2 . 3}^{\circ} \mathbf{1 7 2 . 6}^{\circ}$ |
|  |  |  | $1.595 / 1.5171 .625 / 1.518$ | $141.6^{\circ} 171.4^{\circ}$ |
| spiro[2.2]heptaplane ${ }^{\circ}$ | $\mathbf{4 - 4 2}$ | $C_{2}$ | $\mathbf{1 . 5 7 9 / 1 . 5 2 1} 1.583 / 1.515$ | $\mathbf{1 3 5 . 3}^{\circ} \mathbf{1 4 2 . 3}^{\circ}$ |
|  |  |  | $1.598 / 1.5231 .602 / 1.526$ | $135.1^{\circ} 142.2^{\circ}$ |
| spiro[2.2]bioctaplane | $\mathbf{4 - 4 3}$ | $D_{2}$ | $\mathbf{1 . 5 6 0 / 1 . 5 0 2}$ | $\mathbf{1 3 8 8 . 7}^{\circ}$ |
|  |  |  | $1.580 / 1.511$ | $138.4^{\circ}$ |
| spiro[2.2]octaplane | $\mathbf{4 - 2 8}$ | $D_{2}$ | $\mathbf{1 . 5 5 1 / 1 . 4 9 9}$ | $\mathbf{1 3 7 . 9}^{\circ}$ |
| spiro[2.2]binonaplane | $\mathbf{4 - 4 4}$ | $D_{2}$ | $1.571 / 1.506$ | $137.5^{\circ}$ |

[^60]molecules have by far the largest alternation in $\mathrm{C}^{\alpha}-\mathrm{C}^{\beta}$ bond lengths (and consequently the largest values for $\alpha_{\text {plan }}$ ). On the other hand, the largest spiroalkaplanes we have examined, 4-28 and 4-44 have the least pronounced bond length alternation and the smallest values for $\angle \mathrm{C}^{\beta} \mathrm{C}^{\alpha} \mathrm{C}^{\beta}$ (138 ${ }^{\circ}$ and $137^{\circ}$, respectively, compared with an MP2/6$31 \mathrm{G}(\mathrm{d})$ calculated angle of $115^{\circ}$ for the equivalent angle in octamethylspiropentane). This suggests that a cage which would reduce the $\angle \mathrm{C}^{\beta} \mathrm{C}^{\alpha} \mathrm{C}^{\beta}$ angle may help in achieving absolute planarity.

The spiroalkaplanes (4-VII) are also found to have a remarkably low barrier to inversion at the central carbon atom $\left(\mathrm{C}^{0}\right)$. Values for $\Delta \mathrm{E}_{\text {plan }}$ calculated at the MP2/6$311+\mathrm{G}(2 \mathrm{~d}, \mathrm{p}) / / \mathrm{MP} 2 / 6-311+\mathrm{G}(2 \mathrm{~d}, \mathrm{p})($ red $)$ level for $\mathbf{4 - 2 8}$ and 4-39-4-44 are in the range $5-15 \mathrm{~kJ} \mathrm{~mol}^{-1}$ while the B3-LYP/6-311+G(2d,p)//B3-LYP/6-31G(d) values are in the range $10-20 \mathrm{~kJ} \mathrm{~mol}^{-1}$ (see Table 4-9 on page 170). Rapid conversion between the two equivalent isomers is expected to occur at room temperature.

The pair of cyclic hydrocarbon caps introduced in the spiroalkaplanes has resulted in an almost complete reduction in the $437 \mathrm{~kJ} \mathrm{~mol}^{-1}$ barrier to planar-tetracoordination
in spiropentane (see Section 4.3.2). Work towards overcoming the final impediment to planarity is detailed in the next section.

### 4.3.5 Dimethanospiroalkaplane Structures

Further flattening at the central tetracoordinate carbon atom $\left(\mathrm{C}^{0}\right)$ can be achieved by strapping together the cyclic hydrocarbon caps of a spiroalkaplane (4-VII) with hydrocarbon bridges. In particular, we have used methylene bridges to link pairs of methylene groups between the caps of spiroalkaplanes built with caps of at least eight carbon atoms (specifically spiro[2.2]bioctaplane (4-43), spiro[2.2]octaplane (4-28), and spiro[2.2]binonaplane (4-44)). This modification to the spiroalkaplane structures is

expected to make the cage more rigid by preventing the linked pair of methylene groups from twisting in an anti fashion. It is also expected to help in reducing the $\mathrm{C}^{\beta} \mathrm{C}^{\alpha} \mathrm{C}^{\beta}$



angles and thereby reduce the bond-length alternation in the $\mathrm{C}^{\alpha}-\mathrm{C}^{\beta}$ bonds. We refer to the resulting molecules, dimethanospiro[2.2]bioctaplane 4-47, dimethanospiro[2.2]octaplane 4-29 and dimethanospiro[2.2]binonaplane 4-48, collectively as dimethanospiroalkaplanes (4-VIII). Initial structures were determined using the AM1 method
without symmetry constraints. In all three cases a $D_{2}$ symmetry structure resulted. These structures were then re-optimized in $D_{2}$ symmetry at the B3-LYP/6-31G(d) and MP2/6-311+G(2d,p)(red $)^{38}$ levels. In the case of both 4-29 and 4-48 the MP2 optimization resulted in a $D_{2 \mathrm{~h}}$ symmetry structure. Structures for all molecules with $D_{2 \mathrm{~h}}$ symmetry imposed were also determined by optimization at the B3-LYP/6-31G(d) and MP2/6$311+\mathrm{G}(2 \mathrm{~d}, \mathrm{p})($ red $)$ levels. The nature of the resulting B3-LYP stationary points were examined by analytic force constant analysis. The extremely challenging task ${ }^{\dagger}$ of determining second derivatives for the $D_{2 \mathrm{~h}}$ symmetry MP2/6-311+G(2d,p)(red) optimized structures was also undertaken in order to establish without doubt the nature of these stationary points. Where appropriate, improved energy differences were calculated at the MP2/6-311+G(2d,p)/MP2/6-311+G(2d,p)(red) and B3-LYP/6-311+G(2d,p)//B3-LYP/6-31G(d) levels. General structural features, the symmetry of equilibrium structures, the number of imaginary vibrational frequencies for the $D_{2 \mathrm{~h}}$ symmetry structures, the distortion from planar-tetracoordination at $C^{0}, \alpha_{\text {plan }}$, and the values for $\Delta \mathrm{E}_{\text {plan }}$, the barrier to inversion at $\mathrm{C}^{0}$, for the three dimethanospiroalkaplanes explored in this work, 4-47, 4-29 and 4-48, are given in Table 4-11. More detailed structural data (all bond lengths and the most distorted CCC angles) are given in Figure 4-8 on page 180.

Optimizations at the MP2/6-311+G(2d,p)(red) level, which are substantiated by numerical force constant analyses which give no imaginary frequencies, predict quite conclusively that the dimethanospiroalkaplanes, dimethanospiro[2.2]octaplane (4-29) and dimethanospiro[2.2]binonaplane (4-48) have an exactly planar-tetracoordinate central carbon atom $\left(\alpha_{\text {plan }}=0.0^{\circ}\right)$. The third dimethanospiroalkaplane examined here, dimethanospiro[2.2]binonaplane (4-47), is predicted from the MP2 calculations to have a $D_{2}$ symmetry equilibrium structure. However, although the MP2 predicted distortion from planar-tetracoordination at $\mathrm{C}^{0}$ is $2.2^{\circ}$, the difference between the energies of the distorted $\left(D_{2}\right)$ and 'planar' $\left(D_{2 \mathrm{~h}}\right)$ structures, $\Delta \mathrm{E}_{\text {plan }}[\mathrm{MP} 2]$, is almost negligible (0.4 $\mathrm{kJ} \mathrm{mol}^{-1}$ ). Calculations at the B3-LYP/6-31G(d) level differ in that they predict $D_{2}$ symmetry equilibrium structures for all three molecules, 4-47, 4-29 and 4-48. However, the B3-LYP/6-311+G(2d,p)//B3-LYP/6-31G(d) calculated difference in the energy of the $D_{2}$ and $D_{2 \mathrm{~h}}$ symmetry structures $\left(\Delta \mathrm{E}_{\text {plan }}\right)$ is remarkably small for 4-29 and 4-48 (0.6 and 0.2

[^61]Table 4-11. Structural features, the distortion from planarity, $\alpha_{\text {plan }}\left({ }^{\circ}\right)$, and the inversion barrier at $\mathrm{C}^{0}$, $\Delta \mathrm{E}_{\text {plan }}\left(\mathrm{kJ} \mathrm{mol}^{-1}\right)$, for the dimethanospiroalkaplanes.

| Molecule |  | Sym. ${ }^{\text {a }}$ | Cap Structure ${ }^{\text {b }}$ | Molecular Formula | $n i^{\text {c }}$ | $\alpha_{\text {plan }}{ }^{\text {d }}$ | $\Delta \mathrm{E}_{\text {plan }}{ }^{\text {e }}$ |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| dimethanospiro[2.2]bioctaplane | 4-47 | $D_{2} / D_{2}$ |  | $\mathrm{C}_{23} \mathrm{H}_{20}$ | 1/1 | $\begin{aligned} & 2.2^{\circ} \\ & 2.6^{\circ} \end{aligned}$ | $\begin{gathered} \mathbf{0 . 4} \\ 5.1 \end{gathered}$ |
| dimethanospiro[2.2]octaplane | 4-29 | $\boldsymbol{D}_{2 \mathrm{~h}} / D_{2}$ |  | $\mathrm{C}_{23} \mathrm{H}_{24}$ | 0/1 | $\begin{aligned} & \mathbf{0 . 0}^{\text {of }} \\ & 1.8^{\circ} \end{aligned}$ | $\begin{aligned} & \mathbf{0 . 0}^{\mathrm{f}} \\ & 0.6 \end{aligned}$ |
| dimethanospiro[2.2]binonaplane | 4-48 | $D_{2 \mathrm{~h}} / D_{2}$ |  | $\mathrm{C}_{25} \mathrm{H}_{24}$ | 0/1 | $\begin{aligned} & \mathbf{0 . 0}^{\text {of }} \\ & 1.7^{\circ} \end{aligned}$ | $\begin{aligned} & \mathbf{0 . 0}^{\mathrm{f}} \\ & 0.2 \end{aligned}$ |

[^62]$\mathrm{kJ} \mathrm{mol}^{-1}$, respectively). ${ }^{\dagger}$ It seems likely that the B3-LYP predicted distortions from pla-nar-tetracoordination at $\mathrm{C}^{0}$ in 4-29 and 4-48 are an artifact of the B3-LYP/6-31G(d) calculations. Dimethanospirooctaplane (4-29) and dimethanospirobinonaplane (4-48) are the first neutral saturated hydrocarbons predicted to contain an exactly planar-tetracoordinate carbon atom.

A detailed examination of the structures of the dimethanospiro[2.2]alkaplanes examined here (see Figure 4-8) reveals that the alternation in $\mathrm{C}^{\alpha}-\mathrm{C}^{\beta}$ bond lengths is reduced considerably to either nothing (for the $D_{2 \mathrm{~h}}$ symmetry MP2 structures) or $0.03-0.04 \AA$ for the $D_{2}$ symmetry structures. It can also be seen that the corresponding

[^63]
$$
\alpha_{\text {plan }}=2.2 / 2.6
$$

$\alpha_{\text {plan }}=0.0 / 1.8$
$$
4-29\left(\boldsymbol{D}_{2 \mathrm{~h}} / D_{2}\right)
$$
$$
4-47\left(D_{2} / D_{2}\right)
$$

$\alpha_{\text {plan }}=0.0 / 1.7$
4-48 $\left(\boldsymbol{D}_{2 \mathrm{~h}} / D_{2}\right)$

Figure 4-8. Structural parameters (MP2/6-311+G(2d,p)(red) ${ }^{38}$ values in bold type, B3-LYP/6-31G(d) values in plain text, all values in $\AA$ or degrees) for dimethanospirobioctaplane (4-47), dimethanospirooctaplane (4-29), and dimethanospirobinonaplane (4-48). All unique bond lengths and some close-contact distances ( $\AA$ ) are shown. CCC angles significantly distorted from the tetrahedral ideal and the distortion from planartetracoordination at $\mathrm{C}^{0}, \alpha_{\text {plan }}\left({ }^{\circ}\right)$, are also given.
$\mathrm{C}^{\beta} \mathrm{C}^{\alpha} \mathrm{C}^{\beta}$ angles in 4-47, 4-29 and 4-48 (135.5 ${ }^{\circ}, 134.2^{\circ}$ and $134.4^{\circ}$, respectively $)^{\dagger}$ are slightly reduced from those in the parent spiroalkaplanes, 4-43, 4-28 and 4-44 (138.7 ${ }^{\circ}$, $137.9^{\circ}$ and $137.0^{\circ}$, respectively). ${ }^{\ddagger}$ This is consistent with the expectation that bond-

[^64]length alternation in the $\mathrm{C}^{\alpha}-\mathrm{C}^{\beta}$ bond pairs will be decreased by a reduction in the $C^{\beta} C^{\alpha} C^{\beta}$ angle.

Very long carbon-carbon bonds can indicate a potential source of kinetic instability via facile $\mathrm{C}-\mathrm{C}$ cleavage or molecular rearrangement. Examination of the calculated C-C bond lengths for 4-47, 4-29 and 4-48 reveals no bonds longer than $1.60 \AA$ (see Figure 4-8 on page 180). It is worth noting, however, that, with the exception of the shortest C-C bond in 4-48 (1.525 A compared with $1.534 \AA$ in twistboat-twistboat bicyclo[3.3.1]nonane (TBTB-4-54)), the $\mathrm{C}-\mathrm{C}$ bonds of the capping units (derived from cisbicyclo[3.3.0]octane, crown cyclooctane and bicyclo[3.3.1]nonane) are all longer than the corresponding bonds of the unincorporated cyclic hydrocarbons. ${ }^{\dagger}$ It appears that the entire cage surrounding $\mathrm{C}^{0}$ is slightly expanded. This is consistent with our intention to design a cage that 'clamps down' the bonding at $\mathrm{C}^{0}$ to give planar-tetracoordination.

One other structural feature that is worth noting is the $\mathrm{H}-\mathrm{H}$ close contact between the topmost and bottommost methylene hydrogens in dimethanospirooctaplane (4-29). This distance ( $1.86 \AA$ ) is markedly shorter than in the corresponding spiroalkaplane 4$28(2.24 \AA)$. This close contact must induce some distortionary forces into the capping unit of 4-29 and may prove to be a problem synthetically. This close-contact situation is overcome in dimethanospirobinonaplane (4-48) by introducing a methylene bridge at this position.

Finally, it can also be seen that the MP2/6-311+G(2d,p)(red) $\mathrm{C}^{0}-\mathrm{C}^{\alpha}$ bonds in the dimethanospiroalkaplanes 4-47, 4-29 and 4-48 (1.51, 1.50, $1.51 \AA$, respectively), are longer than those in the corresponding spiroalkaplanes, 4-43, 4-28 and 4-44 (all of which are $1.48 \AA$ ), and that the $\mathrm{C}^{\alpha}-\mathrm{C}^{\alpha}$ bonds (1.47, 1.44 and $1.45 \AA$, respectively) are shorter (the $\mathrm{C}^{\alpha}-\mathrm{C}^{\alpha}$ bonds of 4-43, 4-28 and 4-44 are $1.514,1.504$ and $1.494 \AA$, respectively). The $\mathrm{C}^{\alpha}-\mathrm{C}^{\alpha}$ bonds in 4-47, 4-29 and 4-48 are even shorter than the $\mathrm{C}-\mathrm{C}$ bonds of cyclopropane (which are calculated at the MP2/6-31G(d) level to be $1.504 \AA$ ), suggesting they may possess some $\mathrm{C}=\mathrm{C}$ double bond character.

Both dimethanospirooctaplane (4-29) and dimethanospirobinonaplane (4-48) are expected to be good targets for attempts at synthesis of a planar-tetracoordinate carbon

[^65]

Figure 4-9. Calculated potential energy curves for inversion at $\mathrm{C}^{0}$ determined at the $\mathrm{MP} 2 / 6-311+\mathrm{G}(2 \mathrm{~d}, \mathrm{p}) / / \mathrm{MP} 2 / 6-311+\mathrm{G}(2 \mathrm{~d}, \mathrm{p})(\mathrm{red})$ level are given as relative energy, $E_{\text {rel }}$, $\left(\mathrm{kJ} \mathrm{mol}^{-1}\right)$ against angle of distortion from planarity at $\mathrm{C}^{0}, \alpha_{\text {plan }}\left({ }^{\circ}\right)$, for the three species typifying the three alkaplane families: - octaplane (4-27), O - spiro[2.2]octaplane (4-28), and $\boldsymbol{\square}$ - dimethanospiro[2.2]octaplane (4-29). In all cases, this inversion mode corresponds to the lowest-energy vibrational mode.
atom in a neutral saturated hydrocarbon. Dimethanospirobioctaplane (4-47) is predicted to have a substantial degree of flattening at $\mathrm{C}^{0}\left(\alpha_{\text {plan }}=2.2^{\circ}\right)$ and an almost negligible barrier to inversion at $\mathrm{C}^{0}\left(\Delta \mathrm{E}_{\text {plan }}=0.4 \mathrm{~kJ} \mathrm{~mol}^{-1}\right)$, which is expected to be below the zero-point energy for the inversion mode, suggesting that this molecule might be best described as pseudo-planar-tetracoordinate.

The remarkable progression in the alkaplane families from considerably planarized in the alkaplanes (4-VI), through almost planar-tetracoordinate in the spiroalkaplanes (4-VII), to exactly planar-tetracoordinate in the dimethanospiroalkaplanes (4-VIII) is well-illustrated by Figure 4-9, which shows the reduction in the barrier to inversion at $\mathrm{C}^{0}$ ( $\Delta \mathrm{E}_{\text {plan }}$ ) from octaplane (4-27), through spirooctaplane (4-28), to dimethanospirooctaplane (4-29). Firstly, the effect of forming bonds between adjacent pairs of $\mathrm{C}^{\alpha}$ atoms
dramatically reduces the barrier to inversion ( $\Delta \mathrm{E}_{\text {plan }}$ drops from 58.6 to $7.4 \mathrm{~kJ} \mathrm{~mol}^{-1}$ ). This might partly reflect the dramatic reduction in the energy difference between 'planar' and tetrahedral-like structures for neopentane and spiropentane ( $\Delta \mathrm{E}_{\mathrm{PT}}=880$ and $440 \mathrm{~kJ} \mathrm{~mol}^{-1}$, respectively) (see Section 4.3.2). The introduction of a pair of methylene bridges between the caps then reduces this barrier to zero, giving a broadened potential energy well with an equilibrium structure with $D_{2 \mathrm{~h}}$ symmetry.

### 4.3.6 Strain Energies and Heats of Formation

Determining the total strain energies (SEs) of our novel hydrocarbons allows for a comparison with other strained hydrocarbons. ${ }^{43}$ We have chosen to use a method of calculating strain energies which has been used to great effect by Schulman and Disch. ${ }^{32}$ This method determines the strain energy as the negative of the calculated enthalpy change of a homodesmic reaction in which the number of quaternary $(\mathrm{C})$, tertiary $(\mathrm{CH})$ and secondary $\left(\mathrm{CH}_{2}\right)$ carbons present in the target hydrocarbon are balanced with product neopentane, isobutane and propane molecules. The number of primary $\left(\mathrm{CH}_{3}\right)$ carbons on each side of the reaction is then balanced using ethane. This preserves the number and type of $\mathrm{C}-\mathrm{C}$ bonds on each side of the reaction and is found to give good cancellation of errors when the MP2 method is used to calculate energies (see also Section 3.2 on page 97). If these product molecules are defined as being strain free (which is usual), the enthalpy change of this homodesmic reaction gives the total strain of the target hydrocarbon. The resulting reaction enthalpy change can then be used in conjunction with experimental heats of formation for ethane, propane, isobutane and neopentane to give calculated heats of formation $\left(\Delta H_{\mathrm{f}}(\mathrm{calc})\right)$ for the target hydrocarbon.

Previous work, using MP2/6-31G(d)//HF/6-31G(d) calculated energies, has shown this type of approach to yield heats of formation for a number of hydrocarbons, some with significant strain energies, to within $13 \mathrm{~kJ} \mathrm{~mol}^{-1}$. We have used MP2/6$311+G(2 d, p)$ energies (calculated at MP2/6-311+G(2d,p), MP2/6-31G(d) or HF/6$31 \mathrm{G}(\mathrm{d})$ geometries) and appropriately scaled ${ }^{34}$ B3-LYP/6-31G(d) frequencies for the ZPVE and $H^{298}-H^{0}$ corrections. A comparison of the resulting calculated and experimental heats of formation is given in Table 4-12 and Table 4-13 for molecules for which experimental heats of formation are available. The applicable homodesmic reactions, calculated $S E s, S E / \mathrm{Cs}$ and $\Delta H_{\mathrm{f}} \mathrm{s}$ for a number of small cyclic hydrocarbons and well-

Table 4-12. Calculated strain energies $(S E)^{\text {a }}$ and strain per carbon atom (SE/C), and calculated and experimental heats of formation $\left(\Delta H_{\mathrm{f}}\right)$ at $298 \mathrm{~K}\left(\mathrm{~kJ} \mathrm{~mol}^{-1}\right)$ for a variety of known and previously explored hydrocarbons.

| Molecule | Homodesmic reaction ${ }^{\text {b }}$ | $\begin{gathered} S E \\ (\mathrm{calc})^{\mathrm{c}} \end{gathered}$ | $\begin{aligned} & S E / \mathrm{C} \\ & \text { (calc) } \end{aligned}$ | $\begin{gathered} \Delta H_{\mathrm{f}} \\ \text { (calc) } \end{gathered}$ | $\Delta H_{\mathrm{f}}(\exp )^{\text {d }}$ |
| :---: | :---: | :---: | :---: | :---: | :---: |
| Simple Alicyclic Hydrocarbons |  |  |  |  |  |
| cyclopropane | 4-49 + 3 eth $\rightarrow 3$ pro | 124 | 41.5 | 62 | $53.3 \pm 0.6$ |
| cyclobutane | $\mathbf{4 - 5 0}+4$ eth $\rightarrow 4$ pro | 115 | 28.7 | 32 | $28.5 \pm 0.6$ |
| cyclopentane | $\mathbf{4 - 5 1}+5$ eth $\rightarrow 5$ pro | 29 | 5.9 | -75 | -76.4 |
| cyclohexane (chair) | C-4-52 + 6 eth $\rightarrow 6$ pro | 1 | 0.1 | $-124$ | $-123.1 \pm 0.8$ |
| cyclooctane (boat-chair) | BC-4-53 + 8 eth $\rightarrow 8$ pro | 42 | 5.3 | -125 | $-124.4 \pm 1.0$ |
| bicyclo[3.3.1]nonane (chair-chair) | CC-4-54 + 10 eth $\rightarrow 7$ pro +2 iso | 28 | 3.1 | -135 | $-127.5 \pm 2.3$ |
| Strained Hydrocarbons |  |  |  |  |  |
| tetrahedrane | 4-55 + 6 eth $\rightarrow 4$ iso | 602 | 150.5 | 568 | $(535.0 \pm 4.0)^{\text {e }}$ |
| pyramidane | $\mathbf{4 - 5 6}+8$ eth $\rightarrow$ neo +4 iso | 644 | 128.8 | 610 |  |
| [1.1.1]propellane | $\mathbf{4 - 5 7}+7$ eth $\rightarrow 2$ neo +3 pro | 429 | 85.9 | 366 | $351.0 \pm 4.0^{\text {f }}$ |
| spiropentane | $\mathbf{4 - 5 8}+6$ eth $\rightarrow$ neo +4 pro | 282 | 56.4 | 198 | $185.1 \pm 0.8$ |
| prismane | $\mathbf{4 - 5 9}+9$ eth $\rightarrow 6$ iso | 640 | 106.7 | 589 |  |
| cubane | $\mathbf{4 - 6 0}+12$ eth $\rightarrow 8$ iso | 712 | 89.0 | 644 | $622.2 \pm 3.7$ |
| tetramethyltetrahedrane | 4-61 + 6 eth $\rightarrow 4$ neo | 593 | 74.1 | 425 |  |
| tetra-tert-butyltetrahedrane | 4-62 + 10 eth $\rightarrow 8$ neo | 527 | 26.3 | 22 | $25.9 \pm 8.8^{\text {g }}$ |
| pagodane | $\mathbf{4 - 6 3}+30$ eth $\rightarrow 4$ pro +12 iso +4 neo | 348 | 17.4 | 163 | $200.3 \pm 3.8^{\text {h }}$ |
| dodecahedrane | 4-64 + 30 eth $\rightarrow 20$ iso | 245 | 12.3 | 77 | $76.1 \pm 4.2^{\text {i }}$ |

[^66]known strained hydrocarbons, the hydrocarbons we have used as caps in designing the alkaplanes, a number of [3.m.3]- and [n.n.n.n]fenestranes, and all the alkaplanes examined in this work (4-27-4-36, 4-39-4-44, 4-47 and 4-48), are listed in Tables 4-12, 4-$13,4-14$ and 4-15, respectively.


4-55 $\left(T_{d}\right)$


4-59 $\left(D_{3 \mathrm{~h}}\right)$


4-60 $\left(O_{\mathrm{h}}\right)$


4-63 $\left(D_{2 h}\right)$

A comparison of calculated and experimental heats of formation for the simple cyclic and bicyclic hydrocarbons listed in Table 4-12 (4-49, 4-50, 4-51, C-4-52, BC-453 and CC-4-54) shows that for these relatively unstrained molecules our method gives $\Delta H_{\mathrm{f}} \mathrm{s}$ in good agreement with experiment, with results to within $12 \mathrm{~kJ} \mathrm{~mol}^{-1}$ (and to within $7 \mathrm{~kJ} \mathrm{~mol}^{-1}$ if cyclopropane is excluded). For the capping hydrocarbons listed in Table 4-13 for which we have experimental heats of formation (4-65-4-68), this impressive agreement is maintained. However, for experimentally-known, highlystrained hydrocarbons (4-57, 4-58, 4-60, 4-62, 4-63 and 4-64), the differences between theory and experiment appear to be somewhat larger (see Table 4-12). The largest difference is associated with the calculated $\Delta H_{\mathrm{f}}$ of [1.1.1.1]pagodane $\left(\mathbf{4 - 6 3}{ }^{44}\right)$, which differs from the experimental value ${ }^{33 \mathrm{e}}$ by $37 \mathrm{~kJ} \mathrm{~mol}^{-1}$. Relatively large discrepancies between the calculated and experimental $\Delta H_{\mathrm{f}} \mathrm{s}$ are also found for cubane (4-60) (22 $\mathrm{kJ} \mathrm{mol}^{-1}$ ) and tetrahedrane $(\mathbf{4 - 5 5})^{\dagger}\left(33 \mathrm{~kJ} \mathrm{~mol}^{-1}\right)$.

We have also calculated strain energies (SEs) for the appropriate equilibrium structures of the cyclic hydrocarbons used as caps in building the alkaplanes (Table 4-13). The caps are calculated to have strain energies lying in a small range ( $S E=28-63$ $\mathrm{kJ} \mathrm{mol}^{-1}$ ), except bicyclo[2.2.0]hexane (4-65) which has a calculated $S E$ of 238 $\mathrm{kJ} \mathrm{mol}^{-1}$. When considering the strain energies of the alkaplanes it should be remembered that there is an inherent contribution to the total strain energy from the pairs of

[^67]Table 4-13. Calculated strain energies $(S E)^{\mathrm{a}}$ and strain per carbon atom ( $S E / \mathrm{C}$ ) and calculated and experimental heats of formation $\left(\Delta H_{\mathrm{f}}\right)$ at $298 \mathrm{~K}\left(\mathrm{~kJ} \mathrm{~mol}^{-1}\right)$ for the capping hydrocarbons.

| Molecule | Homodesmic reaction ${ }^{\text {b }}$ | $\begin{gathered} S E \\ (\mathrm{calc})^{\mathrm{c}} \end{gathered}$ | $\begin{aligned} & S E / \mathrm{C} \\ & \text { (calc) } \end{aligned}$ | $\begin{gathered} \Delta H_{\mathrm{f}} \\ (\mathrm{calc}) \end{gathered}$ | $\Delta H_{\mathrm{f}}(\exp )^{\text {d }}$ |
| :---: | :---: | :---: | :---: | :---: | :---: |
| Capping Hydrocarbons |  |  |  |  |  |
| bicyclo[2.2.0]hexane | 4-65 + 7 eth $\rightarrow 4$ pro +2 iso | 238 | 39.7 | 138 | $125 .{ }^{\text {e }}$ |
| cyclohexane (twistboat) | TB-4-52 + 6 eth $\rightarrow 6$ pro | 28 | 4.6 | -97 |  |
| cycloheptane | 4-66 + 7 eth $\rightarrow 7$ pro | 27 | 3.9 | -119 | $-118.1 \pm 1.0^{\text {f }}$ |
| norbornane | $\mathbf{4 - 6 7}+8$ eth $\rightarrow 5$ pro +2 iso | 62 | 8.9 | -59 | $-54.9 \pm 4.7$ |
| cis-bicyclo[3.3.0]octane | 4-68 +9 eth $\rightarrow 6$ pro +2 iso | 49 | 6.1 | -93 | $-93.3 \pm 1.5$ |
| cyclooctane (crown) | $\mathbf{C r - 4 - 5 3}+8$ eth $\rightarrow 8$ pro | 52 | 6.4 | -115 |  |
| bicyclo[3.3.1]nonane (twistboat-twistboat) | TBTB-4-54 +10 eth $\rightarrow 7$ pro +2 iso | 63 | 7.0 | $-100$ |  |

${ }^{\text {a }}$ MP2/6-311+G(2d,p)//MP2/6-31G(d) values corrected to $298 \mathrm{~K}\left(\mathrm{~kJ} \mathrm{~mol}^{-1}\right)$. ${ }^{\mathrm{b}}$ The abbreviations "eth", "pro", "iso" and "neo" indicate ethane, propane, isobutane and neopentane, respectively. ${ }^{\text {c }}$ The strain energy ( $S E$ ) is determined as the negative of the enthalpy change for the given homodesmic reaction.
${ }^{\mathrm{d}}$ Taken from Ref. 33b unless otherwise noted. ${ }^{\mathrm{e}}$ From Ref. 33c. ${ }^{\mathrm{f}}$ From 33h.
capping units based on TB-4-52, Cr-4-53, TBTB-4-54, 4-66, 4-67 and 4-68 of approximately $60-120 \mathrm{~kJ} \mathrm{~mol}^{-1}$, while a pair of caps based on $\mathbf{4 - 6 5}$ will contribute $480 \mathrm{~kJ} \mathrm{~mol}^{-1}$. The examination of bond lengths in Sections 4.3.3-4.3.5, indicates that the strain attributable to the caps will in fact be greater than this, particularly in the case of molecules like spirohexaplane (4-39) where a number of cyclohexane $\mathrm{C}-\mathrm{C}$ bond lengths are significantly lengthened after incorporation into the alkaplane.

The calculated strain energies (SEs) for the three families of alkaplanes indicate that, in general, the alkaplanes $(\mathbf{4}-\mathrm{VI})\left(S E=1180-1770 \mathrm{~kJ} \mathrm{~mol}^{-1}\right)$ are more strained than the two families of spiroalkaplanes (4-VII and 4-VIII) (SE = 875-1625 kJ mol ${ }^{-1}$ ) (see Table 4-15 on page 189). These strain energies are quite large. By comparison, cubane $(4-60)\left(S E=712 \mathrm{~kJ} \mathrm{~mol}^{-1}\right)$ has the largest total strain energy of all known hydrocar-

Table 4-14. Calculated strain energies $(S E)$, ${ }^{\text {a }}$ strain per carbon atom $(S E / C)$ and calculated heats of formation $\left(\Delta H_{\mathrm{f}}\right)$ at $298 \mathrm{~K}^{\left(\mathrm{kJ} \mathrm{mol}^{-1}\right)}$ for a number of bridged spiropentanes and fenestranes.

| Molecule | Homodesmic reaction ${ }^{\text {b }}$ | $\begin{gathered} S E \\ (\mathrm{calc})^{\mathrm{c}} \end{gathered}$ | $\begin{aligned} & S E / \mathrm{C} \\ & \text { (calc) } \end{aligned}$ | $\begin{gathered} \Delta H_{\mathrm{f}} \\ \text { (calc) } \end{gathered}$ |
| :---: | :---: | :---: | :---: | :---: |
| Bridged Spiropentanes |  |  |  |  |
| [3.3.3]fenestrane | $\mathbf{4 - 2 6}+7$ eth $\rightarrow$ neo +2 iso +2 pro | 585 | 116.9 | 526 |
| [3.4.3]fenestrane | $\mathbf{4 - 2 5}+8$ eth $\rightarrow$ neo +2 iso +3 pro | 498 | 83.0 | 418 |
| [3.5.3]fenestrane | $\mathbf{4 - 4 5}+9$ eth $\rightarrow$ neo +2 iso +4 pro | 354 | 50.5 | 253 |
| tetracyclo[3.3.1. $0^{2,4} .0^{2,8}$ ]nonane | $4-46+12$ eth $\rightarrow$ neo +4 pro +4 iso | 424 | 47.1 | 307 |
| Fenestranes |  |  |  |  |
| trans,cis,cis,cis[4.4.4.4]fenestrane | $\boldsymbol{C}_{\text {s }} \mathbf{- 4 - 1 8}+12$ eth $\rightarrow$ neo +4 iso +4 pro | 663 | 73.7 | 546 |
| all-cis- <br> [4.4.4.4]fenestrane | $\boldsymbol{D}_{2 \mathrm{~d}} \mathbf{- 4 - 1 8}+12$ eth $\rightarrow$ neo +4 iso +4 pro | 719 | 79.9 | 602 |
| all-trans- <br> [4.4.4.4]fenestrane | $\boldsymbol{C}_{\mathbf{2 v}} \mathbf{- 4 - 1 8}+12$ eth $\rightarrow$ neo +4 iso +4 pro | 735 | 81.7 | 618 |
| trans,cis,trans,cis[4.4.4.4]fenestrane | $\boldsymbol{C}_{\mathbf{2}}^{\mathbf{- 4 - 1 8}+12}$ eth $\rightarrow$ neo +4 iso +4 pro | 1098 | 122.0 | 981 |
| [5.5.5.5]fenestrane | all-cis-4-19 +16 eth $\rightarrow$ neo +4 iso +8 pro | 59 | 4.5 | -142 |
| [5.5.5.5]fenestrane | all-trans-4-19 +16 eth $\rightarrow$ neo +4 iso +8 pro | 637 | 49.0 | 436 |

${ }^{\text {a }}$ MP2/6-311+G(2d,p)//MP2/6-31G(d) values corrected to $298 \mathrm{~K}\left(\mathrm{~kJ} \mathrm{~mol}^{-1}\right) .{ }^{\mathrm{b}}$ The abbreviations "eth", "pro", "iso" and "neo" indicate ethane, propane, isobutane and neopentane, respectively. ${ }^{\text {c }}$ The strain energy $(S E)$ is determined as the negative of the enthalpy change for the given homodesmic reaction.
bons. The least strained of all the alkaplanes we have examined are amongst those based on eight-membered primary-ring caps, 4-28, 4-29, 4-43, 4-44, 4-47 and 4-48 (SE $\left.=875-1065 \mathrm{~kJ} \mathrm{~mol}^{-1}\right)$. Of these, spirooctaplane (4-28) $\left(S E=873 \mathrm{~kJ} \mathrm{~mol}^{-1}\right)$, which is approximately $160 \mathrm{~kJ} \mathrm{~mol}^{-1}$ more strained than cubane, is the least strained alkaplane. However, strain accumulates and cubane is only a $\mathrm{C}_{8} \mathrm{H}_{8}$ hydrocarbon while spirooctaplane is $\mathrm{C}_{21} \mathrm{H}_{24}$. As such, comparisons between molecules often examine strain per carbon (SE/C) or strain per $\mathrm{C}-\mathrm{C}$ bond in order to introduce some size consistency. We have calculated that prismane (4-59) has the highest strain per carbon atom of all isolated hydro-
carbons (SE/C $=107 \mathrm{~kJ} \mathrm{~mol}^{-1}$ ), while, as far we are aware, [3.3.3]fenestrane (or tricyclo[2.1.0.0 $\left.{ }^{1,3}\right]$ pentane $)^{16}(\mathbf{4 - 2 6})$, has the highest strain per carbon of any observed ${ }^{\dagger}$ hydrocarbon ( $117 \mathrm{~kJ} \mathrm{~mol}^{-1}$ ). In comparison, the least strained alkaplanes (4-28, 4-29, 443, 4-44, 4-47 and 4-48) have strain energies per carbon of only $39-46 \mathrm{~kJ} \mathrm{~mol}^{-1}$. Comparison of $S E / \mathrm{C}$ of the alkaplanes with cubane ( $S E=89 \mathrm{~kJ} \mathrm{~mol}^{-1}$ ) or prismane is somewhat misleading because in 4-59 and 4-60 the strain is quite clearly, equally distributed throughout the molecule, whereas the alkaplanes have a very highly strained central region and considerably less strained caps. ${ }^{*}$ Comparison with bridged spiropentanes (425, 4-26, 4-45, 4-46) (SE/C $=47-117 \mathrm{~kJ} \mathrm{~mol}^{-1}$ ) is likely to be more meaningful (see Table 4-14). Like the alkaplanes, the bridged spiropentanes contain a highly distorted spiro[2.2] carbon and a progressively less strained surrounding structure. Interestingly, the least strained alkaplanes (4-28, 4-29, 4-43, 4-44, 4-47 and 4-48) are found to have lower strain per carbon than the synthetically-isolable bridged spiropentanes 4-45 (SE/C $\left.=50.5 \mathrm{~kJ} \mathrm{~mol}^{-1}\right)$ and $4-46\left(S E / \mathrm{C}=47.1 \mathrm{~kJ} \mathrm{~mol}^{-1}\right)$. However, this is almost certainly affected by the fact that the alkaplanes concerned have from 21 to 25 carbon atoms, compared with only 7 and 9 carbon atoms in 4-45 and 4-46.

Of the parent alkaplanes (4-VI), the $S_{4}$ symmetry isomer of octaplane (4-27) is clearly the least strained ( $S E=1179 \mathrm{~kJ} \mathrm{~mol}^{-1}$ ). All the B-type ( $D_{2}$ symmetry) structures (4-31, 4-32, 4-34, 4-35 and 4-36) are very highly strained with SEs around 1500 $\mathrm{kJ} \mathrm{mol}^{-1}$, indicating that the $\mathbf{B}$-type orientation of the central $\mathrm{C}(\mathrm{CH})_{4}$ moiety is unfavorable. Bihexaplane (4-30) (also a B-type alkaplane), has the highest strain of all the alkaplanes $\left(S E=1772 \mathrm{~kJ} \mathrm{~mol}^{-1}\right)$, reflecting in part the much greater strain inherent in the bicyclo[2.2.0]hexane caps.

The SEs of the spiroalkaplanes (4-VII) are consistent with the size of the primary ring of the capping subunit. Thus, spirohexaplane (4-39) and spirobiheptaplane (4-40) (both of which have six-membered primary-ring caps) have strain energies around 1700 $\mathrm{kJ} \mathrm{mol}^{-1}$, the two spiroheptaplane isomers (4-41 and 4-42) have considerably lower strain energies $1200-1300 \mathrm{~kJ} \mathrm{~mol}^{-1}$, and the three spiroalkaplanes with eight-membered

[^68]Table 4-15. Calculated strain energies (SE), ${ }^{\text {a }}$ strain per carbon atom (SE/C) and calculated heats of formation $\left(\Delta H_{\mathrm{f}}\right)$ at $298 \mathrm{~K}\left(\mathrm{~kJ} \mathrm{~mol}^{-1}\right)$ for the alkaplanes.

| Molecule | Homodesmic reaction ${ }^{\text {b }}$ | $\begin{gathered} S E \\ (\mathrm{calc})^{\mathrm{c}} \end{gathered}$ | $\begin{aligned} & S E / \mathrm{C} \\ & \text { (calc) } \end{aligned}$ | $\begin{gathered} \Delta H_{\mathrm{f}} \\ \text { (calc) } \end{gathered}$ |
| :---: | :---: | :---: | :---: | :---: |
| Alkaplanes |  |  |  |  |
| bihexaplane ${ }^{\text {d }}$ | $\mathbf{4 - 3 0}+26$ eth $\rightarrow$ neo +16 iso | 1772 | 104.2 | 1637 |
| hexaplane | $\mathbf{4 - 3 1}+24$ eth $\rightarrow$ neo +12 iso +4 pro | 1467 | 86.3 | 1282 |
| biheptaplane ${ }^{\text {d }}$ | 4-32 +28 eth $\rightarrow$ neo +16 iso +2 pro | 1519 | 79.9 | 1342 |
| heptaplane | $\mathbf{4 - 3 3}+26$ eth $\rightarrow$ neo +12 iso +6 pro | 1285 | 67.6 | 1058 |
| bioctaplane $^{\text {d }}$ | 4-34 +30 eth $\rightarrow$ neo +16 iso +4 pro | 1480 | 70.5 | 1262 |
| octaplane (A-type) | $\mathbf{4 - 2 7}+28$ eth $\rightarrow$ neo +12 iso +8 pro | 1179 | 56.1 | 910 |
| octaplane (B-type) ${ }^{\text {d }}$ | 4-35 +28 eth $\rightarrow$ neo +12 iso +8 pro | 1486 | 70.7 | 1218 |
| binonaplane ${ }^{\text {d }}$ | $\mathbf{4 - 3 6}+32$ eth $\rightarrow$ neo +16 iso +6 pro | 1533 | 66.7 | 1273 |
| Spiroalkaplanes |  |  |  |  |
| spirohexaplane | $\mathbf{4 - 3 9}+26$ eth $\rightarrow 5$ neo +8 iso +4 pro | 1625 | 95.6 | 1473 |
| spirobiheptaplane | $4-40+30$ eth $\rightarrow 5$ neo +12 iso +2 pro | 1742 | 91.7 | 1598 |
| spiroheptaplane (isomer a) | $\mathbf{4 - 4 1}+28$ eth $\rightarrow 5$ neo +8 iso +6 pro | 1302 | 68.5 | 1109 |
| spiroheptaplane (isomer b) | $\mathbf{4 - 4 2}+28$ eth $\rightarrow 5$ neo +8 iso +6 pro | 1166 | 61.4 | 972 |
| spirobioctaplane | $4-43+32$ eth $\rightarrow 5$ neo +12 iso +4 pro | 977 | 46.5 | 791 |
| spirooctaplane | $\mathbf{4 - 2 8}+30$ eth $\rightarrow 5$ neo +8 iso +8 pro | 873 | 41.6 | 638 |
| spirobinonaplane | $4-44+34$ eth $\rightarrow 5$ neo +12 iso +6 pro | 904 | 39.3 | 677 |
| Dimethanospiroalkaplanes |  |  |  |  |
| dimethanospirobioctaplane | 4-47 +36 eth $\rightarrow 5$ neo +16 iso +2 pro | 1040 | 45.2 | 862 |
| dimethanospirooctaplane | $\mathbf{4 - 2 9}+34$ eth $\rightarrow 5$ neo +12 iso +6 pro | 1064 | 46.2 | 836 |
| dimethanospirobinonaplane | 4-48 +38 eth $\rightarrow 5$ neo +16 iso +4 pro | 980 | 39.2 | 760 |

[^69]primary-ring caps (4-28, 4-43 and 4-44) have calculated SEs of about 900-1000 $\mathrm{kJ} \mathrm{mol}^{-1}$.

Adding methylene bridges to the three spiroalkaplanes 4-28, 4-43 and 4-44 to give the dimethanospiroalkaplanes (4-VIII) has the effect of increasing the strain energy by approximately $80-190 \mathrm{~kJ} \mathrm{~mol}^{-1}$. The smallest increase $\left(76 \mathrm{~kJ} \mathrm{~mol}^{-1}\right)$ is for dimethanospirobinonaplane (4-48) which is also the least strained dimethanospiroalkaplane ( $S E=$ $980 \mathrm{~kJ} \mathrm{~mol}^{-1}$ ). The introduction of a very short $\mathrm{H}-\mathrm{H}$ close contact in dimethanospirooctaplane $(r(H-H)=1.84 \AA)$ (which was noted in Section 4.3 .5 on page 177 ) probably contributes significantly to the much greater ( $190 \mathrm{~kJ} \mathrm{~mol}^{-1}$ ) difference between the SEs of 4-28 and 4-29. The considerably lower strain in 4-48 suggests that while both 4-29 and 4-48 are predicted to contain a planar-tetracoordinate carbon atom, 4-48 is likely to be a more viable target.

The total strain energies and heats of formation of a number of isomers of [4.4.4.4]and [5.5.5.5]fenestrane (4-18 and 4-19) are given in Table 4-14 on page 187. Despite considerable effort on the part of synthetic chemists, only the least strained of all of these structures, all-cis-4-19 $\left(S E(\right.$ calc $\left.)=59 \mathrm{~kJ} \mathrm{~mol}^{-1}\right)$, has been synthesized to date. However, unlike the fenestranes, the alkaplanes surround the most strained, central region by a less strained periphery. Although the larger, rigid cage structures of the alkaplanes will undoubtedly add to the complexity of synthesis, it is likely that this situation will also aid in protecting the most reactive central $\mathrm{C}^{0}-\mathrm{C}^{\alpha}$ bonds, thereby allowing more strain to be introduced at $\mathrm{C}^{0}$ (a necessity for the achievement of planar-tetracoordination) than has so far been possible in syntheses of [k.l.m.n]fenestranes.

The alkaplane families are all found to have extremely large total strain energies. Lowest total strain energies are predicted for the spiroalkaplanes (4-VII) and dimethanospiroalkaplanes (4-VIII) in which the capping subunits have an eight-membered primary ring (4-28, 4-29, 4-43, 4-44, 4-47 and 4-48). These molecules, particularly 4-48, are therefore suggested as the best targets for potential synthesis.

### 4.3.7 Ionization Energies

A striking feature of all the alkaplane families (4-VI, 4-VII and 4-VIII) is that the highest occupied molecular orbital (HOMO) is basically a $p$-type lone pair orbital local-
ized on the central quaternary carbon atom (see Figure 4-10). This should give the alkaplanes interesting chemical and physical properties unlike those of other saturated hydrocarbons. As an example of such properties, we have calculated the adiabatic ion-


Figure 4-10. An iso-surface of the highest occupied molecular orbital (HOMO) of dimethanospiro[2.2] octaplane (4-29) (the iso-surface is drawn at $0.080 e^{\AA^{-3}}$ ).
ization energy for octaplane (4-27) ${ }^{45}$, spirooctaplane (4-28) and dimethanospirooctaplane (4-29) at the UMP2/6-311+G(2d,p)//UMP2/6-31G(d) level. This yields values for the $I E_{\mathrm{a}}$ of $5.23,4.97$ and 4.96 eV , respectively. Test calculations on small molecules for which accurate experimental data ${ }^{36}$ are available (including $\mathrm{NH}_{3}, \mathrm{H}_{2} \mathrm{O},{ }^{3} \mathrm{CH}_{2}$ and $\left.\mathrm{CH}_{4}\right)^{\dagger}$ suggest that the calculated $I E_{\mathrm{a}} \mathrm{s}$ will be too low by about $0.1-0.2 \mathrm{eV}$. The corrected values of just above 5 eV are considerably lower than the ionization energy of tetra-tertbutyltetrahedrane, which has an $I E_{\mathrm{a}}$ equal to 7.1 eV (the lowest experimental value for a saturated hydrocarbon from a recent compendium ${ }^{36}$ ). In fact, the alkaplanes are pre-

[^70]

Figure 4-11. Structural parameters (MP2/6-311+G(2d,p)(red) ${ }^{38}$ values in bold type, B3-LYP/6-31G(d) values in plain text, all values in $\AA$ or degrees) for octaplane radical cation (4-27 ${ }^{\circ}$ ), spirooctaplane radical cation (4-28 ${ }^{\bullet+}$ ), and dimethanospirooctaplane (4$\mathbf{2 9}^{\boldsymbol{+}}$ ). All unique bond lengths and some close-contact distances ( $\AA$ ) are shown. Angles significantly distorted from the tetrahedral ideal are also given.
dicted to have an ionization energy comparable to that of the alkali metals lithium and sodium (5.39 and 5.14 eV , respectively ${ }^{36}$ ).

The radical cations which result from ionization of octaplane, spirooctaplane and dimethanospirooctaplane, $\mathbf{4 - 2 7 ^ { + }}, \mathbf{4 - 2 8}{ }^{++}$and $\mathbf{4 - 2 9}{ }^{\bullet+}$, respectively, are predicted to contain an exactly planar-tetracoordinate carbon atom. High symmetry structures ( $C_{4 \mathrm{~h}}, D_{2 \mathrm{~h}}$ and $D_{2 h}$, respectively) for $\mathbf{4 - 2 7 ^ { + + }}, \mathbf{4 - 2 8}{ }^{++}$and $\mathbf{4 - 2 9 ^ { + + }}$, calculated at the $\mathrm{HF} / 6-31 \mathrm{G}(\mathrm{d})$ and B3-LYP/6-31G(d) levels, were found via analytic force constant analysis to have no imaginary frequencies.

A comparison of the structures of these radical cations with the corresponding neu-
tral species reveals only minor structural changes (see Figure 4-11 on page 192). The central $\mathrm{C}^{0}-\mathrm{C}^{\alpha}$ bonds are lengthened by about $0.02 \AA$ (from 1.59 to $1.61 \AA$ for $\mathbf{4 - 2 7}$, from 1.48 to 1.49 for $\mathbf{4 - 2 8}$, and from 1.50 to $1.52 \AA$ for $\mathbf{4 - 2 9}$ ). For both $\mathbf{4 - 2 7}{ }^{++}$and $\mathbf{4 - 2 8}{ }^{++}$, where the neutral species is distorted from planar-tetracoordination at $\mathrm{C}^{0}$, the $\mathrm{C}^{\alpha}-\mathrm{C}^{\beta}$ bonds are alternately lengthened and shortened in the ions to values that correspond roughly to the average of the two lengths in the neutral molecules (from 1.60/1.51 to 1.56 for 4-27, and from $1.55 / 1.50$ to 1.53 for 4-28). The $C^{\alpha}-C^{\beta}$ bond lengths are relatively unchanged for $\mathbf{4 - 2 9}{ }^{+}$( $1.50 \AA$ ). In all the radical cation structures examined (Figure 4-11), the central carbon atom ( $\mathrm{C}^{0}$ ) has an exactly planar-tetracoordinate bonding environment.

Removing one of the electrons from the high-energy HOMO appears to significantly reduce the preference for a tetrahedral-like bonding arrangement. ${ }^{\dagger}$ The result is that the bicapped alkaplane cage structures now exert easily enough pressure on the bonding arrangement at $\mathrm{C}^{0}$ to impose planar-tetracoordination. These molecules $\left(\mathbf{4 - 2 7 ^ { + }}\right.$, $\mathbf{4 - 2 8}{ }^{+}$and $\mathbf{4 - 2 9}{ }^{\boldsymbol{+}}$ ) are the first saturated hydrocarbon radical cations found to contain a planar-tetracoordinate-carbon atom.

### 4.3.8 Triplets and Stability

An examination of the electronic structure of square-planar methane reveals a relatively low-lying lowest unoccupied molecular orbital (LUMO). This has lead to speculation as to whether square-planar methane would in fact prefer a triplet or open-shell singlet configuration ${ }^{3}$ (see Section 1.3). However, our calculations (see Section 4.3.1), and calculations by Schleyer and coworkers ${ }^{46}$ and more recently by Gordon and Schmidt ${ }^{4 \mathrm{a}}$ indicate that the closed-shell singlet is the preferred configuration for squareplanar methane. In fact, it has been predicted in the present work that both of the openshell configurations lie approximately $100 \mathrm{~kJ} \mathrm{~mol}^{-1}$ above the $D_{4 \mathrm{~h}}$ closed-shell singlet configuration and around $150 \mathrm{~kJ} \mathrm{~mol}^{-1}$ above the lowest $\left(C_{2 \mathrm{v}}\right)$ closed-shell singlet con-

[^71]figuration. ${ }^{\dagger}$ The large separation between the closed- and open-shell surfaces for planar methane suggests that interference from low-lying open-shell states may not be a concern for the stability of the alkaplanes. However, in going from four hydrogen substituents to four carbon substituents the situation may change.

Calculations on the 'planar' neopentane ( $C_{4 \mathrm{~h}}$ symmetry) and 'planar' spiropentane model systems (Table 4-16) indicated that the $C_{4 \mathrm{~h}}$ 'planar' neopentane triplet is in fact lower in energy than the closed-shell singlet, with our best calculations predicting the difference to be $91.2 \mathrm{~kJ} \mathrm{~mol}^{-1}$. This suggests that an alkaplane (4-VI) with $\alpha_{\text {plan }}=0.0^{\circ}$

Table 4-16. Energies of the 'planar' neopentane and spiropentane triplets relative to their respective tetrahedral and tetrahedral-like ground state singlets, $\Delta \mathrm{E}_{\mathrm{PT}}$ (triplet) $\left(\mathrm{kJ} \mathrm{mol}^{-1}\right)$, and the energy difference between the 'planar' singlet and triplet, $\left.\mathrm{T}-\mathrm{S}\left(\mathrm{kJ} \mathrm{mol}^{-1}\right)\right)^{\mathrm{a}}$

| method | 'planar' neopentane$\left(C_{4 \mathrm{~h}}\right)$ |  | $\begin{gathered} \text { 'planar' spiropentane } \\ \left(D_{2 \mathrm{~h}}\right) \end{gathered}$ |  |
| :---: | :---: | :---: | :---: | :---: |
|  | $\Delta \mathrm{E}_{\mathrm{PT}}$ (triplet) | T-S | $\Delta \mathrm{E}_{\mathrm{PT}}($ triplet $)$ | T-S |
| UB3-LYP/6-31G(d) | 764.8 | -116.8 | 482.4 | 51.2 |
| UB3-LYP/6-311+G(2d,p) | 756.2 | -101.8 | 477.5 | 56.1 |
| UB3-LYP/6-311+G(3df, 2p) | 756.5 | -98.2 | 479.4 | 59.9 |
| UMP2(full)/6-31G(d) ${ }^{\text {b }}$ | 836.1 | -91.3 | 536.8 | 77.8 |
| UMP2(full)/6-311+G(2d,p) ${ }^{\text {b }}$ | 805.0 | -64.8 | 519.7 | 89.5 |
| UMP2(full)/6-311+G(3df, 2p $)^{\text {b }}$ | 805.6 | -57.3 | 520.8 | 95.6 |
| $\operatorname{URCCSD}(\mathrm{T})(\mathrm{fc}) / 6-311+\mathrm{G}(2 \mathrm{~d}, \mathrm{p})^{\mathrm{c}}$ | 781.2 | -98.7 | 503.7 | 60.3 |
| $\operatorname{URCCSD}(\mathrm{T})(\mathrm{fc}) / 6-311+\mathrm{G}(3 \mathrm{df}, 2 \mathrm{p})^{\text {c }}$ | 786.9 | -91.2 | 506.4 | 66.4 |
| $\mathrm{URCCSD}(\mathrm{T})(\mathrm{fc}) / \mathrm{AVTZ}^{\text {c }}$ | - | - | 505.1 | 67.6 |

[^72][^73]is likely to prefer the triplet over a singlet configuration. However, all the alkaplanes based on template 4-VI which have been examined is the present work have equilibrium structures that are distorted from planar-tetracoordination at $\mathrm{C}^{0}$ and this distortion leads to a considerable drop in the energy ( $\Delta \mathrm{E}_{\text {plan }}=35-140 \mathrm{~kJ} \mathrm{~mol}^{-1}$ ) (see Section 4.3.4). This lowering on distortion is of the order of the singlet-triplet energy difference in $C_{4 \mathrm{~h}}$ 'planar' neopentane, suggesting that 'planar' triplet alkaplane species may well be similar in energy to the singlet equilibrium structures. The situation for 'planar' spiropentane is quite different. Our best calculations predict the 'planar' spiropentane triplet to be $67.6 \mathrm{~kJ} \mathrm{~mol}^{-1}$ higher than the closed-shell singlet.

More conclusive information about the relative energies of the singlet and triplet configurations in all the alkaplane families (4-VI, 4-VII and 4-VIII) can be gained from triplet energy calculations at a number of geometries for the A-type octaplane (4-27) and spirooctaplane (4-28). An examination of the results in Table 4-16 reveals that in general, the UB3-LYP calculations give an energy for the triplet that is slightly too low compared with the large basis set $\operatorname{CCSD}(\mathrm{T})$ calculations while the UMP2 calculations indicate an energy for the triplet that is too high. $\operatorname{CCSD}(\mathrm{T})$ calculations on a complete alkaplane system are not possible at this time but calculations at the UMP2/6-31G(d) and UB3-LYP/6-311+G(2d,p) levels are possible. From the results in Table 4-16, we expect that true triplet energy will probably lie between values calculated at these two levels.

In order to gain some idea of where the alkaplane and spiroalkaplane triplet surfaces lie relative to the singlet surfaces, we began by calculating single point energies for the triplet configuration at both the singlet equilibrium and 'planar' geometries of 4$\mathbf{2 7}$ and 4-28 (see Table 4-17). These energies predict quite clearly that the triplet surface lies well above the singlet surface at the equilibrium geometries of all the alkaplanes. However, as might be expected from the calculations on the model systems (neopentane and spiropentane), as $S_{4}$ octaplane (4-27) approaches planar-tetracoordination at $\mathrm{C}^{0}\left(C_{4 \mathrm{~h}}\right.$ symmetry) the triplet and closed-shell singlet surfaces become quite close ( $\mathrm{T}-\mathrm{S}$ (vertical) is expected to be in the range 11 to $44 \mathrm{~kJ} \mathrm{~mol}^{-1}$ ).

Optimization of the triplet configuration in $D_{2 \mathrm{~h}}\left(C_{4 \mathrm{~h}}\right)$ symmetry leads to a saddle point. Distortion along the down-hill mode proceeds via a $C_{2 \mathrm{~h}}\left(C_{\mathrm{s}}\right)$ symmetry structure to a $C_{\mathrm{s}}$ symmetry equilibrium structure in which most of the alkaplane structure is intact

Table 4-17. Vertical triplet energy differences, $\mathrm{T}-\mathrm{S}$ (vertical) $\left(\mathrm{kJ} \mathrm{mol}^{-1}\right)$, for the 'planar' and equilibrium geometries of octaplane (4-27) and spirooctaplane (4-28). ${ }^{\text {a }}$

|  |  | T-S(vertical) |  |
| :--- | :---: | :---: | :---: |
| structure |  | UB3-LYP/6-311+G(2d,p)// <br> B3-LYP/6-31G(d) | UMP2/6-31G(d)// <br> MP2/6-31G(d) |
| octaplane $S_{4}$ (singlet) | $\boldsymbol{S}_{\mathbf{4}} \mathbf{- 4 - 2 7}$ | 168.6 | 240.1 |
| octaplane $C_{4 \mathrm{~h}}$ (singlet) | $\boldsymbol{C}_{\mathbf{4 h}} \mathbf{- 4 - 2 7}$ | 11.4 | 44.2 |
| spiro[2.2]octaplane $D_{2}$ (singlet) | $\boldsymbol{D}_{\mathbf{2}} \mathbf{- 4 - 2 8}$ | 193.6 | 285.6 |
| spiro[2.2]octaplane $D_{2 \mathrm{~h}}$ (singlet) | $\boldsymbol{D}_{\mathbf{2 h}} \mathbf{- 4 - 2 8}$ | 129.3 | 187.5 |

${ }^{\text {a }}$ Energy differences between the singlet and triplet electronic configurations are calculated at singlet optimized stationary points.
except that one of the $\mathrm{C}^{0}-\mathrm{C}^{\alpha}$ bonds has undergone homolytic cleavage. This distortion is barrier-less and considerably exothermic. As a result, excitation to the triplet surface is likely to lead to homolytic cleavage. For the alkaplanes to be stable, a relatively large singlet-triplet separation is required. An indication of the proximity of the optimized triplet surface to the closed-shell singlet surface can be gleaned from the relative energy differences listed in Table 4-18.

Table 4-18. Energy differences ( $\mathrm{kJ} \mathrm{mol}^{-1}$ ) between stationary points on the optimized singlet and triplet potential energy surfaces for octaplane (4-27) and spirooctaplane (4-28).

| molecule | T-S difference ${ }^{\mathrm{a}}$ | UB3-LYP/6-311+G(2d,p)// <br> UB3-LYP/6-31G(d) | UMP2/6-31G(d)// <br> UMP2/6-31G(d) |
| :---: | :---: | :---: | :---: |
|  | $C_{\mathrm{s}}$ triplet $-S_{4}$ | -182.9 | -101.9 |
| octaplane (4-27) | $C_{4 \mathrm{~h}}$ triplet $-S_{4}$ | 55.6 | 97.3 |
|  | $C_{4 \mathrm{~h}}$ triplet $-C_{4 \mathrm{~h}}$ | -16.9 | 27.3 |
|  | $C_{\mathrm{s}}$ triplet $-D_{2}$ | 18.1 | 83.8 |
| spirooctaplane (4-28) | $D_{2 \mathrm{~h}}$ triplet $-D_{2}$ | 128.8 | 176.8 |
|  | $D_{2 \mathrm{~h}}$ triplet $-D_{2 \mathrm{~h}}$ | 113.7 | 164.1 |

[^74]Considering octaplane (4-27) first, it can be seen that the energy of the optimized $C_{4 \mathrm{~h}}$ triplet (a saddle point) is substantially higher than that for the $S_{4}$ symmetry equilibrium structure (between 56 and $97 \mathrm{~kJ} \mathrm{~mol}^{-1}$ ). However, the energy of the $C_{4 \mathrm{~h}}$ singlet (the saddle point for inversion between equivalent $S_{4}$ symmetry equilibrium structures) is relatively close to the optimized $C_{4 \mathrm{~h}}$ triplet energy. Preliminary calculations on the other alkaplanes (4-VI) indicate that this is a general trend. This, in combination with results from calculations on the 'planar' neopentane and the fact that the triplet surface leads, without barrier, in a highly exothermic process, to $\mathrm{C}^{0}-\mathrm{C}^{\alpha}$ cleavage, suggests strongly that no structures based on a neopentane subunit can achieve planar-tetracoordination.


Figure 4-12. Structural parameters (MP2/6-31G(d) values in bold type, B3-LYP/6$31 \mathrm{G}(\mathrm{d})$ values in plain text, all values in $\AA$ or degrees) for triplet octaplane (triplet-427) and triplet spirooctaplane (triplet-4-28). Selected bond lengths and the dissociated CC distance are shown. Selected angles are also given. The two-dimensional structural elements show a top-down view of a slice of the molecule through the central $\mathrm{C}(\mathrm{C})_{4}$ and $\mathrm{C}(\mathrm{CH})_{4}$ regions.

Spirooctaplane (4-28) is entirely different. The energy difference between the $D_{2 \mathrm{~h}}$ symmetry triplet geometry and the $D_{2}$ and $D_{2 \mathrm{~h}}$ singlet structures of spirooctaplane sug-
gest that the triplet surface in spirooctaplane lies well above the singlet surface for geometries close to the singlet equilibrium structure (by greater than $100 \mathrm{~kJ} \mathrm{~mol}^{-1}$ at least). Only at the triplet equilibrium geometry, a geometry that can only be reached from the singlet equilibrium structure after inversion at one of the $\mathrm{C}^{\alpha}$ atoms and cleavage of the corresponding $\mathrm{C}^{0}-\mathrm{C}^{\alpha}$ bond (see Figure 4-12), does the triplet energy approach the singlet energy. As a result, we expect the spiroalkaplanes (4-VII) and closely related dimethanospiroalkaplanes (4-VIII) not to suffer from triplet instability problems.


Figure 4-13. Calculated potential energy curves for homolytic $\mathrm{C}^{0}-\mathrm{C}^{\alpha}$ bond cleavage in dimethanospirooctaplane (4-29) determined at the O - UMP2(fc)/6-31G(d) and $\boldsymbol{\square}$ -UB3-LYP/6-31G(d) levels are given as relative energy, $E_{\text {rel }}$, $\left(\mathrm{kJ} \mathrm{mol}^{-1}\right)$ against C ${ }^{0}-\mathrm{C}^{\alpha}$ bond length, $r\left(\mathrm{C}^{0}-\mathrm{C}^{\alpha}\right)(\AA)$. Optimized geometries at fixed values of $r\left(\mathrm{C}^{0}-\mathrm{C}^{\alpha}\right)$ were determined at the UB3-LYP/6-31G(d) level.

Calculations on the triplets suggest that one of the lowest-energy routes to decom-
position of the spiroalkaplanes (4-VII) is likely to be via homolytic $\mathrm{C}-\mathrm{C}$ cleavage at $\mathrm{C}^{0}-\mathrm{C}^{\alpha}$, as was seen in Chapter 3 when examining the hemispiroalkaplanes (4-V) (see Section 3.3.6). Unlike cleavage in a free $\mathrm{C}-\mathrm{C}$ bond, which is endothermic and a monotonically uphill process leading to an open-shell singlet biradical, homolytic cleavage of the $\mathrm{C}^{0}-\mathrm{C}^{\alpha}$ bond is hindered by the rigid cage structure such that bond separation requires inversion at $\mathrm{C}^{\alpha}$. This is fortunate because the energy of the biradical product, at least for dimethanospirooctaplane (4-29), is probably close to that of the closed-shell equilibrium structure. Since it can be expected that the high energy biradical will react further to give decomposition products, a large barrier to this $\mathrm{C}-\mathrm{C}$ cleavage would be advantageous.

An accurate determination of this barrier is likely to require (8/8)CASPT2 energies with a reasonably large basis set (with at least two sets of $d$-functions and diffuse functions ${ }^{\dagger}$ ). ${ }^{47}$ Calculations of this size are currently beyond our means. As a preliminary indication of the magnitude of the barrier, we have determined geometries and energies for points along the potential curve for $\mathrm{C}^{0}-\mathrm{C}^{\alpha}$ cleavage at fixed $\mathrm{C}^{0}-\mathrm{C}^{\alpha}$ distances, optimized at the UB3-LYP/6-31G(d) level, for dimethanospirooctaplane (4-29). ${ }^{\ddagger}$ A second estimate of the energy of the cleavage process was then determined by UMP2/6-31G(d) single point energies at the UB3-LYP optimized geometries (see Figure 4-13). It seems likely that a substantial barrier (probably between 40 and $160 \mathrm{~kJ} \mathrm{~mol}^{-1}$ ) to this $\mathrm{C}-\mathrm{C}$ bond cleavage exists. Since a barrier of only $40 \mathrm{~kJ} \mathrm{~mol}^{-1}$ will make isolation very difficult but $160 \mathrm{~kJ} \mathrm{~mol}^{-1}$, if this is indeed the lowest barrier to decomposition, would suggest that 4-29 is quite stable, more work on establishing an accurate determination of the barrier height is required. ${ }^{\S}$ Potential decomposition routes via $\mathrm{C}^{\alpha}-\mathrm{C}^{\beta}$ cleavage also need to be examined.

It is possible that the structures based on 4-VI (the parent alkaplanes) will suffer from low-lying triplet instability problems and not prove to be good synthetic targets. On the other hand, the spiroalkaplanes (4-VII) and dimethanospiroalkaplanes (4-VIII) do not suffer from such problems and no obvious source of kinetic instability has yet

[^75]been identified. Spiro[2.2]octaplane (4-28), dimethanospiro[2.2]octaplane (4-29) and dimethanospiro[2.2]binonaplane (4-48) are expected to be good synthetic targets.

### 4.3.9 Synthetic Considerations

Design of a viable and complete synthetic strategy is beyond the scope of this work and best left to the ingenuity of the synthetic organic chemists. A number of observations are, however, of value.


4-69 $\left(D_{2 \mathrm{~h}}\right)$


4-70 $\left(D_{2 \mathrm{~d}}\right)$


4-71 ( $C_{2 v}$ )

Firstly, it can be seen that the well-known cage hydrocarbon, pagodane ${ }^{44}(4-63)$, is spiro[2.2]bioctaplane (4-43) without the central carbon atom $\left(\mathrm{C}^{0}\right)$. Further, there is a pagodane isomer, ${ }^{49}$ 4-69 (referred to as a bis-methano-bridged [1.1.1.1]pagodane), which bears the same relationship to dimethanospiro[2.2]bioctaplane (4-47). Prinzbach and coworkers ${ }^{50}$ have also had considerable success in expanding the pagodane synthesis to make a number of other pagodane isomers (e.g. [1.1.1.1]isopagodane (4-70) and [2.2.1.1]isopagodane (4-71)). It appears that complex, rigid cage structures like those proposed in this work, but without the crucial central carbon atom, can be synthesized. The problem, however, is how to get a carbon atom into the center of cage compounds like 4-69.

One suggestion ${ }^{48}$ has been to fire positively charged carbon atoms at a pagodane cage and hope that some are included in much the same way the cations are inserted into buckminsterfullerenes. The problem here is that the very rigid, inflexible cages do not have the same ability to disperse localized energy in the way that buckminsterfullerenes can and would almost certainly disintegrate under such a bombardment.

A more likely, but still completely hypothetical, route might involve the inclusion of the target carbon atom at some stage in a pagodane synthesis. As an example, consider the synthesis of [1.1.1.1]pagodane which is outlined in Scheme 1. ${ }^{44}$ One could

isodrin
4-72

Phase 1


4-73


4-63

Phase $3 \boxed{\square}$


4-74

Scheme 1
imagine how the cyclization steps of the second phase in the synthesis of [1.1.1.1] pagodane could be modified to effect the necessary inclusion of carbon, giving a hemispiroalkaplane (4-75) (see Scheme 2). This might be achieved via reaction with carbon suboxide (OCCCO). Alternatively, Skattebøl's method for synthesis of distorted


4-73


4-75


4-43

Scheme 2
spiropentanes, which we have already referred to in Section 3.3.4 as a potential route to hemispiroalkaplanes (4-V), might be employed. However, the success of these approaches all depend on the ability to achieve carbene insertion to give an endo isomer at the appropriate aromatic $\mathrm{C}-\mathrm{C}$ bonds in $\mathbf{4 - 7 3}$. This is not likely to be an easy task. However, if this can be achieved, the synthesis could proceed with formation of the
upper cap, probably via Diels-Alder condensations as is usual when synthesizing pagodanes.

Clearly, this discussion has been purely speculative, but it does serve to indicate that complex, rigid cage compounds of an analogous nature to the spiroalkaplanes and dimethanospiroalkaplanes are well-known and might indeed be synthetically achievable.

### 4.4 Concluding Remarks

The successful synthesis of rigid saturated hydrocarbon systems such as tetracyclo[3.3.1.0 $\left.0^{2,4} \cdot 0^{2,8}\right]$ nonane (4-46), prismane (4-59), cubane (4-60), pagodane (4-63) and the bis-methano-bridged [1.1.1.1]pagodane 4-69 reflects the skills of organic chemists in synthesizing systems of this nature today. For this reason, we might be optimistic that if we can design a saturated cage-type hydrocarbon containing a planar-tetracoordinate carbon there would be a reasonable prospect of its successful synthesis. What is needed is a good target molecule for attempts at synthesis. Molecular orbital techniques allow us to examine, relatively straightforwardly, a range of potential target molecules in order to identify the one that is most suitable. The challenging synthetic task might then be reduced to a (still challenging) single molecule.


We have examined three families of novel, saturated hydrocarbons, the alkaplanes (4-VI), the spiroalkaplanes (4-VII) and the dimethanospiroalkaplanes (4-VIII), for molecules that would be suitable as synthetic targets in achieving planar-tetracoordinate carbon. The parent alkaplanes based on template $\mathbf{4}$-VI are predicted to have a considerable degree of flattening at the central carbon atom $\left(\alpha_{\text {plan }}=5-9^{\circ}\right)$. However, the barrier to inversion through a 'planar' structure is significant $\left(35-140 \mathrm{~kJ} \mathrm{~mol}^{-1}\right)$ and, of all the novel hydrocarbons studied here, these molecules are the least likely to be good syn-
thetic targets considering their very high strain energies ( $1180-1770 \mathrm{~kJ} \mathrm{~mol}^{-1}$ ), potential problems from a low-lying triplet surface (as seen from the examination of $S_{4}$ octaplane (4-27)), and, in some cases (in particular 4-33), elongated $\mathrm{C}-\mathrm{C}$ bonds.

The spiroalkaplanes (4-VII) with an eight-membered primary-ring cap (4-28, 4-43 and 4-44) are much more attractive synthetic targets. They are closer to planarity at the central carbon atom ( $\alpha_{\text {plan }} \approx 3^{\circ}$ ) than the alkaplanes (4-VI), and the barrier to inversion is reduced to $5-15 \mathrm{~kJ} \mathrm{~mol}^{-1}$. Although they are calculated to have quite large total strain energies ( $873-977 \mathrm{~kJ} \mathrm{~mol}^{-1}$ ), taking the size of these structures into consideration $\left(\mathrm{C}_{21} \mathrm{H}_{20}, \mathrm{C}_{21} \mathrm{H}_{24}\right.$ and $\mathrm{C}_{23} \mathrm{H}_{24}$, respectively), these strain energies do not appear to be prohibitive when compared with those for other highly-strained hydrocarbons that have been synthesized (cf. cubane (4-60), $\mathrm{C}_{8} \mathrm{H}_{8}$ with $S E=712 \mathrm{~kJ} \mathrm{~mol}^{-1}$, and tetracyclo[3.3.1. $\left.0^{2,4} .0^{2,8}\right]$ nonane (4-46), $\mathrm{C}_{9} \mathrm{H}_{12}$ with $S E=424 \mathrm{~kJ} \mathrm{~mol}^{-1}$ ). However, the spiroalkaplanes 4-28, 4-43 and 4-44 do not have the desired property of exact planar-tetracoordination at the central carbon atom. The smaller spiroalkaplanes (4-39, 4-40, 4-41 and 4-42) look less promising. Although they are also close to planarity at the central carbon atom ( $\alpha_{\text {plan }}=3-4^{\circ}$ ), they are found to have very strained structures with large values for the $\mathrm{C}^{\beta} \mathrm{C}^{\alpha} \mathrm{C}^{\beta}$ angle (up to $174^{\circ}$ ) and bond lengths in some of these molecules are calculated to be in excess of $1.60 \AA$. Consequently, they have very high strain energies (1165-1740 $\mathrm{kJ} \mathrm{mol}^{-1}$ ) and, as a result, are expected to be more difficult to synthesize than the larger spiroalkaplanes (4-28, 4-43 and 4-44).

We have examined three dimethanospiroalkaplanes (4-VIII), spiroalkaplanes with a pair of methano-bridges between the caps. Calculations in the present work predict dimethanospiro[2.2]octaplane (4-29) and dimethanospiro[2.2]binonaplane (4-48) to be exactly planar-tetracoordinate. They are the first neutral, saturated hydrocarbons to contain an exactly planar-tetracoordinate carbon atom. Examination of the calculated structures reveals no glaringly long $\mathrm{C}-\mathrm{C}$ bonds (all bonds are shorter than $1.60 \AA$ ) in these molecules that might give an immediate indication of kinetic instability. These two molecules are found to have quite high strain energies (1064 and $980 \mathrm{~kJ} \mathrm{~mol}^{-1}$, respectively) but preliminary examination of potential decomposition routes suggests that these molecules lie in relatively deep potential energy wells. Provided that these local minima on the $\mathrm{C}_{23} \mathrm{H}_{24}$ and $\mathrm{C}_{25} \mathrm{H}_{24}$ potential energy surfaces can be attained, the resulting molecules are expected to be relatively stable. A large proportion of the total
strain energy in these molecules is expected to be concentrated at the central carbon atom $\left(\mathrm{C}^{0}\right)$, but this region is well protected by the surrounding hydrocarbon cage. The fairly large $C^{\beta} C^{\alpha} C^{\beta}$ angles of $134-135^{\circ}$ suggest that significant strain is also present at the $\mathrm{C}^{\alpha}$ atoms which are quite exposed. It seems likely that a major source of instability in these molecules will result from reactivity at $\mathrm{C}^{\alpha}$ and some protection of these positions may be necessary. This might be achieved by alkyl substitutions at $\mathrm{C}^{\beta}, \mathrm{C}^{\gamma}$ (the carbon atoms across a five-membered ring from the $\mathrm{C}^{\alpha}-\mathrm{C}^{\alpha}$ bonds) and possibly at the methano-bridging carbons. The somewhat higher strain energy in 4-29 may be attributed in part to the rather short H-H close contact ( $1.86 \AA$ ), and we therefore suggest dimethanospiro[2.2]binonaplane (4-48) as the preferred target.


4-47 $\left(D_{2}\right)$


4-29 $\left(D_{2}\right)$


4-48 $\left(D_{2}\right)$

A third dimethanospiroalkaplane (4-VIII), namely dimethanospiro[2.2]bioctaplane (4-47), which has the same outer cage structure as a synthetically available bis-methanobridged [1.1.1.1]pagodane (4-69), has also been considered. It has a calculated strain energy ( $1040 \mathrm{~kJ} \mathrm{~mol}^{-1}$ ) similar to that of the other dimethanospiroalkaplanes studied here (4-29 and 4-48) and no bond lengths over 1.60 Å. Although this molecule is not found to have a planar-tetracoordinate carbon atom, the barrier to inversion at the central carbon atom is expected to be very small ( $0.4 \mathrm{~kJ} \mathrm{~mol}^{-1}$ from MP2 calculations). Such a small barrier will be below the zero-point energy for the inversion mode. In this case the term pseudo-planar-tetracoordination may be appropriate.

The spiroalkaplanes 4-28, 4-43 and 4-44 and dimethanospiroalkaplanes 4-29, 4-47 and 4-48 are a remarkable group of molecules that are predicted to have high strain energies but are expected to have good kinetic stability. The extremely planarized coordination at the central tetracoordinate carbon atom of these molecules, imposed in a manner that preserves the $\sigma^{2} \pi^{2}$ electronic structure of the planar- or near-planar tetraco-
ordinate carbon, is expected to give these saturated hydrocarbons quite unique properties. As an example, we have calculated the ionization energies ( $I E_{\mathrm{a}}$ ) of 4-28 and 4-29 to be approximately 5 eV ! This is comparable to the ionization energy of the alkali metals lithium and sodium ( 5.39 and 5.14 eV , respectively). Clearly, successful synthesis of any of these molecules will result in compounds with quite remarkable properties.


4-43 $\left(D_{2}\right)$


4-28 $\left(D_{2}\right)$


4-44 $\left(D_{2}\right)$

Our recommended synthetic target is dimethanospirobinonaplane (4-48), a $\mathrm{C}_{25} \mathrm{H}_{24}$ saturated cage hydrocarbon with an exactly planar-tetracoordinate central carbon atom, moderate strain and remarkable properties. A very considerable synthetic challenge lies ahead, but, by pin-pointing the appropriate target molecule with the desired properties, attempts at synthesizing compounds that would not have achieved the desired aim can be avoided. It seems likely that such use of high-level computational techniques as an aid to synthesis will become more prominent in the future as the processing power of supercomputers and the algorithms for performing high-level quantum chemistry calculations continue to improve.

## References

(1) (a) Hoffmann, R.; Alder, R.; Wilcox Jr, C. F. "Planar tetracoordinate carbon," J. Am. Chem. Soc. 1970, 92, 4992-4993; (b) Hoffmann, R. "The theoretical design of novel stabilized systems," Pure Appl. Chem. 1971, 28, 181-194.
(2) (a) van't Hoff, J. H. "Sur les formules de structure dans l'espace," Arch. Neerl. Sci. Exactes Nat. 1874, 9, 445-454. For a translation see, van't Hoff, J. H. "A suggestion looking into the extension into space of the structural formulas at present used in chemistry. And a note upon the relation between the optical activity and the chemical constitution of organic compounds" in Classics in the Theory of Chemical Combinations; Benfey, O. T., Ed.; Dover: New York, 1963; Vol. I, pp 151-160; (b) le Bel, J. A. "Sur les relations qui existent entre les formules atomiques des corps organiques, et le pouvoir rotatoire de leurs dissolutions," Bull. Chim. Soc. Fr. 1874, 22, 337-347. For a translation see, le Bel, J. A.
"On the relations which exist between the atomic formulas of organic compounds and the rotatory power of their solutions" in Classics in the Theory of Chemical Combinations; Benfey, O. T., Ed.; Dover: New York, 1963; Vol. I, pp 161-171.
(a) Monkhorst, H. J. "Activation energy for interconversion of enantiomers containing an asymmetric carbon atom without breaking bonds," J. Chem. Soc., Chem. Commun. 1968, 1111-1112; (b) Lathan, W. A.; Hehre, W. J.; Curtiss, L. A.; Pople, J. A. "Molecular orbital theory of the electronic structure of organic compounds. X. A systematic study of geometries and energies of $\mathrm{AH}_{4}$ molecules and cations," J. Am. Chem. Soc. 1971, 93, 6377-6387; (c) Durmaz, S.; Murrell, J. N.; Pedley, J. B. "Calculation of the lowest-energy state of planar methane," J. Chem. Soc., Chem. Commun. 1972, 933-934; (d) Murrell, J. N.; Pedley, J. B.; Durmaz, S. "Potential energy surfaces for the reaction $\mathrm{CH}_{2}+\mathrm{H}_{2} \rightarrow$ $\mathrm{CH}_{4}$," J. Chem. Soc., Faraday Trans. 2 1973, 69, 1370-1380; (e) Firestone, R. "Linnett planar methane," J. Chem. Soc., Chem. Commun. 1973, 163; (f) Wiberg, K. B.; Ellison, G. B. "Distorted geometries at carbon," Tetrahedron 1974, 30, 1573-1578; (g) Wiberg, K. B.; Ellison, G. B.; Wendoloski, J. J. "Electronic states of organic molecules. I. Potential functions for the deformation of methane," J. Am. Chem. Soc. 1976, 98, 1212; (h) Minkin, V. I.; Minyaev, R. M.; Zacharov, I. I. "Semiempirical and ab initio calculations on the automerization of methane," J. Chem. Soc., Chem. Commun. 1977, 213-214; (i) Crans, D. C.; Snyder, J. P. "Tetracoordinate planar carbon: a singlet radical," J. Am. Chem. Soc. 1980, 102, 7152-7154; (j) Krogh-Jesperson, M.-B.; Chandrasekhar, J.; Würthwein, E.-U.; Collins, J. B.; Schleyer, P. v. R. "Molecular orbital study of tetrahedral, planar, and pyramidal structures of the isoelectronic series $\mathrm{BH}_{4}^{-}, \mathrm{CH}_{4}, \mathrm{NH}_{4}^{+}, \mathrm{SiH}_{4}$, and $\mathrm{PH}_{4}^{+}$, J. Am. Chem. Soc. 1980, 102, 2263-2268.
(4) (a) Gordon, M. S.; Schmidt, M. W. "Does methane invert through square planar?" J. Am. Chem. Soc. 1993, 115, 7486-7492; (b) Pepper, M. J. M.; Shavitt, I.; Schleyer, P. v. R.; Glukhovtsev, M. N.; Janoschek, R.; Quack, M. "Is stereomutation of methane possible?" J. Comput. Chem. 1995, 16, 207-225. (c) See also, Minkin, V. I.; Minyaev, R. M.; Zacharov, I. I. "Semiempirical and ab initio calculations on the automerization of methane," J. Chem. Soc., Chem. Commun. 1977, 213-214.
(5) Wong, M. W.; Radom, L. "Methane dication: planar but not square," J. Am. Chem. Soc. 1989, 111, 1155-1156.
(6) Benson, S. W. Thermochemical kinetics: Methods for the estimation of thermochemical data and rate parameters; 2nd ed.; Wiley: New York, 1976, p 309.
(7) (a) Collins, J. B.; Dill, J. D.; Jemmis, E. D.; Apeloig, Y.; Schleyer, P. v. R.; Seeger, R.; Pople, J. A. "Stabilization of planar tetracoordinate carbon," J. Am. Chem. Soc. 1976, 98, 5419-5427; (b) Bolton, E. E.; Laidig, W. D.; Schleyer, P. V.; Schaefer, H. F. "Singlet $\mathrm{C}_{2} \mathrm{H}_{2} \mathrm{Li}_{2}$ - Acetylenic and 1,2-dilithioethene isomers - A remarkably congested potential energy hypersurface for a simple organometallic system," J. Am. Chem. Soc. 1994, 116, 9602-9612; (c) Bolton, E. E.; Laidig, W. D.; Schleyer, P. v. R.; Schaefer, H. F. "Does singlet 1,1-dilithioethene really prefer a perpendicular structure," J. Phys. Chem. 1995, 99, 17551-17557; (d) Sorger, K.; Schleyer, P. v. R. "Planar and inherently non-tetrahedral tetracoordinate carbon: a status report," J. Mol. Struct., Theochem. 1995, 338, 317-346; (e) Gribanova, T. N.; Minyaev, R. M.; Minkin, V. I. "Planar tetracoordinate carbon in organoboron compounds: ab initio computational study," Coll. Czech. Chem. Commun. 1999, 64, 1780-1789.
(8) (a) Sorger, K.; Schleyer, P. v. R.; Stalke, D. "Towards planar tetracoordinate carbon in the puckered ladder structure of dilithiated 1-di-tert-butylhydroxymethyl-3,3-dimethycyclopropene," J. Chem. Soc., Chem. Commun. 1995, 2279-2280; (b) Sorger, K.; Schleyer, P. v. R.; Stalke, D. "Dimeric [3,3-dimethyl-2-(trimethylsilyl)cyclopropenyl]lithium-tetramethylenediamine: distortion of the cyclopropenyl geometry due to strong rehybridization at the lithiated carbon," J. Am. Chem. Soc. 1996, 118, 1086-1091; (c) Sorger, K.; Schleyer, P. v. R.; Fleischer, R.; Stalke, D. "Toward planar tetracoordinate carbon in the puckered ladder structures of chelated cyclopropenyllithium aggregates," J. Am. Chem. Soc. 1996, 118, 6924-6933.
(9) (a) Chacon, S. T.; Chisholm, M. H.; Folting, K.; Huffman, J. C.; Hampden-Smith, M. J. "Allene adducts of ditungsten hexaalkoxides. Three modes of allene coordination to dinuclear centers as seen in the structures of $\mathrm{W}_{2}(\mathrm{O}-t \mathrm{Bu})_{6}\left(\mathrm{C}_{3} \mathrm{H}_{4}\right), \mathrm{W}_{2}(\mathrm{O}-t \mathrm{Bu})_{6}\left(\mathrm{C}_{3} \mathrm{H}_{4}\right)_{2}$, and $\mathrm{W}_{2}(\mathrm{O}-t \mathrm{Bu})_{6}\left(\mathrm{C}_{3} \mathrm{H}_{4}\right)(\mathrm{CO})_{2}, "$ Organometallics 1991, 10, 3722-3735; (b) Leoni, P.; Pasquali, M.; Pieri, G.; Albinati, A.; Pregosin, P. S.; Rüegger, H. "A stable palladium(I) dimer with one 14 e palladium center and its reversible reaction with $\mathrm{CS}_{2}$, affording a new complex with a planar four-coordinate carbon," Organometallics 1995, 14, 3143-3145; (c) Gunale, A.; Pritzkow, H.; Siebert, W.; Steiner, D.; Berndt, A. "Dicobalt and diplatinum complexes of diborylcarbenes," Angew. Chem., Int. Ed. 1995, 34, 1111-1113; (d) Gunale, A.; Steiner, D.; Schweikart, D.; Pritzkow, H.; Berndt, A.; Siebert, W. "Unusual mono- and dinuclear cobalt and platinum complexes of rearranged boriranylideneborane and diboretanylideneborane ligands - Dicobalt- $\mu$-diborylcarbene complexes as derivatives of planar methane," Chem. Eur. J. 1998, 4, 44-52.
(10) (a) Cotton, F. A.; Millar, M. "The probable existence of a triple bond between two vanadium atoms," J. Am. Chem. Soc. 1977, 99, 7886-7891; (b) Buchwald, S. L.; Lucas, E. A.; Davies, W. M. "A bimetallic zirconium complex containing an in-plane bridging aromatic ring," J. Am. Chem. Soc. 1989, 111, 397-398.
(11) Key contributions from Erker's group include: (a) Erker, G.; Zwettler, R.; Krüger, C.; Noe, R.; Werner, S. "Planar tetracoordinate carbon in $\mathrm{Cp}_{2} \mathrm{Zr}\left(\mu-\eta^{1}, \eta^{2}-\mathrm{Me}_{3} \mathrm{SiCCPh}\right)(\mu-$ Cl)AlMe ${ }_{2}$," J. Am. Chem. Soc. 1990, 112, 9620-9621; (b) Ahlers, W.; Erker, G.; Fröhlich, R.; Peuchert, U. "Synthesis, structure, and dynamic behavior of ( $\mu$-aldimido) $\left(\mu-\eta^{1}, \eta^{2}\right.$ -alkyne)-biszirconocene cation complexes that contain planar-tetracoordinate carbon," Chem. Ber. -Recueil 1997, 130, 1069-1077.
(12) For reviews, see: (a) Albrecht, M.; Erker, G.; Krüger, C. "The synthesis of stable, isolable planar-tetracoordinate carbon compounds," Synlett 1993, 441-448; (b) Röttger, D.; Erker, G. "Compounds containing planar-tetracoordinate carbon," Angew. Chem., Int. Ed. 1997, 36, 813-827; Angew. Chem. 1997, 109, 840-856; (c) Erker, G. "Using bent metallocenes for stabilizing unusual coordination geometries at carbon," Chem. Soc. Rev. 1999, 28, 307-314; (c) Choukroun, R.; Cassoux, P. "Planar tetracoordination of carbon in groups 4 and 5 organometallic chemistry," Acc. Chem. Res. 1999, 32, 494-502.
(13) For reviews, see: (a) Liebman, J. F.; Greenberg, A. "A survey of strained organic molecules," Chem. Rev. 1975, 76, 311-365; (b) Greenberg, A.; Liebman, J. F. "A potpourri of pathologies" in Strained Organic Molecules; Academic Press: New York, 1978; Vol. 38, pp 342-385; (c) Krohn, K. "Fenestrane - Blick auf strukturelle Pathalogien," Nach. Chem. Tech. Lab. 1987, 35, 264-266; (d) Venepalli, B. R.; Agosta, W. C. "Fenestranes and the flattening of tetrahedral carbon," Chem. Rev. 1987, 87, 399-410; (e) Agosta, W. C.
"Inverted and planar carbon" in The Chemistry of the Alkanes and Cycloalkanes; Patai, S. and Rappoport, Z., Ed.; Wiley: New York, 1992, pp 927-962; (f) Luef, W.; Keese, R. "Planarizing distortions in carbon compounds," Adv. Strain Org. Chem. 1993, 3, 229-267; (g) Thommen, M.; Keese, R. "Fenestranes in recent synthetic developments," Synlett 1997, 231-240.
(14) (a) Keese, R. "Tetrakoordinierter Kohlenstoff mit planoider Konfiguration," Nach. Chem. Tech. Lab. 1982, 30, 844-849; (b) Keese, R. Planarization of tetracoordinate carbon. Synthesis and structure of [5.5.5.5]fenestranes; Chizhov, O. S., Ed.; Blackwell: Oxford, 1986, pp 43-52; (c) Luef, W.; Keese, R. "62. Angular distortions at tetracoordinate carbon. Planoid distortions in $\alpha, \alpha^{\prime}$-bridged spiro[4.4]nonanes and [5.5.5.5]fenestranes," Helv. Chim. Acta 1987, 70, 543-553; (d) van der Waals, A.; Keese, R. "Synthesis of a [5.5.5.5]fenestrenedione via tandem Pauson-Khand tetracyclization," J. Chem. Soc., Chem. Commun. 1992, 570-571; (e) Keese, R.; Guidetti-Grept, R.; Herzog, B. "Synthesis of [5.5.5.5]fenestranes by Pd-catalyzed carbonylation-cyclization," Tetrahedron Lett. 1992, 33, 1207-1210; (f) Brunvoll, J.; Guidetti-Grept, R.; Hargittai, I.; Keese, R. "204. Synthesis and electron-diffraction structure of all-cis-[5.5.5.5]fenestrane," Helv. Chim. Acta 1993, 76, 2838-2846; (g) Guidetti-Grept, R. G.; Herzog, B.; Debrunner, B.; Siljegovic, V.; Keese, R.; Frey, H.-M.; Hauser, A.; König, O.; Lüthi, S.; Birrer, J.; Nyffeler, D.; Förster, M.; Bürgi, H.-B. "A [5.5.5.5]fenestrane derivative," Acta Crystallogr., Sect. C: Cryst. Struct. Commun. 1995, C51, 495-497.
(15) (a) Hoeve, W. T.; Wynberg, H. "Synthetic approaches to planar carbon. 1,"J. Org. Chem. 1980, 45, 2925-2930; (b) Hoeve, W. T.; Wynberg, H. "Synthetic approaches to planar carbon. 2," J. Org. Chem. 1980, 45, 2930-2937; (c) Rao, V. B.; George, C. F.; Wolff, S.; Agosta, W. C. "Synthetic and structural studies in the [4.4.4.5]fenestrane series," J. Am. Chem. Soc. 1985, 107, 5732-5739; (d) Smit, W. A.; Buhanjuk, S. M.; Simonyan, S. O.; Shashkov, A. S.; Struchkov, Y. T.; Yanovsky, A. I.; Caple, R.; Gybin, A. S.; Anderson, L. G.; Whiteford, J. A. "An efficient protocol for the synthesis of fenestrane derivatives," Tetrahedron Lett. 1991, 32, 2105-2108; (e) Luef, W.; Keese, R. "Angular distortions at tetracoordinate carbon: Planoid distortions in small spiroalkanes," J. Mol. Struct., Theochem. 1992, 257, 353-368; (f) Venugopal, D.; Agosta, W. C. "Cation, carbene, and radical centers in a [4.4.4.5]fenestrane," Tetrahedron 1992, 48, 6757-6762; (g) Keese, R. "Two stereoisomeric [4.5.5.5]fenestranes formed by intramolecular [2 + 2] cycloaddition," Angew. Chem., Int. Ed. 1992, 31, 344-345; (h) Hirschi, D.; Luef, W.; Gerber, P.; Keese, R. " 147. Synthesis and structure of [4.5.5.5]fenestranes (= tetracyclo[5.4.1.0 $0^{4,12} .0^{9,12}$ ]dodecanes)," Helv. Chim. Acta 1992, 75, 1897-1908.
(16) (a) Wiberg, K. B.; Olli, L. K.; Golombeski, N.; Adams, R. D. "Tricyclo[4.2.0.0 $0^{1,4}$ ]octane," J. Am. Chem. Soc. 1980, 102, 7467-7475; (b) Wiberg, K. B.; Wendoloski, J. J. "Enthalpies of formation of fused cyclobutane derivatives," J. Am. Chem. Soc. 1982, 104, 5679-5686; (c) Wiberg, K. B. "Structures and energies of the tricyclo[4.1.0.0 ${ }^{1,3}$ ]heptanes and the tetracyclo[4.2.1. $0^{2,9} .0^{5,9}$ ]nonanes. Extended group equivalents for converting $a b$ initio energies to heats of formation," J. Org. Chem. 1985, 50, 5285-5291.
(17) For theoretical work by Minkin and coworkers relating to fenestranes (4-II), see: (a) Minkin, V. I.; Minyaev, R. M.; Natanzon, V. I. "Structure of fenestranes and the eightelectron rule," J. Org. Chem. USSR (Engl. Transl.) 1980, 16, 589-596; (b) Minkin, V. I.; Minyaev, R. M. "The nonclassical polyhedral organic molecules and ions" in Progress in

Theoretical Organic Chemistry; Csizmadia, I. G., Ed.; Elsevier: Amsterdam, 1982; Vol. 3, pp 121-155; (c) Minkin, V. I.; Minyaev, R. M.; Zhdanov, Y. A. "Nontetrahedral tetracoordinate carbon atom in organic compounds" in Nonclassical Structures of Organic Compounds; Mir: Moscow, 1987, pp 248-306 (translated by B. V. Rassadin).
(a) Würthwein, E.-U.; Chandrasekhar, J.; Jemmis, E. D.; Schleyer, P. v. R. "The [4.4.4.4]fenestranes and [2.2.2.2]paddlane. Prospects for the realization of planar tetracoordinate carbon?" Tetrahedron Lett. 1981, 22, 843-846; (b) Schulman, J. M.; Sabio, M. L.; Disch, R. L. "Structure and energetics of [4.4.4.4]fenestrane," J. Am. Chem. Soc. 1983, 105, 743-744.
(a) Böhm, M. C.; Gleiter, R.; Schang, P. "On the planarity of tetracyclo[5.5.1.0 $\left.0^{4,13} .0^{10,13}\right]$ tridecahexaene," Tetrahedron Lett. 1979, 28, 2575-2578; (b) Chandrasekhar, J.; Würthwein, E.-U.; Schleyer, P. v. R. "On the planarity of tetracoordinate carbon enclosed by annulene perimeter," Tetrahedron 1981, 37, 921-927.
(a) Wiberg, K. B.; Hiatt, J. E.; Burgmaier, G. J. "Distorted geometries about bridgehead carbons," Tetrahedron Lett. 1968, 5855-5857; (b) Hahn, E. H.; Bohm, H.; Ginsburg, D. "The synthesis of paddlanes: compounds in which quaternary bridgehead carbons are joined by four chains," Tetrahedron Lett. 1973, 507-510; (c) Wiberg, K. B.; O'Donnell, M. J. "Preparation and Diels-Alder reactions of the $[n](1,4)$ naphthalenophanes. Isolation of a paddlane derivative containing the tricyclo[14.2.2.2 ${ }^{1,6}$ docosane ring system," J. Am. Chem. Soc. 1979, 101, 6660-6666; (d) Wiberg, K. B. "Bonding in small ring paddlanes," Tetrahedron Lett. 1985, 26, 5967-5970. (e) See also, Dodziuk, H. "Unusual saturated hydrocarbons: Interaction between theoretical and synthetic chemistry," Top. Stereochem. 1994, 21, 351-380.
(a) Wynberg, H.; Helder, R. "The synthesis of [2.2](9,10)anthraceno(2,5)furanophane and its reaction with dimethyl acetylenedicarboxylate," Tetrahedron Lett. 1971, 45, 4317-4320; (b) Helder, R.; Wynberg, H. "Diels-Alder addition of dicyanocetylene to [8](2,5)furanophane. Synthesis of a paddlane," Tetrahedron Lett. 1973, 4321-4; (c) Wynberg, H.; Hulshof, L. A. "Optical activity of hydrocarbons," Tetrahedron 1974, 30, 177582; (d) Vögtle, F.; Koo Tze Mew, P. "Triptycenophanes - Synthesis via ‘double nonbenzylic sulfone pyrolysis'," Angew. Chem., Int. Ed. 1978, 17, 60-61; (e) Warner, P.; Chem, B.-L.; Bronski, C. A.; Karcher, B. A.; Jacobson, R. A. "Synthesis of some [n.1.3.1]- and [n.1.2.1]paddlanes," Tetrahedron Lett. 1981, 22, 375-6; (f) Eaton, P. E.; Leipzig, B. D. "Toward tricyclo[2.2.2.2]decane. 1. [n.2.2.2]Paddlane systems, n = 10-14," J. Am. Chem. Soc. 1983, 105, 1656-1658; (g) Tobe, Y.; Fujita, H.; Wakaki, I.; Terashima, K.; Kobiro, K.; Kakiuchi, K.; Odaira, Y. "Water-soluble macrocyclic paddlanes and propellane as a new class of host molecules," J. Chem. Soc., Perkin Trans. 1 1984, 2681-4; (h) Schwartz, M. H.; Rosenfeld, S. M.; Lee, C. I.; Jasinski, J. P.; Dardon, E. H. "The structure of 9,10-dihydro-9,10-bis(hydroxymethyl)-9,10-ethanoanthracene-11,12-anhydride," Tetrahedron Lett. 1992, 33, 6275-8; (i) Lee, W. B.; Oh, D. W. "The reaction of [1.1.1]propellane with methylene," Bull. Korean Chem. Soc. 1999, 20, 629-630.
(22) (a) Wiberg, K. B.; McClusky, J. V.; Schulte, G. K. "The reaction of a bridged spiropentane with Zeise's dimer," Tetrahedron Lett. 1986, 27, 3083-3086; (b) Wiberg, K. B.; McClusky, J. V. "Tricyclo[2.1.0.0 ${ }^{1,3}$ ]pentane," Tetrahedron Lett. 1987, 28, 5411-5414; (c) Wiberg, K. B.; Chaves, A. "Predominant inversion of configuration in an intramolecular carbene addition to an alkene," J. Am. Chem. Soc. 1989, 111, 8052-8053; (d) Wiberg, K.
B.; McMurdie, N.; McClusky, J. V.; Hadad, C. M. "Tricyclo[2.1.0.0 ${ }^{1,3}$ ]pentane," J. Am. Chem. Soc. 1993, 115, 10653-10657; (e) Wiberg, K. B.; Snoonian, J. R. "Bridged spiropentanes - ring expansion," Tetrahedron Lett. 1995, 36, 1171-1174; (f) Wiberg, K. B.; Snoonian, J. R.; Lahti, P. M. "Ring contraction of a two-carbon bridged spiropentane," Tetrahedron Lett. 1996, 37, 8285-8288; (g) Wiberg, K. B.; Snoonian, J. R. "Synthesis, reactions, and structural studies of two-carbon bridged spiropentanes," J. Org. Chem. 1998, 63, 1402-1407; (h) Wiberg, K. B.; Snoonian, J. R. "Ring expansion and contraction of a two-carbon bridged spiropentane," J. Org. Chem. 1998, 63, 1390-1401.
(23) See also: (a) Dodziuk, H.; Nowinski, K. S. "In quest for planar and pyramidal carbon atom. Part 2. AM1 study of small bridged spiropentanes," J. Mol. Struct., Theochem. 1994, 311, 97-100; (b) Dodziuk, H.; Leszczynski, J.; Nowinski, K. S. "The quest for a planar and pyramidal carbon atom. 3. Can a tetrahedrally coordinated carbon form a nearly linear C-C-C bond angle," J. Org. Chem. 1995, 60, 6860-6863.
(24) For an initial communication on the structures for octaplane and a number of other alkaplanes, see: McGrath, M. P.; Radom, L. "Alkaplanes: a class of neutral hydrocarbons containing a potentially planar tetracoordinate carbon," J. Am. Chem. Soc. 1993, 115, 3320-3321.
(25) For a description of some of the basis sets and theoretical methods used, see: Hehre, W. J.; Radom, L.; Schleyer, P. v. R.; Pople, J. A. Ab Initio Molecular Orbital Theory; Wiley: New York, 1986.
(26) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Zakrzewski, V. G.; Petersson, G. A.; Montgomery, J., J. A.; Stratmann, R. E.; Burant, J. C.; Dapprich, S.; Millam, J. M.; Daniels, A. D.; Kudin, K. N.; Strain, M. C.; Farkas, O.; Tomasi, J.; Barone, V.; Cossi, M.; Cammi, R.; Mennucci, B.; Pomelli, C.; Adamo, C.; Clifford, S.; Ochterski, J.; Petersson, G. A.; Ayala, P. Y.; Cui, Q.; Morokuma, K.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Cioslowski, J.; Ortiz, J. V.; Baboul, A. G.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Challacombe, M.; Gill, P. M. W.; Johnson, B. G.; Chen, W.; Wong, M. W.; Andres, J. L.; Gonzalez, C.; Head-Gordon, M.; Replogle, E. S.; Pople, J. A. GAUSSIAN 98, Revision A.7; Gaussian, Inc.: Pittsburgh PA, 1998.
(27) Molpro is a package of $a b$ initio programs written by H.-J. Werner and P. J. Knowles with contributions from J. Almlöf, R. D. Amos, A. Berning, D. L. Cooper, M. J. O. Deegan, A. J. Dobbyn, F. Eckert, S. T. Elbert, C. Hampel, R. Lindh, W. A. Lloyd, W. Meyer, A. Nicklass, K. Peterson, R. Pitzer, A. J. Stone, P. R. Taylor, M. E. Mura, P. Pulay, M. Schütz, H. Stoll and T. Thorsteinsson.
(28) (a) Knowles, P. J.; Hampel, C.; Werner, H.-J. "Coupled cluster theory for high spin, open shell reference wave functions," J. Chem. Phys. 1993, 99, 5219-5227; (b) Werner, H.-J.; Knowles, P. J. "An efficient internally contracted multiconfiguration-reference configuration interaction method," J. Chem. Phys. 1988, 89, 5803-5814; (c) Knowles, P. J.; Werner, H.-J. "An efficient method for the evaluation of coupling coefficients in configuration interaction calculations," Chem. Phys. Lett. 1988, 145, 514-522.
(29) For a description of these methods and their application, see: Jensen, F. Introduction to Computational Chemistry; John Wiley \& Sons: Chichester, 1998, and references therein.
(30) (a) Bauschlicher, C. W., Jr.; Langhoff, S. R.; Taylor, P. R.; Handy, N. C.; Knowles, P. J. "Benchmark full configuration-interaction calculations on hydrogen fluoride and amidogen $\left(\mathrm{NH}_{2}\right)$," J. Chem. Phys. 1986, 85, 1469-1474. (b) For the original formulation of the Davidson correction, see: Langhoff, S. R.; Davidson, E. R. "Configuration interaction calculations on the nitrogen molecule," Int. J. Quantum Chem. 1974, 8, 61-72.
(31) Dewar, M. J. S.; Zoebisch, E. G.; Healy, E. F.; Stewart, J. J. P. "Development and use of quantum mechanical molecular models. 76. AM1: a new general purpose quantum mechanical molecular model," J. Am. Chem. Soc. 1985, 107, 3902-3909.
(a) Schulman, J. M.; Sabio, M. L.; Disch, R. L. "Structure and energetics of [4.4.4.4]fenestrane," J. Am. Chem. Soc. 1983, 105, 743-744; (b) Schulman, J. M.; Disch, R. L. "Ab initio heats of formation of medium-sized hydrocarbons. The heat of formation of dodecahedrane," J. Am. Chem. Soc. 1984, 106, 1202-1204; (c) Disch, R. L.; Schulman, J. M.; Sabio, M. L. "Ab initio heats of formation of medium-sized hydrocarbons. 2. Use of second-order correlation energies," J. Am. Chem. Soc. 1985, 107, 1904-1906; (d) Disch, R. L.; Schulman, J. M. "Ab initio heats of formation of medium-sized hydrocarbons. 7. The [n]prismanes," J. Am. Chem. Soc. 1988, 110, 2102-2105; (e) Schulman, J. M.; Disch, R. L. "A theoretical study of pagodane and related systems," J. Mol. Struct., Theochem. 1995, 358, 51-54.
(a) The experimental heats of formation of the small unstrained hydrocarbons (ethane propane, isobutane and neopentane) were taken from: Afeefy, H. Y.; Liebman, J. F.; Stein, S. E. "Neutral Thermochemical Data" in NIST Chemistry WebBook, NIST Standard Reference Database Number 69; Mallard, W. G. and Linstrom, P. J., Ed.; National Institute of Standards and Technology: Gaithersburg MD, May 1999, (http://webbook.nist.gov); (b) Most other experimental values for the heats of formation, given in Tables 4-12 and 4-13, were taken from: Pedley, J. B.; Naylor, R. D.; Kirby, S. P. Thermochemical Data of Organic Compounds; 2nd ed.; Chapman and Hall: London, 1986; (c) The heat of formation of [1.1.1]propellane (4-57) is quoted from: Wiberg, K. B.; Ochterski, J. W. "Comparison of different $a b$ initio theoretical models for calculating isodesmic reaction energies for small-ring and related compounds," J. Comput. Chem. 1997, 18, 108-114; (d) The G2 value for the heat of formation of tetrahedrane (4-55) is given in the absence of an experimental value: Glukhovtsev, M. N.; Laiter, S.; Pross, A. "Thermochemistry of cyclobutadiene and tetrahedrane: A high-level computational study," J. Phys. Chem. 1995, 99, 6828-6831; (e) Beckhaus, H.-D.; Rüchardt, C.; Lagerwall, D. R.; Paquette, L. A.; Wahl, F.; Prinzbach, H. "Experimental enthalpies of formation and strain energies for the caged $\mathrm{C}_{20} \mathrm{H}_{20}$ pagodane and dodecahedrane frameworks," J. Am. Chem. Soc. 1994, 116, 11775-11778; (f) Beckhaus, H.-D.; Rüchardt, C.; Lagerwall, D. R.; Paquette, L. A.; Wahl, F.; Prinzbach, H. "Experimental enthalpies of formation and strain energies for the caged $\mathrm{C}_{20} \mathrm{H}_{20}$ pagodane and dodecahedrane frameworks (Vol 116, Pg 11775, 1994)," J. Am. Chem. Soc. 1995, 117, 8885; (g) Disch, R. L.; Schulman, J. M. "Heat of formation of dodecahedrane," J. Phys. Chem. 1996, 100, 3504-3506; (h) Pedley, J. B.; Naylor, R. D.; Kirby, S. P. Thermochemical data of organic compounds; 2nd ed.; Chapman and Hall: London, 1986.
(a) Pople, J. A.; Scott, A. P.; Wong, M. W.; Radom, L. "Scaling factors for obtaining fundamental vibrational frequencies and zero-point energies from HF/6-31G* and MP2/631G* harmonic frequencies," Isr. J. Chem. 1993, 33, 345; (b) Scott, A. P.; Radom, L.
"Harmonic vibrational frequencies: an evaluation of Hartree-Fock, Møller-Plesset, quadratic configuration interaction, density functional theory, and semi-empirical scale factors," J. Phys. Chem. 1996, 100, 16502-16513.
(35) Lias, S. G.; Liebman, J. F.; Levin, R. D. "Evaluated gas phase basicities and proton affinities of molecules; heats of formation of protonated molecules," J. Phys. Chem. Ref. Data 1984, 13, 695-808.
(36) Lias, S. G. "Ionization energy evaluation" in NIST Chemistry WebBook, NIST Standard Reference Database Number 69; Mallard, W. G. and Linstrom, P. J., Ed.; National Institute of Standards and Technology: Gaithersburg MD 20899, February 2000, (http://webbook.nist.gov).
(37) (a) Benson, S. W. Thermochemical kinetics: Methods for the estimation of thermochemical data and rate parameters; 2nd ed.; Wiley: New York, 1976, p 120. (b) See also: Johnson, W. T. G.; Hrovat, D. A.; Borden, W. T. "Ab initio calculations on spiropentane stereomutations lead to a reinterpretation of the experimental results," J. Am. Chem. Soc. 1999, 121, 7766-7772.
(38) The designation $6-311+\mathrm{G}(2 \mathrm{~d}, \mathrm{p})($ red $)$ refers to our enhanced $6-31 \mathrm{G}(\mathrm{d})$ basis, which is designed to afford $6-311+G(2 d, p)$ at the central carbon atom without the added computational cost of using such a large basis for the entire molecule. The usual 6-31G(d) basis (but with a set of five spherical $d$-functions instead of the usual six Cartesian functions) is enhanced to $6-311+G(2 d)$ at the central carbon atom $\left(\mathrm{C}^{0}\right)$ and to $6-311+\mathrm{G}(\mathrm{d})$ at the four adjacent carbon atoms $\left(\mathrm{C}^{\alpha}\right)$. An examination of the use of this basis is given in Section 4.2 on page 145.
(39) (a) Skattebøl, L. "Chemistry of gem-dihalocyclopropanes. II. The reaction of dienes with dibromocarbene," J. Org. Chem. 1964, 29, 2951-2956; (b) Skattebøl, L. "Chemistry of gem-dihalocyclopropanes. V. Formation of tricyclo[4.1.0.04,6]heptane and derivatives," $J$. Org. Chem. 1966, 31, 2789-2794; (c) Becher, G.; Skattebøl, L. "Thermal reactions of meso- and racemic deca-2,3,7,8-tetraene," Tetrahedron Lett. 1979, 14, 1261-1264;
(40) See also: (a) Brinker, U. H.; Streu, J. "4,5-Benzotricyclo[4.1.0.0 ${ }^{1,3}$ ]hept-4-ene," Angew. Chem., Int. Ed. 1980, 19, 631-632; Angew. Chem. 1980, 92, 641; (b) Brinker, U. H.; Wilk, G.; Gomann, K. "Thermolysis and reactions of 4,5-benzotricyclo[4.1.0.0 ${ }^{1,3}$ ]hept-4ene and $o$-(propadienyl)styrene," Angew. Chem., Int. Ed. 1983, 22, 868-869; Angew. Chem. 1983, 95, 892; (c) Brinker, U. H.; Gomann, K.; Zorn, R. "Tricyclo[4.1.0.0 ${ }^{1,3}$ ]hept-4-enes as intermediates," Angew. Chem., Int. Ed. 1983, 22, 869-870; Angew. Chem. 1983, 95, 893; (d) Wiberg, K. B.; Chaves, A. "Predominant inversion of configuration in an intramolecular carbene addition to an alkene," J. Am. Chem. Soc. 1989, 111, 8052-8053; (e) Miebach, T.; Wuster, H.; Brinker, U. H. "Carbene rearrangements. 42. Intramolecular addition versus novel carbon hydrogen bond insertion reactions of N -alkenyl-substituted cyclopropylidenes," J. Org. Chem. 1993, 58, 6520-6523; (f) Miebach, T.; Brinker, U. H. "trans-Tricyclo[5.1.0.0 ${ }^{1,3}$ ]octane," J. Org. Chem. 1993, 58, 6524-6525.
(41) Baird, M. S. "Tetracyclo[3.3.1. $\left.0^{2,4} \cdot 0^{2,8}\right]$ nonane. A strained spiro-compound," J. Chem. Soc., Chem. Commun. 1974, 197-198.
(42) (a) For an overview, see: Kaupp, G.; Boy, J. "Overlong C-C single bonds," Angew. Chem., Int. Ed. 1997, 36, 48-49. (b) Komatsu, K.; Nishinaga, T.; Takeuchi, K.; Lindner, H. J.; Richter, J. "A polycyclic pentamer of bicyclo[2.2.2]octene - a hydrocarbon mole-
cule with a long C-C single bond connecting two cofacially disposed cyclopentadiene rings," J. Org. Chem. 1994, 59, 7322-7328; (c) Kammermeier, S.; Jones, P. G.; Herges, R. "[2+2] Cycloaddition products of tetradehydrodianthracene - Experimental and theoretical proof of extraordinary long C-C single bonds," Angew. Chem., Int. Ed. 1997, 36, 1757-1760; (d) Toyota, A.; Muramatsu, T.; Koseki, S. "Structural properties of 3,10-diaz-adispiro[5.0.5.3]pentadeca-1,4,8,11-tetraene and its homologues - a generation of an unusually long C-C single bond by through-bond interaction," J. Mol. Struct., Theochem. 1997, 393, 85-91; (e) Bettinger, H. F.; Schleyer, P. V.; Schaefer, H. F. "Tetraphenyldihydrocyclobutaarenes - What causes the extremely long 1.72 -Ångstrom C-C single bond," J. Chem. Soc., Chem. Commun. 1998, 769-770.
(43) For general aspects of the treatment of strain in hydrocarbons, see: (a) Schleyer, P. v. R.; Williams, J. E.; Blanchard, K. R. "The evaluation of strain in hydrocarbons. The strain in adamantane and its origin," J. Am. Chem. Soc. 1970, 92, 2377- 2386; (b) Greenberg, A.; Liebman, J. F. Strained Organic Molecules; Academic: New York, 1978; Ch. 1, pp 1-24; (c) Wiberg, K. B. "The concept of strain in organic chemistry," Angew. Chem., Int. Ed. 1986, 25, 312-322; (d) Wiberg, K. B.; Bader, R. F. W.; Lau, C. D. H. "Theoretical analysis of hydrocarbon properties. 2. Additivity of group properties and the origin of strain energy," J. Am. Chem. Soc. 1987, 109, 1001-1012; (e) Haufe, G.; Mann, G. Chemistry of alicyclic compounds. Structure and chemical transformations; Elsevier: Amsterdam, 1989, pp 79-158; (f) Halton, B. "Strain in organic chemistry: a perspective," in Advances in strain in organic chemistry; Halton, B., Ed.; JAI Press: London, 1991; Vol. 1, pp 1-17; (g) Grimme, S. "Theoretical bond and strain energies of molecules derived from properties of the charge density at bond critical points," J. Am. Chem. Soc. 1996, 118, 1529-1534; (h) Wiberg, K. B.; Ochterski, J. W. "Comparison of different ab initio theoretical models for calculating isodesmic reaction energies for small-ring and related compounds," $J$. Comput. Chem. 1997, 18, 108-114.
(44) For a leading review detailing the synthesis of dodecahedrane via the pagodane route, see: Prinzbach, H.; Fessner, W.-D. "Novel organic polycycles - an adventure in molecular architecture" in Organic Synthesis: Modern Trends; Chizhov, O., Ed.; Blackwell: Oxford, 1987, pp 23-42.
(45) Lyons, J. E.; Rasmussen, D. R.; McGrath, M. P.; Nobes, R. H.; Radom, L. "Octaplane: a saturated hydrocarbon with a remarkably low ionization energy leading to a cation with a planar tetracoordinate carbon atom," Angew. Chem., Int. Ed. 1994, 33, 1667-1668; Angew. Chem. 1994, 106, 1722.
(46) Krogh-Jesperson, M.-B.; Chandrasekhar, J.; Würthwein, E.-U.; Collins, J. B.; Schleyer, P. v. R. "Molecular orbital study of tetrahedral, planar, and pyramidal structures of the isoelectronic series $\mathrm{BH}_{4}^{-}, \mathrm{CH}_{4}, \mathrm{NH}_{4}^{+}, \mathrm{SiH}_{4}$, and $\mathrm{PH}_{4}^{+}$," J. Am. Chem. Soc. 1980, 102, 2263-2268
(47) For a description of CASPT2 and other MCSCF methods, and for leading references, see: (a) Schmidt, M. W.; Gordon, M. S. "The construction and interpretation of MCSCF wavefunctions," Annu. Rev. Phys. Chem. 1998, 49, 233-266; (b) Bally, T.; Borden, W. T. "Calculations on open-shell molecules: a beginner's guide" in Reviews in Computational Chemistry; Liptowitz, K. B. and Boyd, D. B., Ed.; Wiley-VCH: New York, 1999; Vol. 13, pp 1-97.
(48) Schwartz, H. private communication.
(49) Sharma, V.; Keller, M.; Weiler, A.; Hunkler, D.; Prinzbach, H. "From pagodanes to nonpentagonal (homo)dodecahedranes - the undecacyclo[10.10.0.0 $0^{2,20} \cdot 0^{3,10} .0^{4,19} .0^{5,9} .0^{6,18} .0^{7,15}$ $.0^{8,13} .0^{19,22} .0^{16,21}$ ]docosane cage," Angew. Chem., Int. Ed. 1997, 35, 2858-2861; Angew. Chem. 1997, 108, 3029-3031.
(50) (a) Sedelmeier, G.; Fessner, W.-D.; Pinkos, R.; Grund, C.; Murty, B. A. R. C.; Hunkler, D.; Rihs, G.; Fritz, H.; Krüger, C.; Prinzbach, H. "Studien im Umfeld funktioalisierter/ anellierter acs-Tetracyclo[7.2.1.0 $\left.{ }^{4,11} .0^{6,10}\right]$ dodeca-2,7-dien-Gerüste - Röntgenstrukturanalysen einer 'face-to-face'-Dibenzoverbindung und eines Tetraoxadihydro-pagodans," Chem. Ber. 1986, 119, 3442-3472; (b) Prinzbach, H.; Fessner, W.-D. "Novel organic polycycles - an adventure in molecular architecture" in Organic Synthesis: Modern Trends; Chizhov, O., Ed.; Blackwell: Oxford, 1987, pp 23-42; (c) Fessner, W.-D.; Prinzbach, H. "The pagodane route to dodecahedrane" in Cage Hydrocarbons; Olah, G., Ed.; Wiley: New York, 1990, pp 353-405; (d) Prinzbach, H.; Weber, K. "From an insecticide to Plato's universe - The pagodane route to dodecahedranes - New pathways and new perspectives," Angew. Chem., Int. Ed. 1994, 33, 2239-2257; Angew. Chem. 1994, 106, 2329; (e) Wollenweber, M.; Pinkos, R.; Leonhardt, J.; Prinzbach, H. "Isopagodanes - Precursors of Unusual Cage Ions," Angew. Chem., Int. Ed. 1994, 33, 117-120; Angew. Chem. 1994, 106, 84; (f) Pinkos, R.; Weiler, A.; Voss, T.; Weber, K.; Wahl, F.; Melder, J. P.; Fritz, H.; Hunkler, D.; Prinzbach, H. "From pagodanes to homologous, non-pentagonal dodecahedranes," Liebigs Ann./Recueil 1997, 2069-2088; (g) Prakash, G. K. S.; Weber, K.; Olah, G. A.; Prinzbach, H.; Wollenweber, M.; Etzkorn, M.; Voss, T.; Herges, R. "Long-lived [1.1.1.1]- and [2.2.1.1]-'isopagodane' dications: Novel 4C/2e sigma-bishomoaromatic dications," J. Chem. Soc., Chem. Commun. 1999, 1029-1030.

# Appendix A Nomenclature 

## A. 1 Fenestranes

Hydrocarbons that consist of three or four rings that are fused in a manner such that a single carbon atom is common to all rings are often referred to as fenestranes (A-I or A-II). Fenestranes of type A-I are known as [l.m.n]fenestranes, where $l, m, n \geq 3$, and


A-I


A-I
fenestranes of type A-II are known as [k.l.m.n]fenestranes, where $k, l, m, n \geq 3$. The rings are usually listed with the smallest first, and we suggest that proceeding clockwise around the structure as a convenient mechanism for indicating the positioning of these rings. Thus, $\mathbf{A - 1}$ is a [4.4.4.5]fenestrane and A-2 is a [3.5.3.5]fenestrane. Unsaturated fenestranes have also been considered. Introducing a single $\mathrm{C}=\mathrm{C}$ double bond, e.g. A-3, gives a fenestrene. Thus A-3 is a [4.5.5.5]fenestrene while A-4 is [5.5.5.5]fenestratetraene. Normally, carbon numbering proceeds around the ring as indicated in A-1, A-2


A-1


A-2


A-3


A-4
and A-3. We have used a numbering scheme that would allow ready comparison between all the hydrocarbons considered in this work. This scheme labels the target, pla-nar-tetracoordinate carbon atom as $\mathrm{C}^{0}$ and refers to other carbon atoms through their bonding separation from $\mathrm{C}^{0}$. Thus, $\mathrm{C}^{0}$ (which is quaternary in all cases) is surrounded by four $\mathrm{C}^{\alpha}$ atoms (often referred to as $\mathrm{C}^{\alpha, \mathrm{i}}$, where $i=1 \ldots 4$ ) (see A-II).

Various stereoisomers are possible for each fenestrane skeleton. This becomes important when considering strain as some of these isomers are highly strained while others are not. There are two main methods for indicating stereoisomerism. The first, which has been used in the present work, describes the structure in terms of the number of cis- and trans-bicyclo[x.y.0]alkane subunits. Thus, $\mathbf{A - 1}$ is a cis,cis,cis,trans-[4.4.4.5]fenestrane, $\mathbf{A - 2}$ is all-cis-[3.5.3.5]fenestrane, and $\mathbf{A - 3}$ is cis,cis,trans-[4.5.5.5]fenestrene. It is occasionally of value to indicate the trans-fused ring bonds as in A-3. The alternative method describes the orientation of the bridgehead substituents as above ( $\alpha$ ) or below ( $\beta$ ) the plane of projection. Thus, $\mathbf{A} \mathbf{- 1}$ is a $1 \alpha, 3 \alpha, 5 \beta, 7 \alpha-[4.4 .4 .5]$ fenestrane and A-3 is a $4 \beta, 7 \alpha, 9 \alpha-[4.5 .5 .5]$ fenestrene.


A-5


A- 6


A-7

Table A-1. Trivial names for a number of fenestranes and their corresponding IUPAC names.

| Trivial Name |  | Fenestrane Nomenclature | IUPAC Name |
| :--- | :---: | :---: | :---: |
| pyramidane | A-5 | $[3.3 .3 .3]$ fenestrane | tetracyclo[5.5.1.0 $\left.0^{4,13} .0^{10,13}\right]$ tridecane |
| windowpane | A-6 | $[4.4 .4 .4]$ fenestrane | tetracyclo[3.3.1.0 $\left.0^{3,9} .0^{7,9}\right]$ nonane |
| staurane | A-7 | $[5.5 .5 .5]$ fenestrane | tetracyclo[2.1.0.0 $\left.0^{1,3} .0^{2,5}\right]$ pentane |

A few fenestranes have received particular trivial names. The most noteworthy are given along with IUPAC names in Table A-1.

## A. 2 Alkaplanes

We have designed a number of novel hydrocarbon cage systems which involve either capping or bicapping a neopentane or spiropentane subunit with a cyclic hydrocarbon. Because the systematic names for these molecules which result from the IUPAC nomenclature rules are cumbersome and rather undescriptive, a system of trivial names has been developed.


A-8


A-9

The alkaplanes are constructed by bicapping a neopentane subunit with identical cycloalkanes. In recognition of the close approach to planar-tetracoordination at the central carbon atom, the suffix "-plane" has been chosen. The nature of the capping cycloalkanes are then indicated by a prefix which is derived from the systematic name for the cyclic hydrocarbon by removing the word "cyclo". This is best illustrated by a few examples. The alkaplane which results from bicapping a neopentane subunit with crown cyclooctane is called octaplane (A-8). Similarly, using norbornane (or bicyclo [2.2.1]heptane) for the caps gives biheptaplane (A-9). ${ }^{\dagger}$

The saturated, polycyclic, hydrocarbon cage systems that result from bicapping spiropentane with cycloalkanes have a spiro[2.2] carbon atom at the center. We refer to these molecules as the spiroalkaplanes. Because molecules with other central moieties are also possible, it is suggested that the prefix "spiro[2.2]-" be used to indicate the nature of the spiro junction. For example, bicapping spiro[2.2]pentane with cyclooctane rings gives spiro[2.2]octaplane (A-10), while bicapping spiro[4.4]nonane with bicy-clo[2.2.0]-hexane results in a molecule we would name spiro[4.4]bihexaplane (A-11).

[^76]

A-10


A-11

Another structural modification to the basic alkaplane skeleton that has been employed in this work is to place a methylene bridge linking the alkaplane caps. The prefix "dimethano-" has been used to indicate this structural feature. Consequently, the doubly methano-bridged derivative of the alkaplane which results from bicapping spiropentane with bicyclo[3.3.1]octane is named dimethanospiro[2.2]bioctaplane (A-12).


A-12

No attempt has been made to number the entire systems. However, a system which labels the central atom as $\mathrm{C}^{0}$ and refers to the other carbon atoms through their bonding separation from $\mathrm{C}^{0}$ has been used. Thus, the carbon atoms directly attached to $\mathrm{C}^{0}$, which are in the central region of the molecule, are labelled $\mathrm{C}^{\alpha}$. Where these atoms need to be distinguished they are referred to as $\mathrm{C}^{\alpha, i}$, where $i=1 \ldots 4$. The atoms in the caps which bond to the $\mathrm{C}^{\alpha}$ atoms are then labelled $\mathrm{C}^{\beta}$, and so on (see A-8 and A-10).

There are two important types of alkaplane isomers. Stereoisomers result from inversion at the $\mathrm{C}^{\alpha}$ positions in the parent alkaplanes (i.e. those constructed from a neopentane subunit). This amounts to changing the orientation of the central methine ( CH ) groups. An example of this type of isomerism can be seen in the $S_{4}$ and $D_{2}$ symmetry
structures of octaplane ( $\boldsymbol{S}_{\mathbf{4}} \mathbf{- A - 8}$ and $\boldsymbol{D}_{\mathbf{2}} \mathbf{- A - 8}$ ). Structural isomers for all alkaplane families result from altering the relative orientation of the central and capping subunits. These isomers are only possible when neither the central subunit nor the cap have fourfold symmetry.

$S_{4}$-A-8

$D_{2}$-A-8

A list of names of some of the alkaplanes presented in the present work, together with corresponding IUPAC names, is given in Table A-2.


A-13


A-14


A-15

Molecules which result from applying a single cap to neopentane or spiropentane are referred to by the prefix "hemi-". In all other respects the nomenclature we have used for these molecules, the hemialkaplanes and hemispiroalkaplanes, follows that given above for the alkaplanes. Thus, the molecule which results from capping neopentane with cyclooctane is named hemioctaplane (A-13). ${ }^{\dagger}$ Similarly, the molecule formed by capping spiropentane with bicyclo[3.3.0]octane is called hemispirobioctaplane (A14). A pair of structural isomers which result from changing the orientation of the capping hydrocarbon subunit relative to the spiropentane subunit exists for all the hemisp-

[^77]iroalkaplanes which do not have the potential of four-fold symmetry in the cap. ${ }^{\dagger}$ Where both isomers are considered, we have distinguished them from one another with the label "parallel" or "perpendicular". This refers to the orientation of the major axes of the cap and the spiropentane subunit (cf. A-14 and A-15). A list of names of some of the hemialkaplanes presented in the present work, together with corresponding IUPAC names, is included in Table A-2.

Table A-2. Corresponding IUPAC names for a number of alkaplanes and hemialkaplanes.

| Molecule | IUPAC Alicyclic Hydrocarbon Name ${ }^{\text {a }}$ |  |
| :--- | :--- | :--- |
| octaplane | $\mathbf{A - 8}$ | octacyclo[9.7.1.1 |

${ }^{\text {a }}$ Simpler nomenclature for saturated cage hydrocarbons often results from using the nomenclature for "ortho-fused" and "ortho- and peri-fused" polycyclic hydrocarbons ((IUPAC Hydrocarbon Nomenclature Rules A-21 - A-24 and A-34) rather than that for saturated alicyclic systems (IUPAC Hydrocarbon Nomenclature Rules A-31 and A-32, which are extensions to the von Baeyer system). Using the fused polycyclic hydrocarbon nomenclature, octaplane (A-8) is named hexadecahydro-1,9:3,7:4,12:6,10-tetramethanonaphtha $[1,8-d e]$ naphthalene. Although somewhat simpler, this nomenclature is still cumbersome and fails to indicate the symmetry of the molecule. ${ }^{\text {b }}$ Note that the IUPAC name given by Dodziuk (see footnote on previous page) is incorrect - an indication of the difficulty of using this nomenclature scheme for molecules like the alkaplanes.

[^78]
# Appendix B <br> A Planarity Measure 

## B. 1 Derivation of $\alpha_{\text {plan }}$

## B.1.1 The Problem

The problem we face in comparing the approach to planar-tetracoordination in the alkaplane families is how to relate molecules of differing symmetry, in which a unique parameter for the deviation from planar-tetracoordination at the central carbon atom is not always obvious. In the higher symmetry species, especially the $S_{4}$ and $D_{2}$ molecules like octaplane and spirooctaplane, the central carbon atom $\left(\mathrm{C}^{0}\right)$ must lie at the origin, and the angles made by the four coordinating bonds $\left(\mathrm{C}^{0}-\mathrm{C}^{\alpha}\right)$ to the xy -plane (with the z -axis running through the centers of the caps) will all be equal. Clearly, this angle, which will be $0.0^{\circ}$ when the arrangement is exactly planar-tetracoordinate, gives a good indication of the deviation from planar tetracoordination. The problem is how to arrive at the equivalent measure when symmetry is reduced, for example, to $C_{2}$ or even $C_{1}$, so that the central atom no longer lies at the origin and the xy-plane is no longer a uniquely defined plane through $\mathrm{C}^{0}$.

The first step is to recognize that the unique plane in the high-symmetry molecules is in fact the best-fit plane through $\mathrm{C}^{0}$ which minimizes the distances of the $\mathrm{C}^{\alpha}$ atoms to this plane. What is required is a means of determining this best-fit plane (which runs through $\mathrm{C}^{0}$ ) even in cases where no symmetry is present. There is one further complication. When symmetry is lowered, the $\mathrm{C}^{0}-\mathrm{C}^{\alpha}$ bond lengths need not be equal. We have chosen not to weight the measure towards the further placed $\mathrm{C}^{\alpha}$ atoms and so normalized bond lengths have been used. Also, a measure based on distances of the $\mathrm{C}^{\alpha}$ atoms from the plane is dependent on the absolute $\mathrm{C}^{0}-\mathrm{C}^{\alpha}$ distances. Expression as an angular measure is pre-
ferred. Hence we would like to determine $\alpha_{i}$ values for each $\mathrm{C}^{\alpha, i}$, where $i=1 \ldots 4$, as the angles made by the $\mathrm{C}^{0}-\mathrm{C}^{\alpha}$ bonds with the best-fit plane which minimizes the sum of the squared sines of these angles (i.e. the squared distances of the unit vectors to the plane).

Finally, a list of $\alpha_{i}$ values can be cumbersome so all four values are averaged to give a single measure, although it is recognized that in some cases where the $\alpha_{i}$ values vary greatly this may give a somewhat misleading result and the list of $\alpha_{i}$ values should be quoted.

## B.1.2 The Solution

We define a system of five particles $\left(\mathrm{C}^{0}\right.$ and $\left.\mathrm{C}^{\alpha, i} ; i=1 \ldots 4\right)$ where $\mathrm{C}^{0}$ lies at the origin. To determine the best-fit plane through $\mathrm{C}^{0}$, we first define an arbitrary plane (see Figure B-1) with normal $\mathbf{u}$. The vectors from $\mathrm{C}^{0}$ to $\mathrm{C}^{\alpha, i}$ are defined as $\mathbf{u}_{i}=\left(\mathrm{u}_{x i}, \mathrm{u}_{y i}, \mathrm{u}_{z i}\right)$


Figure B-1. The deviation from planar-tetracoordination in the central $C^{0}\left(C^{\alpha}\right)_{4}$ moiety of the alkaplanes can be determined by finding the plane through $\mathrm{C}^{0}$, defined by the normal to the plane, $\hat{\mathbf{u}}$, which minimizes the sum of squared distances $d_{i}$ made by the unit vectors $\hat{\mathbf{u}}_{i}$ with the plane.
with corresponding unit vectors $\hat{\mathbf{u}}_{i}=\left(\hat{\mathrm{u}}_{x i}, \hat{\mathrm{u}}_{y i}, \hat{\mathrm{u}}_{z i}\right)$, where $i=1 \ldots 4$. The distances of the unit vectors to atoms $\mathrm{C}^{\alpha, i}$ from the arbitrary plane are then defined as $d_{\mathrm{i}}=\sin \alpha_{i}$. The angles $\alpha_{i}$ then give the deviation from planar-tetracoordination of the atoms $\mathrm{C}^{\alpha, i}$. A convenient definition of the best-fit plane minimizes the sum of the squared distances of the unit vectors to atoms $\mathrm{C}^{\alpha, i}$ from the plane. We label this sum as $s^{2}$.

$$
\begin{aligned}
& s^{2}=\sum_{i} d_{i}^{2}=\frac{\sum_{i}\left(\hat{\mathbf{u}}_{i} \cdot \mathbf{u}\right)^{2}}{|\mathbf{u}|^{2}} \\
& s^{2}=\frac{\sum_{i}\left(\hat{\mathrm{u}}_{x i}^{2} x^{2}+2 \hat{\mathbf{u}}_{y i} y \hat{\mathrm{u}}_{x i} x+\hat{\mathrm{u}}_{y i}^{2} y^{2}+\hat{\mathrm{u}}_{z i}^{2} z^{2}+2 \hat{\mathrm{u}}_{y i} y \hat{\mathrm{u}}_{z i} z+2 \hat{\mathrm{u}}_{x i} x \hat{\mathrm{u}}_{z i} z\right)}{x^{2}+y^{2}+z^{2}},
\end{aligned}
$$

where $\quad \hat{\mathbf{u}}_{i}=\left[\begin{array}{c}\hat{\mathrm{u}}_{x i} \\ \hat{\mathrm{u}}_{y i} \\ \hat{\mathrm{u}}_{z i}\end{array}\right]$, for $i=1 \ldots 4$, are constants, and

$$
\mathbf{u}=\left[\begin{array}{l}
x  \tag{B-1}\\
y \\
z
\end{array}\right] \text {, the normal to the plane, is variable. }
$$

Note that minimizing the sum of $d_{i}^{2}$,s is identical to minimizing the sum of $\sin ^{2} \alpha_{i}$ 's, which, for small values of $\alpha_{i}$, is equivalent to minimizing the sum of $\alpha_{i}{ }^{2}$ s.

For $s^{2}$ to be a minimum, we require $\nabla s^{2}=\mathbf{0}$, i.e. we want to find a minimum with respect to rotations of the plane. This can also be written as

$$
\nabla s^{2}=\mathbf{0}=\left[\begin{array}{c}
\frac{\partial s^{2}}{\partial x}  \tag{B-2}\\
\frac{\partial s^{2}}{\partial y} \\
\frac{\partial s^{2}}{\partial z}
\end{array}\right] \text {. }
$$

Inspection of the formula for $s^{2}$ (Equation B-1) gives

$$
\begin{align*}
& \nabla s^{2}=\mathbf{0}=2|\mathbf{u}|^{-2} \sum_{i}\left[\begin{array}{ccc}
\hat{\mathrm{u}}_{x i}^{2} & \hat{\mathrm{u}}_{x i} \hat{\mathrm{u}}_{y i} & \hat{\mathrm{u}}_{x i} \hat{\mathrm{u}}_{z i} \\
\hat{\mathrm{u}}_{y i} \hat{\mathrm{u}}_{x i} & \hat{\mathrm{u}}_{y i}^{2} & \hat{\mathrm{u}}_{y i} \hat{\mathrm{u}}_{z i} \\
\hat{\mathrm{u}}_{z i} \hat{u}_{x i} \hat{\mathrm{u}}_{z i} \hat{u}_{y i} & \hat{\mathrm{u}}_{z i}^{2}
\end{array}\right]\left[\begin{array}{l}
x \\
y \\
z
\end{array}\right]-2|\mathbf{u}|^{-4} \sum_{i}\left(\hat{\mathbf{u}}_{i} \cdot \mathbf{u}\right)^{2}\left[\begin{array}{l}
x \\
y \\
z
\end{array}\right]  \tag{B-3}\\
& \mathbf{0}=\sum_{i}\left[\begin{array}{c}
\hat{\mathrm{u}}_{x i} \\
\hat{\mathrm{u}}_{y i} \\
\hat{\mathrm{u}}_{z i}
\end{array}\right]\left[\begin{array}{ll}
\hat{\mathrm{u}}_{x i} \hat{\mathrm{u}}_{y i} & \hat{\mathrm{u}}_{z i}
\end{array}\right]\left[\begin{array}{c}
x \\
y \\
z
\end{array}\right]-|\mathbf{u}|^{-2} \sum_{i}\left(\hat{\mathbf{u}}_{i} \cdot \mathbf{u}\right)^{2}\left[\begin{array}{l}
x \\
y \\
z
\end{array}\right],
\end{align*}
$$

which can also be written

$$
\begin{equation*}
\mathbf{0}=\sum_{i} \hat{\mathbf{u}}_{i} \hat{\mathbf{u}}_{i}^{\mathrm{T}} \mathbf{u}-|\mathbf{u}|^{-2} \sum_{i}\left(\hat{\mathbf{u}}_{i} \cdot \mathbf{u}\right)^{2} \mathbf{u} . \tag{B-5}
\end{equation*}
$$

Now, let $\quad \mathbf{W}=\sum_{i}\left[\begin{array}{c}\hat{\mathrm{u}}_{x i} \\ \hat{\mathrm{u}}_{y i} \\ \hat{\mathrm{u}}_{z i}\end{array}\right]\left[\hat{\mathrm{u}}_{x i} \hat{\mathrm{u}}_{y i} \hat{\mathrm{u}}_{z i}\right]=\sum_{i} \hat{\mathbf{u}}_{i} \hat{\mathbf{u}}_{i}^{\mathrm{T}}$,
i.e. the outer product of $\hat{\mathbf{u}}_{i}$ with itself. $\mathbf{W}$ is a $3 \times 3$ matrix which we will refer to as the geometry tensor. Substituting for $\mathbf{W}$ and $s^{2}$, we can rewrite Equation B-5 as

$$
\begin{align*}
& \mathbf{0}=\mathbf{W} \mathbf{u}-s^{2} \mathbf{u}  \tag{B-7}\\
& \mathbf{W u}=s^{2} \mathbf{u} . \tag{B-8}
\end{align*}
$$

Clearly, this is an eigenvalue problem. The smallest eigenvalue of $\mathbf{W}, s_{\text {min }}^{2}$, is the minimum value for $s^{2}$ and the associated eigenvector, $\mathbf{u}_{\text {min }}$, defines the best-fit plane. Because $\mathbf{W}$ is $3 \times 3$, it will have three eigenvalues. The other two values are expected to give two other extrema, the maximum and a point of inflection in $s^{2}$. Further, since $\mathbf{W}$ is real and symmetric, the eigenvectors are orthogonal to each other.

The angles $\alpha_{i}$ are calculated from Equation B-9,

$$
\begin{equation*}
\alpha_{i}=\sin ^{-1}\left(\hat{\mathbf{u}}_{i} \cdot \mathbf{u}_{\text {min }}\right) \tag{B-9}
\end{equation*}
$$

and $\alpha_{\text {plan }}$ is given by

$$
\begin{equation*}
\alpha_{\text {plan }}=\frac{1}{4} \sum_{i} \alpha_{i}, \text { where } i=1 \ldots 4 . \tag{B-10}
\end{equation*}
$$

Thus, $\alpha_{\text {plan }}$, the average of the angles $\alpha_{i}$ made by the $\mathrm{C}^{0}-\mathrm{C}^{\alpha, i}$ bonds to the best-fit plane, which is defined by $\mathbf{u}_{\text {min }}$, can be calculated from the cartesian coordinates $\left(\mathrm{u}_{x i}, \mathrm{u}_{y i}\right.$, $\mathrm{u}_{z i}$ ) of the five carbon atoms ( $\mathrm{C}^{0}$ and $\mathrm{C}^{\alpha, i}$, for $\left.i=1 \ldots 4\right)$.

## B. 2 A Program to Calculate $\alpha_{\text {plan }}$

We include here a simple Fortran program for calculating the $\alpha_{i}$ 's and $\alpha_{\text {plan }}$ given the cartesian coordinates of the five carbon atoms ( $\mathrm{C}^{0}$ and $\mathrm{C}^{\alpha, i}$, for $i=1 \ldots 4$ ). This program reads in the coordinates for the central atom $\left(\mathrm{C}^{0}\right)$, followed by the coordinates for the four $\mathrm{C}^{\alpha}$ atoms. The origin of the coordinate system is then translated to $\mathrm{C}^{0}$. The geometry tensor, $\mathbf{W}$, is then calculated and its eigenvectors and eigenvalues are determined. The diagonalization routine, RSM (see Section B.2.2), orders the eigenvectors and eigenvalues such that the eigenvector corresponding to the best-fit plane (i.e. the eigenvector that minimizes $\left.d^{2}\right)$ is listed first $(k=1)$. This vector is then used with Equation B-9 to give the angles $\alpha_{i}$. The average of these four angles gives $\alpha_{\text {plan }}$. Fortran source code to calculate $\alpha_{i} ; i=1 \ldots 4$, and $\alpha_{\text {plan }}$ from the Cartesian coordinates of the atoms is given in the following section.

## B.2.1 The Main Program ALPHA_PLAN

The source code for the program ALPHA_PLAN for calculating $\alpha_{\text {plan }}$ (and related parameters) is given below. The code is also included on the CD-ROM in the inside back cover with file name 'alpha.f'.

## PROGRAM APLHA_PLAN



```
IMPLICIT DOUBLE PRECISION (A-H,K,O-Z)
DIMENSION SQSUM(4),SRSQS(4),AV ANG IN(3)
DIMENSION ANG (4,3),DOT (4,3),ANG_IN (4,3)
DIMENSION ORIG(1,3), COORD (4,3), CART (4,3)
DIMENSION W(3,3),EVAL (3),EVEC (3,3)
INTEGER*4 IWORK(3),FWORK (24),ATMASS (4)
```

C
C Universal constants

```
AMU = 1.6605402D-27
HART = 4.3597482D-18
BOLTZ = 1.380658D-23
PLANCK = 6.6260755D-34
BOHR = 0.529177249D-10
AV = 6.0221367D+23
SLGHT = 2.99792458D+10
PI = 3.141592654D0
```

C -------------------------------------------------------------------------
C DATA IN THE INPUT FILE:
C NATOM :-- NUMBER OF ALPHA ATOMS (SET TO 4)
C ORIG :-- COORDINATES OF THE ATOM TO BE AT THE ORIGIN
C COORD :-- CARTESIAN COORDINATES OF THE FOUR ALPHA ATOMS

C READING IN THE DATA
C read in molecular information on the molecule from UNIT 5
$\mathrm{NATOM}=4$
$\operatorname{READ}(5, *)$ ATMASS (I), (ORIG(1, J) , J=1, 3)
DO 100 I=1,NATOM
$\operatorname{READ}(5, *)$ ATMASS (I) , (COORD (I, J) , J=1, 3)
100 CONTINUE
CDRR Translate first atom to origin
do $150 j=1$, NATOM
do 150 i=1,3
$\operatorname{COORD}(j, i)=\operatorname{COORD}(j, i)-\operatorname{ORIG}(1, i)$

```
CDRR Output the geometry to UNIT 6
    WRITE (6,*) ' CARTESIAN CO-ORDINATES'
    WRITE (6,*) ' '
    DO 200 I=1,NATOM
        WRITE (6,1200) I,ATMASS (I) ,(COORD (I,J) ,J=1, 3)
200 CONTINUE
    WRITE (6,*) ' '
CDRR Normalize coordinates
CDRR uses dummy vectors sqsum(4) and srsqs(4)
    do 206 j=1,NATOM
        sqsum(j) = 0.0
        do 202 i=1,3
            sqsum(j) = COORD(j,i)*COORD(j,i) + sqsum(j)
            continue
        srsqs(j) = dsqre(sqsum(j))
        do 204 i=1,3
            CART(j,i) = COORD(j,i)/srsqs(j)
            continue
206 continue
CDRR For curiosity sake we determine the angles to the xy, xz and yz
CDRR planes at the input orientation.
CDRR
CDRR Find angles to planes xy (k=1),yz(k=2) and xz(k=3) in input orientation
CDRR and write them to output (UNIT 6).
CDRR
CDRR ang_in :-- angles to plane in input geometry
CDRR av_ang_in :-- average of input angles
CDRR
    do 701 k=1,3
        do 601 j=1,NATOM
            ang_in(j,k) = 360*asin(CART(j,k))/(2*PI)
601 continue
7 0 1 ~ c o n t i n u e
    do 801 j=1,NATOM
        write(6,1500) j,(ang_in(j,k),k=1,3)
8 0 1 ~ c o n t i n u e
    do 901 k=1,3
        av_ang_in(k) = 0.0
        do-901 j=1,NATOM
        av_ang_in(k) = abs(ang_in(j,k)/4) + av_ang_in(k)
9 0 1 ~ c o n t i n u e
    write(6,*) ' '
    write(6,1700) (av_ang_in(k),k=1,3)
    write(6,*) ' '
CDRR Calculate the W-matrix where W[3\times3] = CARTt[3\times4] CART[4\times3]
CDRR where CARTt is the hypothetic transpose of CART
CDRR ----------------------------------------------------
CDRR CART :-- the 3 x NATOM matrix of coords
CDRR -----------------------------------------------------------------------------------
    do 300 i=1,3
    do 300 j=1,3
        do 250 k=1,NATOM
```

```
    w(i,j) = CART(k,i)*CART(k,j) + w(i,j)
250 continue
300 continue
CDRR Find the eigenvalues and eigenvectors of the geometry tensor, W
CDRR which is a Real Symmetric Matrix (RSM)
    call RSM(3,3,W,EVAL,3,EVEC,FWORK,IWORK,0)
CDRR Write out the eigenvalues (EVAL) and eigenvectors (EVEC) of W
    write(6,1300) (eval(i),i=1,3)
    write(6,*) ' '
    do 400 i=1,3
        write(6,1400) (evec(i,j),j=1,3)
400 continue
CDRR Find angle to normals k -- evec(i,k)
    do 700 k=1,3
            do 600 j=1,NATOM
            dot (j,k) = 0.0
            do 500 i=1,3
                dot(j,k) = (evec(i,k)*CART(j,i)) + dot(j,k)
            continue
            ang(j,k) = 360*asin(dot(j,k))/(2*PI)
            continue
7 0 0 ~ c o n t i n u e ~
CDRR Write out the angles, ang(j,k), which is 3x3
CDRR to the planes defined by the norms k
        do 800 j=1,NATOM
            write(6,1500) j,(ang(j,k) ,k=1,3)
    800 continue
CDRR Average these angles (av_ang) for k=1 (the best-fit plane)
    av_ang = 0.0
    do 900 j=1,NATOM
    av_ang = abs(ang(j,1)/4) + av_ang
    900 continue
CDRR Write out av_ang for k=1 (the best-fit plane)
    write(6,*) ' '
    write(6,1600) av_ang
    write(6,*) ' '
1200 FORMAT(i4,3x,i4,4x,3f12.6)
1300 FORMAT(' eigenvalues: ',3F12.6)
1350 FORMAT(' ',3F12.6)
1400 FORMAT(' eigenvector: ',3F12.6)
1500 FORMAT(' ALPHA[i] for',i2,': ',3F12.3)
1600 FORMAT(' ALPHA[PLAN]:',F12.2)
1700 FORMAT(' Avg ANGLE: ',3F12.4)
STOP
END
```


## B.2.2 Eigenvector Routines from NETLIB

The preceding program requires a subroutine for calculating the eigenvalues and eigenvectors of a real symmetric matrix, subroutine RSM. The header is given below and the code is included on the CD-ROM in the inside back cover in the file named 'eigen.f'.

C
C REFERENCE FOR DIAGONALIZATION ROUTINE
C NETLIB@DRACU.CS.UOW.EDU.AU
subroutine rsm(nm,n,a,w,m,z,fwork,iwork,ierr)
integer $n, n m, m$,iwork ( n ), ierr
integer k1,k2,k3,k4,k5,k6,k7
double precision $a(n m, n), w(n), z(n m, m), f w o r k(1)$
subroutines from the eigensystem subroutine package (eispack)
to find all of the eigenvalues and some of the eigenvectors
of a real symmetric matrix.
on input
nm must be set to the row dimension of the two-dimensional
array parameters as declared in the calling program
dimension statement.
$n$ is the order of the matrix $a$.
a contains the real symmetric matrix.
$m$ the eigenvectors corresponding to the first $m$ eigenvalues
are to be computed.
if $m=0$ then no eigenvectors are computed.
if $m=n$ then all of the eigenvectors are computed.
on output
w contains all $n$ eigenvalues in ascending order.
z contains the orthonormal eigenvectors associated with
the first m eigenvalues.
ierr is an integer output variable set equal to an error
completion code described in the documentation for tqlrat,
imtqlv and tinvit. the normal completion code is zero.
fwork is a temporary storage array of dimension 8*n.
iwork is an integer temporary storage array of dimension $n$.
questions and comments should be directed to burton s. garbow,
mathematics and computer science div, argonne national laboratory
this version dated august 1983.

## Appendix C Computational Data

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Section C. 2 contains Gaussian archive files. These have not been included in the printed matter but are included on the CD-ROM (inside back cover) in the file 'thesis.pdf'. .

## C. 1 Energies and Enthalpy Contributions

## C.1.1 Data for Chapter 1

## C.1.1.1 Fenestranes

Table C-1. MP2(fc)/6-311+G(3df,2p)//MP2(fc)/6-31G(d) total energies (hartree) for the fenestranes in Chapter 1.

| Molecule |  | Sym. | $E$ |
| :--- | :---: | :---: | :---: |
| all-trans-[4.4.4.4]fenestrane | $(\mathbf{1 - 4 8})$ | $C_{2 \mathrm{v}}$ | -349.1539306 |
| all-cis-[4.4.4.4]fenestrane | $(\mathbf{1 - 4 9 )}$ | $D_{2 \mathrm{~d}}$ | -349.1607971 |
| trans,trans,cis,cis-[4.4.4.4]fenestrane | $(\mathbf{1 - 5 0})$ | $C_{2}$ | -349.0150907 |
| trans,cis,cis,cis-[4.4.4.4]fenestrane | $(\mathbf{1 - 5 1})$ | $C_{\mathrm{s}}$ | -349.1836319 |
| all-cis-[5.5.5.5]fenestrane | $(\mathbf{1 - 5 2})$ | $D_{2}$ | -506.2892489 |
| all-trans-[5.5.5.5]fenestrane | $(\mathbf{1 - 5 3 )}$ | $D_{2 \mathrm{~d}}$ | -506.0674567 |

## C.1.2 Data for Chapter 3

## C.1.2.1 Neutral Species

Table C-2. B3-LYP/6-31G(d) ${ }^{\text {a }}$ thermochemical data (hartree) for the neutral species in Chapter 3.

| Molecule |  | Sym. | $E$ | $Z P V E^{\text {b }}$ | $H^{298}-H^{0}$ |
| :---: | :---: | :---: | :---: | :---: | :---: |
| basic hydrocarbons |  |  |  |  |  |
| ethane |  | $D_{2 \mathrm{~d}}$ | -79.829013 | 0.0737831 | 0.0044157 |
| propane |  | $C_{2 \mathrm{v}}$ | -119.142160 | 0.1021191 | 0.0054652 |
| isobutane |  | $C_{3 v}$ | -158.456043 | 0.1297674 | 0.0066542 |
| neopentane |  | $T_{\text {d }}$ | -197.769659 | 0.1579172 | 0.0076174 |
| small strained hydrocarbons |  |  |  |  |  |
| spiropentane | (3-41) |  | -195.268152 | 0.1133145 | 0.0058481 |
| capping hydrocarbons |  |  |  |  |  |
| cyclobutane | (3-46) | $D_{2 \mathrm{~d}}$ | -157.208854 | 0.1093110 | 0.0050656 |
| bicyclo[2.2.0]hexane | (3-47) | $C_{2}$ | -234.594172 | 0.1432814 | 0.0063780 |
| twistboat-cyclohexane | (TB-3-48) | $C_{2}$ | -235.866051 | 0.1678498 | 0.0069375 |

Table C-2. (Continued) B3-LYP/6-31G(d) ${ }^{\text {a }}$ thermochemical data (hartree) for the neutral species in Chapter 3.

| Molecule |  | Sym. | $E$ | $Z P V E^{\text {b }}$ | $H^{298}-H^{0 \mathrm{~b}}$ |
| :---: | :---: | :---: | :---: | :---: | :---: |
| bicyclo[2.2.1]heptane | (3-49) | $C_{2 \mathrm{v}}$ | -273.963973 | 0.1745935 | 0.0065260 |
| cis-bicyclo[3.3.0]octane | (3-50) | $C_{2 \mathrm{v}}$ | -313.283957 | 0.2025357 | 0.0079612 |
| crown-cyclooctane (Crow | -3-51) | $C_{4 \mathrm{v}}$ | -314.484396 | 0.2245220 | 0.0092362 |
| $t b, t b$-bicyclo[3.3.1]nonane (TBTB-3-52) |  | $C_{2}$ | -352.587810 | 0.2325913 | 0.0085701 |
| hemialkaplanes |  |  |  |  |  |
| hemibihexaplane | (3-25) | $C_{2}$ | -427.284504 | 0.2174725 | 0.0080879 |
| hemihexaplane | (3-2) | $C_{2}$ | -428.541638 | 0.2423461 | 0.0084548 |
| hemibiheptaplane | (3-3) | $C_{2}$ | -466.642613 | 0.2479687 | 0.0087029 |
| hemibioctaplane | (3-26) | $C_{2}$ | -505.981218 | 0.2788840 | 0.0092102 |
| hemioctaplane | (3-1) | $C_{2 \mathrm{v}}$ | -507.194398 | 0.3020702 | 0.0102851 |
| hemibinonaplane | (3-27) | $C_{2}$ | -545.276533 | 0.3088827 | 0.0098241 |
| hemispiroalkaplanes |  |  |  |  |  |
| hemispirobutaplane | (3-28) | $C_{2 v}$ | -347.469641 | 0.1341244 | 0.0067582 |
| hemispirobihexaplane (perp) | (3-29) | $C_{2 \mathrm{v}}$ | -424.933169 | 0.1713001 | 0.0072969 |
| hemispirobihexaplane (par) | (3-30) | $C_{2}$ | -424.847680 | 0.1680346 | 0.0082826 |
| hemispirohexaplane (perp) | (3-31) | $C_{2 \mathrm{v}}$ | -426.187898 | 0.1959131 | 0.0076746 |
| hemispirohexaplane (par) | (3-32) | $C_{2 v}$ | -426.148961 | 0.1930312 | 0.0085830 |
| hemispirobiheptaplane (perp) | (3-33) | $C_{2 \mathrm{v}}$ | -464.300822 | 0.2020111 | 0.0078253 |
| hemispirobiheptaplane (par) | (3-34) | $C_{2 v}$ | -464.233349 | 0.1995533 | 0.0084594 |
| hemispirobioctaplane (perp) | (3-4) | $C_{2 v}$ | -503.635837 | 0.2307424 | 0.0088967 |
| hemispirobioctaplane (par) | (3-35) | $C_{2 v}$ | -503.591748 | 0.2299550 | 0.0091810 |
| hemispirooctaplane | (3-5) | $C_{2 v}$ | -504.827596 | 0.2529552 | 0.0100956 |
| hemispirobinonaplane (perp) | (3-6) | $C_{2 v}$ | -542.941268 | 0.2604139 | 0.0096160 |
| hemispirobinonaplane (par) | (3-36) | $C_{2 v}$ | -542.879539 | 0.2604497 | 0.0098266 |
| tetramethylhemispirooctaplane | (3-24) | $C_{2 v}$ | -662.098919 | 0.3617009 | 0.0167526 |

[^79]Table C-3. MP2(fc)/6-311+G(2d,p)//MP2(fc)/6-31G(d) thermochemical data (hartree) for the neutral species in Chapter 3.

| Molecule |  | Sym. | $E$ | $Z P V E^{a}$ | $H^{298}-H^{0} \mathrm{a}$ |
| :---: | :---: | :---: | :---: | :---: | :---: |
| small molecules |  |  |  |  |  |
| $\mathrm{CH}_{4}$ |  | $T_{\text {d }}$ | -40.388143 | 0.0448131 | 0.0038004 |
| $\mathrm{NH}_{3}$ |  | $C_{3 \mathrm{v}}$ | -56.426926 | 0.0341139 | 0.0037976 |
| $\mathrm{H}_{2} \mathrm{O}$ |  | $C_{2 v}$ | -76.289814 | 0.0207170 | 0.0037783 |
| basic hydrocarbons |  |  |  |  |  |
| ethane |  | $D_{2 \mathrm{~d}}$ | -79.586293 | 0.0746137 | 0.0043387 |
| propane |  | $C_{2 \mathrm{v}}$ | -118.788770 | 0.1032196 | 0.0053211 |
| isobutane |  | $C_{3 v}$ | -157.994623 | 0.1311487 | 0.0063946 |
| neopentane |  | $T_{\text {d }}$ | -197.202810 | 0.1588111 | 0.0075510 |
| small strained hydrocarbons |  |  |  |  |  |
| cyclopropane | (3-39) | $D_{3 \mathrm{~h}}$ | -117.556366 | 0.0811014 | 0.0042035 |
| tetrahedrane | (3-40) | $T_{\text {d }}$ | -154.218426 | 0.0583614 | 0.0047255 |
| pyramidane | (3-15) | $C_{4 \mathrm{v}}$ | -192.231067 | 0.0654932 | 0.0051149 |
| spiropentane | (3-41) | $D_{2 \mathrm{~d}}$ | -194.725260 | 0.1144318 | 0.0056528 |
| [1.1.1]propellane | (3-42) | $D_{3}$ | -193.494912 | 0.0925433 | 0.0047095 |
| prismane | (3-43) | $D_{3 \mathrm{~h}}$ | -231.433482 | 0.0957157 | 0.0048784 |
| cubane | (3-44) | $O_{\text {h }}$ | -308.634567 | 0.1303275 | 0.0053988 |
| tetrakis(tert-butyl)tetrahedrane | (3-45) | T | -781.547815 | 0.5073666 | 0.0258508 |
| other alicyclic hydrocarbons |  |  |  |  |  |
| 3-21 |  | $C_{2 v}$ | -270.632696 | 0.1241388 | 0.0065134 |
| 3-22 |  | $C_{2 v}$ | -308.640978 | 0.1296209 | 0.0065911 |
| 3-23 |  | $C_{2 v}$ | -347.858521 | 0.1594824 | 0.0076312 |
| chair-cyclohexane | (C-3-48) | $D_{3 \mathrm{~d}}$ | -235.212723 | 0.1692813 | 0.0064070 |
| boat,chair-cyclooctane | (BC-3-51) | $C_{2 \mathrm{v}}$ | -313.602824 | 0.2269198 | 0.0085873 |
| ch,ch-bicyclo[3.3.1]nonane | (CC-3-52) |  | -351.634296 | 0.2342256 | 0.0081440 |
|  |  | apping | hydrocarbons |  |  |
| cyclobutane | (3-46) | $D_{2 \mathrm{~d}}$ | -156.762947 | 0.1103487 | 0.0048595 |
| bicyclo[2.2.0]hexane | (3-47) | $C_{2}$ | -233.943322 | 0.1442915 | 0.0060266 |
| twistboat-cyclohexane | (TB-3-48) | $C_{2}$ | -235.202775 | 0.1692357 | 0.0066539 |
| bicyclo[2.2.1]heptane | (3-49) | $C_{2 v}$ | -273.214927 | 0.1755026 | 0.0063557 |

Table C-3. (Continued) MP2(fc)/6-311+G(2d,p)//MP2(fc)/6-31G(d) thermochemical data (hartree) for the neutral species in Chapter 3.

| Molecule |  | Sym. | $E$ | $Z P V E^{a}$ | $H^{298}-H^{0}$ a |
| :---: | :---: | :---: | :---: | :---: | :---: |
| cis-bicyclo[3.3.0]octane | (3-50) | $C_{2 v}$ | -312.422527 | 0.2039460 | 0.0076471 |
| crown-cyclooctane (Crow | n-3-51) | $C_{4 \mathrm{v}}$ | -313.598858 | 0.2258430 | 0.0091908 |
| $t b, t b$-bicyclo[3.3.1]nonane (TBT | -3-52) | $C_{2}$ | -351.621005 | 0.2342693 | 0.0081731 |
| bridged spiropentanes |  |  |  |  |  |
| [3.3.3]fenestrane (pyramidane) | (3-15) | $C_{1}$ | -193.431958 | 0.0903832 | 0.0051984 |
| [3.4.3]fenestrane | (3-53) | $C_{2}$ | -232.667793 | 0.1196215 | 0.0058130 |
| [3.5.3]fenestrane | (3-12) | $C_{2}$ | -271.926235 | 0.1496244 | 0.0064921 |
| tetracyclo[3.3.1. $\left.0^{2,4} .0^{2,8}\right]$ nonane | (3-54) | $C_{1}$ | -349.128388 | 0.1858377 | 0.0072737 |
| hemialkaplanes |  |  |  |  |  |
| hemihexaplane | (3-2) | $C_{2}$ | -427.411788 | 0.2435267 | 0.0078861 |
| hemibiheptaplane | (3-3) | $C_{2}$ | -465.427336 | 0.2490389 | 0.0080870 |
| hemioctaplane | (3-1) | $C_{2 v}$ | -505.845710 | 0.3034066 | 0.0098056 |
| hemispiroalkaplanes |  |  |  |  |  |
| hemispirobioctaplane | (3-4) | $C_{2 v}$ | -502.341667 | 0.2318886 | 0.0083333 |
| hemispirooctaplane | (3-5) | $C_{2 v}$ | -503.508547 | 0.2544729 | 0.0094998 |
| hemispirobinonaplane | (3-6) | $C_{2 v}$ | -541.538657 | 0.2618384 | 0.0090060 |
| tetramethylhemispirooctaplane | (3-24) | $C_{2 v}$ | -660.363420 | 0.3642070 | 0.0157620 |

${ }^{\text {a }}$ The thermochemical corrections are calculated from the MP2(fc)/6-31G(d) frequencies and scaled by $0.9670(Z P V E)$ or $1.0211\left(H^{298}-H^{0}\right)$. We have used a set of five spherical $d$-functions rather than the usual six Cartesian functions for the $6-31 \mathrm{G}(\mathrm{d})$ basis set.

## C.1.2.2 Protonated Species

Table C-4. MP2(fc)/6-311+G(2d,p)//MP2(fc)/6-31G(d) thermochemical data (hartree) for the protonated species in Chapter 3.

|  | Molecule | Sym. | $E$ | $Z P V E^{a}$ |
| :--- | :---: | :---: | :---: | :---: |
| $\mathrm{CH}_{5}{ }^{+}$ | small molecules | $H^{298}-H^{0 \mathrm{a}}$ |  |  |
| $\mathrm{NH}_{4}{ }^{+}$ | $C_{2 \mathrm{v}}$ | -40.592328 | 0.0474515 | 0.0057386 |
| $\mathrm{OH}_{3}{ }^{+}$ | $T_{\mathrm{d}}$ | -56.763779 | 0.0488557 | 0.0037897 |
|  | $C_{3 \mathrm{v}}$ | -76.561764 | 0.0333690 | 0.0038191 |

Table C-4. (Continued) MP2(fc)/6-311+G(2d,p)//MP2(fc)/6-31G(d) thermochemical data (hartree) for the protonated species in Chapter 3.

| Molecule | Sym. | $E$ | $Z P V E^{a}$ | $H^{298}-H^{0}$ a |
| :---: | :---: | :---: | :---: | :---: |
| small strained hydrocarbons |  |  |  |  |
| $(\mathrm{CH})_{5}^{+}\left(\right.$protonated pyramidane) (3-15-H ${ }^{+}$) | $C_{4 \mathrm{v}}$ | -192.608907 | 0.0786334 | 0.0048061 |
| other alicyclic hydrocarbons |  |  |  |  |
| 3-21-H ${ }^{+}$ | $C_{2 \mathrm{v}}$ | -271.060887 | 0.1385916 | 0.0061131 |
| 3-22-H ${ }^{+}$ | $C_{2 \mathrm{v}}$ | -309.070147 | 0.1440256 | 0.0062034 |
| 3-23-H ${ }^{+}$ | $C_{2 v}$ | -348.289818 | 0.1739992 | 0.0072285 |
| hemialkaplanes |  |  |  |  |
| protonated hemioctaplane (3-1-H ${ }^{+}$) | $C_{4 \mathrm{v}}$ | -506.282263 | 0.3155558 | 0.0105022 |
| hemispiroalkaplanes |  |  |  |  |
| protonated hemispirooctaplane (3-5-H ${ }^{+}$) | $C_{2 \mathrm{v}}$ | -502.800776 | 0.2472377 | 0.0080142 |
| protonated hemispirobioctaplane (3-4-H ${ }^{+}$) | $C_{2 v}$ | -503.969100 | 0.2701497 | 0.0091580 |
| protonated hemispirobinonaplane (3-6-H ${ }^{+}$) | $C_{2 v}$ | -542.000536 | 0.2773413 | 0.0086999 |
| protonated <br> tetramethylhemispirooctaplane (3-24- $\mathbf{H}^{+}$) | $C_{2 v}$ | -660.830685 | 0.3798746 | 0.0153697 |

${ }^{\text {a }}$ The thermochemical corrections are calculated from the MP2(fc)/6-31G(d) frequencies and scaled by $0.9670(Z P V E)$ or $1.0211\left(H^{298}-H^{0}\right)$. We have used a set of five spherical $d$-functions rather than the usual six Cartesian functions for the $6-31 \mathrm{G}(\mathrm{d})$ basis set.

## C.1.3 Data for Chapter 4

## C.1.3.1 Methane and Methane Fragments

Table C-5. Total energies (hartree) for the three lowest states of methane for geometry optimized methods.

|  | ground state | triplet $^{\mathrm{a}}$ | open singlet $^{\mathrm{a}}$ | closed-shell singlet |  |
| :--- | :---: | :---: | :---: | :---: | :---: |
| Method | $T_{\mathrm{d}}$ | $D_{4 \mathrm{~h}}$ | $D_{4 \mathrm{~h}}$ | $D_{4 \mathrm{~h}}$ | $C_{2 \mathrm{v}}$ |
| UB3-LYP |  |  |  |  |  |
| $6-31 \mathrm{G}(\mathrm{d})$ | -40.518389 | -40.266909 | -40.270757 | -40.278591 | -40.287522 |
| $6-311+\mathrm{G}(2 \mathrm{~d}, \mathrm{p})$ | -40.534896 | -40.288373 | -40.291301 | -40.320689 | -40.334869 |
| $6-311+\mathrm{G}(3 \mathrm{df}, 2 \mathrm{p})$ | -40.536788 | -40.290293 | -40.293090 | -40.325124 | -40.339871 |

Table C-5. (Continued) Total energies (hartree) for the three lowest states of methane for geometry optimized methods.

|  | ground state | triplet $^{\mathrm{a}}$ | open singlet $^{\mathrm{a}}$ | closed-shell singlet |  |
| :--- | :---: | :---: | :---: | :---: | :---: |
| Method | $T_{\mathrm{d}}$ | $D_{4 \mathrm{~h}}$ | $D_{4 \mathrm{~h}}$ | $D_{4 \mathrm{~h}}$ | $C_{2 \mathrm{v}}$ |
| UMP2(full) |  |  |  |  |  |
| 6-31G(d) | -40.337043 | -40.067534 | -40.072476 | -40.082393 | -40.096750 |
| 6-311+G(2d,p) | -40.408195 | -40.144985 | -40.145656 | -40.186385 | -40.203813 |
| 6-311+G(3df,2p) | -40.427561 | -40.164906 | -40.164481 | -40.211216 | -40.228583 |

${ }^{a}$ A UHF reference wavefunction was used for single-determinant calculations on the open-shell systems.

Table C-6. Total energies (hartree) for the three lowest states of methane at $\mathrm{UCCSD}(\mathrm{T})($ full $) / 6-311+\mathrm{G}(3 \mathrm{df}, 2 \mathrm{p})$ optimized geometries.

| Species | Method |  |
| :--- | :---: | :---: |
|  | UCCSD(T)(fc)/AVQZ | MRCI+Q/AV5Z |
| $\mathrm{CH}_{4}$ closed-shell singlet $\left(T_{\mathrm{d}}\right)$ | -40.451728 | -40.455101 |
| ${ }^{3} \mathrm{CH}_{4}$ triplet $\left(D_{4 \mathrm{~h}}\right)$ | $-40.193364^{\mathrm{a}}$ | -40.196568 |
| ${ }^{1} \mathrm{CH}_{4}$ open-shell singlet $\left(D_{4 \mathrm{~h}}\right)$ | $-40.194507^{\mathrm{b}}$ | -40.198851 |
| $\mathrm{CH}_{4}$ closed-shell singlet $\left(D_{4 \mathrm{~h}}\right)$ | -40.233333 | -40.236862 |
| $\mathrm{CH}_{4}$ closed-shell singlet $\left(C_{2 \mathrm{v}}\right)$ | -40.252782 | -40.256244 |
| $\mathrm{CH}_{3}{ }^{\circ}$ | - | -39.776614 |
| $\mathrm{H}^{\circ}$ | - | -0.499995 |
| $\mathrm{H}_{2}$ | - | -1.174252 |
| ${ }^{3} \mathrm{CH}_{2}$ triplet | - | -39.090696 |
| ${ }^{1} \mathrm{CH}_{2}$ closed-shell singlet | - | -39.076960 |

${ }^{\text {a }}$ Calculated with Molpro's URCCSD(T) method. ${ }^{\text {b }}$ Calculated with Gaussian 98's UCCSD (T) method.

## C.1.3.2 Neopentane and Spiropentane

Table C-7. UB3-LYP total energies (hartree) for neopentane species in Chapter 4.

|  |  | Basis Set |  |  |  |
| :--- | :--- | :---: | :---: | :---: | :---: |
| Species | $6-31 \mathrm{G}(\mathrm{d})^{\mathrm{a}}$ | $6-311+\mathrm{G}(2 \mathrm{~d}, \mathrm{p})$ | $6-311+\mathrm{G}(3 \mathrm{df}, 2 \mathrm{p})$ |  |  |
| ground state <br> tetrahedral | $T_{\mathrm{d}}$ | -197.773086 | -197.835553 | -197.843552 |  |
|  | $\mathbf{A}\left(C_{4 \mathrm{~h}}\right)$ | -197.437283 | -197.508729 | -197.518008 |  |
| 'planar' | $\mathbf{B}\left(D_{2 \mathrm{~h}}\right)$ | -197.438322 | -197.508443 | -197.517564 |  |
| singlet | $\mathbf{C}\left(C_{2 \mathrm{v}}\right)$ | -197.437818 | -197.508636 | -197.517857 |  |
|  | $\mathbf{D}\left(\mathrm{C}_{\mathrm{s}}\right)$ | -197.438250 | -197.508964 | -197.518174 |  |
| 'planar' | $\mathbf{A}\left(C_{4 \mathrm{~h}}\right)$ | -197.481783 | -197.547513 | -197.555408 |  |
| triplet |  |  |  |  |  |

${ }^{\text {a }}$ We have used a set of five spherical $d$-functions rather than the usual six Cartesian functions for the $6-31 \mathrm{G}(\mathrm{d})$ basis set.

Table C-8. UMP2(full) total energies (hartree) for neopentane species in Chapter 4. ${ }^{\text {a,b }}$

|  |  | Basis Set |  |  |  |  |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| Species | $6-31 \mathrm{G}(\mathrm{d})^{\mathrm{b}}$ | $6-311+\mathrm{G}(2 \mathrm{~d}, \mathrm{p})$ <br> $(\mathrm{red})$ | $6-311+\mathrm{G}(2 \mathrm{~d}, \mathrm{p})$ | $6-311+\mathrm{G}(3 \mathrm{df}, 2 \mathrm{p})$ |  |  |
| ground state <br> tetrahedral | $T_{\mathrm{d}}$ | -197.023256 | -197.167636 | -197.304545 | -197.396472 |  |
|  | $\mathbf{A}\left(C_{4 \mathrm{~h}}\right)$ | -196.670036 | -196.830749 | -196.973248 | -197.066299 |  |
| 'planar' | $\mathbf{B}\left(D_{2 \mathrm{~h}}\right)$ | -196.668962 | -196.827791 | -196.972244 | -197.065430 |  |
| singlet | $\mathbf{C}\left(C_{2 \mathrm{v}}\right)$ | -196.669439 | -196.829105 | -196.972446 | -197.065577 |  |
|  | $\mathbf{D}\left(\mathrm{C}_{\mathrm{s}}\right)$ | -196.669978 | -196.828320 | -196.972946 | -197.066079 |  |
| 'planar' <br> triplet | $\mathbf{A}\left(C_{4 \mathrm{~h}}\right)$ | -196.704813 | -196.856152 | -196.997804 | -197.087295 |  |

${ }^{\text {a }}$ Calculated at the MP2(full)/6-31G(d) optimized geometries. ${ }^{\mathrm{b}}$ The usual set of six Cartesian $d$-functions were used for the $6-31 \mathrm{G}(\mathrm{d})$ basis set. ${ }^{\mathrm{c}}$ Our reduced $6-311+\mathrm{G}(2 \mathrm{~d}, \mathrm{p})($ red $)$ basis set is detailed in Section 4.2 on page 145 .

Table C-9. UCCSD(T)(fc) total energies (hartree) for neopentane species in Chapter 4. ${ }^{\text {a }}$

|  |  | Basis Set |  |
| :--- | :--- | :--- | :--- |
| Species | $6-311+\mathrm{G}(2 \mathrm{~d}, \mathrm{p})$ | $6-311+\mathrm{G}(3 \mathrm{df}, 2 \mathrm{p})$ |  |
| ground state <br> tetrahedral | $T_{\mathrm{d}}$ | -197.299463 | -197.384256 |
|  | $\mathbf{A}\left(C_{4 \mathrm{~h}}\right)$ | -196.964349 | -197.049820 |
| 'planar, | $\mathbf{B}\left(D_{2 \mathrm{~h}}\right)$ | -196.963128 | -197.048781 |
| singlet | $\mathbf{C}\left(C_{2 \mathrm{v}}\right)$ | -196.963846 | -197.049429 |
|  | $\mathbf{D}\left(\mathrm{C}_{\mathrm{s}}\right)$ | -196.964139 | -197.049739 |
| 'planar' <br> triplet | $\mathbf{A}\left(C_{4 \mathrm{~h}}\right)$ | -197.001927 | -197.084553 |

${ }^{\text {a }}$ Calculated at MP2(full)/6-311+G(2d,p) optimized geometries.

Table C-10. Total energies (hartree) for spiropentane species in Chapter 4.

| Method | Spiropentane Species |  |  |
| :--- | :---: | :---: | :---: |
|  | ground state <br> $D_{2 \mathrm{~d}}$ | 'planar' singlet <br> $D_{2 \mathrm{~h}}$ | 'planar' triplet <br> $\left(D_{2 \mathrm{~h}}\right)$ |
| UB3-LYP/6-31G(d) | -195.268150 | -195.103933 | -195.084428 |
| UB3-LYP/6-311+G(2d,p) | -195.329146 | -195.168617 | -195.147260 |
| UB3-LYP/6-311+G(3df,2p) | -195.339563 | -195.179784 | -195.156981 |
| UMP2(full)/6-31G(d) |  |  |  |
| UMP2(full)/6-311+G(2d,p)(red) |  |  |  |
| UMP2(full)/6-311+G(2d,p) | -194.729566 | -194.565534 | - |
| UMP2(full)/6-311+G(3df,2p) | -194.827273 | -194.663435 | -194.629267 |
| UCCSD(T)(fc)/6-311+G(2d,p) | -194.922920 | -194.760459 | -194.723242 |
| UCCSD(T)(fc)/6-311+G(3df,2p) | -194.803082 | -194.634231 | -194.611250 |
| UCCSD(T)(fc)/AVTZ ${ }^{\text {d }}$ | -194.890172 | -194.722586 | -194.697289 |

[^80]
## C.1.3.3 Alkaplanes

Table C-11. B3-LYP/6-311+G(2d,p)//B3-LYP/6-31G(d) total energies (hartree) for 'planar' and equilibrium structures for all alkaplanes in Chapter 4.

| Molecule | Sym. $^{\text {a }}$ |  |  |  |
| :--- | :--- | :--- | :--- | :--- |
|  | alkaplanes |  |  |  |
| bihexaplane (equilibrium) | $E$ ('planar') |  |  |  |
| hexaplane | $\mathbf{4 - 3 0}$ | $D_{2}$ | -656.988167 | -656.958204 |
| biheptaplane | $\mathbf{4 - 3 1}$ | $D_{2}$ | -659.486331 | -659.464026 |
| heptaplane | $\mathbf{4 - 3 2}$ | $D_{2}$ | -735.711317 | -735.690024 |
| bioctaplane | $\mathbf{4 - 3 3}$ | $C_{2}$ | -738.204167 | -738.173865 |
| octaplane (A-type) | $\mathbf{4 - 3 4}$ | $D_{2}$ | -814.370074 | -814.317680 |
| octaplane (B-type) | $\mathbf{4 - 2 7}$ | $S_{4}$ | -816.890816 | -816.863205 |
| binonaplane | $\mathbf{4 - 3 5}$ | $D_{2}$ | -816.784278 | -816.758512 |
|  | $\mathbf{4 - 3 6}$ | $D_{2}$ | -892.996246 | -892.957372 |
| spiro[2.2]hexaplane | spiroalkaplanes |  |  |  |
| spiro[2.2]biheptaplane | $\mathbf{4 - 3 9}$ | $D_{2}$ | -657.066828 | -657.059621 |
| spiro[2.2]heptaplane | $\mathbf{4 - 4 0}$ | $D_{2}$ | -733.258374 | -733.252249 |
| spiro[2.2]heptaplane | $\mathbf{4 - 4 1}$ | $C_{2}$ | -735.830186 | -735.822979 |
| spiro[2.2]bioctaplane | $\mathbf{4 - 4 2}$ | $C_{2}$ | -735.866041 | -735.858935 |
| spiro[2.2]octaplane | $\mathbf{4 - 4 3}$ | $D_{2}$ | -812.171956 | -812.163696 |
| spiro[2.2]binonaplane | $\mathbf{4 - 2 8}$ | $D_{2}$ | -814.630983 | -814.625253 |
|  | $\mathbf{4 - 4 4}$ | $D_{2}$ | -890.847667 | -890.843203 |
| dimethanospiro[2.2]bioctaplane | $\mathbf{4 - 4 7}$ | $D_{2}$ | -888.380905 | -888.378965 |
| dimethanospiro[2.2]octaplane | $\mathbf{4 - 2 9}$ | $D_{2}$ | -890.780084 | -890.779850 |
| dimethanospiro[2.2]binonaplane | $\mathbf{4 - 4 8}$ | $D_{2}$ | -967.046504 | -967.046420 |

${ }^{a}$ The symmetry of the equilibrium structure.

Table C-12. MP2(fc)/6-311+G(2d,p)//HF/6-31G(d) total energies (hartree) for 'planar' and equilibrium structures for the parent alkaplanes 4-27 and 4-30-4-36.

| Molecule | Sym. $^{\text {a }}$ | $E$ (equilibrium) | $E$ ('planar') |  |
| :--- | :---: | :---: | :---: | :---: |
| bihexaplane | $\mathbf{4 - 3 0}$ | $D_{2}$ | -655.166506 | -655.142405 |
| hexaplane | $\mathbf{4 - 3 1}$ | $D_{2}$ | -657.633489 | -657.619291 |
| biheptaplane | $\mathbf{4 - 3 2}$ | $D_{2}$ | -733.669617 | -733.632135 |
| heptaplane | $\mathbf{4 - 3 3}$ | $C_{2}$ | -736.112272 | -736.084975 |

Table C-12. (Continued) MP2(fc)/6-311+G(2d,p)//HF/6-31G(d) total energies (hartree) for 'planar' and equilibrium structures for the parent alkaplanes 4-27 and 4-

| Molecule | Sym. $^{\text {a }}$ | $E$ (equilibrium) | $E$ ('planar') |  |
| :--- | :---: | :---: | :---: | :--- |
| bioctaplane | $\mathbf{4 - 3 4}$ | $D_{2}$ | -812.094690 | -812.043090 |
| octaplane (A-type) | $\mathbf{4 - 2 7}$ | $S_{4}$ | -814.561826 | -814.539772 |
| octaplane (B-type) | $\mathbf{4 - 3 5}$ | $D_{2}$ | -814.446853 | -814.424128 |
| binonaplane | $\mathbf{4 - 3 6}$ | $D_{2}$ | -890.481374 | -890.444027 |

${ }^{a}$ The symmetry of the equilibrium structure.

Table C-13. $\operatorname{MP2}(\mathrm{fc}) / 6-311+\mathrm{G}(2 \mathrm{~d}, \mathrm{p}) / / \mathrm{MP} 2(\mathrm{fc}) / 6-311+\mathrm{G}(2 \mathrm{~d}, \mathrm{p})(\mathrm{red})^{\mathrm{a}}$ total energies (hartree) for 'planar' and equilibrium structures for all alkaplanes in Chapter 4.

| Molecule |  | Sym. ${ }^{\text {b }}$ | $E$ (equilibrium) | $E$ ('planar') |
| :---: | :---: | :---: | :---: | :---: |
| alkaplanes |  |  |  |  |
| hexaplane | 4-31 | $D_{2}$ | -657.638609 | -657.622786 |
| heptaplane | 4-33 | $C_{2}$ | -736.116148 | -736.090370 |
| octaplane (A-type) | 4-27 | $S_{4}$ | -814.565397 | -814.543078 |
| spiroalkaplanes |  |  |  |  |
| spiro[2.2]hexaplane | 4-39 | $D_{2}$ | -655.230611 | -655.227177 |
| spiro[2.2]biheptaplane | 4-40 | $D_{2}$ | -731.237233 | -731.235430 |
| spiro[2.2]heptaplane | 4-41 | $C_{2}$ | -733.761328 | -733.756766 |
| spiro[2.2]heptaplane | 4-42 | $C_{2}$ | -733.813880 | -733.808412 |
| spiro[2.2]bioctaplane | 4-43 | $D_{2}$ | -809.939577 | -809.934659 |
| spiro[2.2]octaplane | 4-28 | $D_{2}$ | -812.333476 | -812.330676 |
| spiro[2.2]binonaplane | 4-44 | $D_{2}$ | -888.374420 | -888.372757 |
| dimethanospiroalkaplanes |  |  |  |  |
| dimethanospiro[2.2]bioctaplane | 4-47 | $D_{2}$ | -885.966682 | -885.966520 |
| dimethanospiro[2.2]octaplane | 4-29 | $D_{2 \mathrm{~h}}$ | -888.311809 | $-^{\text {c }}$ |
| dimethanospiro[2.2]binonaplane | 4-48 | $D_{2 \mathrm{~h}}$ | -964.395619 | - ${ }^{\text {c }}$ |

${ }^{\text {a }}$ Our reduced $6-311+G(2 \mathrm{~d}, \mathrm{p})($ red $)$ basis set is detailed in Section 4.2 on page $145 .{ }^{\mathrm{b}}$ The symmetry of the equilibrium structure. ${ }^{\text {c }}$ Equilibrium and 'planar' structures are identical.

Table C-14. Scaled B3-LYP/6-31G(d) ${ }^{\text {a }}$ thermochemical corrections (hartree) for the equilibrium structures for all alkaplanes in Chapter 4.

| Molecule |  | Sym. ${ }^{\text {b }}$ | ZPVE ${ }^{\text {c }}$ | $H^{298}-H^{0 \mathrm{c}}$ |
| :---: | :---: | :---: | :---: | :---: |
| alkaplanes |  |  |  |  |
| bihexaplane | 4-30 | $D_{2}$ | 0.273253 | 0.009986 |
| hexaplane | 4-31 | $D_{2}$ | 0.320226 | 0.010984 |
| biheptaplane | 4-32 | $D_{2}$ | 0.332530 | 0.011366 |
| heptaplane | 4-33 | $C_{2}$ | 0.380107 | 0.013026 |
| bioctaplane | 4-34 | $D_{2}$ | 0.394960 | 0.013016 |
| octaplane (A-type) | 4-27 | $S_{4}$ | 0.438906 | 0.015270 |
| octaplane (B-type) | 4-35 | $D_{2}$ | 0.441490 | 0.014260 |
| binonaplane | 4-36 | $D_{2}$ | 0.454232 | 0.014556 |
| spiroalkaplanes |  |  |  |  |
| spiro[2.2]hexaplane | 4-39 | $D_{2}$ | 0.272164 | 0.010985 |
| spiro[2.2]biheptaplane | 4-40 | $D_{2}$ | 0.285437 | 0.010890 |
| spiro[2.2]heptaplane | 4-41 | $C_{2}$ | 0.332310 | 0.012522 |
| spiro[2.2]heptaplane | 4-42 | $C_{2}$ | 0.333545 | 0.011961 |
| spiro[2.2]bioctaplane | 4-43 | $D_{2}$ | 0.349642 | 0.011445 |
| spiro[2.2]octaplane | 4-28 | $D_{2}$ | 0.393353 | 0.014015 |
| spiro[2.2]binonaplane | 4-44 | $D_{2}$ | 0.409224 | 0.012918 |
| dimethanospiroalkaplanes |  |  |  |  |
| dimethanospiro[2.2]bioctaplane | 4-47 | $D_{2}$ | 0.362299 | 0.011508 |
| dimethanospiro[2.2]octaplane | 4-29 | $D_{2}$ | 0.406474 | 0.013732 |
| dimethanospiro[2.2]binonaplane | 4-48 | $D_{2}$ | 0.420517 | 0.013492 |

${ }^{\text {a }}$ We have used a set of five spherical $d$-functions rather than the usual six Cartesian functions for the $6-31 \mathrm{G}(\mathrm{d})$ basis set. ${ }^{\mathrm{b}}$ The symmetry of the equilibrium structure. ${ }^{\mathrm{c}}$ The thermochemical corrections are calculated from the B3-LYP/6-31G(d) frequencies and scaled by 0.9806 (ZPVE) or 0.9989 $\left(H^{298}-H^{0}\right)$.

## C.1.3.4 Other Neutral Species

Table C-15. MP2(fc)/6-311+G(2d,p)//MP2(fc)/6-31G(d) total energies (hartree) and scaled ${ }^{\text {a }}$ B3-LYP/6$31 \mathrm{G}(\mathrm{d})^{\mathrm{b}}$ thermochemical corrections (hartree) for neutral species other than the alkaplanes in Chapter 4.

| Molecule |  | Sym. ${ }^{\text {c }}$ | $E$ | $Z P V E^{\text {a }}$ | $H^{298}-H^{0} \mathrm{a}$ |
| :---: | :---: | :---: | :---: | :---: | :---: |
| small molecules |  |  |  |  |  |
| ${ }^{3} \mathrm{CH}_{2}$ |  | $C_{2 \mathrm{v}}$ | -39.040266 | 0.017088 | 0.003801 |
| $\mathrm{CH}_{4}$ |  | $T_{\text {d }}$ | -40.388143 | 0.044352 | 0.003808 |
| $\mathrm{NH}_{3}$ |  | $C_{3 \mathrm{v}}$ | -56.426926 | 0.033876 | 0.003803 |
| $\mathrm{H}_{2} \mathrm{O}$ |  | $C_{2 \mathrm{v}}$ | -76.289814 | 0.020725 | 0.003779 |
| unstrained hydrocarbons |  |  |  |  |  |
| ethane |  | $D_{2 \mathrm{~d}}$ | -79.586293 | 0.073783 | 0.004416 |
| propane |  | $C_{2 \mathrm{v}}$ | $-118.788770$ | 0.102119 | 0.005465 |
| isobutane |  | $C_{3 \mathrm{v}}$ | $-157.994623$ | 0.129767 | 0.006654 |
| neopentane |  | $T_{\text {d }}$ | -197.202810 | 0.157917 | 0.007617 |
| simple alicyclic hydrocarbons |  |  |  |  |  |
| cyclopropane | $4-49$ | $D_{3 \mathrm{~h}}$ | -117.556366 | 0.080183 | 0.004303 |
| cyclobutane | 4-50 | $C_{2 \mathrm{v}}$ | -156.762947 | 0.109311 | 0.005066 |
| cyclopentane | 4-51 | $C_{1}$ | -195.999154 | 0.138683 | 0.006179 |
| cyclohexane (chair) | C-4-52 | $D_{3 \mathrm{~d}}$ | -235.212723 | 0.167818 | 0.006666 |
| cyclooctane (boat-chair) | BC-4-53 | $C_{\text {s }}$ | -313.602824 | 0.225190 | 0.008921 |
| bicyclo[3.3.1]nonane (chair-chair) | CC-4-54 | $C_{2 \mathrm{v}}$ | -351.634296 | 0.232804 | 0.008415 |
| strained hydrocarbons |  |  |  |  |  |
| tetrahedrane | 4-55 | $T_{\text {d }}$ | -154.218426 | 0.058785 | 0.004737 |
| pyramidane | 4-56 | $C_{4 \mathrm{v}}$ | -192.231067 | 0.065885 | 0.005165 |
| [1.1.1]propellane | 4-57 | $D_{3}$ | -193.494912 | 0.092133 | 0.004879 |
| spiropentane | 4-58 | $D_{2 \mathrm{~d}}$ | -194.725260 | 0.113315 | 0.005848 |
| prismane | 4-59 | $D_{3 \mathrm{~h}}$ | -231.433482 | 0.095916 | 0.004981 |
| cubane | 4-60 | $O_{\text {h }}$ | -308.634567 | 0.131729 | 0.005451 |
| tetramethyltetrahedrane | 4-61 | $T_{\text {d }}$ | -311.056997 | 0.171424 | 0.010938 |
| tetra-tert-butyltetrahedrane | 4-62 | $T$ | -781.547815 | 0.504021 | 0.027116 |
| pagodane | 4-63 | $D_{2 \mathrm{~h}}$ | -772.154733 | 0.347007 | 0.010838 |
| dodecahedrane | 4-64 | $I_{\mathrm{h}}$ | -772.190079 | 0.353027 | 0.009356 |

Table C-15. (Continued) MP2(fc)/6-311+G(2d,p)//MP2(fc)/6-31G(d) total energies (hartree) and scaled ${ }^{\text {a }}$ B3-LYP/6-31G(d) ${ }^{\text {b }}$ thermochemical corrections (hartree) for neutral species other than the alkaplanes in

| Molecule |  | Sym. ${ }^{\text {c }}$ | $E$ | $Z P V E^{\text {a }}$ | $H^{298}-H^{0}$ a |
| :---: | :---: | :---: | :---: | :---: | :---: |
| capping hydrocarbons |  |  |  |  |  |
| bicyclo[2.2.0]hexane | 4-65 | $C_{2}$ | -233.943322 | 0.143281 | 0.006378 |
| cyclohexane (twistboat) | TB-4-52 | $C_{2}$ | -235.202775 | 0.167850 | 0.006938 |
| cycloheptane | 4-66 | $C_{1}$ | -274.405586 | 0.196323 | 0.007959 |
| norbornane | 4-67 | $C_{2 \mathrm{v}}$ | -273.214927 | 0.174592 | 0.006526 |
| cis-bicyclo[3.3.0]octane | 4-68 | $C_{2 v}$ | -312.422527 | 0.202536 | 0.007961 |
| cyclooctane (crown) | Cr-4-53 | $C_{4 \mathrm{v}}$ | -313.598858 | 0.224522 | 0.009236 |
| bicyclo[3.3.1]nonane (twistboat-twistboat) | TBTB-4-54 | $C_{2}$ | -351.621005 | 0.232591 | 0.008570 |
| bridged spiropentanes |  |  |  |  |  |
| [3.3.3]fenestrane | 4-26 | $C_{1}$ | -193.431958 | 0.089728 | 0.005523 |
| [3.4.3]fenestrane | 4-25 | $C_{2}$ | -232.667793 | 0.119016 | 0.005955 |
| [3.5.3]fenestrane | 4-45 | $C_{2}$ | -271.926235 | 0.148586 | 0.006762 |
| tetracyclo- <br> [3.3.1. $0^{2,4} .0^{2,8}$ ]nonane | 4-46 | $C_{1}$ | -349.128388 | 0.184730 | 0.007566 |
| fenestranes |  |  |  |  |  |
| trans,cis,cis,cis- <br> [4.4.4.4]fenestrane | $C_{\text {s }}$-4-18 | $C_{\text {s }}$ | -349.034915 | 0.182298 | 0.007616 |
| all-cis- <br> [4.4.4.4]fenestrane | $D_{2 \mathrm{~d}}-4-18$ | $D_{2 \mathrm{~d}}$ | -349.012842 | 0.180679 | 0.008372 |
| all-trans- <br> [4.4.4.4]fenestrane | $C_{2 v}-4-18$ | $C_{2 \mathrm{v}}$ | -349.007042 | 0.180883 | 0.008538 |
| trans,cis,trans,cis[4.4.4.4]fenestrane | $C_{2} \mathbf{- 4 - 1 8}$ | $C_{2}$ | -348.867488 | 0.179578 | 0.008429 |
| [5.5.5.5]fenestrane | all-cis-4-19 | $D_{2}$ | -506.079776 | 0.301093 | 0.011140 |
| [5.5.5.5]fenestrane | all-trans-4-19 | $D_{2 \mathrm{~d}}$ | -505.858078 | 0.299702 | 0.010999 |

${ }^{\text {a }}$ The thermochemical corrections are calculated from the B3-LYP/6-31G(d) frequencies and scaled by $0.9806(Z P V E)$ or $0.9989\left(H^{298}-H^{0}\right) .{ }^{\text {b }}$ We have used a set of five spherical $d$-functions rather than the usual six Cartesian functions for the $6-31 \mathrm{G}(\mathrm{d})$ basis set. ${ }^{\mathrm{c}}$ The symmetry of the equilibrium structure.

## C.1.3.5 Ionized Molecules

Table C-16. MP2(fc)/6-311+G(2d,p) total energies (hartree) and scaled ${ }^{\text {a }}$ B3-LYP/6-31G(d) ${ }^{\text {b }}$ thermochemical corrections (hartree) for the ions in Chapter 4.

| Ion |  | Sym. ${ }^{\text {c }}$ | $E$ | $Z P V E^{\text {a }}$ | $H^{298}-H^{0 \mathrm{a}, \mathrm{d}}$ |
| :---: | :---: | :---: | :---: | :---: | :---: |
| small molecules ${ }^{\text {e }}$ |  |  |  |  |  |
| ${ }^{3} \mathrm{CH}_{2}{ }^{+}$ |  | $C_{2 \mathrm{v}}$ | -38.662610 | 0.016237 | 0.003823 |
| $\mathrm{CH}_{4}{ }^{+}$ |  | $C_{2 v}$ | -39.922163 | 0.036501 | 0.004161 |
| $\mathrm{NH}_{3}{ }^{+}$ |  | $C_{3 v}$ | -56.056664 | 0.032211 | 0.003845 |
| $\mathrm{H}_{2} \mathrm{O}^{+}$ |  | $C_{2 v}$ | -75.827104 | 0.018116 | 0.003782 |
| spiropentane ${ }^{+}$ | 4-58 ${ }^{+}$ | $D_{2}$ | -194.377707 | 0.108495 | 0.007674 |
| neopentane ${ }^{\text {- }}$ |  | $C_{3 v}$ | -196.824302 | 0.152192 | 0.009052 |
| alkaplanes ${ }^{\text {f }}$ |  |  |  |  |  |
| octaplane ${ }^{+}$ | 4-27* | $C_{4 \mathrm{~h}}$ | -814.375061 | 0.443003 | 0.014543 |
| spirooctaplane ${ }^{++}$ | 4-28* | $D_{2 \mathrm{~h}}$ | -812.153071 | 0.395619 | 0.014126 |
| dimethanospirooctaplane ${ }^{\text {- }}$ | 4-29 ${ }^{+}$ | $D_{2 \mathrm{~h}}$ | -888.132773 | 0.409740 | 0.013688 |

${ }^{\text {a }}$ The thermochemical corrections are calculated from the B3-LYP/6-31G(d) frequencies and scaled by $0.9806(Z P V E)$ or $0.9989\left(H^{298}-H^{0}\right)$. ${ }^{\text {b }}$ We have used a set of five spherical $d$-functions rather than the usual six Cartesian functions for the $6-31 \mathrm{G}(\mathrm{d})$ basis set. ${ }^{\mathrm{c}}$ The symmetry of the equilibrium structure. ${ }^{\text {d }}$ Note that the temperature corrections for the ions were not used to calculate ionization energies and are simply included for completeness. ${ }^{e}$ Structures optimized at the MP2(fc)/6-31G(d) level. Throughout this work we have used a set of five spherical $d$-functions instead of the usual six Cartesian functions for the $6-31 \mathrm{G}(\mathrm{d})$ basis set. ${ }^{\mathrm{f}}$ Structures optimized at the MP2(fc)/6-311+G(2d,p)(red) level. Our reduced $6-311+G(2 d, p)(r e d)$ basis set is detailed in Section 4.2 on page 145.

## C. 2 Gaussian Archive Files

## C.2.1 Data for Chapter 1

## C.2.1.1 Fenestranes

Table C-17. Gaussian archive files for the MP2/6-31G(d) optimized species in Chapter 1.

## Fenestranes

## 1-48 all-trans-[4.4.4.4]fenestrane

$1 \backslash 1 \backslash G I N C-I X \backslash F O P T \backslash R M P 2-F C \backslash 6-31 G(D) \backslash C 9 H 12 \backslash R A S M U S S E N \backslash 3-J u n-1994 \backslash 1 \backslash \ \# P R M P$ $2=($ DIRECT $) ~ 6-31 G * 5 D ~ S C F=D I R E C T ~ N A M E=R A S M U S S E N ~ F O P T=R E A D F C ~ G E O M=(C H E C K ~$ , NODISTANCE, NOANGLE, NODIHEDRAL) GUESS=CHECK MAXDISK=200000000<br>[4.4.4. 4]fenestrane C2v RMP2/6-31G*<br>0,1\C\X,1,0.5\X,1,0.5,2,90.\X,1,0.5,2,90 $., 3,90 ., 0 \backslash X, 1,0.5,4,90 ., 2,180 ., 0 \backslash X, 1,0.5,2,90 ., 3,180 ., 0 \backslash X, 1,0.5,2,90$. ,
 $\mathrm{x} 1 \mathrm{~b}, 3,0 ., 0 \backslash \mathrm{C}, 1, \mathrm{cc} 1 \mathrm{~b}, 2, \mathrm{ccx} 1 \mathrm{~b}, 6,0 ., 0 \backslash \mathrm{C}, 1, \mathrm{cc} 2,2, \mathrm{ccx} 2,4, \mathrm{ccxx} 2,0 \backslash \mathrm{C}, 1, \mathrm{cc} 2,2$, ccx $2,4,-\operatorname{ccxx} 2,0 \backslash \mathrm{C}, 1, \mathrm{cc} 2,2, \operatorname{ccx} 2,7, \operatorname{ccxx} 2,0 \backslash \mathrm{C}, 1, \mathrm{CC} 2,2, \operatorname{ccx} 2,7,-\operatorname{ccxx} 2,0 \backslash \mathrm{H}, 8$ , hc3a, 1, hcc $3 a, 2,0 ., 0 \backslash H, 9, h c 3 a, 1, h c c 3 a, 2,0 ., 0 \backslash H, 10, h c 3 b, 1, h c c 3 b, 2,0.0 \backslash$ H, 11, hc3b, 1, hcc $3 \mathrm{~b}, 2,0 ., 0 \backslash \mathrm{H}, 12, \mathrm{hc} 4,1, \mathrm{hcc} 4,2, \mathrm{hccx} 4,0 \backslash \mathrm{H}, 12, \mathrm{hc} 5,1, \mathrm{hcc} 5,2, \mathrm{~h}$ CCx5 , $0 \backslash \mathrm{H}, 13, \mathrm{hc} 4,1, \mathrm{hcc} 4,2,-\mathrm{hccx} 4,0 \backslash \mathrm{H}, 13, \mathrm{hc} 5,1, \mathrm{hcc} 5,2,-\mathrm{hccx} 5,0 \backslash \mathrm{H}, 14, \mathrm{hc} 4$, $1, \mathrm{hcc} 4,2, \mathrm{hccx} 4,0 \backslash \mathrm{H}, 14, \mathrm{hc} 5,1, \mathrm{hcc} 5,2, \mathrm{hccx} 5,0 \backslash \mathrm{H}, 15, \mathrm{hc} 4,1, \mathrm{hcc} 4,2,-\mathrm{hccx} 4,0 \backslash$ H, 15, hc5, 1, hcc5, 2 , -hccx $5,0 \backslash \backslash c c 1 a=1.77578849 \backslash c c x 1 a=100.18025781 \backslash c c 1 b=1$. $47463555 \backslash \mathrm{ccx} 1 \mathrm{~b}=116.48801127 \backslash \mathrm{cc} 2=2.25966222 \backslash \mathrm{ccx} 2=120.91849634 \backslash \mathrm{ccxx} 2=40$. $71056557 \backslash \mathrm{hc} 3 \mathrm{a}=1.09415886 \backslash \mathrm{hcc} 3 \mathrm{a}=130.885446 \backslash \mathrm{hc} 3 \mathrm{~b}=1.09740724 \backslash \mathrm{hcc} 3 \mathrm{~b}=104.68$ $213236 \backslash \mathrm{hc} 4=1.09450884 \backslash \mathrm{hcc} 4=118.57671404 \backslash \mathrm{hccx} 4=193.32254798 \backslash \mathrm{hc} 5=1.09458$ $039 \backslash$ hcc5 $=132.83850149 \backslash$ hccx $5=20.87869969 \backslash \backslash$ Version=HP-PARisc-HPUX-G92/DF T-RevG.1 \State=1-A1 \HF=-347.5314018 \MP2=-348.7127039 ${ }_{\text {RMSD }}=7.898 \mathrm{e}-09 \backslash \mathrm{RM}$ $\mathrm{SF}=2.575 \mathrm{e}-05 \backslash$ Dipole=0., 0.,-0.2154305\PG=C02V [C2 (C1) , SGV (C2H2) , SGV' (C2 H2) , X(C4H8)] <br>@

## 1-49 all-cis-[4.4.4.4]fenestrane

$1 \backslash 230 \backslash G I N C-A R G E N T \backslash F O P T \backslash R M P 2-F C \backslash 6-31 G(D) \backslash C 9 H 12 \backslash R A S M U S S E N \backslash 25-M a y-1994 \backslash 1 \backslash$ <br>\#P RMP2=(DIRECT) 6-31G* 5D SCF=DIRECT NAME=RASMUSSEN OPT=READFC MAXDI SK=218750000 GEOM= (CHECK,NODISTANCE, NOANGLE,NODIHEDRAL) GUESS=CHECK <br>[ 4.4.4.4]fenestrane D2d RMP2/6-31G* $5 D \backslash \backslash 0,1 \backslash C \backslash X, 1,0.5 \backslash X, 1,0.5,2,90 . \backslash \mathrm{X}, 1$ $, 0.5,2,90 ., 3,90 ., 0 \backslash X, 1,0.5,4,90 ., 2,180 ., 0 \backslash X, 1,0.5,2,90 ., 3,180 ., 0 \backslash X, 1,0$ $.5,2,90 ., 4,180 ., 0 \backslash C, 1, c c 1,2, \operatorname{ccx} 1,4,0 ., 0 \backslash C, 1, \operatorname{cc} 1,2, \operatorname{ccx} 1,7,0 ., 0 \backslash C, 1, c c 1$, $5, \operatorname{ccx} 1,3,0 ., 0 \backslash \mathrm{C}, 1, \mathrm{cc} 1,5, \operatorname{ccx} 1,6,0 ., 0 \backslash \mathrm{C}, 1, \mathrm{cc} 2,2,90.4,45 ., 0 \backslash \mathrm{C}, 1, \mathrm{cc} 2,2,90$ $., 4,-45 ., 0 \backslash C, 1, \mathrm{Cc} 2,2,90 ., 7,45.0 \backslash \mathrm{C}, 1, \mathrm{cc} 2,2,90 ., 7,-45.0 \backslash \mathrm{H}, 8, \mathrm{hc} 3,1, \mathrm{hcc} 3$ $, 2,0.0 \backslash \mathrm{H}, 9, \mathrm{hc} 3,1, \mathrm{hcc} 3,2,0.0 \backslash \mathrm{H}, 10, \mathrm{hc} 3,1, \mathrm{hcc} 3,5,0.0 \backslash \mathrm{H}, 11, \mathrm{hc} 3,1, \mathrm{hcc} 3,5$ , $0 ., 0 \backslash \mathrm{H}, 12, \mathrm{hc} 4,1$, hcc $4,2, \mathrm{hccx} 4,0 \backslash \mathrm{H}, 12, \mathrm{hc} 4,1, \mathrm{hcc} 4,5, \mathrm{hccx} 4,0 \backslash \mathrm{H}, 13, \mathrm{hc} 4,1, \mathrm{~h}$ Cc4, $2,-\mathrm{hccx} 4,0 \backslash \mathrm{H}, 13, \mathrm{hc} 4,1, \mathrm{hcc} 4,5,-\mathrm{hccx} 4,0 \backslash \mathrm{H}, 14, \mathrm{hc} 4,1, \mathrm{hcc} 4,2, \mathrm{hccx} 4,0 \backslash \mathrm{H}$, $14, \mathrm{hc} 4,1, \mathrm{hcc} 4,5, \mathrm{hccx} 4,0 \backslash \mathrm{H}, 15, \mathrm{hc} 4,1, \mathrm{hcc} 4,2,-\mathrm{hccx} 4,0 \backslash \mathrm{H}, 15, \mathrm{hc} 4,1, \mathrm{hcc} 4,5,-$ hccx $4,0 \backslash \backslash \mathrm{cc} 1=1.48985141 \backslash \mathrm{ccx} 1=65.00898842 \backslash \mathrm{cc} 2=2.07078997 \backslash \mathrm{hc} 3=1.09392002$ $\backslash \mathrm{hcc} 3=120.07850406 \backslash \mathrm{hc} 4=1.09604716 \backslash \mathrm{hcc} 4=125.93415277 \backslash \mathrm{hccx} 4=28.16088107 \backslash$ \Version=IBM-RS6000-G92RevB $\backslash$ State $=1-A 1 \backslash H F=-347.5610013 \backslash M P 2=-348.726771$ $5 \backslash \mathrm{RMSD}=1.281 \mathrm{e}-09 \backslash \mathrm{RMSF}=5.004 \mathrm{e}-06 \backslash \mathrm{Dipole}=0 .,-0 .,-0 . \backslash \mathrm{PG}=\mathrm{D} 02 \mathrm{D} \quad[\mathrm{O}(\mathrm{Cl}), 2 \mathrm{SGD}($ C2H2), X(C4H8)]<br>@

## 1-50 trans,trans,cis,cis-[4.4.4.4]fenestrane

$1 \backslash 224 \backslash$ GINC-ARGENT $\backslash$ FOPT $\backslash$ RMP2-FC $\backslash 6-31 G(D) \backslash C 9 H 12 \backslash R A S M U S S E N \backslash 22-M a y-1994 \backslash 1 \backslash$ <br>\#P RMP2=(DIRECT) 6-31G* 5D SCF=DIRECT NAME=RASMUSSEN FOPT=READFC MAXD ISK=500000000 GEOM=(CHECK,NODISTANCE,NOANGLE,NODIHEDRAL) GUESS=CHECK $\backslash$ [4.4.4.4]fenestrane C2 RMP2/6-31G* $\backslash \backslash 0,1 \backslash C \backslash X, 1,0.5 \backslash X, 1,0.5,2,90 . \backslash \mathrm{X}, 1,0$. $5,2,90 ., 3,90 ., 0 \backslash X, 1,0.5,4,90.2,180 ., 0 \backslash X, 1,0.5,2,90 ., 3,180 ., 0 \backslash X, 1,0.5$, $2,90.4,180 ., 0 \backslash C, 1, c c 1 b, 2, c c x 1 b, 4, c c x x 1 b, 0 \backslash c, 1, c c 1 a, 2, c c x 1 a, 4,-c c x x 1 a$, $0 \backslash c, 1, c c 1 b, 5, c c x 1 b, 7, c c x x 1 b, 0 \backslash c, 1, c c 1 a, 5, c c x 1 a, 7,-c c x x 1 a, 0 \backslash c, 1, c c 2,2, c$ $\mathrm{cx} 2,4,0 ., 0 \backslash \mathrm{C}, 1, \mathrm{cc} 2,5, \mathrm{ccx} 2,7,0 ., 0 \backslash \mathrm{C}, 1, \mathrm{cc} 3,2,90 ., 3,0 ., 0 \backslash \mathrm{C}, 1, \mathrm{cc} 4,5,90 ., 6$, $0 ., 0 \backslash H, 8, h c 3 b, 1, h c c 3 b, 2, h c c x 3 b, 0 \backslash H, 9, h c 3 a, 1, h c c 3 a, 2, h c c x 3 a, 0 \backslash H, 10, h c 3 b$ , 1, hcc $3 \mathrm{~b}, 5, \mathrm{hccx} 3 \mathrm{~b}, 0 \backslash \mathrm{H}, 11, \mathrm{hc} 3 \mathrm{a}, 1, \mathrm{hcc} 3 \mathrm{a}, 5, \mathrm{hccx} 3 \mathrm{a}, 0 \backslash \mathrm{H}, 12, \mathrm{hc} 4,1, \mathrm{hcc} 4,2$, hcc $\mathrm{x} 4,0 \backslash \mathrm{H}, 12, \mathrm{hc} 5,1, \mathrm{hcc} 5,2, \mathrm{hccx} 5,0 \backslash \mathrm{H}, 13, \mathrm{hc} 4,1, \mathrm{hcc} 4,5, \mathrm{hccx} 4,0 \backslash \mathrm{H}, 13, \mathrm{hc} 5,1, \mathrm{hc}$ c5, 5, hccx $5,0 \backslash \mathrm{H}, 14, \mathrm{hc} 6,1, \mathrm{hcc} 6,2, \mathrm{hccx} 6,0 \backslash \mathrm{H}, 14, \mathrm{hc} 6,1, \mathrm{hcc} 6,5, \mathrm{hccx} 6,0 \backslash \mathrm{H}, 15$, hc7, 1, hcc 7,2 , -hccx $7,0 \backslash \mathrm{H}, 15, \mathrm{hc} 7,1, \mathrm{hcc} 7,5,-\mathrm{hccx} 7,0 \backslash \backslash \mathrm{cc} 1 \mathrm{a}=1.5180778 \backslash \mathrm{ccx} 1 \mathrm{a}$ $=81.16994972 \backslash c \operatorname{cxx} 1 \mathrm{a}=42.86958805 \backslash \mathrm{cc} 1 \mathrm{~b}=1.5064807 \backslash \mathrm{ccx} 1 \mathrm{~b}=100.89803796 \backslash \mathrm{ccxx}$ $1 \mathrm{~b}=46.65285943 \backslash \mathrm{cc} 2=2.12128588 \backslash \mathrm{ccx} 2=115.55278552 \backslash \mathrm{cc} 3=2.13596485 \backslash \mathrm{cc} 4=2.2$
 $52227 \backslash \mathrm{hcc} 3 \mathrm{~b}=95.97190955 \backslash \mathrm{hccx} 3 \mathrm{~b}=-15.94811318 \backslash \mathrm{hc} 4=1.09412344 \backslash$ hcc $4=98.858$ $47839 \backslash \mathrm{hccx} 4=196.59682935 \backslash \mathrm{hc5}=1.09995618 \backslash \mathrm{hcc} 5=150.17071593 \backslash \mathrm{hccx} 5=5.5337$ $6631 \backslash$ hc6=1.09652718 $\backslash$ hcc6=125.93953907 $\backslash$ hccx6=-7.37792653 ${ }_{\text {hc7 }}=1.09192345$ $\backslash$ hcc $7=125.19382996 \backslash$ hccx $7=25.3623112 \backslash \backslash$ Version=IBM-RS6000-G92RevB $\backslash$ State $=$ $1-A \backslash H F=-347.3807152 \backslash M P 2=-348.570765 \backslash R M S D=4.888 e-09 \backslash R M S F=9.415 e-03 \backslash D i p o$ le=0.0854325,0.,-0. \PG=C02 [C2 (C1C1C1), X(C6H12)] <br>@

## 1-51 trans,cis,cis,cis-[4.4.4.4]fenestrane

$1 \backslash 1 \backslash G I N C-V P P 09 \backslash F O p t \backslash R M P 2-F C \backslash 6-31 G(d) \backslash C 9 H 12 \backslash R A S M U S S E N \backslash 29-A u g-1996 \backslash 0 \backslash \ \# P$ RMP2 $=($ FULLDIRECT) /6-31G* 5D SCF=DIRECT NAME=RASMUSSEN OPT MAXDISK=750 0000 GEOM $=($ NODISTANCE, NOANGLE,NODIHEDRAL) $\backslash \backslash 4.4 .4 .4]$ fenestrane 5D Cs $\backslash \backslash$ $0,1 \backslash C,-0.0666978099,-0.0671534573,0.5696359847 \backslash C,-0.0666978099,1.38832$ $17126,0.5696359847 \backslash \mathrm{C}, 0.1021884122,-0.6836492613,-0.8727452513 \backslash \mathrm{C},-1.498$ $6607128,1.25020228,-0.1146519102 \backslash C, 1.4846097704,1.25020228,0.234654687$ $\backslash C, 1.4745312107,-0.2837587995,0.7154633397 \backslash C,-1.5999263108,-0.28375879$ $95,0.3554797911 \backslash C, 1.4542275051,-1.3026816755,-0.441118178 \backslash \mathrm{C},-1.3129900$ $398,-1.3026816755,-0.7651274657 \backslash \mathrm{H},-0.1829084406,1.8403535246,1.5621386$ $952 \backslash \mathrm{H}, 0.2000646802,0.0153322195,-1.7086624183 \backslash \mathrm{H},-2.2561383448,1.903966$ $6952,0.3291916494 \backslash \mathrm{H}, 2.1190664518,1.9039666952,0.8414777154 \backslash \mathrm{H},-1.534615$ 0977,1.3617408107,-1.2020442144\H,1.7707900002,1.3617408107,-0.8150193 $658 \backslash \mathrm{H}, 2.0360815395,-0.4833911809,1.6364951841 \backslash \mathrm{H},-2.3590549439,-0.48339$ 11809,1.1218753472\H,1.3453036197,-2.3266419244,-0.0646321062\H,-1.293 9843929,-2.3266419244,-0.3736623199\H,2.2731442532,-1.2786450843,-1.17 $05312568 \backslash \mathrm{H},-1.9412546167,-1.2786450843,-1.6639888018 \backslash \backslash$ Version=Fujitsu-VP-Unix-G94RevD. $2 \backslash$ State $=1-A^{\prime} \backslash H F=-347.5740447 \backslash \mathrm{MP} 2=-348.7458982 \backslash \mathrm{RMSD}=6.5$ $40 \mathrm{e}-09 \backslash \mathrm{RMSF}=1.457 \mathrm{e}-05 \backslash \mathrm{Dipole}=0.0595783,0.0 .0137398 \backslash \mathrm{PG}=\mathrm{CS} \quad[\mathrm{SG}(\mathrm{C} 3 \mathrm{H} 2)$, X( C6H10)] <br>@

## 1-52 all-cis-[5.5.5.5]fenestrane

$1 \backslash 1 \backslash$ GINC-RSCQC6 $\backslash$ FOpt $\backslash$ RMP2-FC $\backslash 6$-31G (d) \C13H20 \RASMUSSEN $\backslash 25-A u g-1996 \backslash 0 \backslash \backslash$ \#P RMP2/6-31G* 5D SCF=(DIRECT) NAME=RASMUSSEN GUESS=CHECK MAXDISK=4500 00000 GEOM $=($ CHECK,NODISTANCE,NOANGLE,NODIHEDRAL) OPT<br>all-cis-[5.5.5.5 ]fenestrane D2 5D <br>0,1\C,0.,0.,0.\C,0.9302059218,-0.934340018,-0.82269 $93958 \backslash C, 0.9302059218,0.934340018,0.8226993958 \backslash C,-0.9302059218,0.934340$ 018,-0.8226993958\C,-0.9302059218,-0.934340018, 0.8226993958\C, 2.317511

2035,-0.7394618541,-0.1943674778\C, 2.3175112035, 0.7394618541, 0.1943674 $778 \backslash \mathrm{C}, 0.3285774885,2.3392233276,0.6933675699 \backslash \mathrm{C},-0.3285774885,2.3392233$ $276,-0.6933675699 \backslash C,-2.3175112035,0.7394618541,-0.1943674778 \backslash C,-2.3175$ $112035,-0.7394618541,0.1943674778 \backslash C,-0.3285774885,-2.3392233276,0.6933$ $675699 \backslash \mathrm{C}, 0.3285774885,-2.3392233276,-0.6933675699 \backslash \mathrm{H}, 0.9746213671,-0.61$ $16696942,-1.8726679448 \backslash \mathrm{H}, 0.9746213671,0.6116696942,1.8726679448 \backslash \mathrm{H},-0.9$ $746213671,0.6116696942,-1.8726679448 \backslash H,-0.9746213671,-0.6116696942,1.8$ $726679448 \backslash \mathrm{H}, 2.4147248861,-1.357694902,0.7084547456 \backslash \mathrm{H}, 3.1326144556,-1.0$ $197214735,-0.8722698397 \backslash \mathrm{H},-1.0736321512,3.1346895354,-0.8167238408 \backslash \mathrm{H}, 0$ $.4344909169,2.4909633656,-1.4669168957 \backslash \mathrm{H},-2.4147248861,1.357694902,0.7$ $084547456 \backslash \mathrm{H},-3.1326144556,1.0197214735,-0.8722698397 \backslash \mathrm{H}, 1.0736321512,-3$ $.1346895354,-0.8167238408 \backslash H,-0.4344909169,-2.4909633656,-1.4669168957 \backslash$ H, 3.1326144556,1.0197214735, 0.8722698397\H,2.4147248861,1.357694902, -0 $.7084547456 \backslash \mathrm{H},-0.4344909169,2.4909633656,1.4669168957 \backslash \mathrm{H}, 1.0736321512,3$ $.1346895354,0.8167238408 \backslash \mathrm{H},-3.1326144556,-1.0197214735,0.8722698397 \backslash \mathrm{H}$, $-2.4147248861,-1.357694902,-0.7084547456 \backslash \mathrm{H}, 0.4344909169,-2.4909633656$, $1.4669168957 \backslash \mathrm{H},-1.0736321512,-3.1346895354,0.8167238408 \backslash \backslash V e r s i o n=I B M-R$ S6000-G94RevD.1 \State=1-A $\backslash H F=-503.9468916 \backslash M P 2=-505.6371177 \backslash R M S D=9.024 e$ $-09 \backslash \mathrm{RMSF}=1.368 \mathrm{e}-05 \backslash \mathrm{Dipole=0.,0.,0}. \mathrm{\backslash PG=D02} \mathrm{\quad[O(C1),X(C12H20)]} \mathrm{\backslash} \mathrm{\backslash @}$

## 1-53 all-trans-[5.5.5.5]fenestrane

$1 \backslash 136 \backslash G I N C-E I G E N \backslash F O P T \backslash R M P 2-F C \backslash 6-31 G(D) \backslash C 13 H 20 \backslash R A S M U S S E N \backslash 28-M a y-1994 \backslash 1 \backslash$ <br>\#P RMP2=(DIRECT) 6-31G* 5D FOPT=READFC NAME=RASMUSSEN SCF=(DIRECT) MA XDISK=218750000 GEOM = (CHECK, NODISTANCE, NOANGLE, NODIHEDRAL) GUESS=CHECK $\backslash$ C13H20 all-trans-[5.5.5.5]fenestrane RMP2/6-31G* D2 <br>0, $1 \backslash C \backslash X, 1,1 . \backslash X$, $1, r 1,2,90 . \backslash X, 1, r 1,2,90 ., 3,-90 ., 0 \backslash X, 1, r 1,2,90 ., 3,180 ., 0 \backslash X, 1, r 1,2,90 ., 4$, $180 ., 0 \backslash X, 1,1 ., 3,90 ., 2,180 ., 0 \backslash C, 1, r 2,7, a 1,6,45 ., 0 \backslash C, 1, r 2,2, a 1,4,45 ., 0 \backslash C$ $, 1, r 2,7, a 1,4,45 ., 0 \backslash C, 1, r 2,2, a 1,6,45 ., 0 \backslash C, 3, r 3,1,90 ., 2, d 1,0 \backslash C, 3, r 3,1,90$ $., 7, d 1,0 \backslash C, 4, r 3,1,90 ., 7,-d 1,0 \backslash C, 4, r 3,1,90 ., 2,-d 1,0 \backslash C, 5, r 3,1,90 ., 2, d 1,0$ $\backslash C, 5, r 3,1,90 ., 7, d 1,0 \backslash C, 6, r 3,1,90 ., 7,-d 1,0 \backslash C, 6, r 3,1,90 ., 2,-d 1,0 \backslash H, 8, r 4$, $1, a 2,10,180 ., 0 \backslash H, 9, r 4,1, a 2,11,180 ., 0 \backslash H, 10, r 4,1, a 2,8,180 ., 0 \backslash H, 11, r 4,1, a$ $2,9,180 ., 0 \backslash H, 12, r 5,8, a 3,13, a 4,-1 \backslash H, 12, r 6,8, a 5,13, a 6,1 \backslash H, 15, r 5,10, a 3,14$ , $\mathrm{a} 4,1 \backslash \mathrm{H}, 15, r 6,10, \mathrm{a} 5,14, \mathrm{a} 6,-1 \backslash \mathrm{H}, 16, r 5,10, \mathrm{a} 3,17, a 4,-1 \backslash \mathrm{H}, 16, r 6,10, a 5,17, a$ $6,1 \backslash H, 19, r 5,8, a 3,18, a 4,1 \backslash H, 19, r 6,8, a 5,18, a 6,-1 \backslash H, 13, r 6,9, a 5,12, a 6,1 \backslash H$, $13, r 5,9, a 3,12, a 4,-1 \backslash H, 14, r 6,9, a 5,15, a 6,-1 \backslash H, 14, r 5,9, a 3,15, a 4,1 \backslash H, 17, r 6$ , 11, a5, 16, a6, 1 \H, 17, r5, 11, a3, 16, a4, -1 \H, 18, r6, 11, a5, 19, a6, -1 \H, 18, r5, 1 $1, a 3,19, a 4,1 \backslash \backslash r 1=2.5254519 \backslash r 2=1.63460817 \backslash r 3=0.77696071 \backslash r 4=1.10915933 \backslash a$ $1=97.94038231 \backslash \mathrm{a} 2=89.58543639 \backslash \mathrm{~d} 1=48.77510316 \backslash r 5=1.09790152 \backslash r 6=1.0967435$ $3 \backslash a 3=114.56061891 \backslash a 4=110.36684386 \backslash a 5=111.44503929 \backslash a 6=113.21983234 \backslash \backslash$ Ver sion $=1 B M-R S 6000-G 92$ RevB $\backslash$ State $=1-A 1 \backslash H F=-503.6875517 \backslash M P 2=-505.4040565 \backslash R M$ $S D=5.508 e-09 \backslash R M S F=1.364 e-05 \backslash D i p o l e=0 ., 0 .,-0 . \backslash P G=D 02 D \quad[O(C 1), 2 S G D(C 2 H 2)$ , X (C8H16) ] <br>@

## C.2.2 Data for Chapter 3

## C.2.2.1 Neutral Hydrocarbons

Table C-18. Gaussian archive files for the B3-LYP/6-31G(d) optimized species in Chapter 3.

## Basic Hydrocarbons

## ethane

$1 \backslash 1 \backslash G I N C-V P P 07 \backslash F O p t \backslash R B 3 L Y P \backslash 6-31 G(d) \backslash C 2 H 6 \backslash R A S M U S S E N \backslash 04-J u l-1999 \backslash 0 \backslash \ \# P$ B 3LYP/6-31G(D) 5D OPT FREQ=NORAMAN NAME=RASMUSSEN MAXDISK=131072000<br>Et hane $\mathrm{D} 3 \mathrm{~d} \backslash \backslash 0,1 \backslash \mathrm{C}, 0 ., 0 .,-0.7655664258 \backslash \mathrm{C}, 0.0 ., 0.7655664258 \backslash \mathrm{H}, 1.021112508$ $1,-0.000000001,-1.1643694313 \backslash \mathrm{H}, 0.5105562541,0.8843093721,1.1643694313$ \H,-0.510556254,0.8843093722,-1.1643694313\H,-1.0211125081,0.000000000 $1,1.1643694313 \backslash \mathrm{H},-0.5105562541,-0.8843093721,-1.1643694313 \backslash \mathrm{H}, 0.5105562$ 54,-0.8843093722,1.1643694313<br>Version=Fujitsu-VP-Unix-G98RevA.6\State $=1-\mathrm{AlG} \backslash \mathrm{HF}=-79.8290131 \backslash \mathrm{RMSD}=4.818 \mathrm{e}-10 \backslash \mathrm{RMSF}=4.469 \mathrm{e}-05 \backslash \mathrm{Dipole}=0 ., 0 ., 0 . \backslash \mathrm{PG}$ =D03D [C3(C1.C1),3SGD (H2)] <br>@

## propane

$1 \backslash 1 \backslash G I N C-V P P 07 \backslash F O p t \backslash R B 3 L Y P \backslash 6-31 G(d) \backslash C 5 H 6 \backslash R A S M U S S E N \backslash 02-N O v-1999 \backslash 0 \backslash \backslash \# P B$ 3LYP/6-31G(D) 5D OPT FREQ=NORAMAN NAME=RASMUSSEN GUESS=CHECK MAXDISK=2 097152000 GEOM=CHECK SYMM=LOOSE $\backslash$ \propellane C1 <br>0,1\C,1.2527557924,0.3 $366966804,0 . \backslash \mathrm{C}, 0 ., 0 ., 0.7895950502 \backslash \mathrm{H}, 1.582406964,1.3735838206,0 . \backslash \mathrm{C},-0.3$ $347900176,-1.2532666811,0 . \backslash \mathrm{C},-0.9179657748,0.9165700008,0 . \backslash \mathrm{H},-0.686625$ 9816,1.9797194431,0.\C,0.,0.,-0.7895950502\H,-1.9807619649,0.683612719 6, 0. \H, 2.0578003209,-0.3952241785, 0. \H, 0.3983550009,-2.0571965402, 0. \H ,-1.3711743392,-1.5844952645,0. <br>Version=Fujitsu-VP-Unix-G98RevA.6\Sta te=1-A1'\HF=-194.0055446\RMSD=2.580e-09\RMSF=4.071e-05\Dipole=0.,0.,0. $\backslash P G=D 03 H[C 3(C 1 . C 1), 3 C 2(C 1), S G H(H 6)] \backslash \backslash @$

## iosbutane

$1 \backslash 1 \backslash G I N C-V P P 06 \backslash F O p t \backslash R B 3 L Y P \backslash 6-31 G(d) \backslash C 4 H 10 \backslash R A S M U S S E N \backslash 04-J u l-1999 \backslash 0 \backslash \ \# P$ B3LYP/6-31G(D) 5D OPT FREQ=NORAMAN NAME=RASMUSSEN MAXDISK=2097152000<br> isobutane C3v <br>0,1\C,0.,0.,0.3735092858\H,0.,0.,1.4741342348\C,1.46217 $08651,0 .,-0.0959984468 \backslash C,-0.7310854326,-1.2662771139,-0.0959984468 \backslash C,-$ $0.7310854326,1.2662771139,-0.0959984468 \backslash \mathrm{H}, 1.9976770071,-0.8863539373,0$ $.2651237172 \backslash \mathrm{H}, 1.9976770071,0.8863539373,0.2651237172 \backslash \mathrm{H}, 1.520545451,0 .$, $-1.1926534036 \backslash \mathrm{H},-1.76644353,-1.2868620681,0.2651237172 \backslash \mathrm{H},-0.2312334771$ ,-2.1732160054,0.2651237172\H,-0.7602727255,-1.3168309881,-1.192653403 $6 \backslash \mathrm{H},-0.2312334771,2.1732160054,0.2651237172 \backslash \mathrm{H},-1.76644353,1.2868620681$ , 0.2651237172\H,-0.7602727255,1.3168309881,-1.1926534036<br>Version=Fuji tsu-VP-Unix-G98RevA. $6 \backslash$ State $=1-\mathrm{Al} \backslash \mathrm{HF}=-158.4560426 \backslash \mathrm{RMSD}=4.160 \mathrm{e}-09 \backslash \mathrm{RMSF}=3$ $.344 \mathrm{e}-05 \backslash$ Dipole=0.,0.,0.0335783\PG=C03V [C3(C1H1), 3SGV(C1H1), X(H6)] <br>@

## neopentane

$1 \backslash 1 \backslash G I N C-V P P 02 \backslash F O p t \backslash R B 3 L Y P \backslash 6-31 G(d) \backslash C 5 H 12 \backslash R A S M U S S E N \backslash 04-J u l-1999 \backslash 0 \backslash \ \# P$ B3LYP/6-31G(D) 5D OPT FREQ=NORAMAN NAME=RASMUSSEN MAXDISK=2097152000<br> Neopentane 5D Td <br>0,1\C,0.,0.,0.\C,0.,0.,1.5404645355\C,1.4523638923,0 ., -0.5134881785\C,-0.7261819461,1.2577840262,-0.5134881785\C,-0.726181

9461,-1.2577840262,-0.5134881785\H, 0.5115788515, -0.886080563,1.9367416 $389 \backslash \mathrm{H},-1.0231577031,0 ., 1.9367416389 \backslash \mathrm{H}, 0.5115788515,0.886080563,1.93674$ $16389 \backslash \mathrm{H}, 1.9965038122,0.886080563,-0.1632593796 \backslash \mathrm{H}, 1.4849249607,0 .,-1.61$ $02228797 \backslash \mathrm{H}, 1.9965038122,-0.886080563,-0.1632593796 \backslash \mathrm{H},-0.7424624803,1.2$ $859827386,-1.6102228798 \backslash \mathrm{H},-0.2308836288,2.1720633016,-0.1632593796 \backslash \mathrm{H}$, -$1.7656201834,1.2859827386,-0.1632593796 \backslash \mathrm{H},-1.7656201834,-1.2859827387$, $-0.1632593796 \backslash \mathrm{H},-0.2308836288,-2.1720633016,-0.1632593796 \backslash \mathrm{H},-0.7424624$ 803,-1.2859827387,-1.6102228798<br>Version=Fujitsu-VP-Unix-G98RevA. $6 \backslash \mathrm{HF}=$ $-197.769659 \backslash \operatorname{RMSD}=3.946 e-10 \backslash \mathrm{RMSF}=6.883 e-06 \backslash \mathrm{Dipole=0.,0.,0}. \mathrm{\backslash PG=TD} \mathrm{\quad[O(C1)}$ , 4C3 (C1) , 6SGD (H2) ] <br>@

## Small Strained Hydrocarbons

## 3-41 spiropentane

$1 \backslash 1 \backslash G I N C-V P P 07 \backslash F O p t \backslash R B 3 L Y P \backslash 6-31 G(d) \backslash C 5 H 8 \backslash R A S M U S S E N \backslash 04-J u l-1999 \backslash 0 \backslash \backslash \# P B$ 3LYP/6-31G(D) 5D OPT FREQ=NORAMAN NAME=RASMUSSEN MAXDISK=131072000<br>Sp iropentane $D 2 d 5 D \backslash \backslash 0,1 \backslash C, 0 ., 0.0 . \backslash C,-0.5408506919,-1.2730959398,-0.540$ $8506919 \backslash C, 0.5408506919,-1.2730959398,0.5408506919 \backslash C,-0.5408506919,1.27$ $30959398,0.5408506919 \backslash \mathrm{C}, 0.5408506919,1.2730959398,-0.5408506919 \backslash \mathrm{H},-1.5$ $450570167,-1.57759691,-0.2526151656 \backslash \mathrm{H}, 1.5450570167,-1.57759691,0.25261$ $51656 \backslash \mathrm{H},-1.5450570167,1.57759691,0.2526151656 \backslash \mathrm{H}, 1.5450570167,1.5775969$ $1,-0.2526151656 \backslash \mathrm{H},-0.2526151656,-1.57759691,-1.5450570167 \backslash \mathrm{H}, 0.25261516$ 56, - $1.57759691,1.5450570167 \backslash \mathrm{H},-0.2526151656,1.57759691,1.5450570167 \backslash \mathrm{H}$, $0.2526151656,1.57759691,-1.5450570167 \backslash$ VVersion=Fujitsu-VP-Unix-G98RevA $.6 \backslash$ State $=1-\mathrm{A} \backslash \mathrm{HF}=-195.2681523 \backslash \mathrm{RMSD}=1.937 e-09 \backslash \mathrm{RMSF}=6.970 e-05 \backslash \mathrm{Dipole=0.}$, 0.,0. \PG=D02D [O (C1), 2SGD (C2) , X (H8) ] <br>@

## Capping Hydrocarbons

## 3-46 cyclobutane

$1 \backslash 1 \backslash G I N C-R S C Q C 2 \backslash F O p t \backslash R B 3 L Y P \backslash 6-31 G(d) \backslash C 4 H 8 \backslash R A S M U S S E N \backslash 06-O c t-1999 \backslash 0 \backslash \backslash \# P$ B3LYP/6-31G* 5D OPT FREQ=NORAMAN NAME=RASMUSSEN MAXDISK=524288000 GEOM $=($ NODISTANCE, NOANGLE, NODIHEDRAL) SYMM=LOOSE <br>cyclobutane C9H14 C2v $\backslash \backslash 0$, $1 \backslash \mathrm{C}, 1.0843616596,0 ., 0.1246890222 \backslash \mathrm{H}, 1.4229567686,0 ., 1.1667669018 \backslash \mathrm{C},-1.0$ $843616596,0 ., 0.1246890222 \backslash \mathrm{H}, 0 .,-1.4229174339,-1.1667734356 \backslash \mathrm{H}, 0 ., 1.4229$ 174339 , - $1.1667734356 \backslash \mathrm{C}, 0 ., 1.0843567499,-0.1246823855 \backslash \mathrm{H}, 0 ., 1.9656739837$ $, 0.5252363824 \backslash \mathrm{H}, 1.9656485967,0 .,-0.5252696688 \backslash \mathrm{H},-1.4229567686,0 ., 1.166$ $7669018 \backslash \mathrm{C}, 0 .,-1.0843567499,-0.1246823855 \backslash \mathrm{H}, 0 .,-1.9656739837,0.52523638$ $24 \backslash H,-1.9656485967,0 .,-0.5252696688 \backslash \backslash V e r s i o n=I B M-R S 6000-G 98 R e v A .6 \backslash$ Stat $\mathrm{e}=1-\mathrm{A} \backslash \mathrm{HF}=-157.2104584 \backslash \mathrm{RMSD}=5.393 \mathrm{e}-09 \backslash \mathrm{RMSF}=2.274 \mathrm{e}-06 \backslash \mathrm{Dipole=0.,0.,-0.0}$ $000059 \backslash \mathrm{PG}=\mathrm{C} 02 \mathrm{~V} \quad\left[\mathrm{SGV}(\mathrm{C} 2 \mathrm{H} 4), \mathrm{SGV}{ }^{\prime}(\mathrm{C} 2 \mathrm{H} 4)\right] \backslash \backslash @$

## 3-47 bicyclo[2.2.0]hexane

$1 \backslash 1 \backslash G I N C-V P P 10 \backslash F O p t \backslash R B 3 L Y P \backslash 6-31 G(d) \backslash C 6 H 10 \backslash R A S M U S S E N \backslash 07-O c t-1999 \backslash 0 \backslash \backslash \# P$ B3LYP/6-31G* 5D OPT=TIGHT FREQ=NORAMAN NAME=RASMUSSEN MAXDISK=20971520 00 GEOM = (CHECK, NODISTANCE,NOANGLE,NODIHEDRAL) GUESS=CHECK <br>bicyclohexa ne $\mathrm{C} 2 \backslash \backslash 0,1 \backslash \mathrm{H},-2.4441359235,-0.4514109433,0.2488085326 \backslash \mathrm{H},-0.8993043219$, $1.0580336958,1.492799176 \backslash \mathrm{H}, 2.4441359235,0.4514109433,0.2488085326 \backslash \mathrm{C},-1$ $.4994445186,-0.2418600554,-0.2634082119 \backslash H, 0.8993043219,-1.0580336958,1$ $.492799176 \backslash \mathrm{C},-0.5053787603,0.6028787473,0.5794953454 \backslash \mathrm{H}, 0.1420181313,1$. $788492794,-1.2195330434 \backslash \mathrm{H}, 0.8929526974,2.3132049674,0.2976236362 \backslash \mathrm{H}, 1.7$ $356323045,-0.1705828355,-1.2513314354 \backslash \mathrm{H},-0.8929526974,-2.3132049674,0$.
$2976236362 \backslash \mathrm{H},-0.1420181313,-1.788492794,-1.2195330434 \backslash \mathrm{C}, 0.5053787603$, $0.6028787473,0.5794953454 \backslash \mathrm{H},-1.7356323045,0.1705828355,-1.2513314354 \backslash \mathrm{C}$ , 0.5053787603,1.4441954783,-0.2441482778\C,1.4994445186, 0.2418600554, $0.2634082119 \backslash C,-0.5053787603,-1.4441954783,-0.2441482778 \backslash \backslash V e r s i o n=F u j i$ tsu-VP-Unix-G98RevA. $6 \backslash$ State=1-A $\backslash H F=-234.5941715 \backslash \mathrm{RMSD}=2.960 \mathrm{e}-10 \backslash \mathrm{RMSF}=1$. 117e-06\Dipole=0., 0., 0.0522987\PG=C02 [X(C6H10)] <br>@

## TB-3-48 twistboat-cyclohexane

$1 \backslash 1 \backslash G I N C-R S C Q C 9 \backslash F O p t \backslash R B 3 L Y P \backslash 6-31 G(d) \backslash C 6 H 12 \backslash R A S M U S S E N \backslash 09-O c t-1999 \backslash 0 \backslash \backslash \# P$ B3LYP/6-31G* 5D OPT=CALCFC NAME=RASMUSSEN MAXDISK=917504000 GEOM=(CH ECK, NODISTANCE,NOANGLE,NODIHEDRAL) GUESS=CHECK<br>Cyclohexane C2 twist<br> $0,1 \backslash \mathrm{H}, 0.4509797272,-1.2156974455,-1.4603209804 \backslash \mathrm{C}, 0.6621170381,-1.22989$ $22507,-0.3820168923 \backslash \mathrm{H},-1.2282907369,-2.1506273973,0.192757875 \backslash \mathrm{H}, 1.2282$ $847748,2.1506377881,0.1926793853 \backslash \mathrm{C},-0.6621060499,1.2298717825,-0.38210$ $04436 \backslash \mathrm{H},-0.4509371527,1.2156206696,-1.4603975376 \backslash \mathrm{H}, 2.1866365881,-0.261$ $1050922,0.8402298211 \backslash \mathrm{H},-2.1886278525,-0.2482848642,-0.8395552683 \backslash \mathrm{H}, 0.4$ $579446953,1.2135816377,1.4601796783 \backslash \mathrm{H},-1.2157991148,2.1576537123,-0.19$ $32636659 \backslash \mathrm{H},-2.186660851,0.2611484717,0.8401527333 \backslash \mathrm{H}, 1.2158045414,-2.15$ $76643724,-0.1931154576 \backslash \mathrm{H},-0.4579865037,-1.2135038481,1.4602299692 \backslash \mathrm{C}, 1$. $528556813,-0.0044479678,0.0001727632 \backslash \mathrm{C}, 0.6692114555,1.2261626662,0.381$ $8797406 \backslash C,-1.5285565789,0.0044478735,0.0001281205 \backslash C,-0.6692227197,-1.2$ $261422104,0.3819247431 \backslash \mathrm{H}, 2.1886521362,0.2482413803,-0.8395047416 \backslash$ Vers ion=IBM-RS6000-G98RevA. $6 \backslash \mathrm{HF}=-235.8660513 \backslash \mathrm{RMSD}=4.879 \mathrm{e}-09 \backslash \mathrm{RMSF}=8.537 \mathrm{e}-07$ \Dipole=0.,0.,-0.0000126\PG=C01 [X(C6H12)] <br>@

## 3-49 bicyclo[2.2.1]heptane

$1 \backslash 1 \backslash G I N C-P C \backslash F O p t \backslash R B 3 L Y P \backslash 6-31 G(d) \backslash C 7 H 12 \backslash R A S M U S S E N \backslash 06-O c t-1999 \backslash 0 \backslash \backslash \# P$ B3L YP/6-31G* 5D OPT FREQ=NORAMAN NAME=RASMUSSEN MAXDISK=2097152000 GEOM= ( NODISTANCE, NOANGLE, NODIHEDRAL) SYMM=LOOSE<br>bicycloheptane C2v<br>0,1\H,0 $.89124767,0 ., 2.0286307551 \backslash \mathrm{H},-0.89124767,0 ., 2.0286307551 \backslash \mathrm{H}, 0 .,-2.155550$ $1936,0.731703749 \backslash \mathrm{H},-2.1615393906,-1.176766414,-0.0182607583 \backslash \mathrm{H}, 0 ., 2.155$ $5501936,0.731703749 \backslash \mathrm{C}, 0 ., 0 ., 1.3892799937 \backslash \mathrm{H}, 1.209269343,1.2063930968$, -1 $.5035338543 \backslash \mathrm{H},-2.1615393906,1.176766414,-0.0182607583 \backslash \mathrm{H}, 1.209269343,-1$ $.2063930968,-1.5035338543 \backslash \mathrm{C}, 0 .,-1.1336730196,0.3401203297 \backslash \mathrm{H},-1.2092693$ $43,-1.2063930968,-1.5035338543 \backslash \mathrm{C}, 0 ., 1.1336730196,0.3401203297 \backslash \mathrm{H},-1.209$ $269343,1.2063930968,-1.5035338543 \backslash C, 1.2556694209,0.7829984181,-0.49377$ $56032 \backslash C, 1.2556694209,-0.7829984181,-0.4937756032 \backslash C,-1.2556694209,-0.78$ $29984181,-0.4937756032 \backslash \mathrm{C},-1.2556694209,0.7829984181,-0.4937756032 \backslash \mathrm{H}, 2$. $1615393906,1.176766414,-0.0182607583 \backslash H, 2.1615393906,-1.176766414,-0.01$ $82607583 \backslash \backslash V e r s i o n=S G I-G 98 R e v A .6 \backslash S t a t e=1-A 1 \backslash H F=-273.9639734 \backslash R M S D=7.084 e$ $-09 \backslash$ RMSF=5.235e-05\Dipole=0.,0.,0.0236245 \PG=C02V [C2 (C1), SGV (C2H2), SG V' (H2) , X (C4H8) ] <br>@

## 3-50 cis-bicyclo[3.3.0]octane

$1 \backslash 1 \backslash G I N C-P C \backslash F O p t \backslash R B 3 L Y P \backslash 6-31 G(d) \backslash C 8 H 14 \backslash R A S M U S S E N \backslash 06-O c t-1999 \backslash 0 \backslash \backslash \# P$ B3L YP/6-31G* 5D OPT FREQ=NORAMAN NAME=RASMUSSEN MAXDISK=2097152000 GEOM= ( NODISTANCE, NOANGLE, NODIHEDRAL) SYMM=LOOSE <br>bicyclooctane C2v C \} 0 , 1 \backslash H , 0 . , 2. $653972206,-1.0200676768 \backslash \mathrm{C}, 0.7883279884,0 .,-0.47661414 \backslash \mathrm{H}, 0 .,-3.11752$ $01911,0.6849926321 \backslash \mathrm{C},-0.7883279884,0 .,-0.47661414 \backslash \mathrm{H},-1.148498892$, $0 .,-1$ $.512944598 \backslash \mathrm{H}, 0 ., 3.1175201911,0.6849926321 \backslash \mathrm{H}, 1.3604887418,1.1548171911$, $1.2829303738 \backslash \mathrm{C}, 0 .,-2.2574215456,0.004818018 \backslash \mathrm{H},-1.3604887418,1.15481719$ 11,1.2829303738\H, 0.,-2.653972206,-1.0200676768\H,-1.3604887418,-1.154

8171911,1.2829303738\H,1.148498892,0.,-1.512944598\H,1.3604887418, -1.1 $548171911,1.2829303738 \backslash C, 1.2067058416,1.3223416119,0.2075309631 \backslash C,-1.2$ $067058416,1.3223416119,0.2075309631 \backslash \mathrm{C},-1.2067058416,-1.3223416119,0.20$ $75309631 \backslash \mathrm{C}, 1.2067058416,-1.3223416119,0.2075309631 \backslash \mathrm{H}, 2.141496567,1.735$ 2086914, - 0.1887179651 \H, -2.141496567,1.7352086914, -0.1887179651 \H, -2.1 $41496567,-1.7352086914,-0.1887179651 \backslash \mathrm{H}, 2.141496567,-1.7352086914,-0.18$ $87179651 \backslash C, 0 ., 2.2574215456,0.004818018 \backslash \backslash V e r s i o n=S G I-G 98 R e v A .6 \backslash S t a t e=1-$ $A 1 \backslash H F=-313.2839567 \backslash R M S D=9.909 e-09 \backslash R M S F=6.120 e-05 \backslash D i p o l e=0 ., 0 .,-0.04961$ $25 \backslash \mathrm{PG}=\mathrm{CO} 2 \mathrm{~V}$ [SGV (C2H4), SGV'(C2H2), X(C4H8)] <br>@

## Crown-3-51 crown-cyclooctane

$1 \backslash 1 \backslash G I N C-P C \backslash F O p t \backslash R B 3 L Y P \backslash 6-31 G(d) \backslash C 8 H 16 \backslash R A S M U S S E N \backslash 06-O c t-1999 \backslash 0 \backslash \backslash \# P B L$ YP/6-31G* 5D OPT FREQ=NORAMAN NAME=RASMUSSEN MAXDISK=2097152000 GEOM=( NODISTANCE, NOANGLE, NODIHEDRAL) SYMM=LOOSE<br>cyclooctane C2v crown<br>0,1\} $\mathrm{H}, 2.0884183234,2.0883264804,-0.0906237867 \backslash \mathrm{C},-1.3234551482,-1.323485268$ $5,-0.2825893268 \backslash \mathrm{H}, 1.2504069793,1.2502280916,-1.3784110848 \backslash \mathrm{H},-1.2504069$ $793,-1.2502280916,-1.3784110848 \backslash H,-1.2504069793,1.2502280916,-1.378411$ $0848 \backslash \mathrm{H}, 2.0884183234,-2.0883264804,-0.0906237867 \backslash \mathrm{H}, 1.2504069793,-1.2502$ $280916,-1.3784110848 \backslash \mathrm{H},-2.0884183234,-2.0883264804,-0.0906237867 \backslash \mathrm{H}, 1.7$ $676852161,0 ., 1.3785194502 \backslash \mathrm{H},-2.0884183234,2.0883264804,-0.0906237867 \backslash \mathrm{H}$ , 0., 1.7685619083,1.378246401 \H, 0., -1.7685619083,1.378246401 \H, -1.76768 52161, 0., 1.3785194502\C, 0., -1. $8717164024,0.2824271181 \backslash C, 1.8713352941,0$ ., 0.2827412411 \C, 0., 1.8717164024, 0.2824271181 \C, -1.8713352941, 0., 0. 282 $7412411 \backslash \mathrm{H}, 0 .,-2.9534014389,0.0901747759 \backslash \mathrm{H}, 2.953152391,0.0 .091190882 \backslash \mathrm{H}$ , 0., 2. $9534014389,0.0901747759 \backslash H,-2.953152391,0 ., 0.091190882 \backslash \mathrm{C}, 1.323455$ $1482,-1.3234852685,-0.2825893268 \backslash \mathrm{C}, 1.3234551482,1.3234852685,-0.282589$ $3268 \backslash C,-1.3234551482,1.3234852685,-0.2825893268 \backslash$ VVersion=SGI-G98RevA. 6 $\backslash$ State $=1-\mathrm{Al} \backslash \mathrm{HF}=-314.4843963 \backslash \mathrm{RMSD}=3.045 \mathrm{e}-09 \backslash \mathrm{RMSF}=8.625 \mathrm{e}-06 \backslash \mathrm{Dipole=0} ., 0$. ,-0.0000416\PG=C02V [SGV (C2H4), SGV' (C2H4) , X (C4H8) ] \@

## TBTB-3-52 twistboat,twistboat-bicyclo[3.3.1]nonane

$1 \backslash 1 \backslash G I N C-V P P 10 \backslash F O p t \backslash R B 3 L Y P \backslash 6-31 G(d) \backslash C 9 H 16 \backslash R A S M U S S E N \backslash 08-O c t-1999 \backslash 0 \backslash \backslash \# P$ B3LYP/6-31G* 5D OPT FREQ=NORAMAN NAME=RASMUSSEN MAXDISK=2097152000 GEO $M=(C H E C K, N O D I S T A N C E, N O A N G L E, N O D I H E D R A L) ~ G U E S S=C H E C K \backslash \backslash$ bicyclononane C2 \} $\backslash 0,1 \backslash H, 0.8768876518,-0.053154862,2.0408447162 \backslash \mathrm{H}, 0.0430778491,-2.145987$ 1824, 1.0752805844\H, -0.0418922727,2.1456955782,1.0759174094\H, 2.861601 $6462,-0.1521103805,-1.1259799457 \backslash \mathrm{H},-2.862621168,0.1522883372,-1.123413$ $6321 \backslash \mathrm{C}, 0.0009032729,-0.0001996236,1.3827171211 \backslash \mathrm{H}, 1.4811584864,1.788560$ $4887,-1.121196821 \backslash \mathrm{H}, 2.6419360284,-0.4394439198,0.5871970222 \backslash \mathrm{H}, 0.576698$ $0715,-0.9814232157,-1.6003066853 \backslash \mathrm{H},-0.8740638626,0.0525519385,2.042192$ $0318 \backslash \mathrm{H},-1.4825821779,-1.7884605494,-1.1199359104 \backslash \mathrm{H},-2.6416700948,0.439$ $3551401,0.5896198118 \backslash \mathrm{H},-0.5783752556,0.981967586,-1.5994910733 \backslash \mathrm{C}, 1.519$ $5288226,1.2723784409,-0.1529561227 \backslash \mathrm{C}, 1.0235100027,-1.1987775536,-0.621$ $6568424 \backslash \mathrm{C},-1.5197891976,-1.2723102304,-0.1516327461 \backslash \mathrm{C},-1.0241897522,1$. $1989457642,-0.6203033499 \backslash \mathrm{H}, 2.1940646446,1.8619002606,0.481376497 \backslash \mathrm{H}, 1.4$ $83472232,-2.1899789437,-0.7203607064 \backslash \mathrm{H},-2.1937064084,-1.8617879768,0.4$ $834021209 \backslash \mathrm{H},-1.4842986675,2.1901557766,-0.7182181314 \backslash \mathrm{C}, 2.1088782473,-0$ $.1498433874,-0.3279601018 \backslash C,-0.096590148,-1.2409592991,0.4715215456 \backslash C$, $-2.1092820714,0.1499132972,-0.3259704864 \backslash C, 0.09708304,1.2408312459,0.4$ $717531012 \backslash$ VVersion=Fujitsu-VP-Unix-G98RevA. $6 \backslash H F=-352.5878101 \backslash \mathrm{RMSD}=3.32$ $2 e-09 \backslash R M S F=9.878 e-06 \backslash D i p o l e=0.0000056,-0.000002,0.0274632 \backslash \mathrm{PG}=\mathrm{C} 01 \quad$ [X (C9 H16) ] <br>@

## Hemialkaplanes

## 3-25 hemibihexaplane

$1 \backslash 1 \backslash$ MHPCC-FR16N09\FOpt\RB3LYP\6-31G(d) \C11H14\RASMUSSEN\02-Nov-1998\0 <br>\#P B3LYP/6-31G* 5D OPT=NEWESTMFC NAME=RASMUSSEN GEOM=(NODISTANCE,NOA NGLE, NODIHEDRAL) <br>Hemibihexaplane C2 <br>0,1\C,0.,0.,1.2361541617\C,1.040 7187436,-1.1941169752,1.1583152289\C,-1.0407187436,1.1941169752,1.1583 $152289 \backslash \mathrm{C}, 1.2485533759,1.0419442656,0.6626121771 \backslash \mathrm{C},-1.2485533759,-1.041$ 9442656, 0.6626121771 \H, 2.0344249429,-1.0239922913, 1.5908281281 \H, 0.700 7810796,-2.1736766193,1.4923602537\H, 0.9818952266,2.0980972714,0.63056 $24895 \backslash \mathrm{H}, 2.0427420382,0.9187942498,1.405406506 \backslash \mathrm{H},-2.0344249429,1.023992$ 2913,1.5908281281\H,-0.7007810796,2.1736766193,1.4923602537\H,-0.98189 52266,-2.0980972714,0.6305624895\H,-2.0427420382,-0.9187942498,1.40540 $6506 \backslash \mathrm{C}, 1.1586660337,-1.0345668493,-0.4679690744 \backslash \mathrm{C}, 1.487419743,0.490075$ $13,-0.6777677247 \backslash C,-1.1586660337,1.0345668493,-0.4679690744 \backslash \mathrm{C},-1.48741$ 9743,-0.49007513,-0.6777677247\H,1.8428193599,-1.7752881564,-0.8971337 $597 \backslash \mathrm{H}, 2.4022814224,0.7524693011,-1.2224803405 \backslash \mathrm{H},-1.8428193599,1.775288$ $1564,-0.8971337597 \backslash \mathrm{H},-2.4022814224,-0.7524693011,-1.2224803405 \backslash \mathrm{H}, 0.151$ 6476946,1.3507337243,-2.325843648\C, 0.1456389714, 0.760041433,-1.405550 $9592 \backslash \mathrm{H},-0.1516476946,-1.3507337243,-2.325843648 \backslash \mathrm{C},-0.1456389714,-0.760$ 041433,-1.4055509592 <br>Version=IBM-RS6000-G94RevE. $2 \backslash$ State $=1-A \backslash H F=-427.2$ $845008 \backslash \mathrm{RMSD}=2.558 \mathrm{e}-09 \backslash \mathrm{RMSF}=5.497 \mathrm{e}-05 \backslash \mathrm{Dipole}=0 ., 0 .,-0.2528374 \backslash \mathrm{PG}=\mathrm{C0} 2 \quad[\mathrm{C}$ 2 (C1), X(C1OH14)]<br>@

## 3-2 hemihexaplane

$1 \backslash 1 \backslash$ MHPCC-FR28N08\FOpt $\backslash$ RB3LYP $\backslash 6-31 G(d) \backslash C 11 H 16 \backslash R A S M U S S E N \backslash 03-N o v-1998 \backslash 0$ <br>\#P B3LYP/6-31G* 5D OPT=NEWESTMFC NAME=RASMUSSEN GUESS=CHECK GEOM=(CH ECK, NODISTANCE,NOANGLE,NODIHEDRAL) <br>Hemihexaplane C2 <br>0,1\C,0.,0.,1.29 $81975204 \backslash \mathrm{C}, 0.4371237973,1.5439182392,0.7134856613 \backslash \mathrm{C},-0.4371237973,-1.5$ $439182392,0.7134856613 \backslash C,-1.5186868481,0.4900464178,1.1696453767 \backslash C, 1.5$ $186868481,-0.4900464178,1.1696453767 \backslash \mathrm{H},-0.0981613561,2.2458966836,1.35$ $58802935 \backslash \mathrm{H}, 1.4964747701,1.7793932092,0.8149506091 \backslash \mathrm{H},-2.2973696576,-0.2$ $190472631,1.4502635733 \backslash \mathrm{H},-1.7756389527,1.4541327954,1.6199427618 \backslash \mathrm{H}, 0.0$ 981613561,-2.2458966836,1.3558802935\H,-1.4964747701,-1.7793932092,0.8 $149506091 \backslash \mathrm{H}, 2.2973696576,0.2190472631,1.4502635733 \backslash \mathrm{H}, 1.7756389527,-1.4$ $541327954,1.6199427618 \backslash C,-0.0236031671,1.4509243113,-0.6906878355 \backslash \mathrm{C},-1$ $.3787183002,0.6622200618,-0.4717272415 \backslash C, 0.0236031671,-1.4509243113,-0$ $.6906878355 \backslash C, 1.3787183002,-0.6622200618,-0.4717272415 \backslash \mathrm{H},-0.1717499661$ , $2.3898626884,-1.2421886231 \backslash \mathrm{H},-2.252330807,1.2131435629,-0.8436651718 \backslash$ H, 0.1717499661,-2.3898626884,-1.2421886231 \H, 2.252330807,-1.2131435629 $,-0.8436651718 \backslash \mathrm{H}, 1.0246237279,0.3525368505,-2.3413539726 \backslash \mathrm{C},-1.17412064$ $93,-0.6390595452,-1.2931858547 \backslash \mathrm{H}, 2.0569477131,1.2910549233,-1.27360266$ $89 \backslash \mathrm{C}, 1.1741206493,0.6390595452,-1.2931858547 \backslash \mathrm{H},-2.0569477131,-1.291054$ 9233,-1.2736026689\H,-1.0246237279,-0.3525368505,-2.3413539726<br>Versio n=IBM-RS6000-G94RevE. $2 \backslash$ State $=1-A \backslash H F=-428.5416326 \backslash$ RMSD $=3.048 e-09 \backslash$ RMSF $=1$ . 523e-05\Dipole=0.,0.,-0.252769\PG=C02 [C2 (C1), X(C10H16)] <br>@

## 3-3 hemibiheptaplane

$1 \backslash 1 \backslash$ MHPCC-FR7N01 \FOpt $\backslash$ RB3LYP $\backslash 6$-31G (d) \C12H16\RASMUSSEN $\backslash 02-N o v-1998 \backslash 0 \backslash$ <br>\#P B3LYP/6-31G* 5D OPT=NEWESTMFC NAME=RASMUSSEN GEOM=(NODISTANCE,NOAN GLE, NODIHEDRAL) <br>Hemibiheptaplane C2 <br>0,1\C,0.,0.,1.5132885243\C,1.387 5703069,-0.8202403168,0.9372455131\C,-1.3875703069,0.8202403168,0.9372
$455131 \backslash C, 0.8396903325,1.3519772205,1.3568108906 \backslash C,-0.8396903325,-1.351$ $9772205,1.3568108906 \backslash \mathrm{H}, 2.1774578089,-0.5159962873,1.6293716606 \backslash \mathrm{H}, 1.328$ $5851374,-1.9076168099,0.9828873315 \backslash \mathrm{H}, 0.3592594584,2.2784955055,1.66697$ $8206 \backslash \mathrm{H}, 1.8541745198,1.3548343789,1.7715935185 \backslash \mathrm{H},-2.1774578089,0.515996$ $2873,1.6293716606 \backslash \mathrm{H},-1.3285851374,1.9076168099,0.9828873315 \backslash \mathrm{H},-0.35925$ $94584,-2.2784955055,1.666978206 \backslash \mathrm{H},-1.8541745198,-1.3548343789,1.771593$ $5185 \backslash \mathrm{C}, 1.4705034508,-0.3095271503,-0.4390320903 \backslash \mathrm{C}, 0.957441845,1.168002$ $1918,-0.2816113064 \backslash C,-1.4705034508,0.3095271503,-0.4390320903 \backslash C,-0.957$ $441845,-1.1680021918,-0.2816113064 \backslash \mathrm{H}, 2.4290888637,-0.3952672974,-0.969$ $6306885 \backslash \mathrm{H}, 1.6418398008,1.9263937416,-0.6823513829 \backslash \mathrm{H},-2.4290888637,0.39$ $52672974,-0.9696306885 \backslash \mathrm{H},-1.6418398008,-1.9263937416,-0.6823513829 \backslash \mathrm{C}, 0$ ., 0., -2. $2459226147 \backslash \mathrm{C},-0.3458855906,1.0743070747,-1.1963804131 \backslash \mathrm{H}, 0.6872$ $282259,-2.0417355349,-1.5783023455 \backslash C, 0.3458855906,-1.0743070747,-1.196$ $3804131 \backslash \mathrm{H},-0.6872282259,2.0417355349,-1.5783023455 \backslash \mathrm{H},-0.8601662812$, - 0 . $2342339979,-2.8848395919 \backslash H, 0.8601662812,0.2342339979,-2.8848395919 \backslash \backslash V e$ rsion=IBM-RS6000-G94RevE.2\State=1-A\HF=-466.6426108\RMSD=5.710e-09\RM $\mathrm{SF}=5.041 \mathrm{e}-05 \backslash \mathrm{Dipole}=0 ., 0 .,-0.2708992 \backslash \mathrm{PG}=\mathrm{C0} 2 \quad[\mathrm{C} 2(\mathrm{ClC1}), \mathrm{X}(\mathrm{ClOH16)]} \mathrm{\backslash} \mathrm{\backslash @}$

## 3-26 hemibioctaplane

$1 \backslash 1 \backslash$ MHPCC-FR34N06\FOpt \RB3LYP\6-31G(d) \C13H18\RASMUSSEN $\backslash 03$-NOV-1998\0 <br>\#P B3LYP/6-31G* 5D OPT=NEWESTMFC NAME=RASMUSSEN GUESS=CHECK GEOM=(CH ECK, NODISTANCE, NOANGLE, NODIHEDRAL) <br>Hemibioctaplane C2 <br>0, $1 \backslash C, 0 ., 0 ., 1$. $3065665413 \backslash C, 0.2729223222,1.6271099085,0.7993319729 \backslash \mathrm{C},-0.2729223222$, -1 $.6271099085,0.7993319729 \backslash \mathrm{C},-1.5579225,0.242056137,1.3876524104 \backslash \mathrm{C}, 1.557$ 9225,-0.242056137,1.3876524104 \H, - $0.3379905982,2.2517414015,1.45628089$ $61 \backslash \mathrm{H}, 1.3091054259,1.884990267,1.0029950826 \backslash \mathrm{H},-2.1666530192,-0.52931008$ $14,1.8653878685 \backslash \mathrm{H},-1.8914503793,1.2029206428,1.7914669412 \backslash \mathrm{H}, 0.33799059$ 82,-2.2517414015, 1.4562808961 \H,-1.3091054259,-1.884990267,1.002995082 $6 \backslash H, 2.1666530192,0.5293100814,1.8653878685 \backslash \mathrm{H}, 1.8914503793,-1.202920642$ $8,1.7914669412 \backslash C,-0.0006318132,1.8008278198,-0.654091958 \backslash C,-1.75443333$ $22,0.2466933949,-0.2536075619 \backslash \mathrm{C}, 0.0006318132,-1.8008278198,-0.65409195$ $8 \backslash \mathrm{C}, 1.7544333322,-0.2466933949,-0.2536075619 \backslash \mathrm{H}, 0.4209330219,2.71352013$ $39,-1.0931703387 \backslash \mathrm{H},-2.7495145339,-0.145362649,-0.4936382137 \backslash \mathrm{H},-0.42093$ $30219,-2.7135201339,-1.0931703387 \backslash \mathrm{H}, 2.7495145339,0.145362649,-0.493638$ $2137 \backslash \mathrm{C},-1.5286496013,1.6671538647,-0.8146812433 \backslash \mathrm{C},-0.6210914889,-0.481$ $0229064,-1.1567566432 \backslash C, 1.5286496013,-1.6671538647,-0.8146812433 \backslash C, 0.6$ $210914889,0.4810229064,-1.1567566432 \backslash \mathrm{H},-2.0658824346,2.4506832941,-0.2$ $655070659 \backslash \mathrm{H},-1.8450748999,1.7209865968,-1.8647043715 \backslash \mathrm{H},-1.0459890244,-$ $0.5544584896,-2.165892284 \backslash \mathrm{H}, 1.0459890244,0.5544584896,-2.165892284 \backslash \mathrm{H}, 2$ $.0658824346,-2.4506832941,-0.2655070659 \backslash H, 1.8450748999,-1.7209865968$, $1.8647043715 \backslash \backslash V e r s i o n=I B M-R S 6000$-G94RevE. $2 \backslash$ State $=1-A \backslash H F=-505.9812107 \backslash R$ $\mathrm{MSD}=4.420 \mathrm{e}-09 \backslash \mathrm{RMSF}=2.589 \mathrm{e}-05 \backslash \mathrm{Dipole}=0 ., 0 .,-0.2235362 \backslash \mathrm{PG}=\mathrm{C} 02 \quad[\mathrm{C} 2(\mathrm{C} 1), \mathrm{X}($ C12H18)] <br>@

## 3-1 hemioctaplane

$1 \backslash 1 \backslash M H P C C-F R 7 N 01 \backslash F O p t \backslash R B 3 L Y P \backslash 6-31 G(d) \backslash C 13 H 20 \backslash R A S M U S S E N \backslash 02-N o v-1998 \backslash 0 \backslash$ <br>\#P B3LYP/6-31G* 5D OPT=NEWESTMFC NAME=RASMUSSEN GEOM= (NODISTANCE,NOAN GLE, NODIHEDRAL) <br>Hemioctaplane $C 2 v \backslash \backslash 0,1 \backslash C, 0 ., 0 ., 1.305833032 \backslash C, 0 .,-1.62$ $29525074,0.8515122638 \backslash C, 0 ., 1.6229525074,0.8515122638 \backslash C, 1.6035664882,0$. , 1.4123961208\C, -1. $6035664882,0 ., 1.4123961208 \backslash \mathrm{H}, 0.8655650883,-2.095125$ $4923,1.3155706308 \backslash \mathrm{H},-0.8655650883,-2.0951254923,1.3155706308 \backslash \mathrm{H}, 2.07846$ $19626,0.8751021171,1.8647668408 \backslash \mathrm{H}, 2.0784619626,-0.8751021171,1.8647668$
$408 \backslash \mathrm{H},-0.8655650883,2.0951254923,1.3155706308 \backslash \mathrm{H}, 0.8655650883,2.0951254$ $923,1.3155706308 \backslash \mathrm{H},-2.0784619626,-0.8751021171,1.8647668408 \backslash \mathrm{H},-2.07846$ $19626,0.8751021171,1.8647668408 \backslash C, 0 .,-1.8087193604,-0.6167172071 \backslash C, 1.8$ $921124543,0 .,-0.2069943773 \backslash \mathrm{C}, 0.1 .8087193604,-0.6167172071 \backslash \mathrm{C},-1.892112$ $4543,0 .,-0.2069943773 \backslash H, 0 .,-2.8704642739,-0.9102691662 \backslash H, 2.9883809616$, $0 .,-0.2923948352 \backslash \mathrm{H}, 0 ., 2.8704642739,-0.9102691662 \backslash \mathrm{H},-2.9883809616,0 .,-0$ $.2923948352 \backslash \mathrm{C}, 1.3984420027,-1.2556246466,-0.9994606695 \backslash \mathrm{C}, 1.3984420027$, $1.2556246466,-0.9994606695 \backslash C,-1.3984420027,1.2556246466,-0.9994606695 \backslash$ C, -1. $3984420027,-1.2556246466,-0.9994606695 \backslash \mathrm{H}, 2.0860480962,-2.08688319$ $21,-0.7889440368 \backslash \mathrm{H}, 1.4984624481,-1.0497082505,-2.0726373658 \backslash \mathrm{H}, 2.086048$ $0962,2.0868831921,-0.7889440368 \backslash H, 1.4984624481,1.0497082505,-2.0726373$ $658 \backslash \mathrm{H},-2.0860480962,2.0868831921,-0.7889440368 \backslash \mathrm{H},-1.4984624481,1.04970$ $82505,-2.0726373658 \backslash \mathrm{H},-2.0860480962,-2.0868831921,-0.7889440368 \backslash \mathrm{H},-1.4$ $984624481,-1.0497082505,-2.0726373658 \backslash \backslash V e r s i o n=I B M-R S 6000-G 94 R e v E .2 \backslash$ St ate $=1-\mathrm{A} 1 \backslash \mathrm{HF}=-507.1943882 \backslash \mathrm{RMSD}=9.309 e-09 \backslash \mathrm{RMSF}=6.677 e-05 \backslash \mathrm{Dipole=0.,0.,-0}$ $.14464 \backslash \mathrm{PG}=\mathrm{C} 02 \mathrm{~V}$ [C2 (C1), SGV (C4H2) ,SGV' (C4H2) , X (C4H16) ] <br>@

## 3-27 hemibinonaplane

$1 \backslash 1 \backslash$ MHPCC-FR24N01 \FOpt \RB3LYP\6-31G(d) \C14H20\RASMUSSEN\03-NOV-1998\0 <br>\#P B3LYP/6-31G* 5D OPT=NEWESTMFC NAME=RASMUSSEN GEOM= (NODISTANCE,NOA NGLE , NODIHEDRAL $\backslash \backslash$ Hemibinonaplane $C 2 \backslash \backslash 0,1 \backslash C, 0 ., 0 ., 1.4586957771 \backslash C,-1.08$ $21350675,1.23307102,0.9993266048 \backslash \mathrm{C}, 1.0821350675,-1.23307102,0.99932660$ $48 \backslash C,-1.1597374487,-1.0705456877,1.5565853208 \backslash C, 1.1597374487,1.0705456$ $877,1.5565853208 \backslash \mathrm{H},-1.9495169103,1.1199011739,1.6555717071 \backslash \mathrm{H},-0.646071$ $1906,2.1975765212,1.2465433492 \backslash \mathrm{H},-0.9424507373,-2.0170568622,2.0560796$ $125 \backslash \mathrm{H},-2.1256668851,-0.7288925529,1.9443628289 \backslash \mathrm{H}, 1.9495169103,-1.11990$ $11739,1.6555717071 \backslash \mathrm{H}, 0.6460711906,-2.1975765212,1.2465433492 \backslash \mathrm{H}, 0.94245$ $07373,2.0170568622,2.0560796125 \backslash \mathrm{H}, 2.1256668851,0.7288925529,1.94436282$ $89 \backslash \mathrm{C},-1.4100688291,1.1963500086,-0.4404186648 \backslash \mathrm{C},-1.3197005896,-1.26011$ $09597,-0.0840279432 \backslash \mathrm{C}, 1.4100688291,-1.1963500086,-0.4404186648 \backslash \mathrm{C}, 1.319$ $7005896,1.2601109597,-0.0840279432 \backslash \mathrm{H},-2.0138389233,2.0516738814,-0.775$ $9247953 \backslash \mathrm{H},-1.8227361426,-2.2241353304,-0.2291267242 \backslash \mathrm{H}, 2.0138389233,-2$. $0516738814,-0.7759247953 \backslash \mathrm{H}, 1.8227361426,2.2241353304,-0.2291267242 \backslash \mathrm{C},-$ $2.2076285759,-0.1202326679,-0.6128759973 \backslash \mathrm{C},-0.0163598793,-1.2370908975$ , - $1.1049765777 \backslash \mathrm{C}, 2.2076285759,0.1202326679,-0.6128759973 \backslash \mathrm{C}, 0.016359879$ $3,1.2370908975,-1.1049765777 \backslash \mathrm{H},-3.1343330339,-0.0371007072,-0.02921015$ $83 \backslash \mathrm{H},-2.5173818373,-0.3140254259,-1.6451194934 \backslash \mathrm{H},-0.1053215457,-2.1475$ $524554,-1.7078342152 \backslash C, 0 ., 0 .,-2.027111439 \backslash H, 3.1343330339,0.0371007072$, $-0.0292101583 \backslash \mathrm{H}, 2.5173818373,0.3140254259,-1.6451194934 \backslash \mathrm{H}, 0.1053215457$ , $2.1475524554,-1.7078342152 \backslash \mathrm{H}, 0.8666192241,-0.0679595938,-2.6917715805$ $\backslash H,-0.8666192241,0.0679595938,-2.6917715805 \backslash \backslash$ Version=IBM-RS6000-G94Rev $E .2 \backslash S t a t e=1-A \backslash H F=-545.2765296 \backslash R M S D=8.074 e-09 \backslash R M S F=7.162 e-05 \backslash D i p o l e=0 .$, $0 .,-0.2335023 \backslash \mathrm{PG}=\mathrm{C0} 2 \quad[\mathrm{C} 2(\mathrm{C} 1 \mathrm{C} 1), \mathrm{X}(\mathrm{C} 12 \mathrm{H} 20)] \backslash \backslash @$

## Hemispiroalkaplanes

## 3-28 hemispirobutaplane

$1 \backslash 1 \backslash$ MHPCC-FR2N05\FOpt \RB3LYP\6-31G(d) \C9H8 \RASMUSSEN $\backslash 30-$ Oct-1998\0<br>\# P B3LYP/6-31G* 5D OPT=NEWESTMFC NAME=RASMUSSEN GEOM=(NODISTANCE,NOANGL E,NODIHEDRAL) <br>Hemispirobutaplane C4v<br>0,1\C,0.,0.,1.4470127318\C,-1.2 $09686106,0.7176138598,0.5962618266 \backslash C, 1.209686106,-0.7176138598,0.59626$ $18266 \backslash \mathrm{C},-1.209686106,-0.7176138598,0.5962618266 \backslash \mathrm{C}, 1.209686106,0.717613$

8598, 0. $5962618266 \backslash \mathrm{H},-1.74678153,1.4516670795,1.1893530357 \backslash \mathrm{H},-1.3566951$ $404,1.3811796206,-1.5993385432 \backslash \mathrm{H}, 1.3566951404,-1.3811796206,-1.5993385$ $432 \backslash \mathrm{H},-1.74678153,-1.4516670795,1.1893530357 \backslash \mathrm{H}, 1.74678153,-1.451667079$ $5,1.1893530357 \backslash \mathrm{H}, 1.3566951404,1.3811796206,-1.5993385432 \backslash \mathrm{H},-1.35669514$ 04, - $1.3811796206,-1.5993385432 \backslash \mathrm{H}, 1.74678153,1.4516670795,1.1893530357 \backslash$ $C,-0.7780997771,0.7862223964,-0.8896840916 \backslash C,-0.7780997771,-0.78622239$ $64,-0.8896840916 \backslash \mathrm{C}, 0.7780997771,-0.7862223964,-0.8896840916 \backslash \mathrm{C}, 0.778099$ 7771, 0.7862223964,-0.8896840916<br>Version=IBM-RS6000-G94RevE.2\State=1$\mathrm{A} 1 \backslash \mathrm{HF}=-347.4696387 \backslash \mathrm{RMSD}=8.300 \mathrm{e}-09 \backslash \mathrm{RMSF}=1.242 \mathrm{e}-04 \backslash \mathrm{Dipole}=0 ., 0 .,-0.97568$ $39 \backslash \mathrm{PG}=\mathrm{C} 02 \mathrm{~V}$ [C2 (C1), X(C8H8)] <br>@

## 3-29 hemispirobihexaplane (perpendicular)

$1 \backslash 1 \backslash$ MHPCC-FR16N02\FOpt \RB3LYP\6-31G(d) \C11H10\RASMUSSEN $\backslash 30-$ Oct-1998\0 <br>\#P B3LYP/6-31G* 5D OPT=NEWESTMFC NAME=RASMUSSEN GEOM= (NODISTANCE,NOA NGLE, NODIHEDRAL) <br>Hemispirobihexaplane (orient b) C2v <br>0,1\C,0.,0.,1.7 $592716178 \backslash C, 1.2150762579,0.7164213807,0.8736181118 \backslash C,-1.2150762579$, -0 . $7164213807,0.8736181118 \backslash C,-1.2150762579,0.7164213807,0.8736181118 \backslash C, 1$. $2150762579,-0.7164213807,0.8736181118 \backslash \mathrm{H},-1.4052772317,0 .,-2.3578439318$ $\backslash \mathrm{H}, 1.818212253,1.329641175,1.5372326177 \backslash \mathrm{H},-1.818212253,1.329641175,1.5$ $372326177 \backslash \mathrm{C},-0.779024346,0 .,-1.4637443945 \backslash \mathrm{H}, 1.4052772317,0 .,-2.3578439$ $318 \backslash \mathrm{H},-1.818212253,-1.329641175,1.5372326177 \backslash \mathrm{H}, 1.818212253,-1.32964117$ $5,1.5372326177 \backslash \mathrm{C}, 0.779024346,0 .,-1.4637443945 \backslash \mathrm{C}, 0.7834083902,1.2307010$ $053,-0.5020492333 \backslash C,-0.7834083902,1.2307010053,-0.5020492333 \backslash C,-0.7834$ 083902 , - $1.2307010053,-0.5020492333 \backslash \mathrm{C}, 0.7834083902,-1.2307010053,-0.502$ $0492333 \backslash \mathrm{H}, 1.2967298778,2.1364911111,-0.8353981657 \backslash \mathrm{H},-1.2967298778,2.13$ $64911111,-0.8353981657 \backslash \mathrm{H},-1.2967298778,-2.1364911111,-0.8353981657 \backslash \mathrm{H}, 1$ $.2967298778,-2.1364911111,-0.8353981657 \backslash \backslash V e r s i o n=I B M-R S 6000-G 94 R e v E .2 \backslash$ State $=1-\mathrm{A} 1 \backslash \mathrm{HF}=-424.9331641 \backslash \mathrm{RMSD}=7.363 e-09 \backslash \mathrm{RMSF}=4.562 e-05 \backslash \mathrm{Dipole=0.,0.}$, $-1.1240561 \backslash \mathrm{PG}=\mathrm{C0} 2 \mathrm{~V} \quad[\mathrm{C} 2(\mathrm{C} 1), \mathrm{SGV}(\mathrm{C} 2 \mathrm{H} 2), \mathrm{X}(\mathrm{C} 8 \mathrm{H} 8)] \backslash \backslash @$

## 3-30 hemispirobihexaplane (parallel)

$1 \backslash 1 \backslash G I N C-P C \backslash F O p t \backslash R B 3 L Y P \backslash 6-31 G(d) \backslash C 11 H 10 \backslash R A S M U S S E N \backslash 09-O c t-1999 \backslash 0 \backslash \backslash \# P$ B3 LYP/6-31G* 5D OPT NAME=RASMUSSEN GEOM= (CHECK,NODISTANCE, NOANGLE,NODIHE DRAL) SYMM=LOOSE GUESS=CHECK <br>Hemispirobihexaplane (orient a) C2v<br>0,1 $\backslash C, 0.0 ., 1.635567735 \backslash C,-0.0493432054,1.4485494573,0.9905553508 \backslash C, 0.049$ $3432054,-1.4485494573,0.9905553508 \backslash C,-1.299369463,0.723540196,0.929250$ $5856 \backslash \mathrm{C}, 1.299369463,-0.723540196,0.9292505856 \backslash \mathrm{H}, 1.1656823286,0.70726466$ $54,-2.3249574872 \backslash \mathrm{H}, 0.3058926115,2.2170955934,1.6727077075 \backslash \mathrm{H},-2.1293120$ $902,0.6645660896,1.6265074451 \backslash C, 0.675141712,0.3991532472,-1.3982348053$ $\backslash \mathrm{H},-1.1656823286,-0.7072646654,-2.3249574872 \backslash \mathrm{H},-0.3058926115,-2.217095$ 5934, 1.6727077075\H,2.1293120902,-0.6645660896,1.6265074451 \C, -0.67514 1712,-0.3991532472,-1.3982348053\C, 0.,1.5374768553,-0.5689578336\C,-1. $3465187323,0.7635740429,-0.600465662 \backslash C, 0 .,-1.5374768553,-0.5689578336 \backslash$ C, 1. $3465187323,-0.7635740429,-0.600465662 \backslash \mathrm{H}, 0.0773028636,2.5539271934$, $-0.9612627094 \backslash H,-2.2452983218,1.2099142739,-1.0325839743 \backslash H,-0.07730286$ $36,-2.5539271934,-0.9612627094 \backslash \mathrm{H}, 2.2452983218,-1.2099142739,-1.0325839$ $743 \backslash$ Version=SGI-G98RevA. $6 \backslash$ State $=1-A \backslash H F=-424.8476803 \backslash R M S D=1.598 e-09 \backslash R M$ $\mathrm{SF}=1.953 \mathrm{e}-06 \backslash \mathrm{Dipole=0.,0.,-0.8707224} \mathrm{\backslash PG=CO2} \mathrm{\quad[C2(C1),X(Cl10H10)]} \mathrm{\backslash} \mathrm{\backslash @}$

## 3-31 hemispirohexaplane (perpendicular)

$1 \backslash 1 \backslash$ MHPCC-FR17N05\FOpt \RB3LYP\6-31G (d) \C11H12\RASMUSSEN\31-Oct-1998\0 <br>\#P B3LYP/6-31G* 5D OPT=NEWESTMFC NAME=RASMUSSEN GEOM= (NODISTANCE,NOA

NGLE, NODIHEDRAL $\backslash \backslash$ Hemispirohexaplane $C 2 v \backslash \backslash 0,1 \backslash C, 0 ., 0 ., 1.796699566 \backslash C, 1$ $.1881557875,0.7159687483,0.9149648001 \backslash \mathrm{C},-1.1881557875,-0.7159687483,0$. $9149648001 \backslash C,-1.1881557875,0.7159687483,0.9149648001 \backslash C, 1.1881557875,-0$ $.7159687483,0.9149648001 \backslash \mathrm{C}, 1.328882301,0 .,-1.3496809816 \backslash \mathrm{H}, 1.7997018946$ , 1. $3414580238,1.5580007761 \backslash \mathrm{H},-1.7997018946,1.3414580238,1.5580007761 \backslash \mathrm{H}$ , 2. $4246565632,0 .,-1.3402535839 \backslash \mathrm{H},-1.0112489188,0 .,-2.3980065601 \backslash \mathrm{H},-1.7$ $997018946,-1.3414580238,1.5580007761 \backslash H, 1.7997018946,-1.3414580238,1.55$ $80007761 \backslash \mathrm{H}, 1.0112489188,0 .,-2.3980065601 \backslash \mathrm{C}, 0.7848621283,1.1786589389$, $0.5074612229 \backslash C,-0.7848621283,1.1786589389,-0.5074612229 \backslash C,-0.784862128$ $3,-1.1786589389,-0.5074612229 \backslash \mathrm{C}, 0.7848621283,-1.1786589389,-0.50746122$ $29 \backslash \mathrm{H}, 1.2060149795,2.1508418285,-0.7798985711 \backslash \mathrm{H},-1.2060149795,2.1508418$ $285,-0.7798985711 \backslash \mathrm{H},-1.2060149795,-2.1508418285,-0.7798985711 \backslash \mathrm{H}, 1.2060$ 149795,-2.1508418285,-0.7798985711 \H,-2.4246565632,0.,-1.3402535839\C, $-1.328882301,0 .,-1.3496809816 \backslash$ \Version=IBM-RS6000-G94RevE. $2 \backslash$ State=1-A1 $\backslash H F=-426.187891 \backslash R M S D=3.632 e-09 \backslash R M S F=3.166 e-05 \backslash D i p o l e=0 ., 0 .,-1.0648417 \backslash$ PG=C02V [C2 (C1), SGV (C2H4), X(C8H8)] <br>@

## 3-32 hemispirohexaplane (parallel)

$1 \backslash 1 \backslash$ MHPCC-FR12N16\FOpt \RB3LYP\6-31G(d) \C11H12 \RASMUSSEN $\backslash 30$-Oct-1998\0 <br>\#P B3LYP/6-31G* 5D OPT=NEWESTMFC NAME=RASMUSSEN GEOM=(NODISTANCE,NOA NGLE, NODIHEDRAL) <br>Hemispirohexaplane (orient a) C2v $\backslash \backslash 0,1 \backslash C, 0 ., 0 ., 1.657$ $0103671 \backslash C, 0.7186234513,1.2754812287,0.9462852685 \backslash C,-0.7186234513,-1.27$ 54812287,0.9462852685\C,-0.7186234513,1.2754812287,0.9462852685\C,0.71 86234513,-1.2754812287,0.9462852685\C,1.4507320197,0.,-1.1981290667 H , $1.4335498008,1.73596083,1.6223931537 \backslash \mathrm{H},-1.4335498008,1.73596083,1.6223$ $931537 \backslash \mathrm{H}, 2.5316513176,0 .,-0.9944272048 \backslash \mathrm{H},-1.3331186315,0 .,-2.290600349$ $9 \backslash \mathrm{H},-1.4335498008,-1.73596083,1.6223931537 \backslash \mathrm{H}, 1.4335498008,-1.73596083$, $1.6223931537 \backslash \mathrm{H}, 1.3331186315,0 .,-2.2906003499 \backslash \mathrm{C}, 0.7898421393,1.23567497$ 89,-0.5912102945\C,-0.7898421393,1.2356749789,-0.5912102945\C,-0.78984 21393,-1.2356749789,-0.5912102945\C,0.7898421393,-1.2356749789,-0.5912 $102945 \backslash \mathrm{H}, 1.2036014307,2.164043351,-1.0014575708 \backslash \mathrm{H},-1.2036014307,2.1640$ 43351,-1.0014575708\H,-1.2036014307,-2.164043351,-1.0014575708\H,1.203 6014307,-2.164043351,-1.0014575708\H,-2.5316513176,0.,-0.9944272048\C, -1.4507320197,0.,-1.1981290667<br>Version=IBM-RS6000-G94RevE.2\State=1-A $1 \backslash H F=-426.1489566 \backslash \mathrm{RMSD}=2.432 \mathrm{e}-09 \backslash \mathrm{RMSF}=4.096 \mathrm{e}-05 \backslash \mathrm{Dipole}=0 ., 0 .,-0.937722$ \PG=C02V [C2 (C1), SGV (C2H4), X(C8H8)] <br>@

## 3-33 hemispirobiheptaplane (perpendicular)

$1 \backslash 1 \backslash$ MHPCC-FR16N06\FOpt \RB3LYP\6-31G(d) \C12H12 \RASMUSSEN $\backslash 30$-Oct-1998\0 <br>\#P B3LYP/6-31G* 5D OPT=NEWESTMFC NAME=RASMUSSEN GEOM= (NODISTANCE,NOA NGLE, NODIHEDRAL) <br>Hemispirobiheptaplane C2v <br>0,1\C,0.,0.,2.0072728322\} C, 1.2023288451,0.7153728311,1.1250703434 \C,-1.2023288451,-0.7153728311 ,1.1250703434\C,-1.2023288451,0.7153728311,1.1250703434\C,1.2023288451 , $-0.7153728311,1.1250703434 \backslash \mathrm{C}, 1.1279030932,0 .,-1.2218684811 \backslash \mathrm{H}, 1.805253$ 5114,1.3405575954,1.7766834432\H,-1.8052535114,1.3405575954,1.77668344 $32 \backslash \mathrm{H}, 0 .,-0.8905153909,-2.9024452149 \backslash \mathrm{C}, 0 ., 0 .,-2.2613694381 \backslash \mathrm{H},-1.8052535$ 114,-1.3405575954,1.7766834432\H,1.8052535114,-1.3405575954,1.77668344 $32 \backslash \mathrm{H}, 0 ., 0.8905153909,-2.9024452149 \backslash \mathrm{C}, 0.7843128227,1.1905120939,-0.2760$ $917221 \backslash \mathrm{C},-0.7843128227,1.1905120939,-0.2760917221 \backslash \mathrm{C},-0.7843128227,-1.1$ 905120939,-0.2760917221\C,0.7843128227,-1.1905120939,-0.2760917221\H,1 . $2313225512,2.1433696236,-0.5744421982 \backslash \mathrm{H},-1.2313225512,2.1433696236,-0$ $.5744421982 \backslash \mathrm{H},-1.2313225512,-2.1433696236,-0.5744421982 \backslash \mathrm{H}, 1.2313225512$
$,-2.1433696236,-0.5744421982 \backslash H,-2.1553331358,0 .,-1.5962800265 \backslash \mathrm{C},-1.127$ $9030932,0 .,-1.2218684811 \backslash \mathrm{H}, 2.1553331358,0 .,-1.5962800265 \backslash$ Version=IBM-RS6000-G94RevE. $2 \backslash$ State=1-A1 \HF=-464.3008149\RMSD=4.160e-09\RMSF=2.992e $-05 \backslash$ Dipole=0., 0.,-1.1304561 \PG=C02V [C2 (C1C1) , SGV (C2H2) , SGV' (H2) , X (C8H 8) ] <br>@

## 3-34 hemispirobiheptaplane (parallel)

$1 \backslash 1 \backslash M H P C C-F R 10 N 15 \backslash F O p t \backslash R B 3 L Y P \backslash 6-31 G(d) \backslash C 12 H 12 \backslash R A S M U S S E N \backslash 01-N O V-1998 \backslash 0$ <br>\#P B3LYP/6-31G* 5D OPT=NEWESTMFC NAME=RASMUSSEN GUESS=CHECK GEOM=(CH ECK, NODISTANCE, NOANGLE, NODIHEDRAL) <br>Hemispirobiheptaplane (orient a) C $2 \mathrm{v} \backslash \backslash 0,1 \backslash \mathrm{C}, 0 ., 0 .,-1.8935577514 \backslash \mathrm{C}, 1.2634264218,0.7209615708,-1.190964175$ $2 \backslash C,-1.2634264218,-0.7209615708,-1.1909641752 \backslash C, 1.2634264218,-0.720961$ 5708, -1.1909641752\C,-1.2634264218, 0.7209615708, -1.1909641752\C,0.,1.1 $562230347,1.1599618556 \backslash \mathrm{H}, 1.7209767547,1.4354801968,-1.8687288873 \backslash \mathrm{H}, 1.7$ $209767547,-1.4354801968,-1.8687288873 \backslash \mathrm{H},-0.8915770195,0 ., 2.8460337296 \backslash$ C, 0., 0., 2. $205392302 \backslash \mathrm{H},-1.7209767547,-1.4354801968,-1.8687288873 \backslash \mathrm{H},-1.7$ $209767547,1.4354801968,-1.8687288873 \backslash \mathrm{H}, 0.8915770195,0 ., 2.8460337296 \backslash \mathrm{C}$, $1.2584738486,0.7842100531,0.350505187 \backslash \mathrm{C}, 1.2584738486,-0.7842100531,0.3$ $50505187 \backslash C,-1.2584738486,-0.7842100531,0.350505187 \backslash C,-1.2584738486,0.7$ $842100531,0.350505187 \backslash \mathrm{H}, 2.1672382783,1.241395016,0.7554029691 \backslash \mathrm{H}, 2.1672$ $382783,-1.241395016,0.7554029691 \backslash \mathrm{H},-2.1672382783,-1.241395016,0.755402$ $9691 \backslash \mathrm{H},-2.1672382783,1.241395016,0.7554029691 \backslash \mathrm{H}, 0 .,-2.1698390018,1.570$ $8511799 \backslash \mathrm{C}, 0 .,-1.1562230347,1.1599618556 \backslash \mathrm{H}, 0 ., 2.1698390018,1.5708511799$ <br>Version=IBM-RS6000-G94RevE.2\State=1-A1 \HF=-464.2333455\RMSD=6.378e$09 \backslash \mathrm{RMSF}=7.558 \mathrm{e}-05 \backslash \mathrm{Dipole}=0 ., 0.0 .9282785 \backslash \mathrm{PG}=\mathrm{C} 02 \mathrm{~V} \quad[\mathrm{C} 2(\mathrm{C} 1 \mathrm{C} 1)$, $\mathrm{SGV}(\mathrm{C} 2 \mathrm{H} 2)$, S GV' (H2) , X (C8H8) ] <br>@

## 3-35 hemispirobioctaplane (parallel)

$1 \backslash 1 \backslash M H P C C-F R 12 N 10 \backslash F O p t \backslash R B 3 L Y P \backslash 6-31 G(d) \backslash C 13 H 14 \backslash R A S M U S S E N \backslash 31-O c t-1998 \backslash 0$ <br>\#P B3LYP/6-31G* 5D OPT=NEWESTMFC NAME=RASMUSSEN GEOM= (NODISTANCE,NOA NGLE, NODIHEDRAL) <br>Hemispirobioctaplane (orient a) C2v $\backslash \backslash 0,1 \backslash C, 0 ., 0 ., 1.8$ $2683815 \backslash \mathrm{C}, 1.2700791092,-0.7188327494,1.1015951919 \backslash \mathrm{C},-1.2700791092,0.71$ $88327494,1.1015951919 \backslash \mathrm{C}, 1.2700791092,0.7188327494,1.1015951919 \backslash \mathrm{C},-1.27$ $00791092,-0.7188327494,1.1015951919 \backslash \mathrm{H}, 0 ., 1.1954134605,-2.1061855423 \backslash \mathrm{H}$, $1.7623763315,-1.3418843588,1.8429292039 \backslash \mathrm{H}, 1.7623763315,1.3418843588,1$. $8429292039 \backslash \mathrm{H}, 0 .,-1.1954134605,-2.1061855423 \backslash \mathrm{H},-3.242338961,0 .,-0.48197$ $85396 \backslash \mathrm{H},-1.7623763315,1.3418843588,1.8429292039 \backslash \mathrm{H},-1.7623763315,-1.341$ $8843588,1.8429292039 \backslash \mathrm{H},-2.3414772587,0 .,-2.0253054161 \backslash \mathrm{C}, 1.3293533453$, -$1.1335526229,-0.3824327524 \backslash \mathrm{C}, 1.3293533453,1.1335526229,-0.3824327524 \backslash \mathrm{C}$ , - $1.3293533453,1.1335526229,-0.3824327524 \backslash C,-1.3293533453,-1.133552622$ $9,-0.3824327524 \backslash \mathrm{H}, 1.6708863278,-2.1605686277,-0.5368127692 \backslash \mathrm{H}, 1.6708863$ $278,2.1605686277,-0.5368127692 \backslash \mathrm{H},-1.6708863278,2.1605686277,-0.5368127$ $692 \backslash \mathrm{H},-1.6708863278,-2.1605686277,-0.5368127692 \backslash \mathrm{C}, 2.2418532408,0 .,-0.9$ $305151814 \backslash \mathrm{C}, 0 ., 0.7909134477,-1.0876893344 \backslash \mathrm{C},-2.2418532408,0 .,-0.930515$ $1814 \backslash \mathrm{C}, 0 .,-0.7909134477,-1.0876893344 \backslash \mathrm{H}, 3.242338961,0 .,-0.4819785396 \backslash \mathrm{H}$ , 2. 3414772587,0.,-2.0253054161 <br>Version=IBM-RS6000-G94RevE. $2 \backslash$ State=1-A $1 \backslash \mathrm{HF}=-503.5917458 \backslash \mathrm{RMSD}=4.141 e-09 \backslash \mathrm{RMSF}=6.413 e-05 \backslash \mathrm{Dipole}=0 ., 0 .,-0.971345$ $1 \backslash \mathrm{PG}=\mathrm{C} 02 \mathrm{~V} \quad\left[\mathrm{C} 2(\mathrm{C} 1), \mathrm{SGV}(\mathrm{C} 2 \mathrm{H} 4), \mathrm{SGV}^{\prime}(\mathrm{C} 2 \mathrm{H} 2), \mathrm{X}(\mathrm{C} 8 \mathrm{H} 8)\right] \backslash \backslash @$

## 3-4 hemispirobioctaplane (perpendicular)

$1 \backslash 1 \backslash$ MHPCC-FR15N05\FOpt \RB3LYP\6-31G (d) \C13H14 \RASMUSSEN $\backslash 30-$ Oct-1998\0 <br>\#P B3LYP/6-31G* 5D OPT=NEWESTMFC NAME=RASMUSSEN GEOM= (NODISTANCE,NOA

NGLE, NODIHEDRAL $\backslash \backslash$ Hemispirobioctaplane $C 2 v \backslash \backslash 0,1 \backslash C, 0 ., 0 ., 1.7511878876 \backslash C$ , 1.2881798615, 0.7160965858,1.0096280155 \C, -1.2881798615, -0.7160965858, $1.0096280155 \backslash C,-1.2881798615,0.7160965858,1.0096280155 \backslash C, 1.2881798615$, $-0.7160965858,1.0096280155 \backslash \mathrm{H},-1.1995039616,0 .,-2.2495613065 \backslash \mathrm{H}, 1.796988$ $7864,1.3188181514,1.7580134468 \backslash \mathrm{H},-1.7969887864,1.3188181514,1.75801344$ $68 \backslash \mathrm{H}, 1.1995039616,0 .,-2.2495613065 \backslash \mathrm{H}, 0 .,-3.0304660247,0.1733670592 \backslash \mathrm{H},-$ $1.7969887864,-1.3188181514,1.7580134468 \backslash \mathrm{H}, 1.7969887864,-1.3188181514,1$ $.7580134468 \backslash \mathrm{H}, 0 .,-2.6858054859,-1.5677676665 \backslash \mathrm{C}, 1.1805898616,1.25456566$ $32,-0.4126178474 \backslash C,-1.1805898616,1.2545656632,-0.4126178474 \backslash \mathrm{C},-1.18058$ $98616,-1.2545656632,-0.4126178474 \backslash \mathrm{C}, 1.1805898616,-1.2545656632,-0.4126$ $178474 \backslash \mathrm{H}, 2.1424979397,1.6892485657,-0.7124086293 \backslash \mathrm{H},-2.1424979397,1.689$ $2485657,-0.7124086293 \backslash \mathrm{H},-2.1424979397,-1.6892485657,-0.7124086293 \backslash \mathrm{H}, 2$. $1424979397,-1.6892485657,-0.7124086293 \backslash C, 0 ., 2.225343209,-0.5717925439 \backslash$ C, -0.7818601081,0.,-1.2390296897\C,0.,-2.225343209,-0.5717925439\C, 0.7 $818601081,0 .,-1.2390296897 \backslash H, 0 ., 3.0304660247,0.1733670592 \backslash \mathrm{H}, 0 ., 2.68580$ $54859,-1.5677676665 \backslash$ Version=IBM-RS6000-G94RevE. $2 \backslash$ State $=1-A 1 \backslash H F=-503.6$ $358308 \backslash \mathrm{RMSD}=8.351 e-09 \backslash \mathrm{RMSF}=5.782 \mathrm{e}-05 \backslash \mathrm{Dipole=0.,0.,-1.0100331} \mathrm{\backslash PG=C02V} \mathrm{\quad[ } \mathrm{\quad]}$ C2 (C1) , SGV (C2H4) ,SGV' (C2H2) , X (C8H8) ] <br>@

## 3-5 hemispirooctaplane

$1 \backslash 1 \backslash$ MHPCC-FR21N03 \FOpt $\backslash$ RB3LYP $\backslash 6$-31G(d) \C13H16\RASMUSSEN $\backslash 01$-Nov-1998\0 <br>\#P B3LYP/6-31G* 5D OPT=NEWESTMFC NAME=RASMUSSEN GEOM= (NODISTANCE,NOA NGLE, NODIHEDRAL) <br>Hemispirooctaplane C2v<br>0,1\C,0.,0.,1.7840845056\C,-$0.7170997587,-1.2902489922,1.0853079711 \backslash C, 0.7170997587,1.2902489922,1$. $0853079711 \backslash C, 0.7170997587,-1.2902489922,1.0853079711 \backslash \mathrm{C},-0.7170997587,1$ $.2902489922,1.0853079711 \backslash \mathrm{H},-2.9687695075,0 .,-0.1328274125 \backslash \mathrm{H},-1.3171889$ 364,-1.7714711776,1.8541829694\H,1.3171889364,-1.7714711776,1.85418296 $94 \backslash \mathrm{H},-2.2949046878,0 .,-1.7596219273 \backslash \mathrm{H}, 0 ., 2.655683968,-1.461291376 \backslash \mathrm{H}, 1$. 3171889364,1.7714711776,1.8541829694 \H,-1.3171889364,1.7714711776,1.85 $41829694 \backslash$ H, $0 ., 1.0562302839,-2.177038643 \backslash$ C, $-1.2560553992,-1.2854250965$, $-0.3492687995 \backslash C, 1.2560553992,-1.2854250965,-0.3492687995 \backslash C, 1.256055399$ $2,1.2854250965,-0.3492687995 \backslash C,-1.2560553992,1.2854250965,-0.349268799$ $5 \backslash \mathrm{H},-1.9665882674,-2.1173799677,-0.4403210801 \backslash \mathrm{H}, 1.9665882674,-2.117379$ 9677,-0.4403210801 \H, 1.9665882674,2.1173799677,-0.4403210801 \Н, -1.9665 882674,2.1173799677,-0.4403210801\C,0.,-1.5869126022,-1.2184169071\C,2 $.024272556,0 .,-0.6951944255 \backslash C, 0 ., 1.5869126022,-1.2184169071 \backslash C,-2.02427$ $2556,0 .,-0.6951944255 \backslash$ H, 0., -2.655683968,-1.461291376\H, 0., -1. 056230283 $9,-2.177038643 \backslash \mathrm{H}, 2.9687695075,0 .,-0.1328274125 \backslash \mathrm{H}, 2.2949046878,0 .,-1.75$ $96219273 \backslash$ VVersion=IBM-RS6000-G94RevE. $2 \backslash$ State $=1-A 1 \backslash H F=-504.8275879 \backslash$ RMSD $=5.700 \mathrm{e}-09 \backslash \mathrm{RMSF}=1.889 \mathrm{e}-05 \backslash \mathrm{Dipole}=0 ., 0 .,-0.8856606 \backslash \mathrm{PG}=\mathrm{CO} 2 \mathrm{~V} \quad[\mathrm{C} 2(\mathrm{Cl}), \mathrm{SGV}($ C2H4), SGV'(C2H4), X(C8H8)]<br>@

## 3-6 hemispirobinonaplane (perpendicular)

$1 \backslash 1 \backslash$ MHPCC-FR7N07\FOpt \RB3LYP\6-31G(d) \C14H16\RASMUSSEN\01-Nov-1998\0\} <br>\#P B3LYP/6-31G* 5D OPT=NEWESTMFC NAME=RASMUSSEN GEOM=(NODISTANCE,NOAN GLE, NODIHEDRAL) <br>Hemispirobinonaplane (orient b) C2v $\backslash \backslash 0,1 \backslash C, 0 ., 0 ., 1.92$ $78095011 \backslash \mathrm{C},-0.7146646383,1.294302478,1.2131482426 \backslash \mathrm{C}, 0.7146646383,-1.29$ $4302478,1.2131482426 \backslash C,-0.7146646383,-1.294302478,1.2131482426 \backslash C, 0.714$ 6646383,1.294302478,1.2131482426\H,-1.3166370932,1.7849830266,1.974986 $478 \backslash \mathrm{H}, 2.6143005638,0 .,-1.3988467176 \backslash \mathrm{H}, 0.8748273764,0 .,-2.7203694708 \backslash \mathrm{H}$, $-1.3166370932,-1.7849830266,1.974986478 \backslash \mathrm{H}, 1.3166370932,-1.7849830266,1$ $.974986478 \backslash \mathrm{H},-0.8748273764,0 .,-2.7203694708 \backslash \mathrm{H}, 0 ., 2.1447859747,-1.75658$
$31854 \backslash \mathrm{H}, 1.3166370932,1.7849830266,1.974986478 \backslash \mathrm{C},-1.2635973832,1.240021$ $4677,-0.2070898871 \backslash C,-1.2635973832,-1.2400214677,-0.2070898871 \backslash C, 1.263$ $5973832,-1.2400214677,-0.2070898871 \backslash \mathrm{C}, 1.2635973832,1.2400214677,-0.207$ $0898871 \backslash \mathrm{H},-1.8590533465,2.1466351194,-0.3766114625 \backslash \mathrm{H},-1.8590533465,-2$. $1466351194,-0.3766114625 \backslash \mathrm{H}, 1.8590533465,-2.1466351194,-0.3766114625 \backslash \mathrm{H}$, $1.8590533465,2.1466351194,-0.3766114625 \backslash \mathrm{C},-2.1500307546,0 .,-0.40585733$ $56 \backslash C, 0 .,-1.2339268281,-1.1486509194 \backslash C, 2.1500307546,0 .,-0.4058573356 \backslash C$, $0 ., 1.2339268281,-1.1486509194 \backslash \mathrm{H},-2.9690082096,0 ., 0.3258478307 \backslash \mathrm{H},-2.614$ $3005638,0 .,-1.3988467176 \backslash \mathrm{H}, 0 .,-2.1447859747,-1.7565831854 \backslash \mathrm{C}, 0 ., 0 .,-2.0$ $586259092 \backslash \mathrm{H}, 2.9690082096,0 ., 0.3258478307 \backslash \backslash V e r s i o n=I B M-R S 6000-G 94 R e v E .2$ $\backslash$ State=1-A1 \HF=-542.941267 $\backslash \mathrm{RMSD}=5.385 e-09 \backslash R M S F=5.534 e-05 \backslash \mathrm{Dipole=0.,0.}$, $-0.9822525 \backslash \mathrm{PG}=\mathrm{C0} 2 \mathrm{~V} \quad\left[\mathrm{C} 2(\mathrm{C} 1 \mathrm{C} 1), \mathrm{SGV}(\mathrm{C} 2 \mathrm{H} 6), \mathrm{SGV}{ }^{\prime}(\mathrm{C} 2 \mathrm{H} 2), \mathrm{X}(\mathrm{C} 8 \mathrm{H} 8)\right] \backslash \backslash @$

## 3-36 hemispirobinonaplane (parallel)

$1 \backslash 1 \backslash$ MHPCC-FR12N12\FOpt \RB3LYP\6-31G (d) \C14H16\RASMUSSEN\31-Oct-1998\0 <br>\#P B3LYP/6-31G* 5D OPT=NEWESTMFC NAME=RASMUSSEN GEOM= (NODISTANCE,NOA NGLE, NODIHEDRAL) <br>Hemispirobinonaplane (orient a) C2v <br>0,1\C,0.,0.,1.9 $963455635 \backslash \mathrm{C},-1.2460479173,0.7191155818,1.2765419647 \backslash \mathrm{C}, 1.2460479173,-0$. $7191155818,1.2765419647 \backslash C,-1.2460479173,-0.7191155818,1.2765419647 \backslash C, 1$ $.2460479173,0.7191155818,1.2765419647 \backslash \mathrm{H},-1.7508127612,1.3285194027,2.0$ $218376264 \backslash \mathrm{H}, 2.5010487661,0 .,-1.7578392739 \backslash \mathrm{H}, 0.8616856833,0 .,-2.6456115$ $284 \backslash \mathrm{H},-1.7508127612,-1.3285194027,2.0218376264 \backslash \mathrm{H}, 1.7508127612,-1.32851$ $94027,2.0218376264 \backslash \mathrm{H},-0.8616856833,0 .,-2.6456115284 \backslash \mathrm{H}, 0 ., 2.1445155457$, $-1.6193274084 \backslash \mathrm{H}, 1.7508127612,1.3285194027,2.0218376264 \backslash \mathrm{C},-1.3454149669$ , 1. $1748685608,-0.1976267296 \backslash C,-1.3454149669,-1.1748685608,-0.197626729$ $6 \backslash C, 1.3454149669,-1.1748685608,-0.1976267296 \backslash \mathrm{C}, 1.3454149669,1.17486856$ 08,-0.1976267296\H,-1.8410022766, 2.1489524534,-0.2496844741 \H, -1. 84100 $22766,-2.1489524534,-0.2496844741 \backslash \mathrm{H}, 1.8410022766,-2.1489524534,-0.2496$ $844741 \backslash \mathrm{H}, 1.8410022766,2.1489524534,-0.2496844741 \backslash \mathrm{C},-2.2386551635,0 .,-0$ $.6963524113 \backslash C, 0 .,-1.2190084972,-1.0342190409 \backslash C, 2.2386551635,0 .,-0.6963$ $524113 \backslash \mathrm{C}, 0 ., 1.2190084972,-1.0342190409 \backslash \mathrm{H},-3.1830316528,0 .,-0.139200857$ $5 \backslash \mathrm{H},-2.5010487661,0 .,-1.7578392739 \backslash \mathrm{H}, 0 .,-2.1445155457,-1.6193274084 \backslash \mathrm{C}$, 0., 0., -1.9783060117 \H, 3.1830316528, 0., - 0.1392008575 \VVersion=IBM-RS600 $0-G 94 R e v E .2 \backslash S t a t e=1-A 1 \backslash H F=-542.8795386 \backslash R M S D=4.082 e-09 \backslash R M S F=4.835 e-05 \backslash D$ ipole=0., 0., -0.961182 \PG=C02V [C2 (C1C1), SGV (C2H6) , SGV' (C2H2) , X (C8H8)] \ \@

## 3-24 tetramethylhemispirooctaplane

$1 \backslash 1 \backslash G I N C-P C \backslash F O p t \backslash R B 3 L Y P \backslash 6-31 G(d) \backslash C 17 H 24 \backslash R A S M U S S E N \backslash 20-A u g-1999 \backslash 0 \backslash \backslash \# P$ B3 LYP/6-31G* 5D OPT=NEWESTMFC NAME=RASMUSSEN MAXDISK=2097152000 GEOM=(CH ECK, NODISTANCE,NOANGLE,NODIHEDRAL) <br>Hemispirooctaplane C2v $\backslash \backslash 0,1 \backslash C, 0 ., 0$ .,1.1699402272\C,-0.7222873702,-1.3174623366,0.5218236479\C, 0.72228737 $02,1.3174623366,0.5218236479 \backslash C, 0.7222873702,-1.3174623366,0.5218236479$ \C, - 0.7222873702,1.3174623366,0.5218236479\H,-2.9607806307,0.,-0.69863 $09439 \backslash \mathrm{C},-1.6020461829,-1.9927931631,1.5541648764 \backslash \mathrm{C}, 1.6020461829,-1.992$ 7931631,1.5541648764 \H,-2.2916232957,0.,-2.3240492198\H,0., 2.655082650 9,-2.0415410972\C,1.6020461829,1.9927931631,1.5541648764\C,-1.60204618 29,1.9927931631,1.5541648764 \H, 0.,1.0526461669,-2.7502213119\C,-1.2508 908549,-1.2891420606,-0.9241087055\C,1.2508908549,-1.2891420606,-0.924 $1087055 \backslash \mathrm{C}, 1.2508908549,1.2891420606,-0.9241087055 \backslash \mathrm{C},-1.2508908549,1.28$ 91420606,-0.9241087055\H,-1.9668893131,-2.11429771,-1.0335454994 \H, 1.9 $668893131,-2.11429771,-1.0335454994 \backslash \mathrm{H}, 1.9668893131,2.11429771,-1.03354$
$54994 \backslash \mathrm{H},-1.9668893131,2.11429771,-1.0335454994 \backslash \mathrm{C}, 0 .,-1.5870782398,-1.7$ $938167122 \backslash \mathrm{C}, 2.0158632512,0 .,-1.2607334672 \backslash \mathrm{C}, 0 ., 1.5870782398,-1.7938167$ $122 \backslash \mathrm{C},-2.0158632512,0 .,-1.2607334672 \backslash \mathrm{H}, 0 .,-2.6550826509,-2.0415410972 \backslash$ H, 0., -1. $0526461669,-2.7502213119 \backslash H, 2.9607806307,0 .,-0.6986309439 \backslash H, 2.2$ $916232957,0 .,-2.3240492198 \backslash H,-1.1513314017,-1.9472568125,2.5467880095 \backslash$ H, -1. $7730881457,-3.0446208059,1.2817871229 \backslash \mathrm{H},-2.5811385439,-1.50129995$ $76,1.6096529375 \backslash \mathrm{H}, 2.5811385439,-1.5012999576,1.6096529375 \backslash \mathrm{H}, 1.77308814$ $57,-3.0446208059,1.2817871229 \backslash \mathrm{H}, 1.1513314017,-1.9472568125,2.546788009$ $5 \backslash \mathrm{H},-1.1513314017,1.9472568125,2.5467880095 \backslash \mathrm{H},-2.5811385439,1.50129995$ $76,1.6096529375 \backslash \mathrm{H},-1.7730881457,3.0446208059,1.2817871229 \backslash \mathrm{H}, 2.58113854$ $39,1.5012999576,1.6096529375 \backslash \mathrm{H}, 1.1513314017,1.9472568125,2.5467880095 \backslash$ H, 1.7730881457, 3.0446208059,1.2817871229<br>Version=SGI-G98RevA.6\State= $1-\mathrm{Al} \backslash \mathrm{HF}=-662.0989194 \backslash \mathrm{RMSD}=4.482 \mathrm{e}-09 \backslash \mathrm{RMSF}=7.118 \mathrm{e}-05 \backslash \mathrm{Dipole=0} ., 0 .,-0.654$ $6519 \backslash \mathrm{PG}=\mathrm{CO} 2 \mathrm{~V}$ [C2 (C1), SGV (C2H4) , SGV' (C2H4) , X (C12H16) ] <br>@

## C.2.2.2 Neutral Species

Table C-19. Guassian archive files for the MP2/6-31G(d) optimized neutral species in Chapter 3.

## Small Molecules

## $\mathrm{CH}_{4}$

$1 \backslash 1 \backslash G I N C-R S C Q C 8 \backslash$ Freq $\backslash$ RMP2-FC $\backslash 6-31 G(d) \backslash C 1 H 4 \backslash R A S M U S S E N \backslash 24-F e b-1999 \backslash 0 \backslash \backslash \# P$ RMP2/6-31G* 5D OPT= (CALCALL, VERYTIGHT) NAME=RASMUSSEN MAXDISK=1048576 $000 \backslash \backslash$ Methane Td singlet $\backslash \backslash 0,1 \backslash \mathrm{C}, 0 ., 0 ., 0 . \backslash \mathrm{H}, 0 ., 0 ., 1.090277068 \backslash \mathrm{H}, 1.027923$ $0776,0 .,-0.3634256893 \backslash H,-0.5139615388,0.8902074983,-0.3634256894 \backslash H,-0$. 5139615388,-0.8902074983,-0.3634256894 <br>Version=IBM-RS6000-G94RevE.1 \H $F=-40.1947226 \backslash M P 2=-40.3312554 \backslash R M S D=4.004 e-09 \backslash R M S F=3.700 e-07 \backslash D i p o l e=0 .$, $0 ., 0 . \backslash$ DipoleDeriv=-0.0271221,0.,0., 0., -0.0271221,0., 0., 0., -0.0271221, 0 $.0743528,0 ., 0 ., 0.0 .0743528,0 ., 0 ., 0 .,-0.1283641,-0.10584,0 ., 0.0637078$, $0 ., 0.0743528,0 ., 0.0637078,0 ., 0.0518287,0.0293046,0.0780258,-0.0318539$, $0.0780258,-0.0607918,0.0551725,-0.0318539,0.0551725,0.0518287,0.029304$ 6, - $0.0780258,-0.0318539,-0.0780258,-0.0607918,-0.0551725,-0.0318539,-0$ $.0551725,0.0518287 \backslash$ Polar=12.1475929, 0.,12.1475929, 0., 0., 12.1475929\PG= $\mathrm{TD}[\mathrm{O}(\mathrm{C} 1), 4 \mathrm{C} 3(\mathrm{H} 1)] \backslash \mathrm{NImag}=0 \backslash \backslash 0.59213776,0 ., 0.59213776,0.0 ., 0.59213776$, $-0.05164684,0 ., 0 ., 0.04907422,0 .,-0.05164684,0 ., 0 ., 0.04907422,0 ., 0 .,-0$. $34080963,0 ., 0 ., 0.36583143,-0.30868043,0.0 .09087510,0.00304727,0 .,-0.0$ $0188482,0.33063619,0 .,-0.05164684,0 ., 0 .,-0.00133219,0 ., 0 ., 0.04907422,0$ $.09087510,0 .,-0.08377604,0.03409458,0 .,-0.00834060,-0.09954719,0 ., 0.08$ 426946 , - 0. 11590524, 0.11129881,-0.04543755,-0.00023732,-0.00189636, 0.00 $094241,-0.01250151,0.02720599,-0.01271125,0.11946471,0.11129881,-0.244$ $42204,0.07870014,-0.00189636,0.00195241,-0.00163230,-0.00217107,0.0019$ $5241,-0.00124381,-0.12191991,0.26024570,-0.04543755,0.07870014,-0.0837$ $7604,-0.01704729,0.02952678,-0.00834060,0.00527846,-0.01163017,0.00392$ $359,0.04977359,-0.08621039,0.08426946,-0.11590524,-0.11129881,-0.04543$ $755,-0.00023732,0.00189636,0.00094241,-0.01250151,-0.02720599,-0.01271$ $125,0.00917937,0.01468853,0.00743279,0.11946471,-0.11129881,-0.2444220$ $4,-0.07870014,0.00189636,0.00195241,0.00163230,0.00217107,0.00195241,0$ $.00124381,-0.01468853,-0.01972847,-0.01038636,0.12191991,0.26024570,-0$ $.04543755,-0.07870014,-0.08377604,-0.01704729,-0.02952678,-0.00834060$,
$0.00527846,0.01163017,0.00392359,0.00743279,0.01038636,0.00392359,0.04$ $977359,0.08621039,0.08426946 \backslash \backslash 0 ., 0 ., 0 ., 0 ., 0 .,-0.00000072,-0.00000068,0$ ., 0.00000024, 0.00000034, -0.00000058, 0.00000024, 0.00000034, 0.00000058, 0 $.00000024 \backslash \backslash \backslash @$

## $\mathrm{NH}_{3}$

$1 \backslash 1 \backslash G I N C-R S C Q C 8 \backslash F r e q \backslash R M P 2-F C \backslash 6-31 G(d) \backslash H 3 N 1 \backslash R A S M U S S E N \backslash 24-F e b-1999 \backslash 0 \backslash \backslash \# P$ MP2/6-31G* 5D NAME=RASMUSSEN OPT= (CALCALL, VERYTIGHT) MAXDISK=10485760 $00 \backslash \backslash$ ammonia $\mathrm{C} 3 \mathrm{~V} \backslash \backslash 0,1 \backslash \mathrm{H}, 0 ., 0.270532406,0.9406828486 \backslash \mathrm{H}, 0.8146552438,0.27$ $0532406,-0.4703414243 \backslash \mathrm{H},-0.8146552438,0.270532406,-0.4703414243 \backslash \mathrm{~N}, 0.0$, $0.1159424597,0 . \backslash \backslash V e r s i o n=I B M-R S 6000-G 94 R e v E .1 \backslash$ State=1-A1 \HF=-56.183190 $8 \backslash M P 2=-56.3519903 \backslash R M S D=5.201 e-09 \backslash R M S F=1.249 e-07 \backslash$ Dipole=0., 0.7693324, 0. \DipoleDeriv=0.1836276,0.,0.,0.,0.2175475,-0.1814189,0.,-0.0909631,0.0 $770651,0.1037057,-0.0787764,0.0461429,-0.1571134,0.2175475,0.0907094,0$ $.0461429,0.0454816,0.1569869,0.1037057,0.0787764,-0.0461429,0.1571134$, $0.2175475,0.0907094,-0.0461429,0.0454816,0.1569869,-0.391039,0 ., 0 ., 0 .$, $-0.6526424,0 ., 0 ., 0 .,-0.391039 \backslash \operatorname{Pol} \operatorname{lar}=9.2290106,0 ., 5.4594397,0 ., 0 ., 9.229$ $0106 \backslash \mathrm{PG}=\mathrm{C0} 3 \mathrm{~V} \quad[\mathrm{C} 3(\mathrm{~N} 1), 3 \mathrm{SGV}(\mathrm{HI})] \backslash \mathrm{NImag}=0 \backslash \backslash 0.06457547,0 ., 0.07675906,0 ., 0$. $14309137,0.41232358,0.00120960,-0.00258731,-0.00466775,0.32538655,0.01$ $589128,0.00166553,-0.01216240,0.12392076,0.07675906,0.03658431,0.01984$ $345,-0.01721743,-0.15057935,-0.07154569,0.15151250,0.00120960,0.002587$ $31,0.00466775,-0.02643094,0.01847859,-0.02062603,0.32538655,-0.0158912$ $8,0.00166553,-0.01216240,-0.01847859,0.00166553,-0.00768105,-0.1239207$ $6,0.07675906,-0.03658431,0.01984345,-0.01721743,0.02062603,-0.00768105$ , 0.01042312, 0.15057935,-0.07154569, 0.15151250,-0.06699468, 0., 0., -0. 300 $16522,-0.15829063,0.13462107,-0.30016522,0.15829063,-0.13462107,0.6673$ 2511, 0., - $0.08009013,-0.11876657,-0.10285486,-0.08009013,0.05938328,0.1$ $0285486,-0.08009013,0.05938328,0 ., 0.24027038,0 \ldots,-0.18277827,-0.3778887$ $3,0.13462107,0.09138914,-0.14471819,-0.13462107,0.09138914,-0.14471819$ , 0., 0., 0.66732511 <br>0., -0.00000012, -0.00000002, -0.00000002, -0.00000012, $0.00000001,0.00000002,-0.00000012,0.00000001,0 ., 0.00000037,0 . \backslash \backslash \backslash @$

## $\mathrm{H}_{2} \mathrm{O}$

$1 \backslash 1 \backslash G I N C-R S C Q C 8 \backslash F r e q \backslash R M P 2-F C \backslash 6-31 G(d) \backslash H 2 O 1 \backslash R A S M U S S E N \backslash 24-F e b-1999 \backslash 0 \backslash \backslash \# P$ MP2/6-31G* 5D OPT= (CALCALL, VERYTIGHT) NAME=RASMUSSEN MAXDISK=10485760 $00 \backslash \backslash$ water $-\mathrm{c} 2 \mathrm{v} \backslash \backslash 0,1 \backslash \mathrm{H},-0.1257249842,0 .,-0.8918185828 \backslash 0,-0.09132278,0$. , 0.0765924466\H, 0.8563072245,0.,0.2790790096<br>Version=IBM-RS6000-G94Re vE. $1 \backslash$ State $=1-\mathrm{A} 1 \backslash \mathrm{HF}=-76.0083941 \backslash \mathrm{MP} 2=-76.1939531 \backslash \mathrm{RMSD}=6.280 e-09 \backslash \mathrm{RMSF}=4.1$ 88e-08\Dipole=0.6619523,0.,-0.5551796\DipoleDeriv=0.3105371,0.,0.05303 $77,0 ., 0.3835736,0 ., 0.0260772,0 ., 0.130366,-0.4328005,0 .,-0.0458262,0 .,-$ $0.7671473,0 .,-0.0458262,0 .,-0.4490056,0.1222634,0 .,-0.0072116,0 ., 0.383$ 5736,0.,0.019749, 0., 0.3186396\Polar=5.9257373,0.,2.7181209, 0.910101, 0. $, 6.2475678 \backslash \mathrm{PG}=\mathrm{C} 02 \mathrm{~V} \quad[\mathrm{C} 2(\mathrm{O} 1), \mathrm{SGV}(\mathrm{H} 2)] \backslash \mathrm{NImag}=0 \backslash \backslash 0.05621492,0 ., 0.00000002$, $0.03449589,0 ., 0.52672941,-0.05077077,0 .,-0.04926609,0.54596409,0 .,-0.0$ $0000004,0 ., 0 ., 0.00000009,0.02286274,0 .,-0.51375519,0.10498184,0 ., 0.583$ $08784,-0.00544414,0 ., 0.01477020,-0.49519332,0 .,-0.12784458,0.50063746$, $0 ., 0.00000003,0 ., 0 \ldots,-0.00000004,0 ., 0 ., 0.00000002,-0.05735863,0 .,-0.012$ $97422,-0.05571575,0 .,-0.06933265,0.11307438,0 ., 0.08230686 \backslash \backslash 0.00000005$, $0 .,-0.00000002,-0.00000008,0 ., 0.00000007,0.00000003,0 .,-0.00000004 \backslash \backslash \backslash @$

## Basic Hydrocarbons

## ethane

$1 \backslash 1 \backslash G I N C-R S C Q C 2 \backslash F O p t \backslash R M P 2-F C \backslash 6-31 G(d) \backslash C 2 H 6 \backslash R A S M U S S E N \backslash 15-J u l-1998 \backslash 0 \backslash \ \# P$ RMP2/6-31G(D) 5D OPT FREQ=NORAMAN MAXDISK=786432000 GEOM=(NODISTANCE, NOANGLE, NODIHEDRAL) NAME=RASMUSSEN \ \Ethane D3d<br>0,1\C,0.,0.,-0.7634609 $439 \backslash \mathrm{C}, 0.0 ., 0.7634609439 \backslash \mathrm{H}, 1.0202526205,0 .,-1.1576074281 \backslash \mathrm{H}, 0.510126310$ $2,0.8835646876,1.1576074281 \backslash \mathrm{H},-0.5101263102,0.8835646876,-1.1576074281$ \H,-1.0202526205,0.,1.1576074281 \H, -0.5101263102,-0.8835646876,-1.1576 $074281 \backslash H, 0.5101263102,-0.8835646876,1.1576074281 \backslash$ Version=IBM-RS6000-G 94RevE.1 \State=1-A1G\HF=-79.2279888\MP2=-79.4921958\RMSD=1.112e-09\RMS F=1.516e-04\Dipole=0.,0.,0.\PG=D03D [C3(C1.C1),3SGD (H2)] <br>@

## propane

1 \1 \GINC-RSCQC9 \FOpt \RMP2-FC\6-31G(d) \C3H8\RASMUSSEN\17-Jul-1998\0<br>\#P RMP2/6-31G* 5D OPT FREQ=NORAMAN MAXDISK=1048576000 GEOM=(NODISTANCE,N OANGLE,NODIHEDRAL) NAME=RASMUSSEN SCF=DIRECT<br>Propane C2v<br>0,1\C,-0.48 99857067,0.,-0.3255239756\C,-0.4853341948,0.,1.2012756464\C,0.91928095 89,0.,-0.9129813677 \H,-1.0374179159, 0.8773340417,-0.6892127663\H,-1.03 74179159,-0.8773340417,-0.6892127663\H,0.0311295648, 0.8841173509,1.588 $6001947 \backslash \mathrm{H}, 0.0311295648,-0.8841173509,1.5886001947 \backslash \mathrm{H},-1.502040705,0 ., 1$. $6054886271 \backslash \mathrm{H}, 1.4764990227,-0.8841173509,-0.587001077 \backslash \mathrm{H}, 1.4764990227,0$. 8841173509,-0.587001077\H,0.8978530176,0.,-2.0068831481 <br>Version=IBM-R S6000-G94RevE.1\State=1-A1 \HF=-118.2625808\MP2=-118.656485\RMSD=3.979e $-09 \backslash$ RMSF $=4.106 e-05 \backslash$ Dipole $=-0.0170699,0 .,-0.0113404 \backslash \mathrm{PG}=\mathrm{C0} 2 \mathrm{~V} \quad[\mathrm{C} 2(\mathrm{C} 1), \mathrm{SGV}$ (C2H2), SGV' (H2) , X(H4) ] <br>@

## isobutane

$1 \backslash 1 \backslash G I N C-R S C Q C 6 \backslash F O p t \backslash R M P 2-F C \backslash 6-31 G(d) \backslash C 4 H 10 \backslash R A S M U S S E N \backslash 15-J u l-1998 \backslash 0 \backslash \ \#$ P RMP2/6-31G* 5D FOPT FREQ=NORAMAN MAXDISK=471859200 GEOM=(NODISTANCE, NOANGLE, NODIHEDRAL) NAME=RASMUSSEN \ \isobutane C3v <br>0,1\C,0.,0.,0.37625 $646 \backslash \mathrm{H}, 0 ., 0 ., 1.4749758138 \backslash \mathrm{C}, 1.4530961503,0 .,-0.0962729279 \backslash \mathrm{C},-0.72654807$ 51,-1.2584181803,-0.0962729279\C,-0.7265480751,1.2584181803,-0.0962729 $279 \backslash \mathrm{H}, 1.9869443455,-0.8861166274,0.2624145809 \backslash \mathrm{H}, 1.9869443455,0.8861166$ $274,0.2624145809 \backslash$ Н, 1.4975950643,0.,-1.1913631188\Н,-1.7608716828,-1.27 76859654, 0.2624145809\H,-0.2260726627,-2.1638025929,0.2624145809\H,-0. 7487975322,-1.2969553703,-1.1913631188\H,-0.2260726627,2.1638025929,0. $2624145809 \backslash \mathrm{H},-1.7608716828,1.2776859654,0.2624145809 \backslash \mathrm{H},-0.7487975322,1$ . $2969553703,-1.1913631188 \backslash \backslash$ Version=IBM-RS6000-G94RevD. 1 \State=1-A1 \HF= $-157.2975405 \backslash \mathrm{MP} 2=-157.8235036 \backslash \mathrm{RMSD}=7.398 \mathrm{e}-09 \backslash \mathrm{RMSF}=4.952 \mathrm{e}-05 \backslash \mathrm{Dipole}=0 .$, $0 ., 0.0318221 \backslash \mathrm{PG}=\mathrm{CO} 3 \mathrm{~V}$ [C3(C1H1), 3SGV(C1H1), X(H6)] <br>@

## neopeantane

$1 \backslash 1 \backslash$ GINC-RSCQC9 \FOpt \RMP2-FC\6-31G(d) \C5H12 \RASMUSSEN $\backslash 16-J u l-1998 \backslash 0 \backslash \backslash \#$ N RMP2/6-31G* 5D OPT=READFC GUESS=CHECK MAXDISK=1048576000 GEOM=(CHECK , NODISTANCE, NOANGLE,NODIHEDRAL) NAME=RASMUSSEN $\backslash \backslash$ Neopentane 5D Td $\backslash \backslash 1 \backslash$ $\mathrm{C}, 0 ., 0 ., 0 . \backslash \mathrm{C}, 0 ., 0 ., 1.5304947093 \backslash \mathrm{C}, 1.44296425,0 .,-0.5101649031 \backslash \mathrm{C},-0.721$ $482125,1.2496436972,-0.5101649031 \backslash C,-0.721482125,-1.2496436972,-0.5101$ 649031 \H, 0.5115604962,-0.8860487706,1.9214710638\H,-1.0231209924,0.,1. $9214710638 \backslash \mathrm{H}, 0.5115604962,0.8860487706,1.9214710638 \backslash \mathrm{H}, 1.9821004575,0.8$ $860487706,-0.1581864934 \backslash \mathrm{H}, 1.4705399613,0 .,-1.6050980769 \backslash \mathrm{H}, 1.9821004575$
, $-0.8860487706,-0.1581864934 \backslash H,-0.7352699806,1.2735249637,-1.605098076$ $9 \backslash H,-0.2237094844,2.1595737343,-0.1581864934 \backslash H,-1.758390973,1.27352496$ $37,-0.1581864934 \backslash H,-1.758390973,-1.2735249637,-0.1581864934 \backslash H,-0.22370$ $94844,-2.1595737343,-0.1581864934 \backslash \mathrm{H},-0.7352699806,-1.2735249637,-1.605$ $0980769 \backslash \backslash$ Version=IBM-RS6000-G94RevE. $1 \backslash \mathrm{HF}=-196.3320553 \backslash \mathrm{MP} 2=-196.9924722$ $\backslash R M S D=3.454 e-09 \backslash R M S F=1.666 e-04 \backslash D i p o l e=0 ., 0 ., 0 . \backslash P G=T D \quad[O(C 1), 4 C 3(C 1), 6 S$ GD (H2) ] <br>@

## Small Strained Hydrocarbons

## 3-39 cyclopropane

$1 \backslash 1 \backslash G I N C-R S C Q C 9 \backslash F O p t \backslash R M P 2-F C \backslash 6-31 G(d) \backslash C 3 H 6 \backslash R A S M U S S E N \backslash 18-O c t-1999 \backslash 0 \backslash \backslash \# P$ MP2/6-31G(D) 5D OPT FREQ=NORAMAN NAME=RASMUSSEN MAXDISK=917504000<br>CY clopropane $\mathrm{D} 3 \mathrm{~h} 5 \mathrm{D} \backslash \backslash 0,1 \backslash \mathrm{C}, 0.4339224791,0.0000000001,0.7515757804 \backslash \mathrm{C}, 0.43$ $39224792,0 .,-0.7515757804 \backslash \mathrm{C},-0.8678449583,0 ., 0 . \backslash \mathrm{H},-1.4576863463,0.9111$ $606953,-0.0000000001 \backslash \mathrm{H},-1.4576863463,-0.9111606953,0 . \backslash \mathrm{H}, 0.7288431731,-$ $0.9111606952,1.2623934067 \backslash \mathrm{H}, 0.7288431731,0.9111606954,1.2623934066 \backslash \mathrm{H}, 0$ $.7288431732,0.9111606952,-1.2623934067 \backslash \mathrm{H}, 0.7288431732,-0.9111606954,-1$ $.2623934066 \backslash \backslash$ Version=IBM-RS6000-G98RevA. $6 \backslash$ State=1-A1' $\backslash H F=-117.0579053 \backslash$ $M P 2=-117.4447365 \backslash R M S D=3.978 e-09 \backslash R M S F=4.052 e-04 \backslash D i p o l e=0 ., 0 ., 0 . \backslash P G=D 03 H$ [3C2 (C1), 3SGV (H2)] <br>@

## 3-40 tetrahedrane

$1 \backslash 1 \backslash G I N C-R S C Q C 6 \backslash F O p t \backslash R M P 2-F C \backslash 6-31 G(d) \backslash C 4 H 4 \backslash R A S M U S S E N \backslash 21-J u l-1998 \backslash 0 \backslash \backslash \# P$ RMP2/6-31G* 5D OPT=TIGHT NAME=RASMUSSEN MAXDISK=471859200 GEOM=CHECK GUESS = CHECK $\backslash \backslash$ Tetrahedrane Td 5D $\backslash \backslash 0,1 \backslash \mathrm{C}, 0.7386392908,0 ., 0.5222968514 \backslash \mathrm{C}$, $-0.5944109979,0.6030964555,0.3183272434 \backslash \mathrm{C},-0.3736623743,-0.8238450792$, $0.006141546 \backslash \mathrm{C}, 0.2294340813,0.2207486237,-0.8467656408 \backslash \mathrm{H},-1.2994377315$, $1.3184249498,0.6958929639 \backslash \mathrm{H},-0.816860707,-1.8010019744,0.0134259908 \backslash \mathrm{H}$, $0.5015642429,0.4825770246,-1.8511084542 \backslash \mathrm{H}, 1.6147341956,-0.0000000001,1$ $.1417894995 \backslash$ Version=IBM-RS6000-G94RevD.I \State=1-A1 \HF=-153.5963695\M $P 2=-154.102365 \backslash R M S D=8.804 e-10 \backslash R M S F=9.554 e-07 \backslash D i p o l e=0 ., 0 ., 0 . \backslash P G=T D \quad[4 C$ $3(. \mathrm{C} 1 \mathrm{HI})] \backslash \backslash @$

## 3-15 pyramidane

$1 \backslash 203 \backslash G I N C-R S C Q C 2 \backslash F O P T \backslash R M P 2-F C \backslash 6-31 G(D) \backslash C 5 H 4 \backslash R A S M U S S E N \backslash 15-M a y-1994 \backslash 1 \backslash \backslash$
 ISK=37500000 OPTCYC=100 GEOM= (CHECK,NODISTANCE,NOANGLE,NODIHEDRAL) 5D GUESS = CHECK $\backslash$ Pyramidane ([3.3.3.3]fenestrane) C4v RMP2/6-31G* 5D $\backslash \backslash 0,1 \backslash$ $C \backslash X, 1,0.5 \backslash X, 1,0.5,2,90 . \backslash X, 1,0.5,2,90 ., 3,90 ., 0 \backslash X, 1,0.5,4,90 ., 2,180 ., 0 \backslash X$ $, 1,0.5,2,90 ., 3,180 ., 0 \backslash X, 1,0.5,2,90 ., 4,180 ., 0 \backslash C, 1, C C, 2, C C x, 4,0 ., 0 \backslash C, 1, c$ $\mathrm{c}, 2, \mathrm{ccx}, 3,0 ., 0 \backslash \mathrm{C}, 1, \mathrm{cc}, 2, \mathrm{ccx}, 7,0 ., 0 \backslash \mathrm{C}, 1, \mathrm{cc}, 2, \mathrm{ccx}, 6,0 ., 0 \backslash \mathrm{H}, 8, \mathrm{hc}, 1, \mathrm{hcc}, 2$, $0 ., 0 \backslash H, 9, h c, 1, h c c, 2,0 ., 0 \backslash H, 10, h c, 1, h c c, 2,0.0 \backslash H, 11, h c, 1, h c c, 2,0 ., 0 \backslash \backslash c c$ $=1.64621025 \backslash \mathrm{ccx}=141.55735791 \backslash \mathrm{hc}=1.0809544 \backslash \mathrm{hcc}=119.23362354 \backslash \backslash$ Version=IB M-RS6000-G92RevB \State=1-A1 \HF=-191.4552433 \MP2=-192.0917766\RMSD=8. 21 $3 e-09 \backslash \mathrm{RMSF}=3.304 \mathrm{e}-05 \backslash \mathrm{Dipole}=-0 .,-0 .,-0.626269 \backslash \mathrm{PG}=\mathrm{C} 04 \mathrm{~V} \quad[\mathrm{C} 4(\mathrm{C} 1)$, $2 \mathrm{SGV}(\mathrm{C} 2 \mathrm{H}$ 2)] <br>@

## 3-41 spiropentane

$1 \backslash 1 \backslash G I N C-P C \backslash F O p t \backslash R M P 2-F C \backslash 6-31 G(d) \backslash C 5 H 8 \backslash R A S M U S S E N \backslash 21-J u l-1998 \backslash 0 \backslash \backslash \# P R M P$ 2/6-31G* 5D OPT=TIGHT NAME=RASMUSSEN MAXDISK=2359296000 GEOM= (CHECK,NO DISTANCE, NOANGLE, NODIHEDRAL) GUESS=CHECK <br>Spiropentane D2d 5D<br>0,1\C,0
$., 0 ., 0 . \backslash C,-0.5395631531,-1.2677687665,-0.5395631531 \backslash C, 0.5395631531,-1$. $2677687665,0.5395631531 \backslash C,-0.5395631531,1.2677687665,0.5395631531 \backslash C, 0$. $5395631531,1.2677687665,-0.5395631531 \backslash \mathrm{H},-1.5420398508,-1.5701905487,-0$ $.2486373311 \backslash \mathrm{H}, 1.5420398508,-1.5701905487,0.2486373311 \backslash \mathrm{H},-1.5420398508$, $1.5701905487,0.2486373311 \backslash \mathrm{H}, 1.5420398508,1.5701905487,-0.2486373311 \backslash \mathrm{H}$, $-0.2486373311,-1.5701905487,-1.5420398508 \backslash H, 0.2486373311,-1.5701905487$ , 1. $5420398508 \backslash \mathrm{H},-0.2486373311,1.5701905487,1.5420398508 \backslash \mathrm{H}, 0.2486373311$ , 1.5701905487,-1.5420398508<br>Version=SGI-G94RevD.3\State=1-A1 \HF=-193. $9162852 \backslash M P 2=-194.558386 \backslash R M S D=7.683 e-09 \backslash R M S F=4.644 e-06 \backslash D i p o l e=0 ., 0 ., 0 . \backslash$ PG=D02D [O (C1) , 2SGD (C2) , X (H8) ] <br>@

## 3-42 [1.1.1]propellane

$1 \backslash 1 \backslash G I N C-P C \backslash F O p t \backslash R M P 2-F C \backslash 6-31 G(d) \backslash C 5 H 6 \backslash R A S M U S S E N \backslash 02-N o v-1999 \backslash 0 \backslash \backslash \# P ~ M P 2$ /6-31G(D) 5D OPT FREQ=NORAMAN NAME=RASMUSSEN SYMM=LOOSE MAXDISK=209715 2000 GEOM=CHECK GUESS=CHECK $\backslash$ \propellane $D 3 \backslash \backslash 0,1 \backslash C, 1.2450733828,0.33463$ 1919, 0. \C, 0., 0., 0.7975429423\H, 1.5719927838, 1.3725496517, 0. \C, -0.33273 $69487,-1.2455811386,0 . \backslash \mathrm{C},-0.9123364342,0.9109492196,0 . \backslash \mathrm{H},-0.678114845$, $1.9736296805,0 . \backslash \mathrm{C}, 0 ., 0 .,-0.7975429423 \backslash \mathrm{H},-1.9746592582,0.6751108594,0 . \backslash$ H, 2. $0482708635,-0.3995501578,0 . \backslash H, 0.4026664745,-2.0476605112,0 . \backslash H,-1.3$ $701560184,-1.5740795227,0 . \backslash \backslash V e r s i o n=S G I-G 98 R e v A .6 \backslash$ State=1-A1'\HF=-192. $6883707 \backslash M P 2=-193.3431179 \backslash R M S D=7.885 e-09 \backslash R M S F=4.599 e-05 \backslash D i p o l e=0 ., 0 ., 0$. $\backslash \mathrm{PG}=\mathrm{D} 03 \mathrm{H} \quad[\mathrm{C} 3(\mathrm{C} 1 . \mathrm{C} 1), 3 \mathrm{C} 2(\mathrm{C} 1), \mathrm{SGH}(\mathrm{H} 6)] \backslash \backslash @$

## 3-43 prismane

$1 \backslash 1 \backslash G I N C-V P P 11 \backslash F O p t \backslash R M P 2-F C \backslash 6-31 G(d) \backslash C 6 H 6 \backslash D R R 501 \backslash 25-F e b-1999 \backslash 0 \backslash \backslash \# P$ MP2 /6-31G* 5D OPT=NEWESTMFC GUESS=CHECK GEOM=CHECK MAXDISK=2621440000<br>Pr ismane $\mathrm{D} 3 \mathrm{~h} \backslash \backslash 0,1 \backslash \mathrm{C},-0.4386937085,0.7598397997,0.7755181988 \backslash \mathrm{C},-0.4386937$ 15, - 0.7598397959, - 0.7755181988\C, -0.4386937085, 0.7598397997, -0.7755181 $988 \backslash \mathrm{C},-0.438693715,-0.7598397959,0.7755181988 \backslash \mathrm{C}, 0.8773874236,-0.000000$ $0038,0.7755181988 \backslash C, 0.8773874236,-0.0000000038,-0.7755181988 \backslash H,-0.8375$ $179288,1.4506236194,1.5116636063 \backslash \mathrm{H},-0.8375179413,-1.4506236122,1.51166$ $36063 \backslash \mathrm{H},-0.8375179288,1.4506236194,-1.5116636063 \backslash \mathrm{H},-0.8375179413,-1.45$ $06236122,-1.5116636063 \backslash \mathrm{H}, 1.6750358701,-0.0000000072,1.5116636063 \backslash \mathrm{H}, 1.6$ 750358701 , - 0.0000000072 ,-1. $5116636063 \backslash$ \Version=Fujitsu-VP-Unix-G98RevA $.6 \backslash$ State $=1-A 1^{\prime} \backslash H F=-230.501355 \backslash M P 2=-231.2617837 \backslash \mathrm{RMSD}=4.078 \mathrm{e}-09 \backslash \mathrm{RMSF}=1.0$ 95e-04\Dipole=0.,0.,0.\PG=D03H [3SGV(C2H2)] <br>@

## 3-44 cubane

$1 \backslash 1 \backslash G I N C-R S C Q C 9 \backslash F O p t \backslash R M P 2-F C \backslash 6-31 G(d) \backslash C 8 H 8 \backslash R A S M U S S E N \backslash 21-J u l-1998 \backslash 0 \backslash \backslash \# P$ RMP2/6-31G* 5D OPT NAME=RASMUSSEN MAXDISK=1048576000 GEOM= (CHECK,NOAN GLE, NODIHEDRAL) GUESS=CHECK <br>Cubane Oh <br>0,1\C,0.782871039, 0.782871039, $0.782871039 \backslash \mathrm{C}, 0.782871039,0.782871039,-0.782871039 \backslash \mathrm{C},-0.782871039,0.78$ $2871039,-0.782871039 \backslash C,-0.782871039,0.782871039,0.782871039 \backslash C, 0.782871$ $039,-0.782871039,0.782871039 \backslash C, 0.782871039,-0.782871039,-0.782871039 \backslash C$ $,-0.782871039,-0.782871039,-0.782871039 \backslash C,-0.782871039,-0.782871039,0$. $782871039 \backslash \mathrm{H}, 1.4140650175,1.4140650175,1.4140650175 \backslash \mathrm{H}, 1.4140650175,1.41$ $40650175,-1.4140650175 \backslash \mathrm{H},-1.4140650175,1.4140650175,-1.4140650175 \backslash \mathrm{H},-1$ $.4140650175,1.4140650175,1.4140650175 \backslash \mathrm{H}, 1.4140650175,-1.4140650175,1.4$ $140650175 \backslash \mathrm{H}, 1.4140650175,-1.4140650175,-1.4140650175 \backslash \mathrm{H},-1.4140650175,-$ $1.4140650175,-1.4140650175 \backslash \mathrm{H},-1.4140650175,-1.4140650175,1.4140650175 \backslash$ \Version=IBM-RS6000-G94RevE.1 \HF=-307.3916541 \MP2=-308.4034279\RMSD=5. $533 \mathrm{e}-10 \backslash \mathrm{RMSF}=1.061 \mathrm{e}-04 \backslash \mathrm{Dipole}=0 ., 0.0 . \backslash \mathrm{PG}=\mathrm{OH} \quad[4 \mathrm{C} 3(\mathrm{H} 1 \mathrm{Cl} . \mathrm{C} 1 \mathrm{H} 1)] \backslash \backslash @$

## 3-45 tetrakis(tert-butyl)tetrahedrane

$1 \backslash 1 \backslash G I N C-P C \backslash F O p t \backslash R M P 2-F C \backslash 6-31 G(d) \backslash C 20 H 36 \backslash R A S M U S S E N \backslash 23-A p r-1999 \backslash 0 \backslash \backslash \# P R$ MP2/6-31G* 5D OPT=NEWESTMFC NAME=RASMUSSEN GUESS=CHECK GEOM=(CHECK,NOD ISTANCE, NOANGLE, NODIHEDRAL) MAXDISK=1800000000<br>tetrakis(tert-butyl) te trahedrane $T d \backslash \backslash 0,1 \backslash C,-1.9656074252,-0.0003653501,1.3897623166 \backslash C,-2.427$ $5498379,-1.4420443962,1.6344561164 \backslash C, 1.6596886932,2.4499807249,1.37366$ $8425 \backslash C, 0.9939344673,2.1924591356,0.0164071156 \backslash C,-0.6103258105,-0.58750$ $91869,-2.2533058693 \backslash C, 2.0512893671,2.2908878604,-1.0899457766 \backslash \mathrm{C}, 1.5819$ 987684,-1. $6045845986,0.8471364371 \backslash C,-0.7469623892,-0.0001388389,0.5281$ $319999 \backslash C,-1.6491333158,0.6624296414,2.7359611345 \backslash C, 1.742248447,-1.4251$ $339443,2.3616732717 \backslash C,-0.0867212267,3.2536574785,-0.223896168 \backslash C,-3.090$ 6567236,0.7782825516,0.6971759743\C,1.084198664, -3.026015093, 0.5582857 $391 \backslash C, 2.9421121206,-1.399766579,0.169017297 \backslash C, 0.6516558785,-0.89007202$ $69,-3.0703507056 \backslash C,-1.3659879763,0.5762904801,-2.9061836115 \backslash C,-1.51114$ 40902,-1.8284966974,-2.2398616963\C, 0.6011849389,-0.6097679171,0.32192 $54511 \backslash C, 0.3777110602,0.8331696824,0.0062349674 \backslash C,-0.2319336098,-0.2232$ 629264,-0.8562924184 \H,-1.6984552793,0.297439927,-3.9133762581\H,-0.72 03512938,1.4561242461,-2.989150523\H,-2.2462001769,0.8484914055,-2.315 $52942 \backslash \mathrm{H}, 1.3382290877,-0.0379398051,-3.0552795085 \backslash \mathrm{H}, 0.3882532284,-1.103$ $1834392,-4.1133903673 \backslash \mathrm{H}, 1.173969194,-1.7614759775,-2.663310603 \backslash \mathrm{H},-1.74$ 82124985,-2.1383342481,-3.2648145869\H,-2.4503394995,-1.6167237621,-1. $7193793271 \backslash \mathrm{H},-1.0162009937,-2.6627897928,-1.7331807334 \backslash \mathrm{H}, 1.5888845353$, $2.1776633562,-2.0754404102 \backslash \mathrm{H}, 2.8101623279,1.5110252767,-0.9730466069 \backslash \mathrm{H}$ , $2.5503627497,3.2667884253,-1.0542664807 \backslash \mathrm{H}, 0.3643564623,4.251967657,-0$ . $2752271706 \backslash \mathrm{H},-0.8184157994,3.2490477312,0.5900076914 \backslash \mathrm{H},-0.6146931489$, $3.0650846494,-1.1638031706 \backslash \mathrm{H}, 2.0660035165,3.4679149782,1.411711641 \backslash \mathrm{H}, 2$ . $4812541721,1.746065218,1.539109692 \backslash \mathrm{H}, 0.9381045967,2.336048448,2.18857$ $64344 \backslash \mathrm{H}, 1.0260079148,-3.2016714572,-0.5204155023 \backslash \mathrm{H}, 0.0902756179,-3.184$ 7662114,0.9879999426\H,1.769611139,-3.7649576684,0.9906082753\H,2.8489 028716,-1.471784875,-0.9190381413\H,3.6545576011,-2.1623795039, 0.50602 1941 \H, 3.3509490463,-0.4150509978, 0.4160502545\H, 2.0483835851, -0.40221 72573,2.6018023295\H,2.5034134912,-2.1134253153,2.7484702859\H, 0.79865 75333,-1.6327830895,2.8758286081 \H,-2.7708064746,1.7985262198, 0.463642 $4403 \backslash \mathrm{H},-3.9723486191,0.8327987738,1.347081005 \backslash \mathrm{H},-3.3818637189,0.285709$ 5419,-0.2357806195\H,-2.612345736,-1.957299425,0.6867736974 \H, -3.35532 09616,-1.450803037,2.219172453\H,-1.6671907748,-2.0010045127,2.1887623 $252 \backslash \mathrm{H},-1.3815613094,1.7140997035,2.5937184139 \backslash \mathrm{H},-0.8138115566,0.157621$ 3671,3.2310827365\H,-2.5222208297,0.6161734506,3.3980092626<br>Version=S GI-G98RevA. $6 \backslash \mathrm{HF}=-778.1615954 \backslash \mathrm{MP} 2=-780.8061327 \backslash \mathrm{RMSD}=7.309 \mathrm{e}-09 \backslash \mathrm{RMSF}=1.38$ 3e-06\Dipole=0., 0., 0. \PG=T [4C3(.C1C1), X(C12H36)] <br>@

## Other Alicylclic Hydrocarbons

## 3-21

$1 \backslash 1 \backslash G I N C-P C \backslash F O p t \backslash R M P 2-F C \backslash 6-31 G(d) \backslash C 7 H 8 \backslash R A S M U S S E N \backslash 24-N o v-1999 \backslash 0 \backslash \backslash$ \# $\operatorname{MP2}$ /6-31G(D) 5D OPT FREQ=NORAMAN NAME=RASMUSSEN SYMM=LOOSE <br>bicyclohexadi ene bound C C1 <br>0,1\H,1.2201394106,0.,1.7921051949\C,0.7136905726,1.04 $20560722,-0.126132103 \backslash C, 0.7136905726,-1.0420560722,-0.126132103 \backslash C,-1.4$ $096565279,0 ., 0.7113044201 \backslash C,-0.7136905726,-1.0420560722,-0.126132103 \backslash C$ , $-0.7136905726,1.0420560722,-0.126132103 \backslash C, 1.4096565279,0 ., 0.711304420$ $1 \backslash H,-1.2515562699,1.8410487578,-0.6259979561 \backslash H,-1.2201394106,0.1 .7921$ $051949 \backslash \mathrm{H}, 2.4863848896,0 ., 0.5332563335 \backslash \mathrm{H},-2.4863848896,0 ., 0.5332563335 \backslash$

C, 0., 0., -1.2758689669 \H, 1.2515562699,1.8410487578, -0.6259979561 $\mathrm{H},-1.2$ 515562699,-1.8410487578,-0.6259979561 \H,1.2515562699,-1.8410487578,-0. 6259979561 <br>Version=SGI-G98RevA. $6 \backslash$ State $=1-A 1 \backslash H F=-269.5052566 \backslash \mathrm{MP2} 2=-270$. $4122029 \backslash \mathrm{RMSD}=4.449 \mathrm{e}-09 \backslash \mathrm{RMSF}=2.028 \mathrm{e}-04 \backslash \mathrm{Dipole}=0 ., 0 ., 0.9837222 \backslash \mathrm{PG}=\mathrm{CO} 2 \mathrm{~V} \quad[$ C2 (C1) , SGV (C2H4), X(C4H4)] <br>@

## 3-22

$1 \backslash 1 \backslash G I N C-P C \backslash F O p t \backslash R M P 2-F C \backslash 6-31 G(d) \backslash C 8 H 8 \backslash R A S M U S S E N \backslash 24-N O v-1999 \backslash 0 \backslash \ \# P$ MP2 /6-31G(D) 5D OPT FREQ=NORAMAN NAME=RASMUSSEN SYMM=LOOSE<br>bicycloheptad iene bound C C1 <br>0,1\H,-2.1733020352,0.,0.9375639\C,-0.713591576,-1.05 $06348393,-0.4236051346 \backslash C,-0.713591576,1.0506348393,-0.4236051346 \backslash C, 1.1$ $397969932,0 ., 0.5922068802 \backslash C, 0.713591576,1.0506348393,-0.4236051346 \backslash C, 0$ $.713591576,-1.0506348393,-0.4236051346 \backslash C,-1.1397969932,0 ., 0.5922068802$ \H, 0.,-0.8999312337,2.2457680308\H,2.1733020352,0., 0.9375639\H,0., 0.89 99312337,2.2457680308\C,0.,0.,1.618898482\C,0.,0.,-1.5599811615\H,-1.3 501132465,-1.7762172623,-0.9150317794 \H,1.3501132465,1.7762172623,-0.9 $150317794 \backslash \mathrm{H},-1.3501132465,1.7762172623,-0.9150317794 \backslash \mathrm{H}, 1.3501132465,-1$ $.7762172623,-0.9150317794 \backslash \backslash$ Version=SGI-G98RevA. $6 \backslash$ State=1-A1 $\backslash H F=-307.36$ $45459 \backslash \mathrm{MP} 2=-308.4002065 \backslash \mathrm{RMSD}=7.001 \mathrm{e}-09 \backslash \mathrm{RMSF}=6.224 \mathrm{e}-05 \backslash$ Dipole=0., 0., 1.06 $71492 \backslash \mathrm{PG}=\mathrm{C0} 2 \mathrm{~V}$ [C2 (C1C1), SGV (C2H2), SGV' (H2), X(C4H4)] <br>@

## 3-23

$1 \backslash 1 \backslash G I N C-P C \backslash F O p t \backslash R M P 2-F C \backslash 6-31 G(d) \backslash C 9 H 10 \backslash R A S M U S S E N \backslash 24-N o v-1999 \backslash 0 \backslash \backslash \# P M P$ 2/6-31G(D) 5D OPT FREQ=NORAMAN NAME=RASMUSSEN SYMM=LOOSE <br>bicyclo[2.2. 2]octadiene bound C C1 <br>0,1\C,-0.7756652921,0.,1.6642919283\C,-0.71369 46106,-1.0416281023,-0.6787384917\C,-0.7136946106,1.0416281023,-0.6787 $384917 \backslash C, 1.3180554807,0.0 .2335370631 \backslash C, 0.7136946106,1.0416281023,-0.6$ $787384917 \backslash \mathrm{C}, 0.7136946106,-1.0416281023,-0.6787384917 \backslash \mathrm{C},-1.3180554807,0$ ., 0.2335370631 \H,1.2838722098,-1.8231175581,-1.170293816\C,0.775665292 $1,0 ., 1.6642919283 \backslash \mathrm{H},-2.4100160174,0 ., 0.1969277029 \backslash \mathrm{H}, 2.4100160174,0.0$. $1969277029 \backslash \mathrm{C}, 0.0 .,-1.827388212 \backslash \mathrm{H},-1.2838722098,-1.8231175581,-1.17029$ $3816 \backslash \mathrm{H}, 1.2838722098,1.8231175581,-1.170293816 \backslash \mathrm{H},-1.2838722098,1.823117$ 5581,-1.170293816\H,1.1622543574,-0.8800777918,2.1918562582\H,-1.16225 43574,-0.8800777918,2.1918562582\H,-1.1622543574,0.8800777918,2.191856 $2582 \backslash H, 1.1622543574,0.8800777918,2.1918562582 \backslash \backslash$ Version=SGI-G98RevA. $6 \backslash \mathrm{~S}$ tate $=1-\mathrm{A} 1 \backslash \mathrm{HF}=-346.4152749 \backslash \mathrm{MP} 2=-347.5800078 \backslash \mathrm{RMSD}=4.218 \mathrm{e}-09 \backslash \mathrm{RMSF}=1.164 \mathrm{e}-$ $04 \backslash$ Dipole=0., 0.,1.0900163\PG=C02V [C2 (C1), SGV (C4H2), X (C4H8)] <br>@

## C-3-48 chair-cyclohexane

$1 \backslash 1 \backslash G I N C-R S C Q C 9 \backslash F O p t \backslash R M P 2-F C \backslash 6-31 G(d) \backslash C 6 H 12 \backslash R A S M U S S E N \backslash 15-J u l-1994 \backslash 0 \backslash \ \#$ P RMP2/6-31G* 5D OPT=READFC FREQ=NORAMAN NAME=RASMUSSEN GUESS=CHECK MA XDISK=1048576000 GEOM=(CHECK,NODISTANCE,NOANGLE,NODIHEDRAL) SCF=DIRECT $\backslash \backslash$ Cyclohexane D3d<br>0,1\C,1.262028478,-0.7286324815,0.2327730824\C,-1.2 $62028478,-0.7286324815,0.2327730824 \backslash C, 0 ., 1.457264963,0.2327730824 \backslash C, 1$. $262028478,0.7286324815,-0.2327730824 \backslash C, 0 .,-1.457264963,-0.2327730824 \backslash C$ , -1.262028478, 0.7286324815,-0.2327730824 \Н, 1.3091102009,-0.7558151269, $1.3303694404 \backslash \mathrm{H},-1.3091102009,-0.7558151269,1.3303694404 \backslash \mathrm{H}, 0 ., 1.5116302$ 538,1.3303694404\H,1.3091102009, 0.7558151269,-1.3303694404\H,0.,-1.511 6302538,-1.3303694404 \Н, -1.3091102009, 0.7558151269,-1.3303694404 \H, 2.1 $574786936,-1.2456209045,-0.1333734436 \backslash \mathrm{H},-2.1574786936,-1.2456209045,-0$ $.1333734436 \backslash \mathrm{H}, 0 ., 2.491241809,-0.1333734436 \backslash \mathrm{H}, 2.1574786936,1.2456209045$ , 0.1333734436\H,0.,-2.491241809,0.1333734436\H,-2.1574786936,1.2456209

045, 0.1333734436<br>Version=IBM-RS6000-G94RevE.I\State=1-A1G\HF=-234.206 $0933 \backslash M P 2=-234.9845819 \backslash R M S D=4.486 e-10 \backslash R M S F=9.825 e-06 \backslash D i p o l e=0 ., 0 ., 0 . \backslash P G$ $=\mathrm{D} 03 \mathrm{D}$ [3SGD (C2H4)] <br>@

## BC-3-51 boat,chair-cyclooctane

$1 \backslash 1 \backslash G I N C-P C \backslash F O p t \backslash R M P 2-F C \backslash 6-31 G(d) \backslash C 8 H 16 \backslash R A S M U S S E N \backslash 28-O c t-1999 \backslash 0 \backslash \backslash \# P$ MP 2/6-31G* 5D OPT FREQ=NORAMAN NAME=RASMUSSEN GUESS=CHECK MAXDISK=209715 2000 GEOM = (CHECK, NODISTANCE, NOANGLE, NODIHEDRAL) SYMM=LOOSE <br>Cyclooctan e Cs chair $\backslash 0,1 \backslash \mathrm{H}, 0.8421492907,1.5393443075,2.1260576805 \backslash \mathrm{C},-0.64042329$ $93,0.0840212168,1.5951715034 \backslash \mathrm{H}, 1.2195503819,-1.0283520645,-1.382311949$ $1 \backslash \mathrm{H}, 1.4994203526,2.3718205749,0 . \backslash \mathrm{H},-0.930294668,0.1128934931,2.6529254$ $063 \backslash \mathrm{H},-1.5825447341,0.0661349659,-1.0379780198 \backslash \mathrm{H},-0.930294668,0.112893$ $4931,-2.6529254063 \backslash \mathrm{H}, 0.3200537155,-2.891852403,0 . \backslash \mathrm{H},-1.2690708336,-2.1$ $505871491,0 . \backslash C, 0.1314106124,1.3795526958,1.3039818182 \backslash C,-0.1940418076$, $-1.9211882233,0 . \backslash \mathrm{H},-0.5659485927,2.2278120993,-1.3383199529 \backslash \mathrm{H},-0.56594$ 85927,2.2278120993,1.3383199529\C, 0.1314106124,1.3795526958, -1. 3039818 $182 \backslash C, 0.1393705887,-1.2151054085,-1.3208775205 \backslash C, 0.1393705887,-1.21510$ $54085,1.3208775205 \backslash \mathrm{H},-1.5825447341,0.0661349659,1.0379780198 \backslash \mathrm{H}, 0.84214$ $92907,1.5393443075,-2.1260576805 \backslash \mathrm{H},-0.0797822595,-1.9319571215,-2.1219$ $940359 \backslash \mathrm{H},-0.0797822595,-1.9319571215,2.1219940359 \backslash \mathrm{C}, 0.9273307112,1.434$ $530863,0 . \backslash \mathrm{C},-0.6404232993,0.0840212168,-1.5951715034 \backslash \mathrm{H}, 1.2195503819,-1$ $.0283520645,1.3823119491 \backslash H, 1.6793096861,0.6371897294,0 . \backslash \backslash V e r s i o n=S G I-G$ 98RevA. $6 \backslash$ State=1-A' $\backslash H F=-312.2536114 \backslash M P 2=-313.29633 \backslash \mathrm{RMSD}=3.098 \mathrm{e}-09 \backslash \mathrm{RMSF}$ $=1.755 e-05 \backslash$ Dipole $=0.0051185,-0.0169428,0 . \backslash \mathrm{PG}=\mathrm{CS} \quad[\mathrm{SG}(\mathrm{C} 2 \mathrm{H} 4), \mathrm{X}(\mathrm{C} 6 \mathrm{H} 12)] \backslash \backslash @$

## CC-3-52 chair,chair-bicylclo[3.3.1]nonane

$1 \backslash 1 \backslash G I N C-P C \backslash F O p t \backslash R M P 2-F C \backslash 6-31 G(d) \backslash C 9 H 16 \backslash R A S M U S S E N \backslash 31-O c t-1999 \backslash 0 \backslash \backslash \# P M P$ 2/6-31G(D) 5D OPT FREQ=NORAMAN NAME=RASMUSSEN GUESS=CHECK MAXDISK=2097 152000 GEOM=CHECK $\backslash$ bicyclononane C2v (chair-chair) $\backslash \backslash 0,1 \backslash \mathrm{H}, 0 .,-0.883642$ 8017,-2.1870618961 \H, 2.1415026433, 0.,-1.2818742537 $\mathrm{H},-2.1415026433,0$. , $-1.2818742537 \backslash \mathrm{C},-1.245592464,0 .,-0.6441313481 \backslash \mathrm{H}, 0 .,-2.6119328769,1.321$ $0516261 \backslash \mathrm{C}, 0.0 .,-1.5335229741 \backslash \mathrm{H}, 0 .,-0.967694081,1.9003811462 \backslash \mathrm{H},-1.4260$ $775035,-2.1270815465,-0.5260710812 \backslash \mathrm{C}, 0 .,-1.5664539469,0.9868924176 \backslash \mathrm{H}, 0$ ., 0.8836428017,-2.1870618961 \C, 0.,1.5664539469,0.9868924176\H,-2.14913 $38545,1.2993877615,0.8468196682 \backslash \mathrm{H}, 0 ., 0.967694081,1.9003811462 \backslash \mathrm{C},-1.277$ 1307606,-1.2970347414,0.1791673925\C,1.2771307606,-1.2970347414,0.1791 $673925 \backslash C, 1.2771307606,1.2970347414,0.1791673925 \backslash C,-1.2771307606,1.2970$ $347414,0.1791673925 \backslash \mathrm{H},-2.1491338545,-1.2993877615,0.8468196682 \backslash \mathrm{H}, 2.149$ 1338545,-1.2993877615,0.8468196682 \H, 1.4260775035,2.1270815465,-0.5260 $710812 \backslash \mathrm{H},-1.4260775035,2.1270815465,-0.5260710812 \backslash \mathrm{H}, 1.4260775035,-2.12$ 70815465,-0.5260710812\C,1.245592464,0.,-0.6441313481\H,2.1491338545,1 $.2993877615,0.8468196682 \backslash \mathrm{H}, 0 ., 2.6119328769,1.3210516261 \backslash \backslash$ Version=SGI-G 98RevA. $6 \backslash$ State $=1-A 1 \backslash H F=-350.1387609 \backslash M P 2=-351.3088056 \backslash R M S D=8.617 e-09 \backslash R M$ SF=1.967e-06\Dipole=0., 0., 0.0045253\PG=C02V [C2 (C1) ,SGV (C2H6), SGV' (C2H 2) , X(C4H8)] <br>@

## Capping Hydrocarbons

## 3-46 cyclobutane

$1 \backslash 1 \backslash G I N C-P A L O \backslash F O p t \backslash R M P 2-F C \backslash 6-31 G(d) \backslash C 4 H 8 \backslash R A S M U S S E N \backslash 14-O c t-1999 \backslash 0 \backslash \backslash \# P M$ P2/6-31G* 5D OPT FREQ=NORAMAN NAME=RASMUSSEN GEOM= (CHECK, NODISTANCE,NO ANGLE, NODIHEDRAL) SYMM=LOOSE<br>Cyclobutane C9H14 C2v <br>0,1\C,1.072793747


#### Abstract

3, 0., 0.1469968377\H, 1.3472269869, 0., 1. $2066807509 \backslash \mathrm{C},-1.0727937473,0 ., 0$. $1469968377 \backslash \mathrm{H}, 0 .,-1.3472269869,-1.2066807509 \backslash \mathrm{H}, 0 ., 1.3472269869,-1.20668$ $07509 \backslash \mathrm{C}, 0 ., 1.0727937473,-0.1469968377 \backslash \mathrm{H}, 0 ., 1.9873544538,0.4534118738 \backslash \mathrm{H}$ , 1.9873544538, 0., - 0.4534118738\H, -1.3472269869, 0., 1. $2066807509 \backslash \mathrm{C}, 0 .,-1$ $.0727937473,-0.1469968377 \backslash \mathrm{H}, 0 .,-1.9873544538,0.4534118738 \backslash \mathrm{H},-1.9873544$ 538,0., - 0.4534118738 <br>Version=Sun-SVR4-Unix-G98RevA. $7 \backslash$ State=1-A1 \HF=-1 $56.0956627 \backslash \mathrm{MP} 2=-156.6127414 \backslash \mathrm{RMSD}=3.364 \mathrm{e}-09 \backslash \mathrm{RMSF}=2.033 \mathrm{e}-05 \backslash \mathrm{Dipole=0} ., 0$. , 0. \PG=D02D [2SGD (C2H4)] <br>@


## 3-47 bicylclo[2.2.0]hexane

$1 \backslash 1 \backslash G I N C-P A L O \backslash F O p t \backslash R M P 2-F C \backslash 6-31 G(d) \backslash C 6 H 10 \backslash R A S M U S S E N \backslash 14-O c t-1999 \backslash 0 \backslash \backslash \# P$ MP2/6-31G* 5D OPT FREQ=NORAMAN NAME=RASMUSSEN GEOM= (CHECK, NODISTANCE,N OANGLE, NODIHEDRAL) GUESS=CHECK <br>bicyclohexane $C 2 \backslash \backslash 0,1 \backslash H,-2.4392280943$, $-0.3740737391,-0.1326749111 \backslash \mathrm{H},-1.0349573792,0.9291711906,1.4810359265 \backslash$ H, 2. $4392280943,0.3740737391,-0.1326749111 \backslash \mathrm{C},-1.3833874941,-0.269615732$ $1,-0.3980785304 \backslash \mathrm{H}, 1.0349573792,-0.9291711906,1.4810359265 \backslash \mathrm{C},-0.5231717$ $514,0.5810612547,0.578483969 \backslash \mathrm{H}, 0.1407223773,2.0987563373,-0.9607334387$ $\backslash H, 0.9711704656,2.1803191138,0.6097706412 \backslash H, 1.3288331176,-0.0898063194$ , - $1.4315764871 \backslash \mathrm{H},-0.9711704656,-2.1803191138,0.6097706412 \backslash \mathrm{H},-0.1407223$ $773,-2.0987563373,-0.9607334387 \backslash C, 0.5231717514,-0.5810612547,0.5784839$ $69 \backslash \mathrm{H},-1.3288331176,0.0898063194,-1.4315764871 \backslash \mathrm{C}, 0.4921996743,1.5062504$ $331,-0.1080423938 \backslash C, 1.3833874941,0.2696157321,-0.3980785304 \backslash C,-0.49219$ 96743,-1.5062504331,-0.1080423938<br>Version=Sun-SVR4-Unix-G98RevA.7\Sta $t e=1-A \backslash H F=-232.9630472 \backslash M P 2=-233.7356193 \backslash R M S D=5.448 e-09 \backslash R M S F=9.277 e-06 \backslash$ Dipole=0.,0.,0.040946\PG=C02 [X(C6H10)] <br>@

## TB-3-48 twistboat-cyclohexane

$1 \backslash 1 \backslash G I N C-P A L O \backslash F O p t \backslash R M P 2-F C \backslash 6-31 G(d) \backslash C 6 H 12 \backslash R A S M U S S E N \backslash 14-O c t-1999 \backslash 0 \backslash \backslash \# P$ MP2/6-31G* 5D OPT FREQ=NORAMAN NAME=RASMUSSEN GEOM= (CHECK, NODISTANCE,N OANGLE,NODIHEDRAL) GUESS=CHECK<br>cyclohexane C1 twist <br>0,1\H,0.41836158 95,-1.1785587595,-1.4650738223\C, 0.6510844852,-1.2152970219,-0.3935284 $956 \backslash \mathrm{H},-1.2167945711,-2.1402585613,0.2312197127 \backslash \mathrm{H}, 1.2167879202,2.140270$ $709,0.2311420814 \backslash \mathrm{C},-0.6510731397,1.2152763129,-0.3936111448 \backslash \mathrm{H},-0.41831$ $92628,1.1784817455,-1.4651478164 \backslash \mathrm{H}, 2.1743940834,-0.2742464092,0.836288$ $798 \backslash \mathrm{H},-2.176115863,-0.2615951889,-0.8360876885 \backslash \mathrm{H}, 0.4251206649,1.176217$ $7732,1.4650436518 \backslash \mathrm{H},-1.2043640514,2.1472687958,-0.2313610944 \backslash \mathrm{H},-2.1744$ $184157,0.2742902723,0.8362114426 \backslash \mathrm{H}, 1.2043707147,-2.1472809576,-0.23121$ $3438 \backslash \mathrm{H},-0.4251628263,-1.1761405351,1.4650932016 \backslash \mathrm{C}, 1.5185107858,-0.0044$ $162356,0.0000578879 \backslash \mathrm{C}, 0.6581014319,1.2115230984,0.3935052601 \backslash \mathrm{C},-1.5185$ $107942,0.0044162005,0.0000137657 \backslash \mathrm{C},-0.6581127855,-1.2115023628,0.39354$ $99665 \backslash \mathrm{H}, 2.1761401167,0.2615511672,-0.8360384679 \backslash \backslash V e r s i o n=S u n-S V R 4-U n i x$ -G98RevA. $7 \backslash \mathrm{HF}=-234.1952006 \backslash \mathrm{MP} 2=-234.9740811 \backslash \mathrm{RMSD}=3.080 e-09 \backslash \mathrm{RMSF}=6.353 \mathrm{e}$ -05\Dipole=0.,0.,-0.0000015\PG=C01 [X(C6H12)]<br>@

## 3-49 bicyclo[2.2.1]heptane (norbornane)

$1 \backslash 1 \backslash G I N C-P A L O \backslash F O p t \backslash R M P 2-F C \backslash 6-31 G(d) \backslash C 7 H 12 \backslash R A S M U S S E N \backslash 14-O c t-1999 \backslash 0 \backslash \backslash \# P$ GEOM=ALLCHECK GUESS=TCHECK RMP2 (FC)/6-31G(D) FOPT<br>bicycloheptane C2v $\backslash 0,1 \backslash \mathrm{H}, 0.8928185487,0 ., 2.0181348967 \backslash \mathrm{H},-0.8928185487,0 ., 2.0181348967 \backslash \mathrm{H}$, $0 .,-2.150407647,0.7293974312 \backslash \mathrm{H},-2.1527765812,-1.1717240568,-0.01467211$ $91 \backslash \mathrm{H}, 0 ., 2.150407647,0.7293974312 \backslash \mathrm{C}, 0 ., 0.1 .3815116313 \backslash \mathrm{H}, 1.1998332789$, 1 . 2036410029 , - $1.4995748094 \backslash \mathrm{H},-2.1527765812,1.1717240568,-0.0146721191 \backslash \mathrm{H}$ ,1.1998332789,-1.2036410029,-1.4995748094\C,0.,-1.1276035,0.3383864661
\H,-1.1998332789,-1.2036410029,-1.4995748094\C,0.,1.1276035,0.33838646 $61 \backslash \mathrm{H},-1.1998332789,1.2036410029,-1.4995748094 \backslash \mathrm{C}, 1.2478018377,0.7785122$ 79,-0.4911576801\C,1.2478018377,-0.778512279,-0.4911576801\C,-1.247801 8377,-0.778512279,-0.4911576801 \C,-1.2478018377,0.778512279,-0.4911576 $801 \backslash \mathrm{H}, 2.1527765812,1.1717240568,-0.0146721191 \backslash \mathrm{H}, 2.1527765812,-1.171724$ 0568,-0.0146721191 <br>Version=Sun-SVR4-Unix-G98RevA. $7 \backslash$ State=1-A1 $\backslash H F=-272$ $.059161 \backslash \mathrm{MP} 2=-272.966536 \backslash \mathrm{RMSD}=1.850 \mathrm{e}-09 \backslash \mathrm{RMSF}=5.099 \mathrm{e}-05 \backslash \mathrm{Dipole}=0 ., 0 ., 0.0$ $235243 \backslash \mathrm{PG}=\mathrm{CO} 2 \mathrm{~V}$ [C2(C1), SGV(C2H2), SGV'(H2), X(C4H8)] <br>@

## 3-50 cis-bicyclo[3.3.0]octane (cis-octahydropentalene)

$1 \backslash 1 \backslash G I N C-$ PALO $\backslash$ FOpt $\backslash$ RMP2-FC $\backslash 6-31 G(d) \backslash C 8 H 14 \backslash R A S M U S S E N \backslash 14-O c t-1999 \backslash 0 \backslash \ \# P$ MP2/6-31G* 5D OPT FREQ=NORAMAN NAME=RASMUSSEN GEOM= (CHECK,NODISTANCE,N OANGLE,NODIHEDRAL) SYMM=LOOSE<br>bicyclooctane C2v $\backslash \backslash 0,1 \backslash \mathrm{H}, 0 ., 2.605704831$ $3,-1.0492991401 \backslash C, 0.7833932827,0 .,-0.4706269325 \backslash \mathrm{H}, 0 .,-3.1208686173,0.6$ $428275147 \backslash \mathrm{C},-0.7833932827,0 .,-0.4706269325 \backslash \mathrm{H},-1.1481562816,0 .,-1.50568$ $52336 \backslash \mathrm{H}, 0 ., 3.1208686173,0.6428275147 \backslash \mathrm{H}, 1.3268542036,1.1464261522,1.291$ $5113202 \backslash \mathrm{C}, 0 .,-2.243173019,-0.0134043819 \backslash \mathrm{H},-1.3268542036,1.1464261522,1$ $.2915113202 \backslash \mathrm{H}, 0 .,-2.6057048313,-1.0492991401 \backslash \mathrm{H},-1.3268542036,-1.146426$ 1522,1.2915113202\H,1.1481562816,0.,-1.5056852336\H,1.3268542036,-1.14 64261522,1.2915113202\C,1.1971077748,1.3137914513,0.2140412851\C,-1.19 $71077748,1.3137914513,0.2140412851 \backslash C,-1.1971077748,-1.3137914513,0.214$ $0412851 \backslash \mathrm{C}, 1.1971077748,-1.3137914513,0.2140412851 \backslash \mathrm{H}, 2.1412794302,1.717$ 6253043,-0.167586658\H,-2.1412794302,1.7176253043,-0.167586658\H,-2.14 12794302,-1.7176253043,-0.167586658\H,2.1412794302,-1.7176253043,-0.16 7586658\C,0.,2.243173019,-0.0134043819<br>Version=Sun-SVR4-Unix-G98RevA. $7 \backslash$ State=1-A1 \HF=-311.1001761 \MP2=-312.1362913 \RMSD=4.289e-09\RMSF=1.99 $8 \mathrm{e}-05 \backslash$ Dipole=0., 0.,-0.0455532\PG=C02V [SGV (C2H4), SGV'(C2H2), X(C4H8)] <br> @

## Crown-3-51 crown-cyclooctane

$1 \backslash 1 \backslash G I N C-P A L O \backslash F O p t \backslash R M P 2-F C \backslash 6-31 G(d) \backslash C 8 H 16 \backslash R A S M U S S E N \backslash 14-O c t-1999 \backslash 0 \backslash \ \# P$ MP2/6-31G* 5D OPT FREQ=NORAMAN NAME=RASMUSSEN GEOM= (CHECK,NODISTANCE,N OANGLE,NODIHEDRAL) SYMM=LOOSE <br>cyclooctane C2v crown<br>0,1\H,2.07957831 $2,2.0795209238,-0.1031861573 \backslash C,-1.3141577043,-1.3141564396,-0.28521460$ $16 \backslash \mathrm{H}, 1.2316373,1.2314901386,-1.3783355372 \backslash \mathrm{H},-1.2316373,-1.2314901386,-$ $1.3783355372 \backslash \mathrm{H},-1.2316373,1.2314901386,-1.3783355372 \backslash \mathrm{H}, 2.079578312,-2$. $0795209238,-0.1031861573 \backslash \mathrm{H}, 1.2316373,-1.2314901386,-1.3783355372 \backslash \mathrm{H},-2$. 079578312,-2.0795209238,-0.1031861573\H,1.7413235719,0.,1.3784459928\H ,-2.079578312,2.0795209238,-0.1031861573\H,0.,1.7420719169,1.378227163 \H, 0.,-1.7420719169,1.378227163\H,-1.7413235719,0.,1.3784459928\C,0.,$1.8586262932,0.2850789712 \backslash C, 1.8583715899,0.0 .2853511364 \backslash \mathrm{C}, 0.1 .858626$ 2932,0.2850789712\C,-1.8583715899,0.,0.2853511364\H,0.,-2.9410130209,0 $.1027996538 \backslash \mathrm{H}, 2.9408390112,0 ., 0.103565153 \backslash \mathrm{H}, 0 ., 2.9410130209,0.10279965$ $38 \backslash \mathrm{H},-2.9408390112,0.0 .103565153 \backslash \mathrm{C}, 1.3141577043,-1.3141564396,-0.2852$ $146016 \backslash \mathrm{C}, 1.3141577043,1.3141564396,-0.2852146016 \backslash \mathrm{C},-1.3141577043,1.314$ 1564396,-0.2852146016<br>Version=Sun-SVR4-Unix-G98RevA. 7 \State=1-A1 \HF=$312.253007 \backslash \mathrm{MP} 2=-313.2929085 \backslash \mathrm{RMSD}=2.801 \mathrm{e}-09 \backslash \mathrm{RMSF}=1.218 \mathrm{e}-05 \backslash \mathrm{Dipole}=0 ., 0$. , - 0.0000015 $\backslash \mathrm{PG}=\mathrm{C0} 2 \mathrm{~V}\left[\mathrm{SGV}(\mathrm{C} 2 \mathrm{H} 4), \mathrm{SGV}{ }^{\prime}(\mathrm{C} 2 \mathrm{H} 4), \mathrm{X}(\mathrm{C} 4 \mathrm{H} 8)\right] \backslash \backslash @$

## TBTB-3-52 twistboat,twistboat-bicyclo[3.3.1]nonane

$1 \backslash 1 \backslash G I N C-P A L O \ F O p t \backslash R M P 2-F C \backslash 6-31 G(d) \backslash C 9 H 16 \backslash R A S M U S S E N \backslash 14-O c t-1999 \backslash 0 \backslash \ \# P$ MP2/6-31G* 5D OPT FREQ=NORAMAN NAME=RASMUSSEN GEOM= (CHECK,NODISTANCE,N

OANGLE, NODIHEDRAL) GUESS=CHECK <br>bicyclononane C1 <br>0,1\H,0.8773425467,$0.0470929282,2.0367307775 \backslash \mathrm{H}, 0.0724393412,-2.1392229353,1.0622687007 \backslash \mathrm{H}$, $-0.0713323889,2.1389881426,1.0628204295 \backslash \mathrm{H}, 2.8387029721,-0.1365967746,-$ $1.1306662096 \backslash \mathrm{H},-2.8398750755,0.1368515362,-1.1276716558 \backslash \mathrm{C}, 0.0007073541$ , $-0.000153112,1.3790762965 \backslash \mathrm{H}, 1.4972224082,1.8204334911,-1.0778900843 \backslash \mathrm{H}$ , 2.6175531487,-0.4592800727,0.5754456055\Н, 0.5319438928,-0.918483251,$1.6043704049 \backslash \mathrm{H},-0.8752593117,0.0466392608,2.0376326859 \backslash \mathrm{H},-1.4983281382$ ,-1.8201924878,-1.0767450486\Н, $-2.6169438798,0.4591421447,0.578282992 \backslash$ H, -0.5336135035,0.9188586503,-1.6036078943\C,1.5157475082,1.2742360306 , -0.1263048957\C,0.9933218482,-1.1663520453,-0.6416285897\C,-1.5158724 281,-1.2742132063,-0.1250162259\C,-0.9939890492,1.1665003347,-0.640327 $7903 \backslash \mathrm{H}, 2.1819137884,1.836754068,0.5400095913 \backslash \mathrm{H}, 1.4408587624,-2.1587179$ 408,-0.7764707165\H,-2.1813445273,-1.8368875065,0.5418597873\H,-1.4416 727657,2.1588949926,-0.7744695192\C,2.0881963718,-0.1427580596,-0.3313 $826351 \backslash C,-0.0925522782,-1.2308647746,0.4686909118 \backslash C,-2.0885345068,0.14$ 28289952,-0.3291708637\C,0.0930406349,1.2307611057,0.4688706195<br>Versi on=Sun-SVR4-Unix-G98RevA. $7 \backslash \mathrm{HF}=-350.123117 \backslash \mathrm{MP} 2=-351.2948227 \backslash$ RMSD $=3.543 \mathrm{e}$ $-09 \backslash \mathrm{RMSF}=1.352 \mathrm{e}-05 \backslash \mathrm{Dipole}=0.0000113,-0.000002,0.0213998 \backslash \mathrm{PG}=\mathrm{C01} \quad[\mathrm{X}(\mathrm{C} 9 \mathrm{H} 1$ 6)] <br>@

## Bridged Spiropentanes

## 3-11 [3.3.3]fenestrane (tricyclo $\left[2.1 .0 .0^{1,3}\right]$ pentane)

$1 \backslash 1 \backslash G I N C-P C \backslash F O p t \backslash R M P 2-F C \backslash 6-31 G(d) \backslash C 5 H 6 \backslash R A S M U S S E N \backslash 04-N O v-1999 \backslash 0 \backslash \ \# P$ MP2 /6-31G(D) 5D OPT=(READFC,TIGHT) FREQ=NORAMAN NAME=RASMUSSEN MAXDISK=20 97152000 GEOM=CHECK GUESS=CHECK NOSYMM $\backslash \backslash[3.3 .3]$ fenestrane C1<br>0,1\H,1. 6566522739,-0.91131785,-1.3572958237\C,1.4192235947,-0.2833672819,-0.4 $968373026 \backslash \mathrm{C}, 0.1171830693,0.4372075207,-0.464597015 \backslash \mathrm{C}, 0.386999874,-0.81$ 08699224,0.4658542258\H,2.2772228777,0.2704917096,-0.1130098357\C,-1.3 $582000672,0.4974173326,-0.2359432462 \backslash C,-0.3382647149,0.4232483833,0.91$ 01762225\H,-0.1763322414,-1.6969100637,0.1758023446\H,-0.1417442939,1. 1054353411,1.7320736066\H,-1.8452176421,1.4479944289,-0.4597494011 \H, -$1.9915877595,-0.3773326698,-0.3985105815 \backslash \backslash$ Version=SGI-G98RevA. $6 \backslash \mathrm{HF}=-19$ $2.6284468 \backslash \mathrm{MP} 2=-193.2801211 \backslash \mathrm{RMSD}=9.950 \mathrm{e}-09 \backslash \mathrm{RMSF}=8.340 \mathrm{e}-07 \backslash \mathrm{Dipole}=-0.013$ 197,0.0203119,-0.2202737\PG=C01 [X(C5H6)] <br>@

## 3-53 [3.4.3]fenestrane (tricyclo[3.1.0.0 ${ }^{1,3}$ ]hexane)

$1 \backslash 1 \backslash$ ANU-ARGENT $\backslash$ FOPT $\backslash$ RMP2-FC $\backslash 6$-31G (D) \C6H8 \RASMUSSEN $\backslash 28-N o v-1994 \backslash 1 \backslash$ <br>\#P RMP2/6-31G* 5D FOPT=READFC NAME=RASMUSSEN TEST SCF=DIRECT MAXDISK=2437 50000 GEOM $=(C H E C K, N O D I S T A N C E, N O A N G L E, N O D I H E D R A L) ~ G U E S S=C H E C K \backslash \backslash[3.4 .3] f$ enestrane $\mathrm{C} 2 \backslash \backslash 0,1 \backslash C \backslash C, 1, c l \backslash C, 1, r 1 a, 2, a 1 a \backslash C, 1, r 1 a, 2, a 1 a, 3,180.0 \backslash C, 1, r 2$ $a, 4, a 2 a, 3, d 2 a, 0 \backslash C, 1, r 2 a, 3, a 2 a, 4, d 2 a, 0 \backslash H, 5, h 3 a, 1, h a 3 a, 3, h d 3 a, 0 \backslash H, 6, h 3 a$, $1, h a 3 a, 4, h d 3 a, 0 \backslash H, 3, h 1 a, 1, h a 1 a, 6, h d 1 a, 0 \backslash H, 4, h 2 a, 1, h a 2 a, 5, h d 2 a, 0 \backslash H, 3, h 2$ a,1,ha2a, 6, hd2a, 0\H, 4,h1a,1,ha1a,5,hd1a, 0\H,2,h6a, 1,ha6a,3,hd6a, 0\H,2, h6a, 1, ha6a, 4,hd6a, $0 \backslash \backslash c l=2.1559663 \backslash r 1 a=1.4665557 \backslash r 2 a=1.51612963 \backslash a 1 a=91$. $20037275 \backslash \mathrm{a} 2 \mathrm{a}=61.90646495 \backslash \mathrm{~d} 2 \mathrm{a}=143.94667725 \backslash \mathrm{~h} 3 \mathrm{a}=1.08896925 \backslash \mathrm{ha} 3 \mathrm{a}=123.5396$ $714 \backslash$ hd3a=75.13498892 \ha1a=118.38146571 \ha2a=119.28200678 ha6a=125.8311 $8906 \backslash h d 1 a=101.16031288 \backslash h d 2 a=-112.2781889 \backslash h d 6 a=45.07435081 \backslash h 1 a=1.089056$ $52 \backslash h 2 a=1.09004287 \backslash h 6 a=1.0967593 \backslash \backslash V e r s i o n=I B M-R S 6000-G 92 R e v B \backslash$ State=1-A $H F=-231.704008 \backslash M P 2=-232.4780644 \backslash$ RMSD $=9.758 e-09 \backslash$ RMSF $=1.413 e-05 \backslash$ Dipole $=0$ .,-0.,-0.018111 \PG=C02 [C2(C1C1), X(C4H8)] <br>@

## 3-12 [3.5.3]fenestrane (tricyclo[4.1.0.0 ${ }^{1,3}$ ]heptane

 RMP2/6-31G* 5D FOPT=READFC NAME=RASMUSSEN SCF=DIRECT TEST MAXDISK=243 750000 GEOM $=($ CHECK, NODISTANCE, NOANGLE,NODIHEDRAL) GUESS=CHECK $\backslash$ [3.5.3] fenestrane $7 \mathrm{a} C 2 \backslash \backslash 0,1 \backslash C \backslash \mathrm{X}, 1,1 . \backslash \mathrm{C}, 1, r 1 a, 2, a 1 a \backslash \mathrm{C}, 1, \mathrm{rla}, 2, \mathrm{ala}, 3,180.0 \backslash \mathrm{C}$, $1, r 2 a, 4, a 2 a, 3, d 2 a, 0 \backslash c, 1, r 2 a, 3, a 2 a, 4, d 2 a, 0 \backslash c, 5, r 3 a, 1, a 3 a, 3, d 3 a, 0 \backslash c, 6, r 3$ $a, 1, a 3 a, 4, d 3 a, 0 \backslash H, 5, h 3 a, 1, h a 3 a, 3, h d 3 a, 0 \backslash H, 6, h 3 a, 1, h a 3 a, 4, h d 3 a, 0 \backslash H, 3, h 1$ $a, 1, h a 1 a, 6, h d 1 a, 0 \backslash H, 4, h 2 a, 1, h a 2 a, 5, h d 2 a, 0 \backslash H, 3, h 2 a, 1, h a 2 a, 6, h d 2 a, 0 \backslash H, 4$, h1a, $1, h a 1 a, 5, h d 1 a, 0 \backslash H, 7, h 5 a, 5, h a 5 a, 1, h d 5 a, 0 \backslash H, 8, h 5 a, 6, h a 5 a, 1, h d 5 a, 0 \backslash H$, $7, h 6 a, 5, h a 6 a, 1, h d 6 a, 0 \backslash H, 8, h 6 a, 6, h a 6 a, 1, h d 6 a, 0 \backslash \backslash r 1 a=1.47655571 \backslash r 2 a=1.48$ $170952 \backslash a 1 a=79.02745075 \backslash a 2 a=62.58242051 \backslash d 2 a=139.2418273 \backslash r 3 a=1.53193336 \backslash$ $a 3 a=105.54147758 \backslash d 3 a=-81.91928133 \backslash h 3 a=1.08900735 \backslash h a 3 a=120.72670433 \backslash$ hd 3 $a=56.5921153 \backslash$ hal $a=119.19224468 \backslash$ ha $2 a=118.37541432 \backslash$ ha $5 \mathrm{a}=110.61817981 \backslash$ ha6 $a=112.59519358 \backslash h d 1 a=105.00571988 \backslash h d 2 a=-108.09854561 \backslash h d 5 a=-89.28001905 \backslash$ $h d 6 a=150.901805 \backslash h 1 a=1.08888979 \backslash h 2 a=1.08891854 \backslash h 5 a=1.09789558 \backslash h 6 a=1.096$ $22908 \backslash \backslash$ Version=IBM-RS6000-G92RevB\State=1-A $\backslash H F=-270.7984122 \backslash \mathrm{MP} 2=-271.7$ $006233 \backslash$ RMSD $=3.904 \mathrm{e}-09 \backslash \mathrm{RMSF}=3.199 \mathrm{e}-06 \backslash \mathrm{Dipole}=-0 .,-0 .,-0.0578713 \backslash \mathrm{PG}=\mathrm{C0} 2$ [C2 (C1) , X(C6H10)] <br>@

## 3-54 tetracyclo[3.3.1.0 $\left.0^{2,4} .0^{2,8}\right]$ nonane

$1 \backslash 1 \backslash$ GINC-RSCQC2 $\backslash$ FOpt $\backslash R M P 2-F C \backslash 6-31 G(d) \backslash C 9 H 12 \backslash D A N N E \backslash 03-D e c-1995 \backslash 0 \backslash \backslash \# P R M$ P2/6-31G* 5D FOPT SCF=TIGHT MAXDISK=500000000 GEOM= (NODISTANCE,NOANGLE , NODIHEDRAL) <br>Baird C1 <br>0,1\C,0.1059936544,-1.3141277831,0.4409114962\} $C, 1.2904125998,-0.3786233175,0.6758759938 \backslash C, 1.7286778177,0.4800236689$, $-0.5101625834 \backslash C,-1.3637869152,0.4577062327,1.7125847986 \backslash C,-0.803398263$ $5,0.2874048662,-1.0465308867 \backslash C,-0.7221750908,-1.227431561,-0.827412661$ $8 \backslash C,-0.8605232509,0.9106531054,0.342981284 \backslash C,-0.0648497355,-0.03784865$ $46,1.1851211759 \backslash$ C, $0.5939965325,0.734542203,-1.5518505182 \backslash$ Н, 0.108341666 $9,-2.2421093718,1.012218595 \backslash \mathrm{H}, 2.0865380934,-0.7457571392,1.3257614207 \backslash$ H, - $0.306188867,-1.7455491981,-1.70124994 \backslash \mathrm{H},-1.4110559146,1.252425733,2$ . $4558397805 \backslash \mathrm{H}, 2.1063614559,1.4360780314,-0.1274519919 \backslash \mathrm{H}, 2.5776182857$, -$0.0100345072,-1.0019678827 \backslash \mathrm{H},-2.147530886,-0.2911700938,1.8174153304 \backslash \mathrm{H}$ , -0.5206461582,1.9485706638,0.3699493933\н, 0.5640750926,1.8009010085,$1.805169044 \backslash \mathrm{H}, 0.8117864545,0.1978034662,-2.4833801919 \backslash \mathrm{H},-1.7131772809$, $-1.6575972155,-0.6297549071 \backslash \mathrm{H},-1.5822060325,0.5826460631,-1.7613191528$ $\backslash$ Version=IBM-RS6000-G94RevC. $2 \backslash \mathrm{HF}=-347.6766297 \backslash \mathrm{MP} 2=-348.8427814 \backslash \mathrm{RMSD}=7$ $.392 e-09 \backslash \mathrm{RMSF}=5.271 \mathrm{e}-05 \backslash \mathrm{Dipole}=0.0444677,0.002156,-0.1037839 \backslash \mathrm{PG}=\mathrm{C01} \quad[\mathrm{X}$ (C9H12)] <br>@

## Hemialkaplanes

## 3-2 hemihexaplane

$1 \backslash 1 \backslash$ GINC-VPP05\FOpt \RMP2-FC\6-31G(d) \C11H16\RASMUSSEN\17-Feb-1999\0<br>\# P MP2/6-31G* 5D OPT=NEWESTMFC NAME=RASMUSSEN GEOM= (NODISTANCE,NOANGLE, NODIHEDRAL) MAXDISK=1200000000<br>Hemihexaplane C2 <br>0,1\C,0.,0.,1.276481 $565 \backslash \mathrm{C}, 0.4360476978,1.5129562662,0.7072706509 \backslash \mathrm{C},-0.4360476978,-1.512956$ $2662,0.7072706509 \backslash C,-1.5230309914,0.4926229207,1.1671189615 \backslash \mathrm{C}, 1.523030$ 9914,-0.4926229207,1.1671189615 $\mathrm{H},-0.0823804343,2.2169021668,1.3621202$ $547 \backslash \mathrm{H}, 1.4987237388,1.7397566694,0.7938091648 \backslash \mathrm{H},-2.3049174094,-0.211870$ $0028,1.4550701432 \backslash \mathrm{H},-1.7757291371,1.4628278544,1.6091148526 \backslash \mathrm{H}, 0.082380$ 4343,-2.2169021668,1.3621202547 $\mathrm{H},-1.4987237388,-1.7397566694,0.793809$ $1648 \backslash \mathrm{H}, 2.3049174094,0.2118700028,1.4550701432 \backslash \mathrm{H}, 1.7757291371,-1.462827$
$8544,1.6091148526 \backslash \mathrm{C},-0.0359504491,1.4353721772,-0.6902390776 \backslash \mathrm{C},-1.3797$ $398339,0.6511521254,-0.4591402403 \backslash C, 0.0359504491,-1.4353721772,-0.6902$ $390776 \backslash \mathrm{C}, 1.3797398339,-0.6511521254,-0.4591402403 \backslash \mathrm{H},-0.1860686564,2.37$ $95994059,-1.2332835762 \backslash \mathrm{H},-2.2544779678,1.2002032033,-0.8370924972 \backslash \mathrm{H}, 0$. $1860686564,-2.3795994059,-1.2332835762 \backslash H, 2.2544779678,-1.2002032033,-0$ $.8370924972 \backslash \mathrm{H}, 1.0192961247,0.3351046603,-2.3320148801 \backslash \mathrm{C},-1.1627881439$, $-0.6369214514,-1.2872863828 \backslash \mathrm{H}, 2.035497095,1.3031821324,-1.2735116269 \backslash \mathrm{C}$ , 1.1627881439, 0.6369214514, -1.2872863828\H,-2.035497095,-1.3031821324, $-1.2735116269 \backslash \mathrm{H},-1.0192961247,-0.3351046603,-2.3320148801 \backslash \backslash V e r s i o n=F u j$ itsu-VP-Unix-G94RevE. $2 \backslash$ State $=1-A \backslash H F=-425.5671142 \backslash \mathrm{MP} 2=-427.0331491 \backslash \mathrm{RMSD}$ $=4.676 e-09 \backslash R M S F=2.349 e-05 \backslash D i p o l e=0.0 .,-0.2560482 \backslash \mathrm{PG}=\mathrm{C} 02 \quad$ [C2 (C1) , X (C10 H16)] <br>@

## 3-3 hemibiheptaplane

$1 \backslash 1 \backslash G I N C-V P P 03 \backslash F O p t \backslash R M P 2-F C \backslash 6-31 G(d) \backslash C 12 H 16 \backslash R A S M U S S E N \backslash 17-F e b-1999 \backslash 0 \backslash \ \#$ P MP2/6-31G* 5D OPT=NEWESTMFC NAME=RASMUSSEN GEOM= (NODISTANCE,NOANGLE, NODIHEDRAL) MAXDISK=1200000000<br>Hemibiheptaplane C2<br>0,1\C,0.,0.,1.487 $507086 \backslash \mathrm{C}, 1.35804489,-0.813300473,0.9299323187 \backslash \mathrm{C},-1.35804489,0.81330047$ $3,0.9299323187 \backslash \mathrm{C}, 0.8453488704,1.3543611523,1.3508241782 \backslash \mathrm{C},-0.845348870$ $4,-1.3543611523,1.3508241782 \backslash \mathrm{H}, 2.1403269979,-0.5334652193,1.6416442421$ $\backslash H, 1.2853523563,-1.9009253192,0.9509389608 \backslash \mathrm{H}, 0.3724402613,2.2820668007$ , 1. $6735098272 \backslash \mathrm{H}, 1.866154773,1.348034275,1.7529088232 \backslash \mathrm{H},-2.1403269979$, 0 $.5334652193,1.6416442421 \backslash \mathrm{H},-1.2853523563,1.9009253192,0.9509389608 \backslash \mathrm{H},-$ $0.3724402613,-2.2820668007,1.6735098272 \backslash \mathrm{H},-1.866154773,-1.348034275,1$. $7529088232 \backslash C, 1.4633764411,-0.2915142488,-0.4373380858 \backslash C, 0.9425058554,1$ $.1722923958,-0.2754584635 \backslash C,-1.4633764411,0.2915142488,-0.4373380858 \backslash C$ ,-0.9425058554,-1.1722923958,-0.2754584635\H,2.4272724034,-0. 375907203 $3,-0.9601394377 \backslash \mathrm{H}, 1.6206610633,1.9335484606,-0.6878127879 \backslash \mathrm{H},-2.4272724$ $034,0.3759072033,-0.9601394377 \backslash \mathrm{H},-1.6206610633,-1.9335484606,-0.687812$ $7879 \backslash \mathrm{C}, 0 ., 0 .,-2.2305809453 \backslash \mathrm{C},-0.3530729252,1.0660250709,-1.1861891591 \backslash$ H, 0.7088728076, -2.031455266, -1. $5650891947 \backslash \mathrm{C}, 0.3530729252,-1.0660250709$ , - $1.1861891591 \backslash \mathrm{H},-0.7088728076,2.031455266,-1.5650891947 \backslash \mathrm{H},-0.86112362$ 95,-0.2373351992,-2.8673635865 \H, 0.8611236295, 0.2373351992, -2. 86736358 $65 \backslash \backslash$ Version=Fujitsu-VP-Unix-G94RevE. $2 \backslash$ State $=1-A \backslash H F=-463.4334401 \backslash M P 2=-4$ $65.0287394 \backslash \mathrm{RMSD}=4.984 \mathrm{e}-09 \backslash \mathrm{RMSF}=3.625 \mathrm{e}-05 \backslash \mathrm{Dipole=0.,0.,-0.2755328} \mathrm{\backslash PG=C0}$ 2 [C2 (C1C1), X(C10H16)] <br>@

## 3-1 hemioctaplane

$1 \backslash 1 \backslash G I N C-V P P 01 \backslash F O p t \backslash R M P 2-F C \backslash 6-31 G(d) \backslash C 13 H 20 \backslash R A S M U S S E N \backslash 15-O c t-1998 \backslash 0 \backslash \ \#$ P MP2/6-31G* OPT 5D GEOM=(CHECK,NODISTANCE,NOANGLE,NODIHEDRAL) GUESS=C HECK NAME=RASMUSSEN MAXDISK=1500000000<br>hemioctaplane c2v<br>0,1\C,0.,0. ,1.2848328139\C,1.599530334,0.,0.8385154309\C,-1.599530334,0.,0.838515 $4309 \backslash \mathrm{C}, 0.1 .5988092786,1.4094579635 \backslash \mathrm{C}, 0 .,-1.5988092786,1.4094579635 \backslash \mathrm{H}$, $2.0739579161,0.8652224009,1.3022278131 \backslash \mathrm{H}, 2.0739579161,-0.8652224009,1$. $3022278131 \backslash \mathrm{H},-0.8749931821,2.074445776,1.8635015223 \backslash \mathrm{H}, 0.8749931821,2.0$ 74445776,1.8635015223\H,-2.0739579161,-0.8652224009,1.3022278131 \H,-2. 0739579161,0.8652224009,1.3022278131\H,0.8749931821,-2.074445776,1.863 $5015223 \backslash \mathrm{H},-0.8749931821,-2.074445776,1.8635015223 \backslash \mathrm{C}, 1.791504816,0 .,-0$. $6243520854 \backslash C, 0 ., 1.8802966531,-0.1944572436 \backslash C,-1.791504816,0 .,-0.624352$ $0854 \backslash \mathrm{C}, 0 .,-1.8802966531,-0.1944572436 \backslash \mathrm{H}, 2.8551593361,0 .,-0.9108570214 \backslash$ H, 0., 2.978403744,-0.2826613416\H,-2.8551593361,0., -0.9108570214\H, 0., -$2.978403744,-0.2826613416 \backslash C, 1.2451969758,1.3946798282,-0.9913804209 \backslash \mathrm{C}$,
$-1.2451969758,1.3946798282,-0.9913804209 \backslash \mathrm{C},-1.2451969758,-1.3946798282$ , - 0. $9913804209 \backslash \mathrm{C}, 1.2451969758,-1.3946798282,-0.9913804209 \backslash \mathrm{H}, 2.08153735$ $18,2.0738875561,-0.7727954531 \backslash \mathrm{H}, 1.0374676865,1.5104859205,-2.062633593$ $\backslash H,-2.0815373518,2.0738875561,-0.7727954531 \backslash \mathrm{H},-1.0374676865,1.51048592$ $05,-2.062633593 \backslash H,-2.0815373518,-2.0738875561,-0.7727954531 \backslash \mathrm{H},-1.03746$ $76865,-1.5104859205,-2.062633593 \backslash H, 2.0815373518,-2.0738875561,-0.77279$ $54531 \backslash \mathrm{H}, 1.0374676865,-1.5104859205,-2.062633593 \backslash \backslash V e r s i o n=F u j i t s u-V P-U n$ ix-G94RevE. $2 \backslash$ State $=1-A 1 \backslash H F=-503.6651619 \backslash M P 2=-505.3901423 \backslash R M S D=9.108 e-0$
 ' (C4H2), X(C4H16)] <br>@

## Hemispiroalkaplanes

## 3-4 hemispirobioctaplane (perpendicular)

$1 \backslash 1 \backslash G I N C-V P P 05 \backslash F O p t \backslash R M P 2-F C \backslash 6-31 G(d) \backslash C 13 H 14 \backslash R A S M U S S E N \backslash 18-N o v-1998 \backslash 0 \backslash \backslash \#$ P MP2/6-31G* 5D OPT GEOM= (NODISTANCE, NOANGLE, NODIHEDRAL) NAME=RASMUSSE N MAXDISK=1500000000<br>hemispirobioctaplane $C 2 v \backslash \backslash 0,1 \backslash C, 0 ., 0 ., 1.73352765$ $86 \backslash C, 1.2738509797,0.7179934768,1.0072806465 \backslash C,-1.2738509797,-0.7179934$ $768,1.0072806465 \backslash C,-1.2738509797,0.7179934768,1.0072806465 \backslash C, 1.2738509$ $797,-0.7179934768,1.0072806465 \backslash \mathrm{H},-1.1942394414,0 .,-2.24207899 \backslash \mathrm{H}, 1.7828$ $089284,1.3180988261,1.7600277388 \backslash \mathrm{H},-1.7828089284,1.3180988261,1.760027$ $7388 \backslash H, 1.1942394414,0 .,-2.24207899 \backslash H, 0 .,-3.0247517777,0.1650298251 \backslash H$, -$1.7828089284,-1.3180988261,1.7600277388 \backslash \mathrm{H}, 1.7828089284,-1.3180988261,1$ $.7600277388 \backslash \mathrm{H}, 0 .,-2.6638217742,-1.5764249373 \backslash \mathrm{C}, 1.1742538619,1.24812529$ $28,-0.4094154266 \backslash \mathrm{C},-1.1742538619,1.2481252928,-0.4094154266 \backslash \mathrm{C},-1.17425$ 38619,-1.2481252928, -0.4094154266\C,1.1742538619,-1.2481252928,-0.4094 $154266 \backslash \mathrm{H}, 2.1413853406,1.6749821564,-0.7072148261 \backslash \mathrm{H},-2.1413853406,1.674$ $9821564,-0.7072148261 \backslash \mathrm{H},-2.1413853406,-1.6749821564,-0.7072148261 \backslash \mathrm{H}, 2$. $1413853406,-1.6749821564,-0.7072148261 \backslash C, 0 ., 2.2148295166,-0.575209025 \backslash$ $C,-0.7771100874,0 .,-1.2293105312 \backslash C, 0 .,-2.2148295166,-0.575209025 \backslash C, 0.7$ $771100874,0 .,-1.2293105312 \backslash \mathrm{H}, 0 ., 3.0247517777,0.1650298251 \backslash \mathrm{H}, 0 ., 2.66382$ 17742,-1.5764249373<br>Version=Fujitsu-VP-Unix-G94RevE. $2 \backslash$ State=1-A1 \HF=$500.2598928 \backslash M P 2=-501.9505159 \backslash \operatorname{RMSD}=4.375 e-09 \backslash R M S F=1.110 e-05 \backslash D i p o l e=0 ., 0$ ., -1.0187018 \PG=C02V [C2 (C1), SGV (C2H4), SGV' (C2H2), X (C8H8)] <br>@

## 3-5 hemispirooctaplane

$1 \backslash 1 \backslash G I N C-V P P 07 \backslash F O p t \backslash R M P 2-F C \backslash 6-31 G(d) \backslash C 13 H 16 \backslash R A S M U S S E N \backslash 14-O c t-1998 \backslash 0 \backslash \backslash \#$ P MP2/6-31G* 5D OPT GEOM= (CHECK,NODISTANCE,NOANGLE,NODIHEDRAL) GUESS=C HECK NAME=RASMUSSEN MAXDISK=1500000000<br>hemispirooctaplane C2v<br>0,1\C, 0., 0.,1.7716771708\C,1.2783346408, -0.7190165961,1.0785803182\C,1.27833 $46408,0.7190165961,1.0785803182 \backslash \mathrm{C},-1.2783346408,0.7190165961,1.0785803$ $182 \backslash \mathrm{C},-1.2783346408,-0.7190165961,1.0785803182 \backslash \mathrm{H}, 1.7608344379,-1.31654$ $67772,1.8504065265 \backslash \mathrm{H}, 1.7608344379,1.3165467772,1.8504065265 \backslash \mathrm{H},-1.76083$ $44379,1.3165467772,1.8504065265 \backslash \mathrm{H},-1.7608344379,-1.3165467772,1.850406$ $5265 \backslash \mathrm{C}, 1.2746333188,-1.2497700788,-0.3492391302 \backslash \mathrm{C}, 1.2746333188,1.24977$ $00788,-0.3492391302 \backslash \mathrm{C},-1.2746333188,1.2497700788,-0.3492391302 \backslash \mathrm{C},-1.27$ $46333188,-1.2497700788,-0.3492391302 \backslash H, 2.112281074,-1.9554649094,-0.43$ $69122534 \backslash \mathrm{H}, 2.112281074,1.9554649094,-0.4369122534 \backslash \mathrm{H},-2.112281074,1.955$ $4649094,-0.4369122534 \backslash \mathrm{H},-2.112281074,-1.9554649094,-0.4369122534 \backslash \mathrm{C}, 0$. , $-2.0207544266,-0.6877216534 \backslash C, 0 ., 2.0207544266,-0.6877216534 \backslash C, 1.568066$ $0663,0 .,-1.2136288828 \backslash \mathrm{C},-1.5680660663,0 .,-1.2136288828 \backslash \mathrm{H}, 0 .,-2.9558028$ 459,-0.1098672539\H, 0.,-2.304762728,-1.7489187279\H,2.6370538222,0.,-1


#### Abstract

.4552889298\H,1.0370019927,0.,-2.1719361853\H,0.,2.9558028459,-0.10986 $72539 \backslash \mathrm{H}, 0 ., 2.304762728,-1.7489187279 \backslash \mathrm{H},-2.6370538222,0 .,-1.4552889298 \backslash$ H,-1.0370019927,0.,-2.1719361853 <br>Version=Fujitsu-VP-Unix-G94RevE. $2 \backslash$ St ate $=1-\mathrm{A} \backslash \mathrm{HF}=-501.4021269 \backslash \mathrm{MP} 2=-503.09756 \backslash \mathrm{RMSD}=4.601 \mathrm{e}-09 \backslash \mathrm{RMSF}=6.986 \mathrm{e}-05 \backslash$ Dipole=0., 0.,-0.9138852 \PG=C02V [C2 (C1), SGV (C2H4), SGV'(C2H4), X(C8H8)] \} \@


## 3-6 hemipirobinonaplane (perpendicular)

$1 \backslash 1 \backslash G I N C-V P P 01 \backslash F O p t \backslash R M P 2-F C \backslash 6-31 G(d) \backslash C 14 H 16 \backslash R A S M U S S E N \backslash 14-O c t-1998 \backslash 0 \backslash \backslash \#$ P MP2/6-31G* OPT 5D GEOM=(CHECK,NODISTANCE,NOANGLE,NODIHEDRAL) GUES=CH ECK NAME=RASMUSSEN MAXDISK=1500000000<br> hemipirobinonaplane C2v $\backslash \backslash 0,1 \backslash C$ , 0., 0.,1.9128194161 \C,1.2805403131, -0.7167298894,1.2078267256\C,1.2805 403131,0.7167298894,1.2078267256\C,-1.2805403131,0.7167298894,1.207826 $7256 \backslash \mathrm{C},-1.2805403131,-0.7167298894,1.2078267256 \backslash \mathrm{H}, 1.772788136,-1.31650$ $52836,1.9723381582 \backslash \mathrm{H}, 1.772788136,1.3165052836,1.9723381582 \backslash \mathrm{H},-1.772788$ 136,1.3165052836,1.9723381582 \H,-1.772788136,-1.3165052836,1.972338158 $2 \backslash C, 1.2311286678,-1.2566985619,-0.207267392 \backslash C, 1.2311286678,1.256698561$ $9,-0.207267392 \backslash C,-1.2311286678,1.2566985619,-0.207267392 \backslash C,-1.23112866$ $78,-1.2566985619,-0.207267392 \backslash \mathrm{H}, 2.1429401075,-1.8478899213,-0.37155805$ $81 \backslash \mathrm{H}, 2.1429401075,1.8478899213,-0.3715580581 \backslash \mathrm{H},-2.1429401075,1.8478899$ 213,-0.3715580581 \H,-2.1429401075,-1.8478899213,-0.3715580581\C,0.,-2. $1406631032,-0.4079584916 \backslash \mathrm{C}, 0 ., 2.1406631032,-0.4079584916 \backslash \mathrm{C}, 1.226724368$ 3,0.,-1.1394652181 \C,-1.2267243683,0.,-1.1394652181 \H, 0.,-2.9556120982 , 0.3287524165\H, 0.,-2.6078766174,-1.3999274817\H, 2.1407514764,0.,-1.74 $54936244 \backslash \mathrm{H}, 0.2 .9556120982,0.3287524165 \backslash \mathrm{H}, 0 ., 2.6078766174,-1.399927481$ $7 \backslash \mathrm{H},-2.1407514764,0 .,-1.7454936244 \backslash \mathrm{C}, 0.0 .,-2.046362771 \backslash \mathrm{H}, 0 ., 0.8760842$ 98,-2.7064311911\H,0.,-0.876084298,-2.7064311911 <br>Version=Fujitsu-VP-U nix-G94RevE.2\State=1-A1 \HF=-539.2834904 \MP2=-541.1075704 \RMSD=3.647e$09 \backslash \mathrm{RMSF}=9.630 \mathrm{e}-05 \backslash \mathrm{Dipole=0.,0.,-0.999497} \mathrm{\backslash PG=CO2V} \mathrm{[C2(C1C1)} ,\mathrm{SGV} \mathrm{(C2H6)}$, GV' (C2H2), X(C8H8)]<br>@

## 3-24 tetramethylhemispirooctaplane

$1 \backslash 1 \backslash G I N C-V P P 02 \backslash F O p t \backslash R M P 2-F C \backslash 6-31 G(d) \backslash C 17 H 24 \backslash R A S M U S S E N \backslash 21-A u g-1999 \backslash 0 \backslash \ \#$ P MP2/6-31G* 5D OPT=NEWESTMFC NAME=RASMUSSEN GEOM= (CHECK,NODISTANCE,NO ANGLE, NODIHEDRAL) MAXDISK=1960000000<br>Hemispirooctaplane C2v $\backslash \backslash 0,1 \backslash C, 0$. , 0.,1.1622334045\C,-0.722570835,-1.302844135,0.5149843449\C,0.72257083 $5,1.302844135,0.5149843449 \backslash C, 0.722570835,-1.302844135,0.5149843449 \backslash C,-$ $0.722570835,1.302844135,0.5149843449 \backslash \mathrm{H},-2.9489330463,0 .,-0.6651691337 \backslash$ C, -1.5978637458,-1.96911915,1.5469416098\C,1.5978637458,-1.96911915,1. $5469416098 \backslash \mathrm{H},-2.3099998026,0 .,-2.30616658 \backslash \mathrm{H}, 0 ., 2.6352689217,-2.0307778$ $19 \backslash C, 1.5978637458,1.96911915,1.5469416098 \backslash C,-1.5978637458,1.96911915,1$ $.5469416098 \backslash \mathrm{H}, 0.1 .0333073125,-2.7436572828 \backslash \mathrm{C},-1.2452045102,-1.2772958$ 178,-0.9209830879\C,1.2452045102,-1.2772958178,-0.9209830879\C,1.24520 45102,1.2772958178,-0.9209830879\C,-1.2452045102,1.2772958178,-0.92098 30879 \H,-1.9553497424,-2.1104155172,-1.0244051913\H,1.9553497424,-2.11 04155172,-1.0244051913\H,1.9553497424,2.1104155172,-1.0244051913\H,-1. 9553497424,2.1104155172,-1.0244051913\C,0.,-1.5665329861,-1.7863181877 $\backslash C, 2.0157165959,0 .,-1.2472889993 \backslash C, 0.1 .5665329861,-1.7863181877 \backslash \mathrm{C},-2$. 0157165959, 0.,-1.2472889993\H, 0.,-2.6352689217,-2.030777819\H, 0., -1. 03 33073125,-2.7436572828\H,2.9489330463,0.,-0.6651691337\H,2.3099998026, $0 .,-2.30616658 \backslash$ H, $-1.1411985826,-1.906378102,2.5353318219 \backslash$ н, -1.76373818 84,-3.0219665017,1.2812130749\H,-2.5736854455,-1.4716908712,1.59255995
$52 \backslash \mathrm{H}, 2.5736854455,-1.4716908712,1.5925599552 \backslash \mathrm{H}, 1.7637381884,-3.0219665$ 017,1.2812130749 $\mathrm{H}, 1.1411985826,-1.906378102,2.5353318219 \backslash \mathrm{H},-1.1411985$ $826,1.906378102,2.5353318219 \backslash H,-2.5736854455,1.4716908712,1.5925599552$ $\backslash \mathrm{H},-1.7637381884,3.0219665017,1.2812130749 \backslash \mathrm{H}, 2.5736854455,1.4716908712$ , 1. $5925599552 \backslash \mathrm{H}, 1.1411985826,1.906378102,2.5353318219 \backslash \mathrm{H}, 1.7637381884,3$ .0219665017,1.2812130749<br>Version=Fujitsu-VP-Unix-G98RevA. $6 \backslash$ State=1-A1 $\backslash H F=-657.5536271 \backslash M P 2=-659.7948878 \backslash R M S D=9.398 e-09 \backslash R M S F=1.150 e-04 \backslash D i p o l e$ $=0 ., 0 .,-0.6586146 \backslash \mathrm{PG}=\mathrm{C0} 2 \mathrm{~V} \quad\left[\mathrm{C} 2(\mathrm{C} 1), \mathrm{SGV}(\mathrm{C} 2 \mathrm{H} 4), \mathrm{SGV}{ }^{\prime}(\mathrm{C} 2 \mathrm{H} 4), \mathrm{X}(\mathrm{C} 12 \mathrm{H} 16)\right] \backslash \backslash @$

## C.2.2.3 Protonated Species

Table C-20. Gaussian archive files for the MP2/6-31G(d) optimized protonated species in Chapter 3.

## Small Molecules

## $\mathbf{C H}_{5}{ }^{+}$

$1 \backslash 1 \backslash G I N C-P C \backslash F r e q \backslash R M P 2-F C \backslash 6-31 G(d) \backslash C 1 H 5(1+) \backslash R A S M U S S E N \backslash 24-F e b-1999 \backslash 0 \backslash \backslash \# P$ RMP2/6-31G* 5D OPT= (CALCALL, VERYTIGHT) NAME=RASMUSSEN MAXDISK=5242880 $000 \backslash \backslash$ Methonium ion $\mathrm{C} 4 \mathrm{v} \backslash \backslash 1,1 \backslash \mathrm{H}, 0 ., 0 ., 1.155555194 \backslash \mathrm{C}, 0 ., 0 ., 0.0706464369 \backslash \mathrm{H}$ , - 0.7217602653,-0.7217603967, -0.3948584538\H,0.7217602653, 0.7217603967 $,-0.3948584538 \backslash \mathrm{H}, 0.7217602653,-0.7217603967,-0.3948584538 \backslash \mathrm{H},-0.7217602$ 653, 0.7217603967,-0.3948584538<br>Version=SGI-G98RevA. $6 \backslash$ State $=1-A 1 \backslash H F=-4$ $0.3768274 \backslash M P 2=-40.5269972 \backslash R M S D=6.376 e-09 \backslash R M S F=4.819 e-07 \backslash D i p o l e=0 ., 0 .,-$ $0.5123444 \backslash$ DipoleDeriv=0.1625026, 0., 0., 0., 0.1625026, 0., 0., 0., 0.2537175, $-0.8487441,0 ., 0 ., 0 .,-0.8487442,0 ., 0 ., 0 .,-0.0902411,0.4215604,-0.046327$ $2,0.0199101,-0.0463271,0.4215604,0.0199101,0.0924426,0.0924427,0.20913$ $09,0.4215604,-0.0463272,-0.0199101,-0.0463271,0.4215604,-0.0199101,-0$. $0924426,-0.0924427,0.2091309,0.4215604,0.0463272,-0.0199101,0.0463271$, $0.4215604,0.0199101,-0.0924426,0.0924427,0.2091309,0.4215604,0.0463272$ , 0.0199101, 0.0463271, 0.4215604, -0.0199101, 0.0924426, -0.0924427, 0.20913 $09 \backslash$ Polar $=12.8246288,0 ., 12.8246317,0 ., 0 ., 11.1253127 \backslash \mathrm{PG}=\mathrm{CO} 2 \mathrm{~V} \quad$ [C2 (C1H1), X (H4) ] \NImag=2<br>0.04947601, 0., 0.04947601, 0., 0., 0.38436567, -0.05209548, 0 ., 0., 0.48821927, 0., -0.05209548, 0., 0., 0.48821935, 0., 0., -0.37239576, 0., 0 $., 0.70708355,0.00065487,0.00479607,0.00108431,-0.10903095,-0.13537151$, $-0.06189286,0.13935217,0.00479607,0.00065487,0.00108431,-0.13537148,-0$ $.10903097,-0.06189286,0.11947128,0.13935219,-0.01817002,-0.01817002,-0$ $.00299248,-0.05074396,-0.05074396,-0.08367195,0.06953134,0.06953135,0$. $07692197,0.00065487,0.00479607,-0.00108431,-0.10903095,-0.13537151,0.0$ $6189286,-0.00829085,0.01110415,0.00342887,0.13935217,0.00479607,0.0006$ 5487,-0.00108431,-0.13537148,-0.10903097,0.06189286, 0.01110415,-0.0082 $9085,0.00342887,0.11947128,0.13935219,0.01817002,0.01817002,-0.0029924$ $8,0.05074396,0.05074396,-0.08367195,-0.00342887,-0.00342887,0.00516323$ , - 0.06953134, -0.06953135,0.07692197, 0.00065487, -0.00479607, -0.00108431 , - 0. $10903095,0.13537151,0.06189286,-0.02139683,0.00958373,0.00062384,-$ $0.00128840,-0.00958374,0.00467008,0.13935216,-0.00479607,0.00065487,0$. $00108431,0.13537148,-0.10903097,-0.06189286,-0.00958373,-0.00128841,-0$ $.00467008,0.00958374,-0.02139683,-0.00062384,-0.11947127,0.13935219,0$. $01817002,-0.01817002,-0.00299248,0.05074396,-0.05074396,-0.08367195,-0$ $.00062384,-0.00467008,0.00228962,0.00467008,0.00062384,0.00228962,-0.0$ $6953134,0.06953135,0.07692197,0.00065487,-0.00479607,0.00108431,-0.109$

03095,0.13537151,-0.06189286,-0.00128840,-0.00958374,-0.00467008,-0.02 139683,0.00958373,-0.00062384,-0.00829085,-0.01110415,-0.00342887,0.13 935216,-0.00479607,0.00065487,-0.00108431,0.13537148,-0.10903097,0.061 89286,0.00958374,-0.02139683,0.00062384,-0.00958373,-0.00128841,0.0046 $7008,-0.01110415,-0.00829085,0.00342887,-0.11947127,0.13935219,-0.0181$ $7002,0.01817002,-0.00299248,-0.05074396,0.05074396,-0.08367195,-0.0046$ $7008,-0.00062384,0.00228962,0.00062384,0.00467008,0.00228962,0.0034288$ $7,-0.00342887,0.00516323,0.06953134,-0.06953135,0.07692197 \backslash \backslash 0 ., 0 .,-0.0$ $0000003,0 ., 0 .,-0.00000182,0 .,-0.00000003,0.00000046,0 ., 0.00000003,0.00$ 000046, 0., -0.00000003,0.00000046, 0., 0.00000003, 0.00000046<br>\@

## $\mathbf{N H}_{4}{ }^{+}$

$1 \backslash 1 \backslash$ GINC-RSCQC8 \Freq $\backslash$ RMP2-FC $\backslash 6$-31G (d) \H4N1 (1+) \RASMUSSEN $\backslash 24-F e b-1999 \backslash 0$ <br>\#P RMP2/6-31G* 5D OPT=(CALCALL,VERYTIGHT) NAME=RASMUSSEN MAXDISK=104 $8576000 \backslash \backslash$ Ammonium ion $\mathrm{Td} \backslash \backslash 1,1 \backslash \mathrm{~N}, 0 ., 0.0 . \backslash \mathrm{H}, 0 ., 0 ., 1.0291806106 \backslash \mathrm{H}, 0.9703$ $207851,0 .,-0.3430602035 \backslash \mathrm{H},-0.4851603925,0.8403224497,-0.3430602035 \backslash \mathrm{H},-$ $0.4851603925,-0.8403224497,-0.3430602035 \backslash \backslash$ Version=IBM-RS6000-G94RevE.1 $\backslash H F=-56.5288351 \backslash M P 2=-56.6978168 \backslash R M S D=4.040 e-09 \backslash R M S F=2.674 e-08 \backslash$ Dipole=0 ., 0., 0. \DipoleDeriv=-0.371721,0.,0.,0.,-0.371721,0., 0., 0., -0.371721,0. $3089095,0.0 ., 0 ., 0.3089095,0.0 ., 0 ., 0.4109717,0.3996315,0 .,-0.0320751$, $0 ., 0.3089095,0 .,-0.0320751,0 ., 0.3202498,0.33159,-0.0392838,0.0160375,-$ $0.0392838,0.376951,-0.0277778,0.0160375,-0.0277778,0.3202498,0.33159,0$ $.0392838,0.0160375,0.0392838,0.376951,0.0277778,0.0160375,0.0277778,0$. $3202498 \backslash$ Polar $=7.0538703,0 ., 7.0538703,0 ., 0 ., 7.0538703 \backslash \mathrm{PG}=T \mathrm{D}$ [O(N1),4C3( H1) ] \NImag=0 <br>0.73631658,0.,0.73631658,0.,0.,0.73631658,-0.06813465,0. , 0., 0.05942077,0.,-0.06813465,0.,0.,0.05942077,0., 0.,-0.41596815,0., 0. , 0.43583577,-0.37731998,0.,0.10931352,0.00672323,0.,-0.00221543,0.3940 1188,0.,-0.06813465,0.,0.,-0.00091398,0.,0.,0.05942077,0.10931352,0.,$0.10678281,0.03996297,0 .,-0.00662254,-0.11829582,0 ., 0.10124466,-0.1454$ 3098,0.13388118,-0.05465676,0.00099532,-0.00330701,0.00110771,-0.01170 757,0.03152729,-0.01549033,0.14306855,0.13388118,-0.30002365,0.0946682 9,-0.00330701,0.00481393,-0.00191862,-0.00291122,0.00481393,-0.0024783 $4,-0.14488220,0.31036410,-0.05465676,0.09466829,-0.10678281,-0.0199814$ 8,0.03460894,-0.00662254,0.00559886,-0.01465419,0.00608035,0.05914791, $-0.10244719,0.10124466,-0.14543098,-0.13388118,-0.05465676,0.00099532$, 0.00330701,0.00110771,-0.01170757,-0.03152729,-0.01549033,0.01307467,0 $.01721926,0.00989147,0.14306855,-0.13388118,-0.30002365,-0.09466829,0$. $00330701,0.00481393,0.00191862,0.00291122,0.00481393,0.00247834,-0.017$ 21926,-0.01996831,-0.01217585,0.14488220,0.31036410,-0.05465676,-0.094 66829,-0.10678281,-0.01998148,-0.03460894,-0.00662254,0.00559886,0.014 65419,0.00608035,0.00989147,0.01217585,0.00608035,0.05914791,0.1024471 $9,0.10124466 \backslash \backslash 0 ., 0 ., 0 ., 0 ., 0 .,-0.00000005,-0.00000005,0 ., 0.00000002,0.0$ 0000002,-0.00000004,0.00000002,0.00000002,0.00000004,0.00000002<br>\@

## $\mathrm{H}_{3} \mathrm{O}^{+}$

$1 \backslash 1 \backslash$ GINC-PC $\backslash$ Freq $\backslash$ RMP2-FC $\backslash 6$-31G (d) \H3O1 (1+) \RASMUSSEN $\backslash 24-F e b-1999 \backslash 0 \backslash \ \# P$ MP2/6-31G* 5D NAME=RASMUSSEN OPT=(CALCALL,VERYTIGHT) MAXDISK=52428800 $00 \backslash \backslash$ hydronium ion $\mathrm{C} 3 \mathrm{~V} \backslash \backslash 1,1 \backslash \mathrm{H}, 0.0 .2167009288,0.9462139218 \backslash \mathrm{H}, 0.81944529$ 37,0.2167009288,-0.4731069609\H,-0.8194452937,0.2167009288,-0.47310696 $09 \backslash 0,0 .,-0.0812628483,0 . \backslash \backslash$ Version=SGI-G98RevA. $6 \backslash$ State $=1-A 1 \backslash H F=-76.2858$ $268 \backslash M P 2=-76.4717195 \backslash R M S D=5.354 e-09 \backslash R M S F=2.925 e-09 \backslash \operatorname{Dipole=0.,0.7028654\text {,},~}$ $0 . \backslash$ DipoleDeriv=0.3885066,0.,0.,0.,0.4710783,0.000914,0.,0.0168325,0.62
$83966,0.5684241,0.0145774,-0.1038754,0.0007915,0.4710783,-0.000457,-0$. $1038754,-0.0084163,0.4484791,0.5684241,-0.0145774,0.1038754,-0.0007915$ , 0.4710783,-0.000457, 0.1038754, -0.0084163, 0.4484791, -0.5253548, 0., 0., 0 ., - 0. $4132349,0 ., 0 ., 0 .,-0.5253548 \backslash \operatorname{Pol} a r=5.3980696,0 ., 3.0078704,0 ., 0 ., 5$. $3980696 \backslash \mathrm{PG}=\mathrm{CO} 3 \mathrm{~V}$ [C3(O1), 3SGV(H1)]\NImag=0<br>0.06549709,0.,0.05138116,0. , 0.11988404, 0.42413630, 0.00856702, 0.00133770, -0.00002201, 0.33447650, 0. $01502302,0.00319072,-0.00712890,0.10382263,0.05138116,0.03286859,0.016$ $57477,-0.01039697,-0.15529533,-0.05994202,0.15515689,0.00856702,-0.001$ $33770,0.00002201,-0.01987896,0.01368532,-0.01644530,0.33447650,-0.0150$ $2302,0.00319072,-0.00712890,-0.01368532,0.00319072,-0.00944586,-0.1038$ $2262,0.05138116,-0.03286859,0.01657477,-0.01039697,0.01644530,-0.00944$ $586,0.01804901,0.15529533,-0.05994202,0.15515689,-0.08263113,0 ., 0 .,-0$. $32316456,-0.13253097,0.13887204,-0.32316456,0.13253097,-0.13887204,0.7$ $2896025,0 .,-0.05776261,-0.10562623,-0.09147500,-0.05776261,0.05281312$, $0.09147500,-0.05776261,0.05281312,0 ., 0.17328782,0 .,-0.15303358,-0.4033$ $4237,0.13887204,0.07651679,-0.16280894,-0.13887204,0.07651679,-0.16280$ 894,0., 0., 0.72896025<br>0.,0.,0.,0.,0., 0., 0., 0., 0., 0., 0., 0. <br>\@

## Small Strained Hydrocarbons

## 3-15- $\mathbf{H}^{+} \quad$ protonated pyramidane

$1 \backslash 1 \backslash G I N C-P C \backslash F O p t \backslash R M P 2-F C \backslash 6-31 G(d) \backslash C 5 H 5(1+) \backslash R A S M U S S E N \backslash 17-F e b-1999 \backslash 0 \backslash \backslash \# P$ MP2/6-31G* 5D SCF=DIRECT NAME=RASMUSSEN FOPT=NEWESTMFC GEOM= (NODISTAN CE, NOANGLE, NODIHEDRAL) MAXDISK=1000000000<br>protonated pyramidane ([3.3 .3.3]fenestraneH+) C4v 5D<br>1,1\C,0.,0.,0.8899421624\H,0.,0.,1.97060599 $39 \backslash C, 0 .,-1.0364536682,-0.2835276382 \backslash C, 1.0364536682,0 .,-0.2835276382 \backslash C$, $0 ., 1.0364536682,-0.2835276382 \backslash \mathrm{C},-1.0364536682,0 .,-0.2835276382 \backslash \mathrm{H}, 0 .,-2$ $.1081685675,-0.1263989125 \backslash \mathrm{H}, 2.1081685675,0 .,-0.1263989125 \backslash \mathrm{H}, 0 ., 2.10816$ 85675,-0.1263989125\H,-2.1081685675,0.,-0.1263989125<br>Version=SGI-G98R evA. $6 \backslash$ State $=1-A 1 \backslash H F=-191.8629009 \backslash M P 2=-192.4823114 \backslash$ RMSD $=4.601 e-09 \backslash \mathrm{RMSF}=$ $3.743 e-05 \backslash$ Dipole=0.,0.,0.6205771 \PG=C04V [C4 (C1H1), 2SGV (C2H2)] <br>@

## Other Alicyclic Hydrocarbons

## 3-21-H ${ }^{+}$

$1 \backslash 1 \backslash G I N C-P C \backslash F O p t \backslash R M P 2-F C \backslash 6-31 G(d) \backslash C 7 H 9(1+) \backslash R A S M U S S E N \backslash 24-N O V-1999 \backslash 0 \backslash \backslash \# P$ MP2/6-31G(D) 5D OPT FREQ=NORAMAN NAME=RASMUSSEN SYMM=LOOSE $\backslash \backslash$ hexadiene bound CH+ C2 <br>1,1\H,0.0014792489,-1.2020789748,-1.8134192731\C,1.0540 $084122,-0.7206674473,0.1009063155 \backslash C,-1.0522477668,-0.7232586402,0.1008$ $959501 \backslash \mathrm{C},-0.001741341,1.4174627941,-0.7429497587 \backslash \mathrm{C},-1.0540084122,0.720$ $6674473,0.1009063155 \backslash C, 1.0522477668,0.7232586402,0.1008959501 \backslash C, 0.0017$ $41341,-1.4174627941,-0.7429497587 \backslash \mathrm{H},-1.8421905331,-1.2591803923,0.6211$ $593944 \backslash \mathrm{H},-0.0014792489,1.2020789748,-1.8134192731 \backslash \mathrm{C}, 0 ., 0 ., 1.1019588766$ $\backslash \mathrm{H},-1.8452688375,1.2546591264,0.6211517576 \backslash \mathrm{H}, 0.0030674733,-2.495467100$ $5,-0.5800644144 \backslash \mathrm{H}, 1.8452688375,-1.2546591264,0.6211517576 \backslash \mathrm{H}, 1.84219053$ $31,1.2591803923,0.6211593944 \backslash \mathrm{H},-0.0030674733,2.4954671005,-0.580064414$ $4 \backslash H, 0 ., 0 ., 2.1843617292 \backslash \backslash V e r s i o n=S G I-G 98 R e v A .6 \backslash$ State $=1-A \backslash H F=-269.970372$ $4 \backslash M P 2=-270.8570331 \backslash R M S D=2.649 e-09 \backslash R M S F=6.376 e-05 \backslash D i p o l e=0 ., 0 ., 0.530837$ $1 \backslash \mathrm{PG}=\mathrm{C} 02 \quad[\mathrm{C} 2(\mathrm{C} 1 \mathrm{H} 1), \mathrm{X}(\mathrm{C} 6 \mathrm{H} 8)] \backslash \backslash @$

## 3-22-H ${ }^{+}$

$1 \backslash 1 \backslash G I N C-P C \backslash F O p t \backslash R M P 2-F C \backslash 6-31 G(d) \backslash C 8 H 9(1+) \backslash R A S M U S S E N \backslash 24-N O V-1999 \backslash 0 \backslash \backslash \# P$

MP2/6-31G(D) 5D OPT FREQ=NORAMAN NAME=RASMUSSEN SYMM=LOOSE<br>bicyclohe ptane bound $C H+C 2 v \backslash \backslash 1,1 \backslash H, 2.1791728762,0 .,-0.965561775 \backslash \mathrm{C}, 0.7204233115$ $,-1.0608724593,0.3970652179 \backslash \mathrm{C}, 0.7204233115,1.0608724593,0.3970652179 \backslash \mathrm{C}$ , - 1. $1447217741,0 .,-0.6278436786 \backslash C,-0.7204233115,1.0608724593,0.3970652$ $179 \backslash \mathrm{C},-0.7204233115,-1.0608724593,0.3970652179 \backslash \mathrm{C}, 1.1447217741,0 .,-0.62$ $78436786 \backslash \mathrm{C}, 0 ., 0 ., 1.3847904051 \backslash \mathrm{H},-2.1791728762,0 .,-0.965561775 \backslash \mathrm{H}, 1.3559$ $426885,1.7799365188,0.9045158896 \backslash \mathrm{H},-1.3559426885,1.7799365188,0.904515$ $8896 \backslash \mathrm{H}, 0 ., 0.8957314225,-2.2794306961 \backslash \mathrm{H}, 1.3559426885,-1.7799365188,0.90$ $45158896 \backslash \mathrm{H},-1.3559426885,-1.7799365188,0.9045158896 \backslash \mathrm{C}, 0 ., 0 .,-1.6499608$ $521 \backslash \mathrm{H}, 0 ., 0 ., 2.4675029802 \backslash \mathrm{H}, 0 .,-0.8957314225,-2.2794306961 \backslash \backslash \mathrm{Version=SGI}$ -G98RevA. $6 \backslash$ State=1-A1 \HF=-307.8314485\MP2=-308.8457593 \RMSD=8.521e-09 \} RMSF = 8.588e-05 \Dipole=0., 0., 0.7759493\PG=C02V [C2 (H1C1C1), SGV (C2H2), SG V' (H2) , X (C4H4)] <br>@

## 3-23-H ${ }^{+}$

$1 \backslash 1 \backslash G I N C-P C \backslash F O p t \backslash R M P 2-F C \backslash 6-31 G(d) \backslash C 9 H 11(1+) \backslash R A S M U S S E N \backslash 25-N o v-1999 \backslash 0 \backslash \backslash \#$ P MP2/6-31G(D) 5D OPT=TIGHT FREQ=NORAMAN NAME=RASMUSSEN SYMM=LOOSE<br>bi cyclo[2.2.2]octadiene...CH+ C2<br>1, 1\H,2.4065188274,0.1866031888, -0.27 $44124375 \backslash \mathrm{C}, 0.8121347892,-0.9997660701,0.6272751284 \backslash \mathrm{C}, 0.6514035713,1.10$ $0480479,0.6459180851 \backslash C,-1.3288945608,-0.0995349999,-0.2434602381 \backslash C,-0$. $786984274,0.9901246703,0.6729621736 \backslash \mathrm{C},-0.6262545884,-1.1101212914,0.65$ $42400011 \backslash \mathrm{C}, 1.3185146376,0.1035141227,-0.2931634941 \backslash \mathrm{H},-1.4010045673,1.7$ $136176412,1.2035685815 \backslash \mathrm{H},-2.415383673,-0.1832048679,-0.1838844511 \backslash \mathrm{H}, 1$. $1672873626,1.9106504254,1.1553227638 \backslash H, 0.0527850955,-0.0202350609,2.72$ $88963915 \backslash \mathrm{H}, 1.0522322949,0.9800869474,-2.2323527937 \backslash \mathrm{H}, 1.446006607,-1.73$ $08690832,1.1229575492 \backslash \mathrm{H},-1.1222864178,-1.9279014476,1.1711467577 \backslash \mathrm{C}, 0.7$ $40053402,0.0717625802,-1.7074292698 \backslash C, 0.0318570436,-0.012212334,1.6469$ $530012 \backslash \mathrm{H}, 1.1859787027,-0.7692383194,-2.2477326711 \backslash \mathrm{C},-0.8055457718$, - 0.0 $466562111,-1.6784108033 \backslash \mathrm{H},-1.138050112,-0.9471888587$, - $2.2042770767 \backslash \mathrm{H}$, -$1.2717896127,0.8021337603,-2.1885401179 \backslash \backslash V e r s i o n=S G I-G 98 R e v A .6 \backslash S t a t e=1$ $-\mathrm{A} \backslash \mathrm{HF}=-346.8846141 \backslash \mathrm{MP} 2=-348.0279653 \backslash \mathrm{RMSD}=3.143 \mathrm{e}-09 \backslash \mathrm{RMSF}=2.936 \mathrm{e}-06 \backslash \mathrm{Dipo}$ le=0.0212888,-0.008161,1.1005925\PG=C02 [C2 (C1H1), X(C8H10)] <br>@

## Hemialkaplanes

## 3-1-H $\mathbf{H}^{+} \quad$ protonated hemioctaplane

$1 \backslash 1 \backslash G I N C-V P P 11 \backslash F O p t \backslash R M P 2-F C \backslash 6-31 G(d) \backslash C 13 H 21(1+) \backslash R A S M U S S E N \backslash 15-O c t-1998 \backslash$ $0 \backslash \$ \# MP2/6-31G* 5D OPT GEOM = (CHECK, NODISTANCE, NOANGLE,NODIHEDRAL) GUE $S S=C H E C K$ NAME=RASMUSSEN MAXDISK=1500000000<br>protonated hemioctaplane C $4 \mathrm{v} \backslash \backslash 1,1 \backslash \mathrm{C}, 0.1 .0670174786,1.6715319862 \backslash \mathrm{C}, 1.6715319862,1.0670174786,0 . \backslash$ C, 0., 1.0670174786, -1. $6715319862 \backslash C,-1.6715319862,1.0670174786,0 . \backslash C, 0 ., 1$ $.5193085487,0 . \backslash \mathrm{H}, 0 ., 2.6126269024,0 . \backslash \mathrm{H},-0.8742885458,1.5366369297,2.119$ $3946267 \backslash \mathrm{H}, 0.8742885458,1.5366369297,2.1193946267 \backslash \mathrm{H}, 2.1193946267,1.5366$ $369297,0.8742885458 \backslash \mathrm{H}, 2.1193946267,1.5366369297,-0.8742885458 \backslash \mathrm{H}, 0.8742$ $885458,1.5366369297,-2.1193946267 \backslash \mathrm{H},-0.8742885458,1.5366369297,-2.1193$ $946267 \backslash \mathrm{H},-2.1193946267,1.5366369297,-0.8742885458 \backslash \mathrm{H},-2.1193946267,1.53$ $66369297,0.8742885458 \backslash C, 0 .,-0.4340727046,1.8305011866 \backslash C,-1.8305011866$, $-0.4340727046,0 . \backslash \mathrm{C}, 0 .,-0.4340727046,-1.8305011866 \backslash \mathrm{C}, 1.8305011866,-0.43$ $40727046,0 . \backslash H, 0 .,-0.5990397573,2.9191375339 \backslash \mathrm{H},-2.9191375339,-0.5990397$ $573,0 . \backslash H, 0 .,-0.5990397573,-2.9191375339 \backslash \mathrm{H}, 2.9191375339,-0.5990397573,0$ $. \backslash C,-1.3111684581,-1.0370166978,-1.3111684581 \backslash \mathrm{C}, 1.3111684581,-1.037016$ 6978 ,-1.3111684581 \C,1.3111684581,-1.0370166978,1.3111684581\C,-1.3111
$684581,-1.0370166978,1.3111684581 \backslash \mathrm{H},-2.0765161585,-0.8563010141,-2.076$ $5161585 \backslash \mathrm{H},-1.2200742151,-2.1256210939,-1.2200742151 \backslash \mathrm{H}, 2.0765161585,-0$. $8563010141,-2.0765161585 \backslash \mathrm{H}, 1.2200742151,-2.1256210939,-1.2200742151 \backslash \mathrm{H}$, $2.0765161585,-0.8563010141,2.0765161585 \backslash \mathrm{H}, 1.2200742151,-2.1256210939,1$ $.2200742151 \backslash \mathrm{H},-2.0765161585,-0.8563010141,2.0765161585 \backslash \mathrm{H},-1.2200742151$ , - 2. 1256210939, 1.2200742151 <br>Version=Fujitsu-VP-Unix-G94RevE. $2 \backslash$ State=1 $-\mathrm{A} 1 \backslash \mathrm{HF}=-504.123577 \backslash \mathrm{MP} 2=-505.8312409 \backslash \mathrm{RMSD}=6.441 \mathrm{e}-09 \backslash \mathrm{RMSF}=5.112 \mathrm{e}-05 \backslash \mathrm{Dipo}$ le=0., 0.9534068,0. \PG=C04V [C4 (C1H1), 2SGV (C4H2), 2SGD (C2H4) , X (H8) ] <br>@

## Hemispiroalkaplanes

## 3-4- $\mathbf{H}^{+} \quad$ protonated hemispirobioctaplane (perpendicular)

$1 \backslash 1 \backslash G I N C-V P P 04 \backslash F O p t \backslash R M P 2-F C \backslash 6-31 G(d) \backslash C 13 H 15(1+) \backslash R A S M U S S E N \backslash 11-D e c-1998 \backslash$ $0 \backslash \$ \#P MP2/6-31G* 5D OPT GUESS=CHECK GEOM= (CHECK, NODISTANCE, NOANGLE,NOD IHEDRAL) NAME=RASMUSSEN MAXDISK=1500000000<br>protonated hemispirobiocta plane $\mathrm{C} 2 \mathrm{v} \backslash \backslash 1,1 \backslash \mathrm{C}, 0 ., 0 ., 1.5705407946 \backslash \mathrm{C},-1.3224842426,-0.7199045189,0.97$ $37919491 \backslash C, 1.3224842426,0.7199045189,0.9737919491 \backslash C, 1.3224842426,-0.71$ $99045189,0.9737919491 \backslash \mathrm{C},-1.3224842426,0.7199045189,0.9737919491 \backslash \mathrm{H}, 1.19$ $54441354,0 .,-2.2585690818 \backslash \mathrm{H},-1.781555674,-1.3154178359,1.7615000098 \backslash \mathrm{H}$, $1.781555674,-1.3154178359,1.7615000098 \backslash H,-1.1954441354,0 .,-2.258569081$ $8 \backslash \mathrm{H}, 0 ., 3.0242482827,0.1702057991 \backslash \mathrm{H}, 1.781555674,1.3154178359,1.76150000$ $98 \backslash \mathrm{H},-1.781555674,1.3154178359,1.7615000098 \backslash \mathrm{H}, 0 ., 2.6773738046,-1.56745$ $86658 \backslash C,-1.1796530558,-1.2539879406,-0.4334116508 \backslash C, 1.1796530558,-1.25$ $39879406,-0.4334116508 \backslash C, 1.1796530558,1.2539879406,-0.4334116508 \backslash C,-1$. $1796530558,1.2539879406,-0.4334116508 \backslash \mathrm{H},-2.141582723,-1.6868315599,-0$. $7331785977 \backslash \mathrm{H}, 2.141582723,-1.6868315599,-0.7331785977 \backslash \mathrm{H}, 2.141582723,1.6$ 868315599,-0.7331785977 \H, -2.141582723,1.6868315599, -0.7331785977\C, 0. $,-2.2186896266,-0.5732280184 \backslash C, 0.7789642374,0 .,-1.247548223 \backslash C, 0 ., 2.218$ $6896266,-0.5732280184 \backslash \mathrm{C},-0.7789642374,0 .,-1.247548223 \backslash \mathrm{H}, 0 .,-3.02424828$ $27,0.1702057991 \backslash \mathrm{H}, 0 .,-2.6773738046,-1.5674586658 \backslash \mathrm{H}, 0 ., 0 ., 2.6553012183 \backslash$ \Version=Fujitsu-VP-Unix-G94RevE. $2 \backslash$ State=1-A1 \HF=-500.7538795\MP2=-502 $.4235433 \backslash \mathrm{RMSD}=5.664 \mathrm{e}-09 \backslash \mathrm{RMSF}=5.340 \mathrm{e}-05 \backslash \mathrm{Dipole=0} ., 0 ., 0.9689349 \backslash \mathrm{PG}=\mathrm{C} 02 \mathrm{~V}$ [C2 (C1H1) , SGV (C2H4) , SGV' (C2H2) , X (C8H8) ] <br>@

## 3-5- $\mathrm{H}^{+} \quad$ protonated hemispirooctaplane

$1 \backslash 1 \backslash G I N C-V P P 05 \backslash F O p t \backslash R M P 2-F C \backslash 6-31 G(d) \backslash C 13 H 17(1+) \backslash R A S M U S S E N \backslash 15-O c t-1998 \backslash$ $0 \backslash \ \#$ MP2/6-31G* 5D OPT GEOM = (CHECK, NODISTANCE,NOANGLE, NODIHEDRAL) NAM E=RASMUSSEN MAXDISK=1500000000<br>protonated hemispirooctaplane C2v<br>1,1 $\backslash C, 0 ., 0 ., 1.6169553292 \backslash C, 1.3265300889,-0.7202729449,1.0470931181 \backslash C, 1.32$ $65300889,0.7202729449,1.0470931181 \backslash C,-1.3265300889,0.7202729449,1.0470$ $931181 \backslash \mathrm{C},-1.3265300889,-0.7202729449,1.0470931181 \backslash \mathrm{H}, 0 ., 0 ., 2.7021979838$ $\backslash \mathrm{H}, 1.7552757475,-1.3147613526,1.8520205775 \backslash \mathrm{H}, 1.7552757475,1.3147613526$ , 1. $8520205775 \backslash \mathrm{H},-1.7552757475,1.3147613526,1.8520205775 \backslash \mathrm{H},-1.755275747$ $5,-1.3147613526,1.8520205775 \backslash C, 1.2830653561,-1.2526708826,-0.374369566$ $3 \backslash C, 1.2830653561,1.2526708826,-0.3743695663 \backslash C,-1.2830653561,1.25267088$ $26,-0.3743695663 \backslash \mathrm{C},-1.2830653561,-1.2526708826,-0.3743695663 \backslash \mathrm{H}, 2.11477$ $33822,-1.9624056236,-0.463185833 \backslash \mathrm{H}, 2.1147733822,1.9624056236,-0.463185$ $833 \backslash \mathrm{H},-2.1147733822,1.9624056236,-0.463185833 \backslash \mathrm{H},-2.1147733822,-1.96240$ $56236,-0.463185833 \backslash \mathrm{C}, 0 .,-2.0262959646,-0.6833862646 \backslash \mathrm{C}, 0 ., 2.0262959646$, $-0.6833862646 \backslash \mathrm{C}, 1.5750676278,0 .,-1.2401197246 \backslash \mathrm{C},-1.5750676278,0 .,-1.24$ $01197246 \backslash \mathrm{H}, 0 .,-2.9524275904,-0.0937507578 \backslash \mathrm{H}, 0 .,-2.3280525015,-1.736965$ $0686 \backslash \mathrm{H}, 2.6406787906,0 .,-1.4901859478 \backslash \mathrm{H}, 1.0367838213,0 .,-2.1903793804 \backslash \mathrm{H}$
, 0., 2. $9524275904,-0.0937507578 \backslash \mathrm{H}, 0 ., 2.3280525015,-1.7369650686 \backslash \mathrm{H},-2.64$ $06787906,0 .,-1.4901859478 \backslash \mathrm{H},-1.0367838213,0 .,-2.1903793804 \backslash \backslash V e r s i o n=F u$ jitsu-VP-Unix-G94RevE. $2 \backslash$ State=1-A1 \HF=-501.8974491 \MP2=-503.5719663\RM $S D=8.707 e-09 \backslash \mathrm{RMSF}=2.527 \mathrm{e}-05 \backslash \mathrm{Dipole}=0 ., 0 ., 1.0885024 \backslash \mathrm{PG}=\mathrm{C} 02 \mathrm{~V} \quad[\mathrm{C} 2(\mathrm{C} 1 \mathrm{H} 1), \mathrm{S}$ GV (C2H4) , SGV' (C2H4) , X (C8H8) ] <br>@

## 3-6-H $\mathbf{H}^{+} \quad$ protonated hemispirobinonaplane (perpendicular)

$1 \backslash 1 \backslash G I N C-V P P 11 \backslash F O p t \backslash R M P 2-F C \backslash 6-31 G(d) \backslash C 14 H 17(1+) \backslash R A S M U S S E N \backslash 14-O c t-1998 \backslash$ $0 \backslash \ \# P$ MP2/6-31G* 5D OPT GEOM= (CHECK,NODISTANCE,NOANGLE,NODIHEDRAL) GUE $S S=C H E C K$ NAME=RASMUSSEN MAXDISK=1500000000<br>protonated hemispirobinona plane $C 2 v \backslash \backslash 1,1 \backslash C, 0 ., 0 ., 1.7570873945 \backslash C, 1.3274751966,-0.7182971532,1.176$ $2656426 \backslash C, 1.3274751966,0.7182971532,1.1762656426 \backslash C,-1.3274751966,0.718$ $2971532,1.1762656426 \backslash \mathrm{C},-1.3274751966,-0.7182971532,1.1762656426 \backslash \mathrm{H}, 0 ., 0$ ., 2. $8421833063 \backslash \mathrm{H}, 1.7688240854,-1.313707129,1.9740726198 \backslash \mathrm{H}, 1.7688240854$ , 1. 313707129 , 1. $9740726198 \backslash \mathrm{H},-1.7688240854,1.313707129,1.9740726198 \backslash \mathrm{H}$, -$1.7688240854,-1.313707129,1.9740726198 \backslash C, 1.2377697304,-1.2609901822,-0$ $.2316206102 \backslash C, 1.2377697304,1.2609901822,-0.2316206102 \backslash C,-1.2377697304$, $1.2609901822,-0.2316206102 \backslash \mathrm{C},-1.2377697304,-1.2609901822,-0.2316206102$ $\backslash \mathrm{H}, 2.1436715661,-1.8579401576,-0.3956975638 \backslash \mathrm{H}, 2.1436715661,1.857940157$ $6,-0.3956975638 \backslash \mathrm{H},-2.1436715661,1.8579401576,-0.3956975638 \backslash \mathrm{H},-2.143671$ 5661,-1.8579401576,-0.3956975638\C, 0.,-2.1421448326, -0.4092756081\C, 0. , $2.1421448326,-0.4092756081 \backslash \mathrm{C}, 1.2311051819,0 .,-1.1624971488 \backslash \mathrm{C},-1.23110$ 51819, 0., -1.1624971488\H, 0.,-2.9566690069, 0.3263781092 \H, 0., -2. 6133494 503, -1. $3966757878 \backslash \mathrm{H}, 2.1423028705,0 .,-1.7695780771 \backslash \mathrm{H}, 0 ., 2.9566690069$, 0. $3263781092 \backslash \mathrm{H}, 0 ., 2.6133494503,-1.3966757878 \backslash \mathrm{H},-2.1423028705,0 .,-1.76957$ $80771 \backslash \mathrm{C}, 0 ., 0 .,-2.063315873 \backslash \mathrm{H}, 0 ., 0.8733549863,-2.7243844209 \backslash \mathrm{H}, 0 .,-0.873$ 3549863 ,-2.7243844209<br>Version=Fujitsu-VP-Unix-G94RevE.2\State=1-A1 \HF $=-539.7802565 \backslash M P 2=-541.5832663 \backslash R M S D=7.624 e-09 \backslash R M S F=2.152 e-05 \backslash D i p o l e=0$. , 0., 1. $2054292 \backslash \mathrm{PG}=\mathrm{CO} 2 \mathrm{~V}$ [C2 (H1C1C1), SGV (C2H6) , SGV' (C2H2) , X (C8H8) ] <br>@

## 3-24- $\mathbf{H}^{+} \quad$ protonated tetramethylhemispirooctaplane

$1 \backslash 1 \backslash G I N C-V P P 02 \backslash F O p t \backslash R M P 2-F C \backslash 6-31 G(d) \backslash C 17 H 25(1+) \backslash R A S M U S S E N \backslash 22-A u g-1999 \backslash$ $0 \backslash \ \#$ MP2/6-31G* 5D OPT=NEWESTMFC NAME=RASMUSSEN GEOM = (CHECK, NODISTANC E, NOANGLE, NODIHEDRAL) MAXDISK=1960000000<br>Protonated Tetramethylhemisp irooctaplane $\mathrm{C} 2 \mathrm{v} \backslash \backslash 1,1 \backslash \mathrm{H}, 0 ., 0 ., 2.1088678613 \backslash \mathrm{C}, 0 ., 0 ., 1.0221973507 \backslash \mathrm{C},-0.7$ $257389472,-1.347733367,0.4928059208 \backslash C, 0.7257389472,1.347733367,0.49280$ $59208 \backslash \mathrm{C}, 0.7257389472,-1.347733367,0.4928059208 \backslash \mathrm{C},-0.7257389472,1.34773$ $3367,0.4928059208 \backslash \mathrm{H},-2.9429579271,0 .,-0.6462127853 \backslash \mathrm{C},-1.6039823944,-1$. $9723530078,1.5463773725 \backslash \mathrm{C}, 1.6039823944,-1.9723530078,1.5463773725 \backslash \mathrm{H},-2$ $.3305446584,0 .,-2.2912907311 \backslash \mathrm{H}, 0 ., 2.6372542565,-2.061486401 \backslash \mathrm{C}, 1.603982$ $3944,1.9723530078,1.5463773725 \backslash C,-1.6039823944,1.9723530078,1.54637737$ $25 \backslash \mathrm{H}, 0.1 .032427726,-2.7585551834 \backslash \mathrm{C},-1.2458862013,-1.2842847868,-0.939$ $8269047 \backslash C, 1.2458862013,-1.2842847868,-0.9398269047 \backslash C, 1.2458862013,1.28$ $42847868,-0.9398269047 \backslash \mathrm{C},-1.2458862013,1.2842847868,-0.9398269047 \backslash \mathrm{H},-1$ $.9590681107,-2.1125347399,-1.0428101876 \backslash H, 1.9590681107,-2.1125347399$, $1.0428101876 \backslash \mathrm{H}, 1.9590681107,2.1125347399,-1.0428101876 \backslash \mathrm{H},-1.9590681107$ , 2.1125347399 , - $1.0428101876 \backslash \mathrm{C}, 0 .,-1.5718068762,-1.808396592 \backslash \mathrm{C}, 2.018367$ $6726,0 .,-1.2400293533 \backslash C, 0 ., 1.5718068762,-1.808396592 \backslash C,-2.0183676726,0$ ., -1. $2400293533 \backslash \mathrm{H}, 0 .,-2.6372542565,-2.061486401 \backslash \mathrm{H}, 0 .,-1.032427726,-2.7$ $585551834 \backslash \mathrm{H}, 2.9429579271,0 .,-0.6462127853 \backslash \mathrm{H}, 2.3305446584,0 .,-2.2912907$ $311 \backslash \mathrm{H},-1.1572417727,-1.9366338652,2.5428865891 \backslash \mathrm{H},-1.7713601329,-3.0230$ $124763,1.2848933689 \backslash \mathrm{H},-2.5769562714,-1.4728316455,1.5824292927 \backslash \mathrm{H}, 2.576$

9562714, -1.4728316455, 1.5824292927\H,1.7713601329,-3.0230124763,1.2848 $933689 \backslash \mathrm{H}, 1.1572417727,-1.9366338652,2.5428865891 \backslash \mathrm{H},-1.1572417727,1.936$ $6338652,2.5428865891 \backslash \mathrm{H},-2.5769562714,1.4728316455,1.5824292927 \backslash \mathrm{H},-1.77$ $13601329,3.0230124763,1.2848933689 \backslash \mathrm{H}, 2.5769562714,1.4728316455,1.58242$ $92927 \backslash \mathrm{H}, 1.1572417727,1.9366338652,2.5428865891 \backslash \mathrm{H}, 1.7713601329,3.023012$ 4763, 1.2848933689<br>Version=Fujitsu-VP-Unix-G98RevA. $6 \backslash$ State $=1-A 1 \backslash H F=-65$ $8.0559807 \backslash M P 2=-660.2751644 \backslash R M S D=2.464 e-09 \backslash R M S F=2.783 e-05 \backslash D i p o l e=0 ., 0 .$, $0.5898319 \backslash \mathrm{PG}=\mathrm{C0} 0 \mathrm{~V} \quad\left[\mathrm{C} 2(\mathrm{C} 1 \mathrm{H} 1), \mathrm{SGV}(\mathrm{C} 2 \mathrm{H} 4), \mathrm{SGV}{ }^{\prime}(\mathrm{C} 2 \mathrm{H} 4), \mathrm{X}(\mathrm{C} 12 \mathrm{H} 16)\right] \backslash \backslash @$

## C.2.2.4 Bond Dissociation Geometries

Table C-21. Gaussian archive files for the [8/8]CASSCF/6-31G(d) optimized geometries in the $\mathrm{C}^{0}-\mathrm{C}^{\alpha}$ bond dissociation of hemispirooctaplane (3-5).

## equilibrium <br> $C_{2 v}$

$1 \backslash 1 \backslash G I N C-P A L O \backslash F O p t \backslash C A S S C F \backslash 6-31 G(d) \backslash C 13 H 16 \backslash R A S M U S S E N \backslash 27-S e p-1999 \backslash 0 \backslash \ \# P$ CAS $(8,8) / 6-31 G(D)$ 5D OPT NAME=RASMUSSEN GEOM= (CHECK,NODISTANCE,NOANGLE , NODIHEDRAL) GUESS=(CHECK) <br>hemispirooctaplane C2v <br>0,1\C,0.,0.,1.8604 996298\C,-0.7097160706,-1.3250919308,1.0702054262\C,0.7097160706,1.325 0919308,1.0702054262\C,0.7097160706,-1.3250919308,1.0702054262\C,-0.70 97160706,1.3250919308,1.0702054262 \H, $-2.9340683303,0 .,-0.1060395178 \backslash \mathrm{H}$, $-1.2944710201,-1.8094344783,1.829145273 \backslash \mathrm{H}, 1.2944710201,-1.8094344783,1$ $.829145273 \backslash \mathrm{H},-2.3006611606,0 .,-1.729961963 \backslash \mathrm{H}, 0 ., 2.6442414327,-1.455640$ 3533\H,1.2944710201,1.8094344783,1.829145273\H,-1.2944710201,1.8094344 783,1.829145273\H, 0.,1.0653907371,-2.1733586224\C,-1.2492437184,-1.285 1939152,-0.3552747081\C,1.2492437184,-1.2851939152,-0.3552747081\C,1.2 $492437184,1.2851939152,-0.3552747081 \backslash \mathrm{C},-1.2492437184,1.2851939152,-0.3$ $552747081 \backslash \mathrm{H},-1.9546222904,-2.1040957814,-0.4638895896 \backslash \mathrm{H}, 1.9546222904$, -$2.1040957814,-0.4638895896 \backslash \mathrm{H}, 1.9546222904,2.1040957814,-0.4638895896 \backslash \mathrm{H}$ ,-1.9546222904,2.1040957814,-0.4638895896\C,0.,-1.5842176776,-1.222674 $3205 \backslash \mathrm{C}, 2.0108411557,0 .,-0.6816887489 \backslash \mathrm{C}, 0.1 .5842176776,-1.2226743205 \backslash \mathrm{C}$ ,-2.0108411557,0.,-0.6816887489\H,0.,-2.6442414327,-1.4556403533\H,0., $-1.0653907371,-2.1733586224 \backslash \mathrm{H}, 2.9340683303,0 .,-0.1060395178 \backslash \mathrm{H}, 2.300661$ 1606,0.,-1.729961963<br>Version=Sun-SVR4-Unix-G98RevA.7\State=1-A1 \HF=-5 $01.4922869 \backslash \mathrm{RMSD}=0.000 \mathrm{e}+00 \backslash \mathrm{RMSF}=2.580 \mathrm{e}-05 \backslash \mathrm{Dipole}=0 ., 0 .,-1.0408415 \backslash \mathrm{PG}=\mathrm{C} 0$ 2V [C2 (C1), SGV (C2H4), SGV' (C2H4), X(C8H8)] <br>@

## $\mathrm{C}-\mathrm{C}=1.70 \AA$

$1 \backslash 1 \backslash G I N C-P A L O \backslash F O p t \backslash C A S S C F \backslash 6-31 G(d) \backslash C 13 H 16 \backslash R A S M U S S E N \backslash 04-O c t-1999 \backslash 0 \backslash \ \# P$ CAS $(8,8) / 6-31 G * 5 D$ OPT=MODREDUNDANT NAME=RASMUSSEN GUESS=CHECK GEOM= (N ODISTANCE,NOANGLE,NODIHEDRAL) <br>Hemispirooctaplane diyl inner CC cleava ge $\mathrm{C} 1 \backslash \backslash 0,1 \backslash \mathrm{C},-0.1662341078,0.0069457179,1.8528437253 \backslash \mathrm{C}, 0.7572585144,-1$ $.2292907253,1.1483885003 \backslash C,-0.9470866867,1.2396216112,0.9846608034 \backslash \mathrm{C}, 1$ $.4025985643,0.0339123281,1.1985976758 \backslash C,-1.592471127,-0.0236355366,0.9$ $322386129 \backslash \mathrm{H}, 0.8556906864,-1.967230336,1.9219246194 \backslash \mathrm{H},-0.8903956958,-2$. $0563509491,-1.806631045 \backslash \mathrm{H},-2.214727871,1.1979670674,-1.6644647471 \backslash \mathrm{H}, 2$. $0283031079,0.3388872949,2.0158475504 \backslash \mathrm{H},-1.1781952623,1.9841442617,1.72$ $27473624 \backslash \mathrm{H},-0.7512758284,0.4755115353,-2.2510755393 \backslash \mathrm{H},-1.3228725245,-2$ $.6125024957,-0.2122774538 \backslash \mathrm{H},-2.3549109159,-0.3199855885,1.6275187557 \backslash \mathrm{C}$ , 0.6035295055,-1.6988736204,-0.294307167\C,1.7383712881,0.5254306653,$0.2047069281 \backslash C,-0.540350505,1.6956918357,-0.4122874023 \backslash C,-1.6752337553$
, - 0. $5284874293,-0.5039062332 \backslash \mathrm{H}, 1.0188682703,-2.7003506306,-0.360914968$ $8 \backslash H, 2.7942437366,0.7800574798,-0.2210314099 \backslash \mathrm{H},-0.9365919612,2.69616713$ $37,-0.5605097272 \backslash \mathrm{H},-2.7117089242,-0.7841524368,-0.7045911763 \backslash \mathrm{C}, 1.51303$ $27263,-0.7274103451,-1.0891443163 \backslash C, 0.9736165711,1.7872221031,-0.60632$ $24262 \backslash C,-1.295789462,0.716049709,-1.346318801 \backslash \mathrm{C},-0.8524018607,-1.79330$ $94478,-0.7519966229 \backslash \mathrm{H}, 2.4734090926,-1.2114749354,-1.2349942803 \backslash \mathrm{H}, 1.137$ $4613263,-0.4959877198,-2.0782479707 \backslash \mathrm{H}, 1.3419352162,2.6118612415,0.0003$ $252243 \backslash \mathrm{H}, 1.1977295562$, 2.0402378822 , -1. $6400617191 \backslash \backslash V e r s i o n=$ Sun-SVR4-Uni $x-G 98 R e v A .7 \backslash H F=-501.4922865 \backslash R M S D=0.000 e+00 \backslash R M S F=3.751 e-05 \backslash D i p o l e=0.094$ $0676,-0.0028791,-1.0364805 \backslash \mathrm{PG}=\mathrm{C01}[\mathrm{X}(\mathrm{C} 13 \mathrm{H16})] \backslash \backslash @$

## $\mathrm{C}-\mathrm{C}=1.80 \AA$

$1 \backslash 1 \backslash G I N C-P A L O \backslash F O p t \backslash C A S S C F \backslash 6-31 G(d) \backslash C 13 H 16 \backslash R A S M U S S E N \backslash 06-O c t-1999 \backslash 0 \backslash \backslash \# P$ CAS (8, 8) /6-31G* 5D OPT=MODREDUNDANT NAME=RASMUSSEN GUESS=CHECK GEOM=(C HECK, NODISTANCE, NOANGLE, NODIHEDRAL) <br>Hemispirooctaplane diyl inner CC cleavage $\mathrm{C} 1 \mathrm{CC}=1.8 \backslash \backslash 0,1 \backslash \mathrm{C},-0.0921074696,-0.1209258507,1.8637313774 \backslash \mathrm{C}, 1$ $.2211999328,-0.8555489096,1.0886086748 \backslash C,-1.2519960705,0.8085099787,1$. $0881494591 \backslash C, 1.3894101873,0.5459714864,1.0889049876 \backslash C,-1.4377946018,-0$ $.6077899754,1.0097962433 \backslash \mathrm{H}, 1.6512712503,-1.4967969653,1.8346447238 \backslash \mathrm{H},-$ $0.1892657843,-2.235998881,-1.79305636 \backslash \mathrm{H},-2.5894431965,0.3565433427,-1$. $4981983826 \backslash \mathrm{H}, 1.8250264072,1.086553039,1.9058896213 \backslash \mathrm{H},-1.7158803595,1.4$ $172138945,1.8417056757 \backslash \mathrm{H},-1.0066363963,0.2066498576,-2.1901970959 \backslash \mathrm{H},-0$ $.3223199911,-2.9031088385,-0.1886808861 \backslash \mathrm{H},-2.0368938667,-1.1495510504$, $1.7190156102 \backslash \mathrm{C}, 1.1515864901,-1.3666981322,-0.3537623975 \backslash \mathrm{C}, 1.4330476439$ , 1.114936971,-0.3132041166\C,-1.1192815508,1.3933984286,-0.3210258152\ C, -1.4104113603,-1.0867350159,-0.4340839742 \H, 1.8895694748, -2. 15652942 $83,-0.458491534 \backslash \mathrm{H}, 2.3261545539,1.7288046038,-0.394115355 \backslash \mathrm{H},-1.85483212$ $71,2.1879701854,-0.4080312292 \backslash \mathrm{H},-2.2927382353,-1.6959594365,-0.6075936$ $622 \backslash \mathrm{C}, 1.6056190177,-0.1457954608,-1.1964078157 \backslash \mathrm{C}, 0.2405087195,2.022748$ $3198,-0.6209159524 \backslash \mathrm{C},-1.5415851329,0.22392729,-1.2483535367 \backslash \mathrm{C},-0.19977$ $77607,-1.9719154534,-0.7378822358 \backslash \mathrm{H}, 2.6628408064,-0.2594089354,-1.4138$ $129844 \backslash \mathrm{H}, 1.1048425354,-0.0752076608,-2.1536962224 \backslash \mathrm{H}, 0.340409137,2.9220$ 694835,-0.0169410853\H, 0.2773875236,2.3422547309,-1.6597702226<br>Versio $\mathrm{n}=$ Sun-SVR4-Unix-G98RevA. $7 \backslash \mathrm{HF}=-501.4917292 \backslash \mathrm{RMSD}=0.000 \mathrm{e}+00 \backslash \mathrm{RMSF}=6.296 \mathrm{e}-0$ $4 \backslash$ Dipole=0.1682786,0.0967768,-1.0239216\PG=C01 [X(C13H16)] <br>@

## $\mathrm{C}-\mathrm{C}=1.90 \AA$

$1 \backslash 1 \backslash G I N C-P A L O \backslash F O p t \backslash C A S S C F \backslash 6-31 G(d) \backslash C 13 H 16 \backslash R A S M U S S E N \backslash 01-O c t-1999 \backslash 0 \backslash \backslash \# P$ CAS (8,8)/6-31G* 5D OPT=MODREDUNDANT NAME=RASMUSSEN GUESS=CHECK GEOM=(N ODISTANCE, NOANGLE,NODIHEDRAL) <br>Hemispirooctaplane diyl inner CC cleava ge C1 CC=1.9<br>0,1\C,-0.3242758545,-0.1460368375,1.710311459\C, 0.794755 $296,-1.163259165,1.2341100179 \backslash \mathrm{C},-0.9260877541,1.1965137748,1.102745566$ $4 \backslash C, 1.4589190835,0.0848815657,1.096394959 \backslash \mathrm{C},-1.6410322129,-0.070789423$ $6,0.8861818762 \backslash \mathrm{H}, 1.0612653466,-1.8897413505,1.9861772711 \backslash \mathrm{H},-0.82278502$ $34,-2.075236598,-1.7752182173 \backslash H,-2.1803286459,1.2986994323,-1.60539777$ $22 \backslash \mathrm{H}, 1.8290467726,0.629881831,1.9433326924 \backslash \mathrm{H},-1.2551073512,1.945256876$ $9,1.8042898024 \backslash \mathrm{H},-0.7130907221,0.606999085,-2.220449226 \backslash \mathrm{H},-1.362994102$ $9,-2.566017959,-0.1946993647 \backslash \mathrm{H},-2.4532529883,-0.3516588584,1.538374873$ $3 \backslash C, 0.601868358,-1.7012415691,-0.2205325042 \backslash C, 1.7764984067,0.508335432$ $9,-0.2945812072 \backslash C,-0.5045493862,1.70273149,-0.3095840135 \backslash C,-1.68663809$ $37,-0.4970035558,-0.5598218533 \backslash \mathrm{H}, 0.9944031116,-2.7125604637,-0.2550061$ $622 \backslash \mathrm{H}, 2.8324305001,0.759991952,-0.3691523184 \backslash \mathrm{H},-0.8974684286,2.7113377$

87, - $0.3976792742 \backslash \mathrm{H},-2.7022731816,-0.7547821693,-0.8457121054 \backslash \mathrm{C}, 1.50230$ 81966,-0.7840547589,-1.0970626385\C, 0.991990103, 1.7912075582, -0. 611715 $6557 \backslash \mathrm{C},-1.2696831622,0.7881277154,-1.3081154716 \backslash \mathrm{C},-0.8454803715,-1.772$ 5295131, - 0. $7304707269 \backslash \mathrm{H}, 2.454371572,-1.2814090358,-1.2526691572 \backslash \mathrm{H}, 1.08$ 55615223,-0.6086517785,-2.0810673349\H,1.426484855, 2.5881787904, -0.011 $2598272 \backslash \mathrm{H}, 1.1321811111,2.0784161748,-1.6510227249 \backslash \backslash$ Version=Sun-SVR4-Un ix-G98RevA. $7 \backslash \mathrm{HF}=-501.4917286 \backslash \mathrm{RMSD}=0.000 \mathrm{e}+00 \backslash \mathrm{RMSF}=1.852 \mathrm{e}-03 \backslash \mathrm{Dipole=0.27}$ $32288,0.0765878,-0.6576288 \backslash \mathrm{PG}=\mathrm{CO1} \quad[\mathrm{X}(\mathrm{C} 13 \mathrm{H1} 6)] \backslash \backslash @$

## $\mathrm{C}-\mathrm{C}=2.00 \AA$

$1 \backslash 1 \backslash G I N C-P A L O \backslash F O p t \backslash C A S S C F \backslash 6-31 G(d) \backslash C 13 H 16 \backslash R A S M U S S E N \backslash 30-S e p-1999 \backslash 0 \backslash \backslash \# P$ CAS (8, 8) /6-31G(D) 5D OPT=MODREDUNDANT NAME=RASMUSSEN GUESS=(CHECK) GEO $M=(C H E C K, N O D I S T A N C E, N O A N G L E, N O D I H E D R A L) \backslash \backslash H e m i s p i r o o c t a p l a n e ~ d i y l ~ i n n e r ~$
CC cleavage $C 1 \backslash \backslash 0,1 \backslash C,-0.3497704807,-0.1437744908,1.6695528048 \backslash C, 0.79$ $87194407,-1.1063930429,1.2583719127 \backslash \mathrm{C},-0.9231687381,1.1979497246,1.107$ $5942855 \backslash C, 1.5430345952,0.1044852039,1.0731840822 \backslash C,-1.6707598406,-0.07$ $1441897,0.899115832 \backslash \mathrm{H}, 1.0785451492,-1.8262777928,2.0150763749 \backslash \mathrm{H},-0.823$ $2308391,-2.1032183494,-1.7294037039 \backslash H,-2.1968585733,1.281163092,-1.593$ $7173309 \backslash \mathrm{H}, 1.8520111419,0.7125557225,1.901638585 \backslash \mathrm{H},-1.2509601682,1.9556$ $694194,1.8007039013 \backslash \mathrm{H},-0.7378269096,0.5770042237,-2.2161941906 \backslash \mathrm{H},-1.35$ $64400082,-2.5681383284,-0.1393842838 \backslash H,-2.4949055224,-0.3244288683,1.5$ $489080021 \backslash \mathrm{C}, 0.6034067196,-1.6892799781,-0.1864438995 \backslash \mathrm{C}, 1.8014099304,0$. $5074287487,-0.3329541251 \backslash C,-0.5078748638,1.6860890478,-0.3157929798 \backslash C$, $-1.705046011,-0.5110965725,-0.5445263958 \backslash \mathrm{H}, 0.9956848892,-2.7010241288$, $-0.1936538319 \backslash \mathrm{H}, 2.8483641735,0.7714256192,-0.4700863639 \backslash \mathrm{H},-0.899373861$ $7,2.6944791921,-0.4113115037 \backslash \mathrm{H},-2.7145788721,-0.7807337754,-0.84013526$ $38 \backslash C, 1.500295934,-0.8011048791,-1.0969271595 \backslash C, 0.9859817176,1.77691665$ $61,-0.6399283977 \backslash \mathrm{C},-1.2863135276,0.7676788233,-1.3008795352 \backslash \mathrm{C},-0.84696$ $94576,-1.7800036043,-0.690850005 \backslash \mathrm{H}, 2.4450393341,-1.3116883326,-1.25437$ $33916 \backslash \mathrm{H}, 1.0701540013,-0.6451964035,-2.0786864999 \backslash \mathrm{H}, 1.4233360729,2.5825$ $71582,-0.0531421667 \backslash \mathrm{H}, 1.1033674837,2.0611146897,-1.6833368507 \backslash \backslash V e r s i o n$ $=$ Sun-SVR4-Unix-G98RevA. $7 \backslash H F=-501.4950403 \backslash R M S D=0.000 e+00 \backslash R M S F=3.806 e-03$ \Dipole=0.1331195,0.0666229,-0.4759998\PG=C01 [X(C13H16)]<br>@

## $\mathrm{C}-\mathrm{C}=2.10 \AA$

$1 \backslash 1 \backslash G I N C-P A L O \backslash F O p t \backslash C A S S C F \backslash 6-31 G(d) \backslash C 13 H 16 \backslash R A S M U S S E N \backslash 03-O c t-1999 \backslash 0 \backslash \backslash \# P$ CAS (8,8)/6-31G* 5D OPT=MODREDUNDANT NAME=RASMUSSEN GUESS=CHECK GEOM=(N ODISTANCE,NOANGLE,NODIHEDRAL) <br>Hemispirooctaplane diyl inner CC cleava ge C1 CC=2.1<br>0,1\C,-0.372998451,-0.1527208188,1.6165157652\C,0.774270 $315,-1.0685037896,1.248545663 \backslash C,-0.9136230008,1.181687863,1.0963545238$ $\backslash C, 1.647549585,0.0777717509,1.0928120402 \backslash \mathrm{C},-1.7177741908,-0.0756865078$ , 0.9199216481 \H, 1.0123636707,-1.8040035835,2.0061361507\H,-0. 830342547 $6,-2.0861114884,-1.7317510378 \backslash \mathrm{H},-2.2108972647,1.2781331311,-1.58277456$ $74 \backslash \mathrm{H}, 1.8652272477,0.7331684326,1.9145726949 \backslash \mathrm{H},-1.2006505763,1.93687213$ $73,1.8100011313 \backslash \mathrm{H},-0.7664000389,0.5501458161,-2.2135570294 \backslash \mathrm{H},-1.340939$ $9758,-2.5740327167,-0.1413061856 \backslash \mathrm{H},-2.5719825805,-0.2753663938,1.54783$ $81644 \backslash C, 0.6024818356,-1.664671406,-0.1922801979 \backslash \mathrm{C}, 1.8328435904,0.51312$ $4633,-0.3239902011 \backslash C,-0.510171301,1.6686603397,-0.3207127158 \backslash C,-1.7297$ $015274,-0.5194052549,-0.5323812983 \backslash H, 0.998106154,-2.6747270876,-0.1860$ $398747 \backslash \mathrm{H}, 2.8679971825,0.794190357,-0.5077186194 \backslash \mathrm{H},-0.8985710622,2.6779$ $897399,-0.4180864298 \backslash \mathrm{H},-2.7330579502,-0.7987439526,-0.8385002067 \backslash \mathrm{C}, 1.5$ $123570346,-0.7848398639,-1.0963218941 \backslash C, 0.9888278152,1.7651032571,-0.6$
$263681098 \backslash \mathrm{C},-1.3046319839,0.7542026207,-1.2950707697 \backslash \mathrm{C},-0.8500154054,-$ $1.7723952133,-0.6902374568 \backslash H, 2.4474566693,-1.3112669061,-1.2586413049 \backslash$ H, 1. $0847022192,-0.6117003074,-2.0765164449 \backslash \mathrm{H}, 1.40624034,2.57868813,-0$. $0358165233 \backslash \mathrm{H}, 1.1142626194,2.0527990321,-1.6685618982 \backslash \backslash$ Version=Sun-SVR4 -Unix-G98RevA. $7 \backslash \mathrm{HF}=-501.5021612 \backslash \mathrm{RMSD}=0.000 \mathrm{e}+00 \backslash \mathrm{RMSF}=7.685 \mathrm{e}-03 \backslash \mathrm{Dipole=-}$ $0.0703423,0.056687,-0.2897043 \backslash \mathrm{PG}=\mathrm{C01}[\mathrm{X}(\mathrm{C} 13 \mathrm{H} 16)] \backslash \backslash @$

## dissociated equilibrium

$C_{1}$
$1 \backslash 1 \backslash G I N C-P A L O \backslash F O p t \backslash C A S S C F \backslash 6-31 G(d) \backslash C 13 H 16 \backslash R A S M U S S E N \backslash 29-S e p-1999 \backslash 0 \backslash \ \# P$ CAS $(8,8) / 6-31 G(D)$ 5D OPT NAME=RASMUSSEN GUESS=(CHECK) GEOM= (CHECK,NODI STANCE,NOANGLE,NODIHEDRAL) <br>Hemispirooctaplane diyl inner CC cleavage $\mathrm{C} 1 \backslash \backslash 0,1 \backslash \mathrm{C},-0.5134269499,-0.1439115069,1.62433943 \backslash \mathrm{C}, 0.7338822629,-0.961$ 8530276,1.2402567356\C,-0.9967259209,1.1748904364,1.0634315112\C,1.889 2573667,-0.010668197,1.0956663925\C,-1.8304487133,-0.0737899535,0.9023 $933239 \backslash \mathrm{H}, 0.8932807299,-1.7231793876,1.9960590911 \backslash \mathrm{H},-0.814852445,-2.092$ 3980927,-1.7237076574 \Н, -2.1901183841,1.2742707906,-1.6075929751 \H, 2.2 $046878535,0.6029069667,1.9232154868 \backslash \mathrm{H},-1.2889486558,1.9350384004,1.769$ $6115225 \backslash$ Н, $-0.7534110966,0.5192177722,-2.2240596459 \backslash$ н, $-1.3159172892,-2$. 5733904921,-0.1282006516\H,-2.7430760931,-0.2154574583,1.4575067242\C, $0.5985507039,-1.6080566584,-0.1825147818 \backslash C, 1.916714413,0.5005575105,-0$ $.3181647229 \backslash C,-0.5098291238,1.6376453028,-0.3215965101 \backslash C,-1.7527957501$ , -0.5343290926,-0.5544950358\H,1.0103060427,-2.6099087373,-0.126027518 $2 \backslash H, 2.920893233,0.814791255,-0.5919279089 \backslash \mathrm{H},-0.8667563708,2.6547022449$ , -0.4560452582\H,-2.7379561758,-0.8253654795,-0.905055736\C,1.52694806 79,-0.7649466729,-1.1043402202\C,1.0135716065,1.7355334961,-0.54102527 $32 \backslash \mathrm{C},-1.2962821597,0.7337989087,-1.3111952531 \backslash \mathrm{C},-0.8451508481,-1.76621$ 76803,-0.686233945\H,2.431109207,-1.3328142658,-1.2990731113\H,1.08578 63789,-0.5527216988,-2.0701259528\H,1.3870537077,2.5268253625,0.106296 $0593 \backslash \mathrm{H}, 1.1723296268,2.0855656279,-1.560002376 \backslash \backslash$ Version=Sun-SVR4-Unix-G $98 R e v A .7 \backslash H F=-501.5238781 \backslash R M S D=0.000 e+00 \backslash R M S F=1.402 e-05 \backslash$ Dipole=-0. 12456 91,0.0747013,-0.2473078\PG=C01 [X(C13H16)] <br>@

## C.2.3 Data for Chapter 4

## C.2.3.1 Alkaplanes

Table C-22. Guassian archive files for the B3-LYP/6-31G(d) optimized alkaplanes in Chapter 4.

## Alkaplanes

## 4-30 bihexaplane $\boldsymbol{D}_{\mathbf{2}}$

$1 \backslash 1 \backslash G I N C-P C \backslash F O p t \backslash R B 3 L Y P \backslash 6-31 G(d) \backslash C 17 H 16 \backslash R A S M U S S E N \backslash 01-O c t-1998 \backslash 0 \backslash \backslash \# P$ B3 LYP/6-31G* 5D OPT=(READFC,TIGHT) NAME=RASMUSSEN MAXDISK=5242880000 GUE SS=CHECK SCF=(VSHIFT,NOVARACC,DIRECT) GEOM=(CHECK,NODISTANCE,NOANGLE,N ODIHEDRAL) <br>Bihexaplane $\mathrm{D} 2 \backslash \backslash 0,1 \backslash \mathrm{C}, 0.0 .0 .0 . \backslash \mathrm{C},-1.1386026339,-0.17421696$ $14,-1.1213333851 \backslash C,-1.1386026339,0.1742169614,1.1213333851 \backslash C, 1.1386026$ 339, 0.1742169614,-1.1213333851\C,1.1386026339,-0.1742169614,1.12133338 $51 \backslash C,-0.7714885193,2.2647949552,0.0711069875 \backslash C,-0.7714885193,-2.264794$ 9552,-0.0711069875\C, 0.7714885193,-2.2647949552,0.0711069875\C,0.77148 85193,2.2647949552,-0.0711069875\C,-0.888676217,1.3860402166,-1.365838 $5073 \backslash C,-0.888676217,-1.3860402166,1.3658385073 \backslash C, 0.888676217,-1.386040$
$2166,-1.3658385073 \backslash \mathrm{C}, 0.888676217,1.3860402166,1.3658385073 \backslash \mathrm{C},-0.655126$ $8702,-1.5435323322,-1.5163386948 \backslash C,-0.6551268702,1.5435323322,1.516338$ $6948 \backslash C, 0.6551268702,1.5435323322,-1.5163386948 \backslash C, 0.6551268702,-1.54353$ $23322,1.5163386948 \backslash \mathrm{H}, 1.0542521509,-2.0955793897,2.3822545686 \backslash \mathrm{H}, 1.05425$ 21509, 2.0955793897,-2.3822545686\H,-1.0542521509, 2.0955793897, 2.382254 $5686 \backslash \mathrm{H},-1.0542521509,-2.0955793897,-2.3822545686 \backslash \mathrm{H}, 1.5405671558,1.8674$ 955781, 2. $103348641 \backslash \mathrm{H}, 1.5405671558,-1.8674955781,-2.103348641 \backslash \mathrm{H},-1.5405$ $671558,-1.8674955781,2.103348641 \backslash \mathrm{H},-1.5405671558,1.8674955781,-2.10334$ $8641 \backslash \mathrm{H},-2.1740388229,-0.2849981491,-0.8148564782 \backslash \mathrm{H},-2.1740388229,0.284$ $9981491,0.8148564782 \backslash \mathrm{H}, 2.1740388229,0.2849981491,-0.8148564782 \backslash \mathrm{H}, 2.174$ $0388229,-0.2849981491,0.8148564782 \backslash \mathrm{H},-1.3170717865,3.2153170642,0.0114$ $482617 \backslash \mathrm{H},-1.3170717865,-3.2153170642,-0.0114482617 \backslash \mathrm{H}, 1.3170717865,-3.2$ $153170642,0.0114482617 \backslash \mathrm{H}, 1.3170717865,3.2153170642,-0.0114482617 \backslash \backslash V e r s$ ion=SGI-G94RevE. $2 \backslash$ State=1-A $\backslash H F=-656.8170275 \backslash R M S D=8.285 e-09 \backslash R M S F=1.114 e$ -06\Dipole=0.,0.,0.\PG=D02 [O (C1), X(C16H16)] <br>@

## 4-30 bihexaplane $\boldsymbol{D}_{\mathbf{2 h}}$

$1 \backslash 1 \backslash G I N C-P C \backslash F O p t \backslash R B 3 L Y P \backslash 6-31 G(d) \backslash C 17 H 16 \backslash R A S M U S S E N \backslash 01-O c t-1998 \backslash 0 \backslash \backslash \#$ B3 LYP/6-31G* 5D OPT= (NEWESTMFC, TIGHT) NAME=RASMUSSEN MAXDISK=5242880000 GUESS=CHECK SCF= (VSHIFT, NOVARACC, DIRECT) GEOM= (CHECK, NODISTANCE, NOANGL E, NODIHEDRAL $\backslash \backslash$ Bihexaplane $D 2 h \backslash \backslash 0,1 \backslash C, 0 ., 0 ., 0 . \backslash C, 0 ., 1.124990563,1.1680$ $20437 \backslash \mathrm{C}, 0 .,-1.124990563,-1.168020437 \backslash \mathrm{C}, 0 ., 1.124990563,-1.168020437 \backslash \mathrm{C}, 0$ ., - $1.124990563,1.168020437 \backslash \mathrm{C}, 1.4533998552,1.4257072508,0.7757493909 \backslash \mathrm{C}$, $-1.4533998552,-1.4257072508,-0.7757493909 \backslash \mathrm{C}, 1.4533998552,1.4257072508$, $-0.7757493909 \backslash \mathrm{C},-1.4533998552,1.4257072508,-0.7757493909 \backslash \mathrm{C}, 1.453399855$ $2,-1.4257072508,-0.7757493909 \backslash \mathrm{C},-1.4533998552,1.4257072508,0.775749390$ $9 \backslash C, 1.4533998552,-1.4257072508,0.7757493909 \backslash C,-1.4533998552,-1.4257072$ 508, 0.7757493909\C,2.2474809859, 0., 0.7777511481\C, -2.2474809859, 0., -0. $7777511481 \backslash C, 2.2474809859,0 .,-0.7777511481 \backslash C,-2.2474809859,0 ., 0.777751$ $1481 \backslash \mathrm{H},-3.2104511651,0 .,-1.3147385018 \backslash \mathrm{H}, 3.2104511651,0 ., 1.3147385018 \backslash \mathrm{H}$ ,-3.2104511651,0., 1.3147385018\H,3.2104511651, 0., -1.3147385018\H,1.990 8930234, 2. 2455519179,1.2902344012\H,-1.9908930234, -2.2455519179,-1.290 $2344012 \backslash \mathrm{H}, 1.9908930234,2.2455519179,-1.2902344012 \backslash \mathrm{H},-1.9908930234,2.24$ 55519179,-1.2902344012\H,1.9908930234,-2.2455519179,-1.2902344012\H,-1 $.9908930234,2.2455519179,1.2902344012 \backslash \mathrm{H}, 1.9908930234,-2.2455519179,1.2$ $902344012 \backslash \mathrm{H},-1.9908930234,-2.2455519179,1.2902344012 \backslash \mathrm{H}, 0 ., 0.8607857005$ , 2. $2210110254 \backslash \mathrm{H}, 0 .,-0.8607857005,-2.2210110254 \backslash \mathrm{H}, 0 ., 0.8607857005,-2.22$ $10110254 \backslash \mathrm{H}, 0 .,-0.8607857005,2.2210110254 \backslash \backslash$ Version=SGI-G94RevE.2\State= $1-\mathrm{AG} \backslash \mathrm{HF}=-656.7816749 \backslash \mathrm{RMSD}=3.191 \mathrm{e}-09 \backslash \mathrm{RMSF}=1.270 \mathrm{e}-06 \backslash \mathrm{Dipole=0} ., 0 ., 0 . \backslash \mathrm{PG}=$ D02H [O (C1), SG (C4H4),SG'(C4H4),X(C8H8)]<br>@

## 4-31 hexaplane $\boldsymbol{D}_{\mathbf{2}}$

$1 \backslash 1 \backslash G I N C-P C \backslash F O p t \backslash R B 3 L Y P \backslash 6-31 G(d) \backslash C 17 H 20 \backslash R A S M U S S E N \backslash 28-S e p-1998 \backslash 0 \backslash \ \# P$ B3 LYP/6-31G* 5D OPT=(READFC,TIGHT) MAXDISK=5242880000 GUESS=CHECK SCF=(V SHIFT, NOVARACC,DIRECT) NAME=RASMUSSEN GEOM= (CHECK,NODISTANCE,NOANGLE,N ODIHEDRAL) <br>Hexaplane 5D D2 <br>0,1\C,0.,0.,0.\C,-0.1411364221,1.12660898 55,1.1261066724\C,0.1411364189,1.1266089859,-1.1261066724\C,-0.1411364 189,-1.1266089859,-1.1261066724 \C, 0.1411364221,-1.1266089855,1.1261066 $724 \backslash C,-1.5823322278,0.7171647081,1.3866738589 \backslash C, 1.5823322258,0.7171647$ $126,-1.3866738589 \backslash C,-1.5823322258,-0.7171647126,-1.3866738589 \backslash C, 1.5823$ $322278,-0.7171647081,1.3866738589 \backslash C, 1.4534562217,0.832687213,1.3250308$ $157 \backslash C,-1.4534562241,0.8326872089,-1.3250308157 \backslash C, 1.4534562241,-0.83268$
$72089,-1.3250308157 \backslash \mathrm{C},-1.4534562217,-0.832687213,1.3250308157 \backslash \mathrm{C}, 2.1922$ $212877,1.3338790477,-0.0181647856 \backslash C,-2.1922212877,-1.3338790477,-0.018$ $1647856 \backslash \mathrm{C}, 2.1922212915,-1.3338790415,0.0181647856 \backslash \mathrm{C},-2.1922212915,1.33$ $38790415,0.0181647856 \backslash \mathrm{H},-0.1492852565,2.1813274239,0.8614312691 \backslash \mathrm{H}, 0.14$ $92852504,2.1813274244,-0.8614312691 \backslash \mathrm{H},-0.1492852504,-2.1813274244,-0.8$ $614312691 \backslash \mathrm{H}, 0.1492852565,-2.1813274239,0.8614312691 \backslash \mathrm{H},-2.1602420434,1$. $0904514702,2.2547084932 \backslash \mathrm{H}, 2.1602420403,1.0904514763,-2.2547084932 \backslash \mathrm{H},-2$ $.1602420403,-1.0904514763,-2.2547084932 \backslash H, 2.1602420434,-1.0904514702,2$ $.2547084932 \backslash \mathrm{H},-1.901080923,1.3501102435,-2.185320631 \backslash \mathrm{H}, 1.901080923,-1$. $3501102435,-2.185320631 \backslash \mathrm{H},-1.9010809192,-1.3501102489,2.185320631 \backslash \mathrm{H}, 1$. $9010809192,1.3501102489,2.185320631 \backslash \mathrm{H}, 2.1349751907,2.4278504833,-0.086$ $417727 \backslash \mathrm{H},-2.1349751907,-2.4278504833,-0.086417727 \backslash \mathrm{H}, 2.1349751976,-2.42$ $78504773,0.086417727 \backslash \mathrm{H},-2.1349751976,2.4278504773,0.086417727 \backslash \mathrm{H}, 3.2581$ $13953,1.0943530547,0.0848764622 \backslash \mathrm{H},-3.258113953,-1.0943530547,0.0848764$ $622 \backslash \mathrm{H}, 3.2581139561,-1.0943530455,-0.0848764622 \backslash \mathrm{H},-3.2581139561,1.09435$ 30455 , - 0.0848764622<br>Version=SGI-G94RevE. $2 \backslash$ State=1-A $\backslash H F=-659.3072643 \backslash R$ $\mathrm{MSD}=5.777 \mathrm{e}-09 \backslash \mathrm{RMSF}=1.089 \mathrm{e}-06 \backslash \mathrm{Dipole}=0 ., 0 ., 0 . \backslash \mathrm{PG}=\mathrm{D} 02 \quad[\mathrm{O}(\mathrm{C} 1), \mathrm{X}(\mathrm{C} 16 \mathrm{H} 20)] \backslash$ \@

## 4-31 hexaplane $\boldsymbol{D}_{\mathbf{2 h}}$

$1 \backslash 1 \backslash G I N C-P C \backslash F O p t \backslash R B 3 L Y P \backslash 6-31 G(d) \backslash C 17 H 20 \backslash R A S M U S S E N \backslash 28-S e p-1998 \backslash 0 \backslash \backslash \# P$ B3 LYP/6-31G* 5D OPT=(READFC,TIGHT) MAXDISK=5242880000 GUESS=CHECK SCF=(V SHIFT, NOVARACC,DIRECT) NAME=RASMUSSEN GEOM= (CHECK,NODISTANCE,NOANGLE,N ODIHEDRAL) <br>Hexaplane D2h <br>0,1\C,0.,0.,0.\C,-1.1153173653,-1.140374181 , 0. \C,1.1153173653,-1.140374181,0. \C,1.1153173653,1.140374181,0. \C, -1. $1153173653,1.140374181,0 . \backslash C,-1.3438102116,-0.7741301844,1.5017341745 \backslash \mathrm{C}$ ,1.3438102116,-0.7741301844,-1.5017341745\C,1.3438102116,0.7741301844, $1.5017341745 \backslash C,-1.3438102116,0.7741301844,-1.5017341745 \backslash C,-1.343810211$ 6,-0.7741301844,-1.5017341745\C,1.3438102116,-0.7741301844,1.501734174 $5 \backslash C, 1.3438102116,0.7741301844,-1.5017341745 \backslash C,-1.3438102116,0.77413018$ $44,1.5017341745 \backslash C, 0 .,-1.3394019317,2.1796955621 \backslash C, 0 .,-1.3394019317,-2$. $1796955621 \backslash \mathrm{C}, 0.1 .3394019317,2.1796955621 \backslash \mathrm{C}, 0.1 .3394019317,-2.1796955$ $621 \backslash \mathrm{H},-0.8870151183,-2.2052414523,0 . \backslash \mathrm{H}, 0.8870151183,-2.2052414523,0 . \backslash \mathrm{H}$ , 0.8870151183,2.2052414523,0. \H, -0.8870151183,2.2052414523,0. \H, -2. 215 6276869,-1.2242278578,2.0271300459\H,2.2156276869,-1.2242278578,-2.027 $1300459 \backslash$ H, $2.2156276869,1.2242278578,2.0271300459 \backslash$ Н, $-2.2156276869,1.224$ 2278578,-2.0271300459\H,2.2156276869,-1.2242278578, 2. $0271300459 \backslash$ H, 2.21 56276869,1.2242278578,-2.0271300459\H,-2.2156276869,1.2242278578, 2. 027 $1300459 \backslash$ Н, $-2.2156276869,-1.2242278578,-2.0271300459 \backslash$ н, 0., -2.437536528 , $2.1260988549 \backslash$ Н, 0., $-2.437536528,-2.1260988549 \backslash$ Н, $0 ., 2.437536528,2.126098$ $8549 \backslash \mathrm{H}, 0.2 .437536528,-2.1260988549 \backslash \mathrm{H}, 0 .,-1.0960974618,3.2489283568 \backslash \mathrm{H}$, $0 .,-1.0960974618,-3.2489283568 \backslash \mathrm{H}, 0 ., 1.0960974618,3.2489283568 \backslash \mathrm{H}, 0 ., 1.0$ 960974618,-3.2489283568<br>Version=SGI-G94RevE. $2 \backslash$ State=1-AG\HF=-659.2792 $007 \backslash \mathrm{RMSD}=5.808 \mathrm{e}-09 \backslash \mathrm{RMSF}=5.363 \mathrm{e}-07 \backslash \mathrm{Dipole}=0 ., 0 ., 0 . \backslash \mathrm{PG}=\mathrm{D} 02 \mathrm{H} \quad[\mathrm{O}(\mathrm{C} 1), \mathrm{SG}(\mathrm{C} 4$ H4) , SG" (C4H8) , X (C8H8) ] <br>@

## 4-32 biheptaplane $\boldsymbol{D}_{\mathbf{2}}$

$1 \backslash 1 \backslash G I N C-P C \backslash F O p t \backslash R B 3 L Y P \backslash 6-31 G(d) \backslash C 19 H 20 \backslash R A S M U S S E N \backslash 02-O c t-1998 \backslash 0 \backslash \backslash \# P$ B3 LYP/6-31G* 5D OPT=(READFC,TIGHT) MAXDISK=5242880000 GUESS=CHECK SCF=(V SHIFT,NOVARACC,DIRECT) NAME=RASMUSSEN GEOM=(CHECK,NODISTANCE,NOANGLE,N ODIHEDRAL) <br>Biheptaplane 5D D2<br>0,1\C,0.,0.,0.\C,-1.1145649571,-1.1346 $728476,0.138828225 \backslash C, 1.1145649571,-1.1346728476,-0.138828225 \backslash C, 1.11456$
$49571,1.1346728476,0.138828225 \backslash \mathrm{C},-1.1145649571,1.1346728476,-0.1388282$ $25 \backslash C,-1.4438621624,-0.696583452,1.5456299034 \backslash C, 1.4438621624,-0.6965834$ $52,-1.5456299034 \backslash C, 1.4438621624,0.696583452,1.5456299034 \backslash C,-1.44386216$ $24,0.696583452,-1.5456299034 \backslash C,-1.3241417268,-0.8501682629,-1.43775662$ $37 \backslash \mathrm{C}, 1.3241417268,-0.8501682629,1.4377566237 \backslash \mathrm{C}, 1.3241417268,0.85016826$ $29,-1.4377566237 \backslash C,-1.3241417268,0.8501682629,1.4377566237 \backslash C, 0.0739257$ $313,-1.1310493257,-2.3038063553 \backslash C, 0.0739257313,1.1310493257,2.30380635$ $53 \backslash C,-0.0739257313,1.1310493257,-2.3038063553 \backslash C,-0.0739257313,-1.13104$ $93257,2.3038063553 \backslash \mathrm{C}, 0 ., 0 ., 3.3379672464 \backslash \mathrm{C}, 0 ., 0 .,-3.3379672464 \backslash \mathrm{H},-0.835$ $2158051,-2.1834379317,0.1934862441 \backslash \mathrm{H}, 0.8352158051,-2.1834379317,-0.193$ $4862441 \backslash \mathrm{H}, 0.8352158051,2.1834379317,0.1934862441 \backslash \mathrm{H},-0.8352158051,2.183$ $4379317,-0.1934862441 \backslash H,-2.3268255913,-1.0744458439,2.096372161 \backslash \mathrm{H}, 2.32$ $68255913,-1.0744458439,-2.096372161 \backslash \mathrm{H}, 2.3268255913,1.0744458439,2.0963$ $72161 \backslash \mathrm{H},-2.3268255913,1.0744458439,-2.096372161 \backslash \mathrm{H}, 2.1412609317,-1.4185$ $678612,1.9028421179 \backslash \mathrm{H}, 2.1412609317,1.4185678612,-1.9028421179 \backslash \mathrm{H},-2.141$ $2609317,1.4185678612,1.9028421179 \backslash \mathrm{H},-2.1412609317,-1.4185678612,-1.902$ $8421179 \backslash \mathrm{H}, 0.115127466,-2.151241326,-2.7004154845 \backslash \mathrm{H}, 0.115127466,2.15124$ $1326,2.7004154845 \backslash \mathrm{H},-0.115127466,2.151241326,-2.7004154845 \backslash \mathrm{H},-0.115127$ $466,-2.151241326,2.7004154845 \backslash H, 0.889119765,-0.0354516844,3.9790521402$ $\backslash \mathrm{H},-0.889119765,0.0354516844,3.9790521402 \backslash \mathrm{H}, 0.889119765,0.0354516844,-$ $3.9790521402 \backslash \mathrm{H},-0.889119765,-0.0354516844,-3.9790521402 \backslash \backslash V e r s i o n=S G I-G$ 94RevE. $2 \backslash$ State=1-A $\backslash H F=-735.5164236 \backslash R M S D=6.771 e-09 \backslash R M S F=9.666 e-07 \backslash D i p o l$ $e=0 ., 0 ., 0 . \backslash \mathrm{PG}=\mathrm{D} 02 \quad[\mathrm{O}(\mathrm{C} 1), \mathrm{C} 2 \mathrm{l}(\mathrm{C} 1 . \mathrm{C} 1), \mathrm{X}(\mathrm{C} 16 \mathrm{H} 20)] \backslash \backslash @$

## 4-32 biheptaplane $\boldsymbol{D}_{\mathbf{2 h}}$

$1 \backslash 1 \backslash G I N C-R S C Q C 8 \backslash F O p t \backslash R B 3 L Y P \backslash 6-31 G(d) \backslash C 19 H 20 \backslash D R R 501 \backslash 30-S e p-1998 \backslash 0 \backslash \ \# P B$ 3LYP/6-31G* 5D OPT=(NEWESTMFC,TIGHT) MAXDISK=1048576000 GUESS=CHECK SC F=(VSHIFT,NOVARACC,DIRECT) GEOM=(CHECK,NODISTANCE,NOANGLE,NODIHEDRAL) \} \Biheptaplane 5D D2h<br>0,1\C,0.,0.,0.\C,0.,1.1023722155,1.1507926928\C, 0.,-1.1023722155,1.1507926928\C,0.,-1.1023722155,-1.1507926928\C,0.,1. $1023722155,-1.1507926928 \backslash C, 1.4793036727,1.3672308808,0.7746204063 \backslash C,-1$ $.4793036727,-1.3672308808,0.7746204063 \backslash C, 1.4793036727,-1.3672308808,-0$ $.7746204063 \backslash C,-1.4793036727,1.3672308808,-0.7746204063 \backslash C,-1.4793036727$ , 1.3672308808,0.7746204063\C,1.4793036727,-1.3672308808,0.7746204063\C ,-1.4793036727,-1.3672308808,-0.7746204063\C,1.4793036727,1.3672308808 $,-0.7746204063 \backslash C, 2.2905134216,0 ., 1.1396721755 \backslash C,-2.2905134216,0 ., 1.139$ $6721755 \backslash C, 2.2905134216,0 .,-1.1396721755 \backslash C,-2.2905134216,0 .,-1.13967217$ $55 \backslash \mathrm{C}, 3.3214145987,0.0 . \backslash \mathrm{C},-3.3214145987,0 ., 0 . \backslash \mathrm{H}, 0 ., 0.8653440965,2.2124$ $117761 \backslash \mathrm{H}, 0 .,-0.8653440965,2.2124117761 \backslash \mathrm{H}, 0 .,-0.8653440965,-2.212411776$ $1 \backslash H, 0 ., 0.8653440965,-2.2124117761 \backslash H, 2.0001342288,2.2278330101,1.248402$ $1276 \backslash \mathrm{H},-2.0001342288,-2.2278330101,1.2484021276 \backslash \mathrm{H}, 2.0001342288,-2.2278$ 330101,-1.2484021276\H,-2.0001342288,2.2278330101,-1.2484021276\H, 2.00 01342288,-2.2278330101,1.2484021276\Н, -2.0001342288,-2.2278330101,-1.2 $484021276 \backslash \mathrm{H}, 2.0001342288,2.2278330101,-1.2484021276 \backslash \mathrm{H},-2.0001342288,2$. $2278330101,1.2484021276 \backslash \mathrm{H}, 2.7073923318,0 ., 2.1543281721 \backslash \mathrm{H},-2.7073923318$ , 0., 2. $1543281721 \backslash \mathrm{H}, 2.7073923318,0 .,-2.1543281721 \backslash \mathrm{H},-2.7073923318,0 .,-2$ $.1543281721 \backslash \mathrm{H}, 3.9620553981,-0.8898118765,0 . \backslash \mathrm{H}, 3.9620553981,0.889811876$ $5,0 . \backslash \mathrm{H},-3.9620553981,-0.8898118765,0 . \backslash \mathrm{H},-3.9620553981,0.8898118765,0 . \backslash$ \Version=IBM-RS6000-G94RevE.1\State=1-AG $\backslash H F=-735.4904773 \backslash$ RMSD $=8.946 e-0$ $9 \backslash$ RMSF=1.521e-06\Dipole=0., 0., 0. $\backslash \mathrm{PG}=\mathrm{D} 02 \mathrm{H} \quad\left[\mathrm{O}(\mathrm{C} 1), \mathrm{C} 2(\mathrm{C} 1 . \mathrm{C} 1), \mathrm{SG}(\mathrm{C} 4 \mathrm{H} 4), \mathrm{SG}{ }^{\prime}\right.$ (C4H4), SG" (H4) , X (C8H8) ] <br>@

## 4-33 heptaplane $\boldsymbol{C}_{\mathbf{2}}$

$1 \backslash 1 \backslash$ MHPCC-FR33N06\FOpt $\backslash$ RB3LYP $\backslash 6-31 G(d) \backslash C 19 H 24 \backslash R A S M U S S E N \backslash 04-O c t-1998 \backslash 0$ <br>\#P B3LYP/6-31G* 5D OPT=(NEWESTMFC,TIGHT) SYMM=LOOSE SCF=(VSHIFT,NOVA RACC,DIRECT) NAME=RASMUSSEN GEOM=(CHECK,NODISTANCE,NOANGLE,NODIHEDRAL) $\backslash \backslash$ Heptaplane 5D C1<br>0,1\C,0.,0.0000000007,-0.1240142963\C,-0.234711646 $1,-1.10154545,-1.1875669066 \backslash C, 0.2347116452,1.1015454627,-1.1875668951 \backslash$ C, -0.088061775,1.1205276814,1.0932517979 \C, 0.0880617758,-1.120527693,1 $.0932517859 \backslash C, 1.5609040168,-1.3108903389,-1.0185300716 \backslash C,-1.5609040176$ ,1.3108903497,-1.0185300564\C,1.351657476,0.8066077992,1.5654675176\C, $-1.3516574748,-0.8066078159,1.5654675101 \backslash \mathrm{C},-1.745730041,-1.3864624306$, $-0.9771399121 \backslash C, 1.7457300403,1.386462441,-0.9771398987 \backslash C,-1.4531940774$ $, 0.760529092,1.5688819292 \backslash C, 1.4531940786,-0.7605291087,1.5688819201 \backslash C$, $2.2156083566,1.5558539063,0.4984186776 \backslash C,-2.2190269102,1.5038501206,0$. $4045394814 \backslash C, 2.2190269105,-1.5038501249,0.4045394637 \backslash \mathrm{C},-2.2156083562,-$ $1.5558539116,0.4984186627 \backslash C, 2.2106638514,0.0007479392,-1.6259201068 \backslash C$, $-2.2106638526,-0.0007479219,-1.6259201051 \backslash \mathrm{H},-0.1856409457,-0.862198715$ $8,-2.2498716025 \backslash \mathrm{H}, 0.185640944,0.8621987397,-2.2498715935 \backslash \mathrm{H},-0.07715753$ $77,2.1539236616,0.7410796433 \backslash \mathrm{H}, 0.0771575383,-2.1539236695,0.7410796203$ \H,1.8489605639,-2.1521056022,-1.6641683348\H,-1.8489605651,2.15210561 99,-1.6641683105\Н,-2.1877759255,-2.1968142633,-1.5803071673\H,2.18777 59243,2.1968142801,-1.5803071456\H,1.5901788549,1.215069904,2.55620497 $64 \backslash \mathrm{H},-1.590178853,-1.2150699312,2.5562049647 \backslash \mathrm{H},-1.8098120702,1.1468964$ 247,2.5382645697\H,1.8098120721,-1.1468964517,2.5382645561\H,3.2712451 307,1.2652026985,0.5748792733\H,2.1766140451,2.6254365462,0.7445193753 $\backslash \mathrm{H},-3.2704496598,1.1989733972,0.3351407234 \backslash \mathrm{H},-2.2296711149,2.568599284$ 3,0.6708098658\H,3.27044966,-1.1989734008, 0.3351407082\H,2.2296711154, $-2.5685992915,0.6708098368 \backslash H,-3.2712451303,-1.2652027046,0.5748792623 \backslash$ H, $-2.1766140445,-2.6254365541,0.744519349 \backslash \mathrm{H}, 3.2997403142,-0.0948409453$ ,-1.517208735\H,2.0206723841,0.0476752244,-2.7057140449\H,-3.299740315 3,0.0948409615,-1.5172087315\Н,-2.0206723861,-0.0476751957,-2.70571404 $39 \backslash$ Version=IBM-RS6000-G94RevE.2 \State=1-A $\backslash H F=-738.0029867 \backslash$ RMSD $=4.428 \mathrm{e}$ $-09 \backslash \mathrm{RMSF}=2.394 \mathrm{e}-06 \backslash \mathrm{Dipole=0.,0.,-0.2177733} \mathrm{\backslash PG=C02} \mathrm{\quad[C2(C1),X(C18H24)]} \mathrm{\backslash} \mathrm{\backslash}$ @

## 4-33 heptaplane $\boldsymbol{C}_{2 \mathrm{v}}$

1 \1 \GINC-RSCQC9 \FOpt \RB3LYP\6-31G(d) \C19H24 \RASMUSSEN\01-Oct-1998\0<br>\# P B3LYP/6-31G* 5D OPT=(READFC,TIGHT) MAXDISK=1048576000 GUESS=CHECK SC F= (VSHIFT,NOVARACC,DIRECT) NAME=RASMUSSEN GEOM=(CHECK,NODISTANCE,NOANG LE,NODIHEDRAL) <br>Heptaplane 5D C2v <br>0,1\C,0.,0.,0.041919069\C,0.,-1.067 5356509,-1.2330842502\C,0.,1.0675356509,-1.2330842502\C,0.,1.107237634 $8,1.1175379403 \backslash C, 0 .,-1.1072376348,1.1175379403 \backslash C, 1.5652661114,-1.31832$ 45744,-1.0048014249\C,-1.5652661114,1.3183245744,-1.0048014249\C,1.417 7504104,0.7845794733,1.5938929462\C,-1.4177504104,-0.7845794733,1.5938 $929462 \backslash \mathrm{C},-1.5652661114,-1.3183245744,-1.0048014249 \backslash \mathrm{C}, 1.5652661114,1.31$ 83245744,-1.0048014249\C,-1.4177504104,0.7845794733,1.5938929462\C,1.4 177504104,-0.7845794733,1.5938929462\C,2.1784204283,1.5239963707,0.432 $9000478 \backslash \mathrm{C},-2.1784204283,1.5239963707,0.4329000478 \backslash \mathrm{C}, 2.1784204283,-1.52$ 39963707,0.4329000478\C,-2.1784204283,-1.5239963707,0.4329000478\C,2.1 516823446,0.,-1.6408421439\C,-2.1516823446,0.,-1.6408421439\H,0.,-0.88 43904073,-2.3091673935\H,0., 0.8843904073,-2.3091673935\H,0., 2.13621723 $82,0.7506489703 \backslash \mathrm{H}, 0 .,-2.1362172382,0.7506489703 \backslash \mathrm{H}, 1.9200035464,-2.1542$ $566134,-1.6432538855 \backslash$ Н, $-1.9200035464,2.1542566134,-1.6432538855 \backslash \mathrm{H},-1.9$
$200035464,-2.1542566134,-1.6432538855 \backslash \mathrm{H}, 1.9200035464,2.1542566134,-1.6$ $432538855 \backslash \mathrm{H}, 1.7599603044,1.2027389539,2.5591854392 \backslash \mathrm{H},-1.7599603044,-1$. $2027389539,2.5591854392 \backslash \mathrm{H},-1.7599603044,1.2027389539,2.5591854392 \backslash \mathrm{H}, 1$. $7599603044,-1.2027389539,2.5591854392 \backslash \mathrm{H}, 3.2335877175,1.2275349749,0.38$ $10666395 \backslash \mathrm{H}, 2.1821292399,2.5963428844,0.6764614582 \backslash \mathrm{H},-3.2335877175,1.22$ $75349749,0.3810666395 \backslash \mathrm{H},-2.1821292399,2.5963428844,0.6764614582 \backslash \mathrm{H}, 3.23$ $35877175,-1.2275349749,0.3810666395 \backslash \mathrm{H}, 2.1821292399,-2.5963428844,0.676$ $4614583 \backslash \mathrm{H},-3.2335877175,-1.2275349749,0.3810666395 \backslash \mathrm{H},-2.1821292399$, -2 . $5963428844,0.6764614583 \backslash \mathrm{H}, 3.2397075946,0 .,-1.512802103 \backslash \mathrm{H}, 1.9750951567$, $0 .,-2.7269240904 \backslash \mathrm{H},-3.2397075946,0 .,-1.512802103 \backslash \mathrm{H},-1.9750951567,0 .,-2$ $.7269240904 \backslash \backslash V e r s i o n=I B M-R S 6000-G 94 R e v E .1 \backslash$ State=1-A1 \HF=-737.9692371 \R
 (C4H4) ,SGV' (C2H4) , X (C12H16) ] <br>@

## 4-34 bioctaplane $\boldsymbol{D}_{\mathbf{2}}$

$1 \backslash 1 \backslash G I N C-P C \backslash F O p t \backslash R B 3 L Y P \backslash 6-31 G(d) \backslash C 21 H 24 \backslash R A S M U S S E N \backslash 28-S e p-1998 \backslash 0 \backslash \backslash \# P$ B3 LYP/6-31G* 5D OPT=(READFC,TIGHT) MAXDISK=5242880000 NAME=RASMUSSEN GUE SS=CHECK SCF=(VSHIFT,NOVARACC,DIRECT) GEOM=(CHECK,NODISTANCE,NOANGLE,N ODIHEDRAL) <br>Bioctaplane D2<br>0,1\C,0.,0.,0.\C,0.7835480276,-2.231866940 $6,-0.048613516 \backslash C, 0.7835480276,2.2318669406,0.048613516 \backslash C,-0.7835480276$ , 2. 2318669406,-0.048613516\C,-0.7835480276,-2.2318669406,0.048613516\C ,-0.2599031999,-1.9392084642,-2.3084587247\C,-0.2599031999,1.939208464 $2,2.3084587247 \backslash C, 0.2599031999,1.9392084642,-2.3084587247 \backslash C, 0.259903199$ 9,-1.9392084642,2.3084587247\C,1.0330693373,-1.6783889063,-1.553974684 $1 \backslash C, 1.0330693373,1.6783889063,1.5539746841 \backslash C,-1.0330693373,1.678388906$ 3,-1.5539746841\C,-1.0330693373,-1.6783889063,1.5539746841 \C, 1. 2776291 418,1.3788433159,-1.3270064355\C,1.2776291418,-1.3788433159,1.32700643 $55 \backslash C,-1.2776291418,-1.3788433159,-1.3270064355 \backslash C,-1.2776291418,1.37884$ 33159,1.3270064355\C,1.1817924631,-0.2353578958,-1.078959631\C,1.18179 24631,0.2353578958,1.078959631 \C, -1.1817924631,0.2353578958,-1.0789596 $31 \backslash \mathrm{C},-1.1817924631,-0.2353578958,1.078959631 \backslash \mathrm{H}, 1.1926654658,-3.2462024$ 25,0.0856276075\H,1.1926654658,3.246202425,-0.0856276075\H,-1.19266546 58, 3. $246202425,0.0856276075 \backslash$ Н, $-1.1926654658,-3.246202425,-0.0856276075$ $\backslash \mathrm{H},-0.4245756084,-3.0119641851,-2.4841175941 \backslash \mathrm{H},-0.4245756084,3.0119641$ 851,2.4841175941\H, 0.4245756084,3.0119641851,-2.4841175941 \H, 0.4245756 084,-3.0119641851,2.4841175941 \H,-0.2756629813,-1.4320017693,-3.280660 $5575 \backslash \mathrm{H},-0.2756629813,1.4320017693,3.2806605575 \backslash \mathrm{H}, 0.2756629813,1.432001$ 7693,-3.2806605575\H, 0.2756629813,-1.4320017693,3.2806605575\H,1.92726 94869,-2.092421735,-2.0362122766\H,1.9272694869,2.092421735,2.03621227 $66 \backslash \mathrm{H},-1.9272694869,2.092421735,-2.0362122766 \backslash \mathrm{H},-1.9272694869,-2.092421$ 735,2.0362122766\H,2.3109444969,1.6405989293,-1.5790770654 \H, 2.3109444 969,-1.6405989293,1.5790770654\H,-2.3109444969,-1.6405989293,-1.579077 $0654 \backslash \mathrm{H},-2.3109444969,1.6405989293,1.5790770654 \backslash \mathrm{H}, 2.1610272014,-0.39182$ $15554,-0.6531194849 \backslash \mathrm{H}, 2.1610272014,0.3918215554,0.6531194849 \backslash \mathrm{H},-2.1610$ $272014,0.3918215554,-0.6531194849 \backslash \mathrm{H},-2.1610272014,-0.3918215554,0.6531$ $194849 \backslash$ \Version=SGI-G94RevE. $2 \backslash$ State $=1-A \backslash H F=-814.1531347 \backslash$ RMSD $=4.887 e-09$ $\backslash$ RMSF=1.342e-06\Dipole=0.,0.,0. $\backslash \mathrm{PG}=\mathrm{D} 02$ [O(C1), X(C20H24)] <br>@

## 4-34 bioctaplane $\boldsymbol{D}_{\mathbf{2 h}}$

$1 \backslash 1 \backslash G I N C-P C \backslash F O p t \backslash R B 3 L Y P \backslash 6-31 G(d) \backslash C 21 H 24 \backslash R A S M U S S E N \backslash 30-S e p-1998 \backslash 0 \backslash \backslash \# P$ B3 LYP/6-31G* 5D OPT=(NEWESTMFC,TIGHT) MAXDISK=5242880000 NAME=RASMUSSEN GUESS=CHECK SCF=(VSHIFT,NOVARACC,DIRECT) GEOM=(CHECK,NODISTANCE,NOANGL

E,NODIHEDRAL) <br>Bioctaplane D2h<br>0,1\C,0.,0.,0.\C,0.,1.0961989911,1.238 $6821995 \backslash \mathrm{C}, 0 .,-1.0961989911,1.2386821995 \backslash \mathrm{C}, 0 ., 1.0961989911,-1.238682199$ $5 \backslash C, 0 .,-1.0961989911,-1.2386821995 \backslash C,-1.5184001718,-1.4282322081,1.176$ $1314713 \backslash C, 1.5184001718,1.4282322081,-1.1761314713 \backslash \mathrm{C}, 1.5184001718,-1.42$ $82322081,1.1761314713 \backslash C, 1.5184001718,1.4282322081,1.1761314713 \backslash \mathrm{C}, 1.518$ $4001718,-1.4282322081,-1.1761314713 \backslash C,-1.5184001718,1.4282322081,1.176$ $1314713 \backslash C,-1.5184001718,-1.4282322081,-1.1761314713 \backslash C,-1.5184001718,1$. $4282322081,-1.1761314713 \backslash C,-1.9324065216,-2.296116528,0 . \backslash C, 1.932406521$ $6,2.296116528,0 . \backslash C, 1.9324065216,-2.296116528,0 . \backslash \mathrm{C},-1.9324065216,2.2961$ $16528,0 . \backslash C,-2.1985083225,0.0 .7883277025 \backslash \mathrm{C}, 2.1985083225,0 .,-0.78832770$ $25 \backslash \mathrm{C}, 2.1985083225,0 ., 0.7883277025 \backslash \mathrm{C},-2.1985083225,0 .,-0.7883277025 \backslash \mathrm{H}, 0$ ., - $0.7369385652,-2.2536817357 \backslash \mathrm{H}, 0.0 .7369385652,-2.2536817357 \backslash \mathrm{H}, 0 .,-0$. $7369385652,2.2536817357 \backslash \mathrm{H}, 0.0 .7369385652,2.2536817357 \backslash \mathrm{H},-1.8903446814$ ,-1.8167254075,2.1361922464 \H, 1.8903446814,1.8167254075,-2.1361922464 \} H, 1. $8903446814,-1.8167254075,2.1361922464 \backslash \mathrm{H}, 1.8903446814,1.8167254075$, $2.1361922464 \backslash H, 1.8903446814,-1.8167254075,-2.1361922464 \backslash H,-1.890344681$ $4,1.8167254075,2.1361922464 \backslash \mathrm{H},-1.8903446814,-1.8167254075,-2.136192246$ $4 \backslash \mathrm{H},-1.8903446814,1.8167254075,-2.1361922464 \backslash \mathrm{H},-3.0199874206,-2.457469$ $1065,0 . \backslash H, 3.0199874206,2.4574691065,0 . \backslash H, 3.0199874206,-2.4574691065,0$. $\backslash \mathrm{H},-3.0199874206,2.4574691065,0 . \backslash \mathrm{H},-1.4426066204,-3.2773795704,0 . \backslash \mathrm{H}, 1$. $4426066204,3.2773795704,0 . \backslash H, 1.4426066204,-3.2773795704,0 . \backslash \mathrm{H},-1.442606$ $6204,3.2773795704,0 . \backslash \mathrm{H}, 3.2338540141,0 .,-1.1969555181 \backslash \mathrm{H},-3.2338540141,0$ ., 1.1969555181 \H,-3.2338540141,0., -1.1969555181 \H, 3.2338540141, 0., 1.19 $69555181 \backslash$ Version=SGI-G94RevE. $2 \backslash$ State=1-AG $\backslash \mathrm{HF}=-814.0945985 \backslash \mathrm{RMSD}=3.698 \mathrm{e}$ $-09 \backslash \mathrm{RMSF}=2.388 \mathrm{e}-06 \backslash \mathrm{Dipole}=0 ., 0 ., 0 . \backslash \mathrm{PG}=\mathrm{D} 02 \mathrm{H} \quad\left[\mathrm{O}(\mathrm{C} 1), \mathrm{SG}(\mathrm{C} 4 \mathrm{H} 4), \mathrm{SG} \mathrm{I}^{\prime}(\mathrm{C} 4 \mathrm{H} 4), \mathrm{S}\right.$ G" (C4H8) , X (C8H8) ] <br>@

## 4-27 octaplane (A-type) $\boldsymbol{S}_{\mathbf{4}}$

$1 \backslash 1 \backslash G I N C-R S C Q C 9 \backslash F O p t \backslash R B 3 L Y P \backslash 6-31 G(d) \backslash C 21 H 28 \backslash R A S M U S S E N \backslash 01-O c t-1998 \backslash 0 \backslash \backslash \#$ P B3LYP/6-31G* 5D OPT= (READFC, TIGHT) GUESS=CHECK SCF= (VSHIFT, NOVARACC, DIRECT) MAXDISK=1048576000 GEOM= (CHECK,NODISTANCE,NOANGLE,NODIHEDRAL) NAME=RASMUSSEN <br>Octaplane $S 4 \backslash \backslash 0,1 \backslash C, 0 ., 0 ., 0 . \backslash C, 1.5924922976,0.00648576$ $31,0.1449040324 \backslash \mathrm{C},-0.0064857631,1.5924922976,-0.1449040324 \backslash \mathrm{C},-1.592492$ $2976,-0.0064857631,0.1449040324 \backslash C, 0.0064857631,-1.5924922976,-0.144904$ $0324 \backslash C, 1.8612546156,0.404559246,1.5855089875 \backslash C,-0.404559246,1.86125461$ $56,-1.5855089875 \backslash C,-1.8612546156,-0.404559246,1.5855089875 \backslash C, 0.4045592$ $46,-1.8612546156,-1.5855089875 \backslash C, 1.8494818782,0.3374895529,-1.42355058$ $02 \backslash C,-0.3374895529,1.8494818782,1.4235505802 \backslash C,-1.8494818782,-0.337489$ $5529,-1.4235505802 \backslash C, 0.3374895529,-1.8494818782,1.4235505802 \backslash C, 1.43902$ 73195,-1.0007842564,2.1988114825\C,1.0007842564,1.4390273195,-2.198811 $4825 \backslash \mathrm{C},-1.4390273195,1.0007842564,2.1988114825 \backslash \mathrm{C},-1.0007842564,-1.4390$ $273195,-2.1988114825 \backslash C,-1.649182693,1.0755455881,-2.0678642953 \backslash C,-1.07$ $55455881,-1.649182693,2.0678642953 \backslash C, 1.649182693,-1.0755455881,-2.0678$ $642953 \backslash \mathrm{C}, 1.0755455881,1.649182693,2.0678642953 \backslash \mathrm{H}, 2.0134788048,-1.00286$ $21362,0.1335328689 \backslash \mathrm{H}, 1.0028621362,2.0134788048,-0.1335328689 \backslash \mathrm{H},-2.0134$ $788048,1.0028621362,0.1335328689 \backslash \mathrm{H},-1.0028621362,-2.0134788048,-0.1335$ $328689 \backslash \mathrm{H}, 2.9221533808,0.5612251697,1.8412515615 \backslash \mathrm{H},-0.5612251697,2.9221$ $533808,-1.8412515615 \backslash \mathrm{H},-2.9221533808,-0.5612251697,1.8412515615 \backslash \mathrm{H}, 0.56$ $12251697,-2.9221533808,-1.8412515615 \backslash \mathrm{H},-0.5996970943,2.9070524233,1.57$ $06589104 \backslash \mathrm{H},-2.9070524233,-0.5996970943,-1.5706589104 \backslash \mathrm{H}, 0.5996970943,-2$ $.9070524233,1.5706589104 \backslash \mathrm{H}, 2.9070524233,0.5996970943,-1.5706589104 \backslash \mathrm{H}, 1$ $.1056171277,-0.8839066315,3.2380403627 \backslash \mathrm{H}, 2.3574395984,-1.600124521,2.2$
$442062938 \backslash \mathrm{H}, 0.8839066315,1.1056171277,-3.2380403627 \backslash \mathrm{H}, 1.600124521,2.35$ $74395984,-2.2442062938 \backslash \mathrm{H},-1.1056171277,0.8839066315,3.2380403627 \backslash \mathrm{H},-2$. $3574395984,1.600124521,2.2442062938 \backslash \mathrm{H},-0.8839066315,-1.1056171277,-3.2$ $380403627 \backslash \mathrm{H},-1.600124521,-2.3574395984,-2.2442062938 \backslash \mathrm{H},-1.6300221965,0$ $.991843436,-3.1626513541 \backslash \mathrm{H},-2.5356457911,1.6803201324,-1.8304660102 \backslash \mathrm{H}$, $-0.991843436,-1.6300221965,3.1626513541 \backslash \mathrm{H},-1.6803201324,-2.5356457911$, $1.8304660102 \backslash \mathrm{H}, 1.6300221965,-0.991843436,-3.1626513541 \backslash \mathrm{H}, 2.5356457911$, $-1.6803201324,-1.8304660102 \backslash \mathrm{H}, 0.991843436,1.6300221965,3.1626513541 \backslash \mathrm{H}$, $1.6803201324,2.5356457911,1.8304660102 \backslash \backslash V e r s i o n=I B M-R S 6000-G 94 R e v E .1 \backslash H$
 (C1) , X (C2OH2 8 ) ] <br>@

## 4-27 octaplane (A-type) $\quad \boldsymbol{C}_{4 \mathrm{~h}}$

$1 \backslash 1 \backslash G I N C-P C \backslash F O p t \backslash R B 3 L Y P \backslash 6-31 G(d) \backslash C 21 H 28 \backslash R A S M U S S E N \backslash 01-O c t-1998 \backslash 0 \backslash \backslash \# P$ B3 LYP/6-31G* 5D GUESS=CHECK SCF= (VSHIFT,NOVARACC,DIRECT) MAXDISK=5242880 000 OPT= (NEWESTMFC,TIGHT) NAME=RASMUSSEN GEOM= (CHECK, NODISTANCE,NOANGL E, NODIHEDRAL $\backslash \backslash$ Octaplane $C 4 h \backslash \backslash 0,1 \backslash C, 0 ., 0 ., 0 . \backslash C, 0.3227232345,1.56290705$ $31,0 . \backslash C,-0.3227232345,-1.5629070531,0 . \backslash C, 1.5629070531,-0.3227232345,0$. $\backslash C,-1.5629070531,0.3227232345,0 . \backslash C, 0.7175346531,1.7467191957,1.4932468$ $342 \backslash \mathrm{C},-0.7175346531,-1.7467191957,1.4932468342 \backslash \mathrm{C}, 1.7467191957$, - 0.71753 $46531,-1.4932468342 \backslash C,-1.7467191957,0.7175346531,-1.4932468342 \backslash C, 0.717$ 5346531,1.7467191957,-1.4932468342\C, -0.7175346531,-1.7467191957,-1.49 $32468342 \backslash \mathrm{C}, 1.7467191957,-0.7175346531,1.4932468342 \backslash \mathrm{C},-1.7467191957,0.7$ $175346531,1.4932468342 \backslash C, 0.7268359382,-1.7182003491,2.1247678824 \backslash C, 1.7$ $182003491,0.7268359382,-2.1247678824 \backslash C,-0.7268359382,1.7182003491,2.12$ $47678824 \backslash \mathrm{C},-1.7182003491,-0.7268359382,-2.1247678824 \backslash \mathrm{C}, 1.7182003491,0$. $7268359382,2.1247678824 \backslash C,-0.7268359382,1.7182003491,-2.1247678824 \backslash C$, -$1.7182003491,-0.7268359382,2.1247678824 \backslash \mathrm{C}, 0.7268359382,-1.7182003491,-$ $2.1247678824 \backslash \mathrm{H},-0.5974854084,2.1535191013,0 . \backslash \mathrm{H}, 0.5974854084,-2.1535191$ 013, 0. \H, 2.1535191013, 0.5974854084, 0. \H, -2.1535191013, -0.5974854084, 0. $\backslash \mathrm{H},-2.755833629,1.1182492205,1.6990129514 \backslash \mathrm{H},-1.1182492205,-2.755833629$ , - $1.6990129514 \backslash \mathrm{H}, 2.755833629,-1.1182492205,1.6990129514 \backslash \mathrm{H}, 1.1182492205$ , 2.755833629,-1.6990129514 \H, 1.1182492205,2.755833629,1.6990129514\H, -$1.1182492205,-2.755833629,1.6990129514 \backslash H,-2.755833629,1.1182492205$, -1. $6990129514 \backslash \mathrm{H}, 2.755833629,-1.1182492205,-1.6990129514 \backslash \mathrm{H}, 1.1375153194,-2$ $.7343932756,-2.0361428429 \backslash \mathrm{H}, 2.7343932756,1.1375153194,2.0361428429 \backslash \mathrm{H}$, -$1.1375153194,2.7343932756,-2.0361428429 \backslash H,-2.7343932756,-1.1375153194$, $2.0361428429 \backslash \mathrm{H}, 1.1375153194,-2.7343932756,2.0361428429 \backslash \mathrm{H}, 2.7343932756$, $1.1375153194,-2.0361428429 \backslash \mathrm{H},-1.1375153194,2.7343932756,2.0361428429 \backslash \mathrm{H}$ , - $2.7343932756,-1.1375153194,-2.0361428429 \backslash \mathrm{H}, 0.6649584358,-1.515533894$ $2,3.2024115245 \backslash \mathrm{H}, 1.5155338942,0.6649584358,-3.2024115245 \backslash \mathrm{H},-0.66495843$ $58,1.5155338942,3.2024115245 \backslash \mathrm{H},-1.5155338942,-0.6649584358,-3.20241152$ $45 \backslash \mathrm{H}, 1.5155338942,0.6649584358,3.2024115245 \backslash \mathrm{H}, 0.6649584358,-1.51553389$ $42,-3.2024115245 \backslash \mathrm{H},-0.6649584358,1.5155338942,-3.2024115245 \backslash \mathrm{H},-1.51553$ $38942,-0.6649584358,3.2024115245 \backslash \backslash V e r s i o n=S G I-G 94 R e v E .2 \backslash H F=-816.637084$ $2 \backslash \mathrm{RMSD}=8.425 \mathrm{e}-09 \backslash \mathrm{RMSF}=5.458 \mathrm{e}-06 \backslash \mathrm{Dipole}=0 ., 0 ., 0 . \backslash \mathrm{PG}=\mathrm{C} 04 \mathrm{H} \quad[\mathrm{O}(\mathrm{C} 1), \mathrm{SGH}(\mathrm{C} 4 \mathrm{H}$ 4) , X (C16H24)] <br>@

## 4-35 octaplane (B-type) $\quad \boldsymbol{D}_{\mathbf{2}}$

$1 \backslash 1 \backslash G I N C-P C \backslash F O p t \backslash R B 3 L Y P \backslash 6-31 G(d) \backslash C 21 H 28 \backslash R A S M U S S E N \backslash 28-S e p-1998 \backslash 0 \backslash \backslash \# P$ B3 LYP/6-31G* 5D OPT= (READFC,TIGHT) MAXDISK=5242880000 GUESS=CHECK SCF=(V SHIFT, NOVARACC,DIRECT) NAME=RASMUSSEN GEOM= (CHECK,NODISTANCE,NOANGLE,N

ODIHEDRAL) <br>Octaplane 5D D2 <br>0,1\C,0.,0.,0.\C,-1.1962958272,-1.0933901 $18,0.1788277395 \backslash C, 1.1962958272,-1.093390118,-0.1788277395 \backslash \mathrm{C}, 1.19629582$ $72,1.093390118,0.1788277395 \backslash C,-1.1962958272,1.093390118,-0.1788277395 \backslash$ C, $-1.1991321765,-1.4962724871,1.6444180306 \backslash C, 1.1991321765,-1.496272487$ $1,-1.6444180306 \backslash C, 1.1991321765,1.4962724871,1.6444180306 \backslash \mathrm{C},-1.19913217$ $65,1.4962724871,-1.6444180306 \backslash C,-1.2953886733,-1.3862780044,-1.4093166$ $894 \backslash C, 1.2953886733,-1.3862780044,1.4093166894 \backslash C, 1.2953886733,1.3862780$ $044,-1.4093166894 \backslash C,-1.2953886733,1.3862780044,1.4093166894 \backslash \mathrm{C},-1.61626$ 57483,-0.0274985818,2.2113833593\C,1.6162657483,-0.0274985818,-2.21138 $33593 \backslash C, 1.6162657483,0.0274985818,2.2113833593 \backslash C,-1.6162657483,0.02749$ 85818,-2.2113833593\C,-0.1234946295,-2.1062984588,-2.066619391\C,-0.12 34946295,2.1062984588,2.066619391\C,0.1234946295,2.1062984588,-2.06661 $9391 \backslash \mathrm{C}, 0.1234946295,-2.1062984588,2.066619391 \backslash \mathrm{H},-2.2008612327,-0.69759$ $82332,0.2109824492 \backslash \mathrm{H}, 2.2008612327,-0.6975982332,-0.2109824492 \backslash \mathrm{H}, 2.2008$ 612327,0.6975982332,0.2109824492\H,-2.2008612327,0.6975982332,-0.21098 $24492 \backslash \mathrm{H},-2.0206269005,-2.1732121099,1.9324966649 \backslash \mathrm{H}, 2.0206269005,-2.173$ 2121099,-1.9324966649\H,2.0206269005,2.1732121099,1.9324966649\H,-2.02 06269005,2.1732121099,-1.9324966649\H,2.1974219611,-1.9940174845,1.567 $2359962 \backslash \mathrm{H}, 2.1974219611,1.9940174845,-1.5672359962 \backslash \mathrm{H},-2.1974219611,1.99$ 40174845,1.5672359962 \Н, -2.1974219611,-1.9940174845,-1.5672359962 \H,-1 $.228431252,0.1033727714,3.2291489105 \backslash \mathrm{H},-2.708687033,-0.0688154523,2.31$ $38980697 \backslash \mathrm{H}, 1.228431252,0.1033727714,-3.2291489105 \backslash \mathrm{H}, 2.708687033,-0.068$ $8154523,-2.3138980697 \backslash \mathrm{H}, 1.228431252,-0.1033727714,3.2291489105 \backslash \mathrm{H}, 2.708$ 687033,0.0688154523,2.3138980697 $\backslash \mathrm{H},-1.228431252,-0.1033727714,-3.22914$ $89105 \backslash \mathrm{H},-2.708687033,0.0688154523,-2.3138980697 \backslash \mathrm{H},-0.2455431671,-2.112$ 1180156,-3.1597912592 \H,-0.1209216075,-3.1580983919,-1.7465102582 \H, - 0 . $2455431671,2.1121180156,3.1597912592 \backslash \mathrm{H},-0.1209216075,3.1580983919,1.7$ $465102582 \backslash \mathrm{H}, 0.2455431671,2.1121180156,-3.1597912592 \backslash \mathrm{H}, 0.1209216075,3.1$ 580983919,-1.7465102582\Н, 0.2455431671,-2.1121180156,3.1597912592\н, 0. 1209216075,-3.1580983919,1.7465102582<br>Version=SGI-G94RevE. $2 \backslash$ State=1-A $\backslash H F=-816.5569597 \backslash R M S D=7.279 e-09 \backslash R M S F=1.203 e-06 \backslash D i p o l e=0 ., 0 ., 0 . \backslash P G=D 02$ [ $\mathrm{O}(\mathrm{C} 1), \mathrm{X}(\mathrm{C} 20 \mathrm{H} 28)] \backslash \backslash$ @

## 4-35 octaplane (B-type) $\boldsymbol{D}_{\mathbf{2 h}}$

$1 \backslash 1 \backslash G I N C-P C \backslash F O p t \backslash R B 3 L Y P \backslash 6-31 G(d) \backslash C 21 H 28 \backslash R A S M U S S E N \backslash 30-S e p-1998 \backslash 0 \backslash \backslash \# P$ B3 LYP/6-31G* 5D OPT=(NEWESTMFC,TIGHT) MAXDISK=5242880000 GUESS=CHECK SCF = (VSHIFT, NOVARACC,DIRECT) NAME=RASMUSSEN GEOM=(CHECK,NODISTANCE,NOANGL E,NODIHEDRAL) <br>Octaplane 5D D2h $\backslash \backslash 0,1 \backslash C, 0 ., 0 ., 0 . \backslash C, 0 ., 1.0926184422,1.23$ $07548643 \backslash C, 0 ., 1.0926184422,-1.2307548643 \backslash C, 0 .,-1.0926184422,-1.2307548$ $643 \backslash C, 0 .,-1.0926184422,1.2307548643 \backslash C,-1.5128331978,1.4219780935,1.261$ $5882138 \backslash \mathrm{C}, 1.5128331978,1.4219780935,-1.2615882138 \backslash \mathrm{C},-1.5128331978,-1.4$ $219780935,-1.2615882138 \backslash C, 1.5128331978,-1.4219780935,1.2615882138 \backslash \mathrm{C}, 1$. 5128331978,1.4219780935,1.2615882138\C,-1.5128331978,1.4219780935,-1.2 $615882138 \backslash C, 1.5128331978,-1.4219780935,-1.2615882138 \backslash C,-1.5128331978,-$ $1.4219780935,1.2615882138 \backslash \mathrm{C},-2.1770826768,0 ., 1.6706792543 \backslash \mathrm{C}, 2.17708267$ $68,0 ., 1.6706792543 \backslash C,-2.1770826768,0 .,-1.6706792543 \backslash C, 2.1770826768,0 .$, $-1.6706792543 \backslash C,-2.0689128103,2.0602387398,0 . \backslash C, 2.0689128103,2.0602387$ $398,0 . \backslash C,-2.0689128103,-2.0602387398,0 . \backslash C, 2.0689128103,-2.0602387398,0$ . \H, 0., 0.7339026451, 2.2515484216\H, 0., 0.7339026451, -2.2515484216\H, 0., $-0.7339026451,-2.2515484216 \backslash \mathrm{H}, 0 .,-0.7339026451,2.2515484216 \backslash \mathrm{H},-1.74758$ 20356,2.091899458,2.1102192088\H,1.7475820356,2.091899458,-2.110219208 $8 \backslash H,-1.7475820356,-2.091899458,-2.1102192088 \backslash H, 1.7475820356,-2.0918994$

58, 2. $1102192088 \backslash \mathrm{H},-1.7475820356,2.091899458,-2.1102192088 \backslash \mathrm{H}, 1.74758203$ $56,-2.091899458,-2.1102192088 \backslash \mathrm{H},-1.7475820356,-2.091899458,2.110219208$ $8 \backslash H, 1.7475820356,2.091899458,2.1102192088 \backslash H,-3.2145234702,0 ., 1.3133608$ $416 \backslash \mathrm{H},-2.245941067,0 ., 2.7693678269 \backslash \mathrm{H}, 3.2145234702,0 ., 1.3133608416 \backslash \mathrm{H}, 2$. $245941067,0 ., 2.7693678269 \backslash \mathrm{H},-3.2145234702,0 .,-1.3133608416 \backslash \mathrm{H},-2.245941$ $067,0 .,-2.7693678269 \backslash H, 3.2145234702,0 .,-1.3133608416 \backslash H, 2.245941067,0$. , $-2.7693678269 \backslash \mathrm{H},-3.1684014793,2.0196304299,0 . \backslash \mathrm{H},-1.7972033157,3.126029$ $0143,0 . \backslash \mathrm{H}, 3.1684014793,2.0196304299,0 . \backslash \mathrm{H}, 1.7972033157,3.1260290143,0 . \backslash$ $\mathrm{H},-3.1684014793,-2.0196304299,0 . \backslash \mathrm{H},-1.7972033157,-3.1260290143,0 . \backslash \mathrm{H}, 3$. 1684014793,-2.0196304299, 0. \H, 1.7972033157,-3.1260290143,0. <br>Version=S GI-G94RevE. $2 \backslash$ State=1-AG $\backslash \mathrm{HF}=-816.5278794 \backslash \mathrm{RMSD}=5.416 e-09 \backslash \mathrm{RMSF}=3.878 \mathrm{e}-07 \backslash$ Dipole=0., 0., 0. \PG=D02H [O(C1), SG(C4H4), SG' (C4H8), SG" (C4H8) , X (C8H8)] <br> @

## 4-36 binonaplane $\boldsymbol{D}_{\mathbf{2}}$

$1 \backslash 1 \backslash G I N C-P C \backslash F O p t \backslash R B 3 L Y P \backslash 6-31 G(d) \backslash C 23 H 28 \backslash R A S M U S S E N \backslash 02-O c t-1998 \backslash 0 \backslash \backslash \# P$ B3 LYP/6-31G* 5D OPT=(READFC,TIGHT) NAME=RASMUSSEN MAXDISK=5242880000 GUE SS=CHECK SCF=(VSHIFT,NOVARACC,DIRECT) GEOM=(CHECK,NODISTANCE,NOANGLE,N ODIHEDRAL) <br>Binonaplane $\mathrm{D} 2 \backslash \backslash 0,1 \backslash \mathrm{C}, 0.0 .0 .0 . \backslash \mathrm{C}, 1.1979412572,0.2117415422$ ,-1.0679747858\C,1.1979412572,-0.2117415422,1.0679747858\C,-1.19794125 $72,-0.2117415422,-1.0679747858 \backslash C,-1.1979412572,0.2117415422,1.06797478$ 58\C,1.2266604396,-2.3378697666,0.0924746488\C,1.2266604396,2.33786976 66,-0.0924746488\C,-1.2266604396,2.3378697666,0.0924746488\C,-1.226660 4396,-2.3378697666,-0.0924746488\C,0.227446245,-1.8949219054,-2.283932 $0819 \backslash \mathrm{C}, 0.227446245,1.8949219054,2.2839320819 \backslash \mathrm{C},-0.227446245,1.89492190$ $54,-2.2839320819 \backslash C,-0.227446245,-1.8949219054,2.2839320819 \backslash \mathrm{C}, 1.3145390$ $478,-1.3868861732,-1.3446993413 \backslash C, 1.3145390478,1.3868861732,1.34469934$ $13 \backslash C,-1.3145390478,1.3868861732,-1.3446993413 \backslash C,-1.3145390478,-1.38688$ 61732,1.3446993413\C,1.1003830883,1.6303199691,-1.5841795815\C,1.10038 30883,-1.6303199691,1.5841795815\C,-1.1003830883,-1.6303199691,-1.5841 $795815 \backslash \mathrm{C},-1.1003830883,1.6303199691,1.5841795815 \backslash \mathrm{C}, 0 ., 3.2555138178,0 . \backslash$ C, 0.,-3.2555138178, 0. \H, 0.0320457871,-3.9224684569,-0.8672306926\H, 0.0 320457871,3.9224684569,0.8672306926\H,-0.0320457871,3.9224684569,-0.86 $72306926 \backslash \mathrm{H},-0.0320457871,-3.9224684569,0.8672306926 \backslash \mathrm{H}, 2.1480292934,-2$. 9341346037,0.0858753471\H,2.1480292934,2.9341346037,-0.0858753471\H,-2 $.1480292934,2.9341346037,0.0858753471 \backslash \mathrm{H},-2.1480292934,-2.9341346037,-0$ $.0858753471 \backslash \mathrm{H}, 0.3725735244,-2.9468438684,-2.5572970641 \backslash \mathrm{H}, 0.3725735244$, $2.9468438684,2.5572970641 \backslash \mathrm{H},-0.3725735244,2.9468438684,-2.5572970641 \backslash \mathrm{H}$ , - 0. $3725735244,-2.9468438684,2.5572970641 \backslash \mathrm{H}, 0.2495898074,-1.3288553351$ ,-3.2247619761 \H, 0.2495898074,1.3288553351,3.2247619761 \H, -0.249589807 $4,1.3288553351,-3.2247619761 \backslash H,-0.2495898074,-1.3288553351,3.224761976$ $1 \backslash \mathrm{H}, 2.3083634687,-1.5794750851,-1.7678406042 \backslash \mathrm{H}, 2.3083634687,1.57947508$ $51,1.7678406042 \backslash \mathrm{H},-2.3083634687,1.5794750851,-1.7678406042 \backslash \mathrm{H},-2.308363$ 4687,-1.5794750851,1.7678406042 \H, 1.9518138733,1.95261724,-2.202121619 $2 \backslash \mathrm{H}, 1.9518138733,-1.95261724,2.2021216192 \backslash \mathrm{H},-1.9518138733,-1.95261724$, $-2.2021216192 \backslash \mathrm{H},-1.9518138733,1.95261724,2.2021216192 \backslash \mathrm{H}, 2.1833064452,0$ $.351367271,-0.6538019829 \backslash \mathrm{H}, 2.1833064452,-0.351367271,0.6538019829 \backslash \mathrm{H},-2$ $.1833064452,-0.351367271,-0.6538019829 \backslash \mathrm{H},-2.1833064452,0.351367271,0.6$ $538019829 \backslash \backslash$ Version=SGI-G94RevE.2 ${ }^{\text {State }}=1-A \backslash H F=-892.7549733 \backslash$ RMSD $=7.667 \mathrm{e}$ $-09 \backslash$ RMSF=1.302e-06\Dipole=0., 0., 0. $\backslash \mathrm{PG}=\mathrm{D} 02$ [ $\mathrm{O}(\mathrm{C} 1), \mathrm{C} 2 \mathrm{l}(\mathrm{C} 1 . \mathrm{C} 1), \mathrm{X}(\mathrm{C} 20 \mathrm{H} 28)]$ <br>@

## 4-36 binonaplane $\boldsymbol{D}_{\mathbf{2 h}}$

$1 \backslash 1 \backslash G I N C-P C \backslash F O p t \backslash R B 3 L Y P \backslash 6-31 G(d) \backslash C 23 H 28 \backslash R A S M U S S E N \backslash 03-O c t-1998 \backslash 0 \backslash \backslash \# P$ B3 LYP/6-31G* 5D OPT=(NEWESTMFC,TIGHT) MAXDISK=5242880000 NAME=RASMUSSEN GUESS=CHECK SCF=(VSHIFT,NOVARACC,DIRECT) GEOM=(CHECK,NODISTANCE,NOANGL E,NODIHEDRAL) <br>Binonaplane $D 2 h \backslash \backslash 0,1 \backslash C, 0 ., 0 ., 0 . \backslash C, 0 ., 1.0770677931,1.255$ $2530666 \backslash \mathrm{C}, 0 .,-1.0770677931,1.2552530666 \backslash \mathrm{C}, 0.1 .0770677931,-1.255253066$ $6 \backslash C, 0 .,-1.0770677931,-1.2552530666 \backslash C, 1.495849025,1.4501490941,1.228465$ $261 \backslash C,-1.495849025,-1.4501490941,-1.228465261 \backslash C,-1.495849025,1.4501490$ $941,1.228465261 \backslash C,-1.495849025,-1.4501490941,1.228465261 \backslash C,-1.49584902$ $5,1.4501490941,-1.228465261 \backslash C, 1.495849025,-1.4501490941,1.228465261 \backslash C$, $1.495849025,1.4501490941,-1.228465261 \backslash C, 1.495849025,-1.4501490941,-1.2$ $28465261 \backslash C, 1.8700935684,2.272417991,0 . \backslash C,-1.8700935684,-2.272417991,0$. $\backslash C,-1.8700935684,2.272417991,0 . \backslash C, 1.8700935684,-2.272417991,0 . \backslash C, 2.299$ $7172467,0 ., 1.2441790088 \backslash C,-2.2997172467,0 .,-1.2441790088 \backslash C,-2.29971724$ 67,0.,1.2441790088\C,2.2997172467,0.,-1.2441790088\C,-3.2110974826,0., $0 . \backslash \mathrm{C}, 3.2110974826,0.0 . \backslash \mathrm{H}, 1.7818029727,1.9985979757,2.1434761255 \backslash \mathrm{H},-1$. 7818029727,-1.9985979757,-2.1434761255\H,-1.7818029727,1.9985979757,2. $1434761255 \backslash \mathrm{H},-1.7818029727,-1.9985979757,2.1434761255 \backslash \mathrm{H},-1.7818029727$, $1.9985979757,-2.1434761255 \backslash \mathrm{H}, 1.7818029727,-1.9985979757,2.1434761255 \backslash \mathrm{H}$ ,1.7818029727,1.9985979757,-2.1434761255\Н,1.7818029727,-1.9985979757, $-2.1434761255 \backslash \mathrm{H}, 1.2944089306,3.2072495835,0 . \backslash \mathrm{H},-1.2944089306,-3.207249$ 5835, 0. \H, -1.2944089306,3.2072495835, 0. \H, 1.2944089306,-3.2072495835, 0 . \H, 2. $9243930202,2.5691397417,0 . \backslash H,-2.9243930202,-2.5691397417,0 . \backslash \mathrm{H},-2$ . $9243930202,2.5691397417,0 . \backslash \mathrm{H}, 2.9243930202,-2.5691397417,0 . \backslash \mathrm{H},-2.93148$ $41153,0 .,-2.1466213892 \backslash \mathrm{H}, 2.9314841153,0 ., 2.1466213892 \backslash \mathrm{H}, 2.9314841153,0$ ., $-2.1466213892 \backslash \mathrm{H},-2.9314841153,0 ., 2.1466213892 \backslash \mathrm{H}, 3.8814709073,0.86416$ $37685,0 . \backslash \mathrm{H},-3.8814709073,-0.8641637685,0 . \backslash \mathrm{H},-3.8814709073,0.8641637685$ , $0 . \backslash \mathrm{H}, 3.8814709073,-0.8641637685,0 . \backslash \mathrm{H}, 0 .,-0.7260203977,-2.2739887512 \backslash \mathrm{H}$ , 0., 0.7260203977,-2.2739887512\H,0.,-0.7260203977, 2.2739887512\H, 0., 0. 7260203977,2.2739887512<br>Version=SGI-G94RevE.2\State=1-AG\HF=-892.7118 $497 \backslash \mathrm{RMSD}=6.129 \mathrm{e}-09 \backslash \mathrm{RMSF}=7.942 \mathrm{e}-07 \backslash \mathrm{Dipole}=0.0 .0 . \backslash \mathrm{PG}=\mathrm{D} 02 \mathrm{H} \quad[\mathrm{O}(\mathrm{C} 1)$, C2 (C1 . C1) , SG (C4H4), SG'(C4H4),SG" (C4H12), X(C8H8)] <br>@

## Spiroalkaplanes

## 4-39 spiro[2.2]hexaplane <br> $D_{2}$

$1 \backslash 1 \backslash$ MHPCC-FR12N05 $\$ FOpt $\backslash$ RB3LYP $\backslash 6-31 G(d) \backslash C 17 H 16 \backslash R A S M U S S E N \backslash 30-S e p-1998 \backslash 0$ <br>\#P B3LYP/6-31G* 5D FOPT=(READFC,TIGHT) SCF=(VSHIFT,NOVARACC,DIRECT) GUESS=CHECK NAME=RASMUSSEN GEOM= (CHECK,NODISTANCE,NOANGLE,NODIHEDRAL) TEST <br>Spiro[2.2]hexaplane $\mathrm{D} 2 \backslash \backslash 0,1 \backslash \mathrm{C}, 0.0 .0 .0 . \backslash \mathrm{C},-0.7201724333,-1.267774$ $385,0.1055631101 \backslash C, 0.7201724333,-1.267774385,-0.1055631101 \backslash C, 0.7201724$ $333,1.267774385,0.1055631101 \backslash C,-0.7201724333,1.267774385,-0.1055631101$ $\backslash C,-0.7428360132,-1.3396979929,1.63543201 \backslash C, 0.7428360132,-1.3396979929$ , $-1.63543201 \backslash C, 0.7428360132,1.3396979929,1.63543201 \backslash C,-0.7428360132,1$. $3396979929,-1.63543201 \backslash C,-0.890233517,-1.2661313614,-1.5353338318 \backslash C, 0$. 890233517,-1.2661313614,1.5353338318\C,0.890233517,1.2661313614,-1.535 $3338318 \backslash C,-0.890233517,1.2661313614,1.5353338318 \backslash C,-1.4287503612,-0.04$ $52885448,2.1905378526 \backslash C, 1.4287503612,-0.0452885448,-2.1905378526 \backslash C, 1.4$ $287503612,0.0452885448,2.1905378526 \backslash \mathrm{C},-1.4287503612,0.0452885448,-2.19$ $05378526 \backslash \mathrm{H},-1.0998716415,-2.2370477604,2.1699676009 \backslash \mathrm{H}, 1.0998716415,-2$. $2370477604,-2.1699676009 \backslash \mathrm{H}, 1.0998716415,2.2370477604,2.1699676009 \backslash \mathrm{H},-1$ $.0998716415,2.2370477604,-2.1699676009 \backslash H, 1.3817369928,-2.1488967247,1$.
$965059019 \backslash \mathrm{H}, 1.3817369928,2.1488967247,-1.965059019 \backslash \mathrm{H},-1.3817369928,2.1$ $488967247,1.965059019 \backslash \mathrm{H},-1.3817369928,-2.1488967247,-1.965059019 \backslash \mathrm{H},-1$. $2728276729,0.0340228391,3.276742992 \backslash \mathrm{H},-2.5157026749,-0.1266677698,2.04$ $35026648 \backslash \mathrm{H}, 1.2728276729,0.0340228391,-3.276742992 \backslash \mathrm{H}, 2.5157026749,-0.12$ $66677698,-2.0435026648 \backslash \mathrm{H}, 1.2728276729,-0.0340228391,3.276742992 \backslash \mathrm{H}, 2.51$ $57026749,0.1266677698,2.0435026648 \backslash \mathrm{H},-1.2728276729,-0.0340228391,-3.27$ $6742992 \backslash \mathrm{H},-2.5157026749,0.1266677698,-2.0435026648 \backslash \backslash$ Version=IBM-RS6000 -G94RevE. $2 \backslash$ State=1-A $\backslash \mathrm{HF}=-656.8967398 \backslash \mathrm{RMSD}=5.049 \mathrm{e}-09 \backslash \mathrm{RMSF}=7.725 \mathrm{e}-07 \backslash \mathrm{Dip}$ ole=0.,0., 0.\PG=D02 [O(C1), X(C16H16)] <br>@

## 4-39 spiro[2.2]hexaplane $\quad \boldsymbol{D}_{\mathbf{2 h}}$

$1 \backslash 1 \backslash$ MHPCC-FR3N03 \FOpt \RB3LYP\6-31G(d) \C17H16\RASMUSSEN $\backslash 30-$ Sep-1998\0\} <br>\#P B3LYP/6-31G* 5D FOPT= (NEWESTMFC, TIGHT) SCF= (VSHIFT, NOVARACC, DIRECT ) GUESS=CHECK NAME=RASMUSSEN GEOM=(CHECK,NODISTANCE,NOANGLE, NODIHEDRAL ) TEST<br>Spiro[2.2]hexaplane $\mathrm{D} 2 \mathrm{~h} \backslash \backslash 0,1 \backslash \mathrm{C}, 0 ., 0.0 . \backslash \mathrm{C},-0.7190774954,-1.275$ $9706433,0 . \backslash C, 0.7190774954,-1.2759706433,0 . \backslash C, 0.7190774954,1.2759706433$ , 0. \C, - 0.7190774954, 1.2759706433, 0. \C, - 0. $8160470596,-1.3048384214,1.57$ $89261137 \backslash C, 0.8160470596,-1.3048384214,-1.5789261137 \backslash C, 0.8160470596,1.3$ $048384214,1.5789261137 \backslash C,-0.8160470596,1.3048384214,-1.5789261137 \backslash C,-0$ $.8160470596,-1.3048384214,-1.5789261137 \backslash C, 0.8160470596,-1.3048384214,1$ $.5789261137 \backslash C, 0.8160470596,1.3048384214,-1.5789261137 \backslash C,-0.8160470596$, $1.3048384214,1.5789261137 \backslash C,-1.4334083823,0 ., 2.1784087569 \backslash C,-1.4334083$ 823, 0., - $2.1784087569 \backslash \mathrm{C}, 1.4334083823,0 ., 2.1784087569 \backslash \mathrm{C}, 1.4334083823$, 0 . , $-2.1784087569 \backslash \mathrm{H},-1.2452853467,-2.1950604949,2.0728115959 \backslash \mathrm{H}, 1.245285346$ $7,-2.1950604949,-2.0728115959 \backslash H, 1.2452853467,2.1950604949,2.0728115959$ $\backslash \mathrm{H},-1.2452853467,2.1950604949,-2.0728115959 \backslash \mathrm{H}, 1.2452853467$, - 2.19506049 $49,2.0728115959 \backslash \mathrm{H}, 1.2452853467,2.1950604949,-2.0728115959 \backslash \mathrm{H},-1.2452853$ $467,2.1950604949,2.0728115959 \backslash \mathrm{H},-1.2452853467,-2.1950604949,-2.0728115$ $959 \backslash \mathrm{H},-1.2747212942,0 ., 3.2668454102 \backslash \mathrm{H},-2.5242820181,0 ., 2.0325055946 \backslash \mathrm{H}$, $-1.2747212942,0 .,-3.2668454102 \backslash \mathrm{H},-2.5242820181,0 .,-2.0325055946 \backslash \mathrm{H}, 1.27$ $47212942,0 ., 3.2668454102 \backslash \mathrm{H}, 2.5242820181,0 ., 2.0325055946 \backslash \mathrm{H}, 1.2747212942$ , 0., - $3.2668454102 \backslash \mathrm{H}, 2.5242820181,0 .,-2.0325055946 \backslash \backslash V e r s i o n=I B M-R S 6000-$ G94RevE. $2 \backslash$ State=1-AG $\backslash \mathrm{HF}=-656.8874992 \backslash \mathrm{RMSD}=4.797 \mathrm{e}-09 \backslash \mathrm{RMSF}=1.006 \mathrm{e}-05 \backslash \mathrm{Dip}$ ole=0.,0.,0. \PG=D02H [O(C1), SG(C4),SG'(C4H8),X(C8H8)] <br>@

## 4-40 spiro[2.2]biheptaplane $\boldsymbol{D}_{\mathbf{2}}$

$1 \backslash 1 \backslash$ MHPCC-FR12N05\FOpt \RB3LYP\6-31G (d) \C19H16\RASMUSSEN\30-Sep-1998\0 <br>\#P B3LYP/6-31G* 5D FOPT=(READFC,TIGHT) SCF= (VSHIFT, NOVARACC,DIRECT) GUESS=CHECK NAME=RASMUSSEN GEOM=(CHECK,NODISTANCE,NOANGLE,NODIHEDRAL) \} \Spiro[2.2]biheptaplane D2<br>0,1\C,0.,0., 0.\C, -0.0965496911,1.255304683 $3,0.7240679057 \backslash \mathrm{C}, 0.0965496911,1.2553046833,-0.7240679057 \backslash \mathrm{C},-0.09654969$ 11,-1.2553046833,-0.7240679057\C, 0.0965496911,-1.2553046833, 0.72406790 $57 \backslash C,-1.6210676926,1.3715120302,0.7532870187 \backslash \mathrm{C}, 1.6210676926,1.37151203$ 02,-0.7532870187\C,-1.6210676926,-1.3715120302,-0.7532870187\C,1.62106 76926,-1.3715120302, 0.7532870187\C, 1.54994565,1.2801931754, 0.871780559 $2 \backslash C,-1.54994565,1.2801931754,-0.8717805592 \backslash C, 1.54994565,-1.2801931754$, $-0.8717805592 \backslash C,-1.54994565,-1.2801931754,0.8717805592 \backslash C,-2.3682763236$ , 0.0492345067,1.1638476647\C,2.3682763236,0.0492345067,-1.1638476647\C , - $2.3682763236,-0.0492345067,-1.1638476647 \backslash C, 2.3682763236,-0.049234506$ $7,1.1638476647 \backslash \mathrm{C},-3.4021619924,0 ., 0 . \backslash \mathrm{C}, 3.4021619924,0 ., 0 . \backslash \mathrm{H},-4.0462958$ $452,-0.8881385888,0.0207787977 \backslash \mathrm{H},-4.0462958452,0.8881385888,-0.0207787$ $977 \backslash \mathrm{H}, 4.0462958452,-0.8881385888,-0.0207787977 \backslash \mathrm{H}, 4.0462958452,0.888138$
$5888,0.0207787977 \backslash \mathrm{H},-2.1365664456,2.2628538815,1.1470392983 \backslash \mathrm{H}, 2.136566$ $4456,2.2628538815,-1.1470392983 \backslash H,-2.1365664456,-2.2628538815,-1.14703$ $92983 \backslash \mathrm{H}, 2.1365664456,-2.2628538815,1.1470392983 \backslash \mathrm{H},-1.9853666096,2.1384$ $640576,-1.3987229441 \backslash \mathrm{H}, 1.9853666096,-2.1384640576,-1.3987229441 \backslash \mathrm{H},-1.9$ $853666096,-2.1384640576,1.3987229441 \backslash H, 1.9853666096,2.1384640576,1.398$ $7229441 \backslash \mathrm{H},-2.8093258908,0.0804914785,2.1658787682 \backslash \mathrm{H}, 2.8093258908,0.080$ $4914785,-2.1658787682 \backslash H,-2.8093258908,-0.0804914785,-2.1658787682 \backslash H, 2$. 8093258908,-0.0804914785, 2.1658787682<br>Version=IBM-RS6000-G94RevE. $2 \backslash$ St ate $=1-A \backslash H F=-733.0723986 \backslash R M S D=8.069 e-09 \backslash R M S F=7.720 e-07 \backslash D i p o l e=0 ., 0 ., 0 . \backslash$ PG=D02 [O (C1), C2" (C1.C1), X(C16H16)] <br>@

## 4-40 spiro[2.2]biheptaplane $\boldsymbol{D}_{\mathbf{2 h}}$

$1 \backslash 1 \backslash$ MHPCC-FR17N13 \FOpt $\backslash$ RB3LYP $\backslash 6-31 G(d) \backslash C 19 H 16 \backslash R A S M U S S E N \backslash 30-S e p-1998 \backslash 0$ <br>\#P B3LYP/6-31G* 5D FOPT=(NEWESTMFC,TIGHT) SCF=(VSHIFT, NOVARACC,DIREC T) GUESS=CHECK NAME=RASMUSSEN GEOM= (CHECK,NODISTANCE,NOANGLE,NODIHEDRA L) $\backslash \backslash$ Spiro[2.2]biheptaplane $\mathrm{D} 2 \mathrm{~h} \backslash \backslash 0,1 \backslash \mathrm{C}, 0 ., 0 ., 0 . \backslash \mathrm{C}, 0.1 .2599881409,0.722$ $7562167 \backslash \mathrm{C}, 0 ., 1.2599881409,-0.7227562167 \backslash \mathrm{C}, 0 .,-1.2599881409,-0.72275621$ $67 \backslash C, 0 .,-1.2599881409,0.7227562167 \backslash C,-1.5790774787,1.3273474644,0.8123$ $10072 \backslash \mathrm{C}, 1.5790774787,1.3273474644,-0.812310072 \backslash \mathrm{C},-1.5790774787,-1.3273$ $474644,-0.812310072 \backslash C, 1.5790774787,-1.3273474644,0.812310072 \backslash C, 1.57907$ $74787,1.3273474644,0.812310072 \backslash C,-1.5790774787,1.3273474644,-0.8123100$ $72 \backslash C, 1.5790774787,-1.3273474644,-0.812310072 \backslash C,-1.5790774787,-1.327347$ $4644,0.812310072 \backslash C,-2.3569259498,0 ., 1.167340973 \backslash C, 2.3569259498,0 ., 1.16$ $7340973 \backslash \mathrm{C},-2.3569259498,0 .,-1.167340973 \backslash \mathrm{C}, 2.3569259498,0 .,-1.167340973$ $\backslash \mathrm{C},-3.3895420327,0 ., 0 . \backslash \mathrm{C}, 3.3895420327,0 ., 0 . \backslash \mathrm{H},-4.0333435468,-0.8885153$ 658, 0. \H, -4.0333435468, 0.8885153658, 0. \H,4.0333435468, 0.8885153658, 0. \} H, 4.0333435468,-0.8885153658,0. \H,-2.0654982739,2.2021986409,1.2749577 128\H,2.0654982739,2.2021986409,-1.2749577128\H,-2.0654982739,-2.20219 86409,-1.2749577128\H,2.0654982739,-2.2021986409,1.2749577128\H,-2.065 4982739,2.2021986409,-1.2749577128\H,2.0654982739,-2.2021986409,-1.274 9577128\H,-2.0654982739,-2.2021986409,1.2749577128\H,2.0654982739,2.20 21986409,1.2749577128\H,-2.8049090124,0., 2.1673651633\H,2.8049090124, 0 ., 2.1673651633\H,-2.8049090124,0.,-2.1673651633\H, 2.8049090124,0.,-2.1 $673651633 \backslash$ Version=IBM-RS6000-G94RevE. $2 \backslash$ State $=1-A G \backslash H F=-733.0651059 \backslash$ RMS $\mathrm{D}=5.862 \mathrm{e}-09 \backslash \mathrm{RMSF}=9.295 \mathrm{e}-06 \backslash \mathrm{Dipole}=0 ., 0 ., 0 . \backslash \mathrm{PG}=\mathrm{D} 02 \mathrm{H} \quad$ [O(C1), C2 (C1.C1), SG (C4) , SG' (C4H4) , SG" (H4) , X (C8H8) ] <br>@

## 4-41 spiro[2.2]heptaplane $\boldsymbol{C}_{\mathbf{2}}$

$1 \backslash 1 \backslash$ MHPCC-FR16N05\FOpt \RB3LYP\6-31G(d) \C19H20\RASMUSSEN\30-Sep-1998\0 <br>\#P B3LYP/6-31G* 5D FOPT=(READFC,TIGHT) SCF=(VSHIFT,NOVARACC,DIRECT) GUESS=CHECK NAME=RASMUSSEN TEST GEOM= (CHECK,NODISTANCE,NOANGLE,NODIHED RAL) <br>spiro[2.2]heptaplane C2 <br>0,1\C,0.,0.,0.2150490911\C,-0.661708296 $7,0.2770684153,1.5108399762 \backslash C, 0.6617082967,-0.2770684153,1.5108399762 \backslash$ C, 0.6021730677,-0.4723078799,-1.01253589\C, -0.6021730677,0.4723078799, $-1.01253589 \backslash C,-0.0029515713,1.7627338602,1.487360443 \backslash C, 0.0029515713,-1$ $.7627338602,1.487360443 \backslash C,-1.4775835025,-1.0027377025,1.5536076679 \backslash \mathrm{C}, 1$ $.4775835025,1.0027377025,1.5536076679 \backslash C, 1.8457261035,0.5262241943,-1.0$ $599044639 \backslash \mathrm{C},-1.8457261035,-0.5262241943,-1.0599044639 \backslash \mathrm{C}, 0.2457011799,-$ $1.9456391762,-1.1757741325 \backslash C,-0.2457011799,1.9456391762,-1.1757741325 \backslash$ C, $2.4594856234,0.9463077748,0.3371844126 \backslash C, 0.3514333917,-2.6378121888$, $0.2409469119 \backslash C,-0.3514333917,2.6378121888,0.2409469119 \backslash C,-2.4594856234$ , - 0. $9463077748,0.3371844126 \backslash C, 1.2044341956,1.7862734591,-1.7199607077 \backslash$

C, -1. $2044341956,-1.7862734591,-1.7199607077 \backslash \mathrm{H},-0.1727146601,2.35120077$ $21,2.4001370731 \backslash \mathrm{H}, 0.1727146601,-2.3512007721,2.4001370731 \backslash \mathrm{H},-2.0320164$ $09,-1.2927652028,2.4664618593 \backslash \mathrm{H}, 2.032016409,1.2927652028,2.4664618593 \backslash$ H, 2. 6645157, 0.1509422573,-1. $6874836934 \backslash H,-2.6645157,-0.1509422573,-1.6$ $874836934 \backslash \mathrm{H}, 0.8444322318,-2.5291630716,-1.8901873601 \backslash \mathrm{H},-0.8444322318,2$ $.5291630716,-1.8901873601 \backslash \mathrm{H}, 3.2409395838,0.2266850539,0.6250733184 \backslash \mathrm{H}, 2$ $.9763471335,1.9046453974,0.1979018408 \backslash \mathrm{H}, 1.3807165752,-3.0004188687,0.3$ $822737763 \backslash H,-0.2852948838,-3.5341446027,0.2523780045 \backslash H,-1.3807165752,3$ $.0004188687,0.3822737763 \backslash \mathrm{H}, 0.2852948838,3.5341446027,0.2523780045 \backslash \mathrm{H},-3$ $.2409395838,-0.2266850539,0.6250733184 \backslash \mathrm{H},-2.9763471335,-1.9046453974,0$ $.1979018408 \backslash \mathrm{H},-1.1346530737,-1.626940562,-2.803788563 \backslash \mathrm{H},-1.8153509919$, $-2.6841893102,-1.5584988331 \backslash \mathrm{H}, 1.1346530737,1.626940562,-2.803788563 \backslash \mathrm{H}$, $1.8153509919,2.6841893102,-1.5584988331 \backslash$ VVersion=IBM-RS6000-G94RevE. $2 \backslash$ State $=1-A \backslash H F=-735.6375822 \backslash R M S D=5.567 e-09 \backslash R M S F=2.419 e-06 \backslash D i p o l e=0 ., 0 .,-$ $0.0222923 \backslash \mathrm{PG}=\mathrm{CO} 2[\mathrm{C} 2(\mathrm{C} 1), \mathrm{X}(\mathrm{C} 18 \mathrm{H} 20)] \backslash \backslash @$

## 4-41 spiro[2.2]heptaplane $\quad \boldsymbol{C}_{\mathbf{2 v}}$

$1 \backslash 1 \backslash$ MHPCC-FR17N15 \FOpt $\backslash$ RB3LYP $\backslash 6-31 G(d) \backslash C 19 H 20 \backslash R A S M U S S E N \backslash 30-S e p-1998 \backslash 0$ <br>\#P B3LYP/6-31G* 5D FOPT= (NEWESTMFC,TIGHT) SCF= (VSHIFT, NOVARACC, DIREC T) GUESS=CHECK NAME=RASMUSSEN TEST GEOM= (CHECK,NODISTANCE,NOANGLE,NODI HEDRAL $) \backslash \backslash$ spiro [2.2] heptaplane $C 2 v \backslash \backslash 0,1 \backslash C, 0 ., 0 ., 0.2035403665 \backslash C, 0.760900$ 9493, 0., -1.0171844765\C, -0.7609009493, 0., -1.0171844765\C, -0.7060008668 , 0., 1. $5213893186 \backslash \mathrm{C}, 0.7060008668,0 ., 1.5213893186 \backslash \mathrm{C}, 1.2666528287,1.46995$ $08053,-1.1213210836 \backslash \mathrm{C},-1.2666528287,-1.4699508053,-1.1213210836 \backslash \mathrm{C},-0.8$ $287979847,1.5585618755,1.5167755897 \backslash \mathrm{C}, 0.8287979847,-1.5585618755,1.516$ $7755897 \backslash C, 1.2666528287,-1.4699508053,-1.1213210836 \backslash C,-1.2666528287,1.4$ $699508053,-1.1213210836 \backslash C,-0.8287979847,-1.5585618755,1.5167755897 \backslash C, 0$ $.8287979847,1.5585618755,1.5167755897 \backslash C,-1.6500215621,2.0658733559,0.2$ $8761063 \backslash C,-1.6500215621,-2.0658733559,0.28761063 \backslash C, 1.6500215621,2.0658$ $733559,0.28761063 \backslash C, 1.6500215621,-2.0658733559,0.28761063 \backslash C, 0 ., 2.16085$ $22054,-1.70857787 \backslash \mathrm{C}, 0 .,-2.1608522054,-1.70857787 \backslash \mathrm{H}, 2.1200226394,1.6267$ $809583,-1.798255287 \backslash \mathrm{H},-2.1200226394,-1.6267809583,-1.798255287 \backslash \mathrm{H}, 2.120$ $0226394,-1.6267809583,-1.798255287 \backslash \mathrm{H},-2.1200226394,1.6267809583,-1.798$ $255287 \backslash \mathrm{H},-1.2258623631,2.0395988096,2.4315803834 \backslash \mathrm{H}, 1.2258623631,-2.039$ $5988096,2.4315803834 \backslash \mathrm{H},-1.2258623631,-2.0395988096,2.4315803834 \backslash \mathrm{H}, 1.22$ $58623631,2.0395988096,2.4315803834 \backslash \mathrm{H},-1.5822176094,3.1606535798,0.2281$ $061595 \backslash \mathrm{H},-2.7064649005,1.8458131245,0.5075080957 \backslash \mathrm{H},-1.5822176094,-3.16$ $06535798,0.2281061595 \backslash \mathrm{H},-2.7064649005,-1.8458131245,0.5075080957 \backslash \mathrm{H}, 1.5$ $822176094,3.1606535798,0.2281061595 \backslash \mathrm{H}, 2.7064649005,1.8458131245,0.5075$ $080957 \backslash \mathrm{H}, 1.5822176094,-3.1606535798,0.2281061595 \backslash \mathrm{H}, 2.7064649005,-1.845$ $8131245,0.5075080957 \backslash \mathrm{H}, 0 ., 3.2434455226,-1.5216859907 \backslash \mathrm{H}, 0 ., 2.018034761$, $-2.7973572769 \backslash H, 0 .,-3.2434455226,-1.5216859907 \backslash H, 0 .,-2.018034761,-2.79$ $73572769 \backslash$ VVersion=IBM-RS6000-G94RevE.2 \State=1-A1 \HF=-735.6290084 \RMSD $=7.266 \mathrm{e}-09 \backslash \mathrm{RMSF}=3.656 \mathrm{e}-06 \backslash \mathrm{Dipole}=0 ., 0.0 .088015 \backslash \mathrm{PG}=\mathrm{C} 02 \mathrm{~V} \quad[\mathrm{C} 2(\mathrm{C} 1), \mathrm{SGV}(\mathrm{C} 2$ H4) ,SGV' (C4) , X (C12H16) ] <br>@

## 4-42 spiro[2.2]heptaplane $\quad \boldsymbol{C}_{\mathbf{2}}$

$1 \backslash 1 \backslash$ MHPCC-FR11N05\FOpt \RB3LYP\6-31G(d) \C19H20\RASMUSSEN $\backslash 30-$ Sep-1998\0 <br>\#P B3LYP/6-31G* 5D FOPT=(READFC,TIGHT) SCF=(VSHIFT,NOVARACC,DIRECT) GUESS=CHECK NAME=RASMUSSEN TEST GEOM= (CHECK,NODISTANCE,NOANGLE,NODIHED RAL) <br>spiro[2.2]heptaplane (orient b) C2 $\backslash \backslash 0,1 \backslash C, 0 .,-0.0250859525,0 . \backslash C$, $-1.1206496515,-0.986776845,-0.1581068431 \backslash C, 1.1206496515,-0.986776845,0$
$.1581068431 \backslash C, 1.3202302108,0.5204438543,0.0041460364 \backslash C,-1.3202302108,0$ $.5204438543,-0.0041460364 \backslash C,-0.9140024134,-1.5207649615,1.3335872344 \backslash C$ , $0.9140024134,-1.5207649615,-1.3335872344 \backslash C,-0.6903321226,-1.456712541$ $9,-1.5409061204 \backslash C, 0.6903321226,-1.4567125419,1.5409061204 \backslash C, 1.16633942$ $06,1.0709821818,1.501140406 \backslash C,-1.1663394206,1.0709821818,-1.501140406 \backslash$ C, 1.5165118659, 0.9846108221,-1.4365143874 \C, -1.5165118659, 0.9846108221 , $1.4365143874 \backslash C, 1.2714688086,-0.2464687736,2.3592800689 \backslash C, 1.6760108224$ , $-0.4147888328,-2.1409371223 \backslash C,-1.6760108224,-0.4147888328,2.140937122$ $3 \backslash C,-1.2714688086,-0.2464687736,-2.3592800689 \backslash C,-0.2089138454,1.791169$ 6939, 1. $8002300729 \backslash \mathrm{C}, 0.2089138454,1.7911696939,-1.8002300729 \backslash \mathrm{H},-1.34387$ $66655,-2.509250622,1.5499394424 \backslash H, 1.3438766655,-2.509250622,-1.5499394$ $424 \backslash \mathrm{H},-1.0925007524,-2.4043295426,-1.9378810393 \backslash \mathrm{H}, 1.0925007524,-2.4043$ $295426,1.9378810393 \backslash \mathrm{H}, 1.9719777472,1.7645486215,1.7830295895 \backslash \mathrm{H},-1.9719$ $777472,1.7645486215,-1.7830295895 \backslash \mathrm{H}, 2.3929229277,1.6101595134,-1.67199$ $71689 \backslash \mathrm{H},-2.3929229277,1.6101595134,1.6719971689 \backslash \mathrm{H}, 2.3267979287,-0.4652$ $542256,2.5645562353 \backslash \mathrm{H}, 0.7812734666,-0.1145446195,3.3301422653 \backslash \mathrm{H}, 2.7441$ $089421,-0.6655954016,-2.1257139161 \backslash \mathrm{H}, 1.3718689261,-0.3843786774,-3.193$ $2299712 \backslash \mathrm{H},-2.7441089421,-0.6655954016,2.1257139161 \backslash \mathrm{H},-1.3718689261,-0$. $3843786774,3.1932299712 \backslash \mathrm{H},-2.3267979287,-0.4652542256,-2.5645562353 \backslash \mathrm{H}$, $-0.7812734666,-0.1145446195,-3.3301422653 \backslash H, 0.2383089329,2.7508766599$, $-1.2637802141 \backslash \mathrm{H}, 0.2206618745,2.0428585677,-2.8694404139 \backslash \mathrm{H},-0.238308932$ 9, 2. $7508766599,1.2637802141 \backslash \mathrm{H},-0.2206618745,2.0428585677,2.8694404139 \backslash$ $\backslash$ Version=IBM-RS6000-G94RevE. $2 \backslash$ State $=1-A \backslash H F=-735.6737315 \backslash$ RMSD $=9.836 e-09$ $\backslash \mathrm{RMSF}=4.709 \mathrm{e}-06 \backslash \mathrm{Dipole}=0 ., 0.1939778,0 . \backslash \mathrm{PG}=\mathrm{C0} 2 \quad[\mathrm{C} 2(\mathrm{C} 1), \mathrm{X}(\mathrm{C} 18 \mathrm{H} 20)] \backslash \backslash @$

## 4-42 spiro[2.2]heptaplane $\quad \boldsymbol{C}_{2 \mathrm{v}}$

$1 \backslash 1 \backslash$ MHPCC-FR3N03\FOpt \RB3LYP\6-31G(d) \C19H20\RASMUSSEN $\backslash 30-$ Sep-1998\0\} <br>\#P B3LYP/6-31G* 5D FOPT=(NEWESTMFC,TIGHT) SCF=(VSHIFT, NOVARACC,DIRECT ) GUESS=CHECK NAME=RASMUSSEN TEST GEOM=(CHECK,NODISTANCE,NOANGLE,NODIH EDRAL) <br>spiro[2.2]heptaplane (orient b) C2v $\backslash \backslash 0,1 \backslash C, 0 ., 0 ., 0.0142173285 \backslash$ $C,-1.3383509942,0 ., 0.5175395145 \backslash C, 1.3383509942,0 ., 0.5175395145 \backslash C, 1.085$ $0204883,0 .,-0.9688254999 \backslash C,-1.0850204883,0 .,-0.9688254999 \backslash C,-1.3487233$ $318,1.4809396914,1.0248759156 \backslash \mathrm{C}, 1.3487233318,-1.4809396914,1.024875915$ $6 \backslash C, 0.7996548817,1.4470272957,-1.4911552521 \backslash C,-0.7996548817,-1.4470272$ 957,-1.4911552521 \C, -1. $3487233318,-1.4809396914,1.0248759156 \backslash C, 1.34872$ $33318,1.4809396914,1.0248759156 \backslash \mathrm{C}, 0.7996548817,-1.4470272957,-1.491155$ $2521 \backslash C,-0.7996548817,1.4470272957,-1.4911552521 \backslash \mathrm{C}, 1.47956295,2.2607528$ $9,-0.3339301697 \backslash C, 1.47956295,-2.26075289,-0.3339301697 \backslash C,-1.47956295,2$ $.26075289,-0.3339301697 \backslash C,-1.47956295,-2.26075289,-0.3339301697 \backslash C, 0 ., 1$ $.8128158455,1.7835071876 \backslash \mathrm{C}, 0 .,-1.8128158455,1.7835071876 \backslash \mathrm{H},-2.18525301$ $4,1.7630216408,1.6874524065 \backslash \mathrm{H}, 2.185253014,-1.7630216408,1.6874524065 \backslash \mathrm{H}$ , - $2.185253014,-1.7630216408,1.6874524065 \backslash \mathrm{H}, 2.185253014,1.7630216408,1$. $6874524065 \backslash \mathrm{H}, 1.2319041864,1.744565867,-2.4618379267 \backslash \mathrm{H},-1.2319041864,-1$ $.744565867,-2.4618379267 \backslash \mathrm{H}, 1.2319041864,-1.744565867,-2.4618379267 \backslash \mathrm{H},-$ $1.2319041864,1.744565867,-2.4618379267 \backslash \mathrm{H}, 1.0783091801,3.2772859959,-0$. $2502503396 \backslash \mathrm{H}, 2.5455861922,2.3619681466,-0.5771838035 \backslash \mathrm{H}, 1.0783091801,-3$ $.2772859959,-0.2502503396 \backslash \mathrm{H}, 2.5455861922,-2.3619681466,-0.5771838035 \backslash \mathrm{H}$ , - $1.0783091801,3.2772859959,-0.2502503396 \backslash H,-2.5455861922,2.3619681466$ $,-0.5771838035 \backslash \mathrm{H},-1.0783091801,-3.2772859959,-0.2502503396 \backslash \mathrm{H},-2.545586$ 1922,-2. $3619681466,-0.5771838035 \backslash \mathrm{H}, 0 ., 2.8868403063,2.0148666833 \backslash \mathrm{H}, 0 ., 1$ $.2967505923,2.7553075199 \backslash H, 0 .,-2.8868403063,2.0148666833 \backslash \mathrm{H}, 0 .,-1.29675$ 05923, 2.7553075199<br>Version=IBM-RS6000-G94RevE.2\State=1-A1 \HF=-735. 66
$57582 \backslash \mathrm{RMSD}=9.479 \mathrm{e}-09 \backslash \mathrm{RMSF}=1.118 \mathrm{e}-06 \backslash \mathrm{Dipole}=0 ., 0.0 .0270617 \backslash \mathrm{PG}=\mathrm{CO} 2 \mathrm{~V} \quad[\mathrm{C} 2$ (C1), SGV (C2H4), SGV' (C4) , X(C12H16)] <br>@

## 4-43 spiro[2.2]bioctaplane $\quad \boldsymbol{D}_{\mathbf{2}}$

$1 \backslash 1 \backslash$ MHPCC-FR12N06\FOpt \RB3LYP\6-31G(d) \C21H20\RASMUSSEN $\backslash 30-$ Sep-1998\0 <br>\#P B3LYP/6-31G* 5D FOPT=(READFC,TIGHT) SCF=(VSHIFT,NOVARACC,DIRECT) GUESS=CHECK NAME=RASMUSSEN GEOM=(CHECK,NODISTANCE,NOANGLE,NODIHEDRAL) \} $\backslash$ Spiro[2.2]bioctaplane 5D D2<br>0,1\C,0.,0., 0.\C,0.0948959618, 0.74763288 $43,1.2694259537 \backslash C,-0.0948959618,-0.7476328843,1.2694259537 \backslash \mathrm{C}, 0.0948959$ 618,-0.7476328843,-1.2694259537\C,-0.0948959618, 0.7476328843,-1.269425 $9537 \backslash C, 1.5142235722,1.26440915,1.2843556919 \backslash C,-1.5142235722,-1.2644091$ $5,1.2843556919 \backslash C, 1.5142235722,-1.26440915,-1.2843556919 \backslash C,-1.514223572$ $2,1.26440915,-1.2843556919 \backslash \mathrm{C},-1.3714944824,1.3272074886,1.1722952669 \backslash \mathrm{C}$ ,1.3714944824,-1.3272074886,1.1722952669\C,-1.3714944824,-1.3272074886 ,-1.1722952669\C,1.3714944824,1.3272074886,-1.1722952669\C,1.656922427 , 2. $2261248136,0.0655078626 \backslash \mathrm{C},-1.656922427,-2.2261248136,0.0655078626 \backslash \mathrm{C}$ , 1.656922427,-2.2261248136,-0.0655078626\C,-1.656922427,2.2261248136,$0.0655078626 \backslash C,-2.2377105972,0.0435703501,0.796743881 \backslash C, 2.2377105972,0$ $.0435703501,-0.796743881 \backslash C,-2.2377105972,-0.0435703501,-0.796743881 \backslash C$, $2.2377105972,-0.0435703501,0.796743881 \backslash \mathrm{H}, 1.9177868056,1.6907501295,2.2$ $14729309 \backslash \mathrm{H},-1.9177868056,-1.6907501295,2.214729309 \backslash \mathrm{H}, 1.9177868056,-1.6$ 907501295,-2.214729309\H,-1.9177868056,1.6907501295,-2.214729309\H,1.7 037719649,-1.7985643084,2.1059224003\H,-1.7037719649,-1.7985643084, -2. $1059224003 \backslash \mathrm{H}, 1.7037719649,1.7985643084,-2.1059224003 \backslash \mathrm{H},-1.7037719649,1$ . $7985643084,2.1059224003 \backslash \mathrm{H}, 1.0192323129,3.112242331,0.1399951805 \backslash \mathrm{H},-1$. 0192323129,-3.112242331,0.1399951805 \H, 1.0192323129,-3.112242331,-0.13 99951805\H,-1.0192323129,3.112242331,-0.1399951805\H,2.6924234834, 2. 58 48955002, 0.0013570579\Н, -2.6924234834,-2.5848955002,0.0013570579\H,2.6 924234834,-2.5848955002,-0.0013570579\H,-2.6924234834,2.5848955002,-0. $0013570579 \backslash \mathrm{H},-3.2561059698,0.1342258458,1.2005647571$ पН, 3.2561059698, 0. 1342258458,-1.2005647571\H,-3.2561059698,-0.1342258458,-1.2005647571 \H , 3.2561059698,-0.1342258458,1.2005647571<br>Version=IBM-RS6000-G94RevE. 2 $\backslash$ State=1-A $\backslash H F=-811.9647258 \backslash R M S D=6.467 e-09 \backslash R M S F=2.979 e-07 \backslash D i p o l e=0 ., 0 .$, $0 . \backslash \mathrm{PG}=\mathrm{D} 02[\mathrm{O}(\mathrm{C} 1), \mathrm{X}(\mathrm{C} 2 \mathrm{OH} 20)] \backslash \backslash @$

## 4-43 spiro[2.2]bioctaplane $\quad D_{\mathbf{2 h}}$

$1 \backslash 1 \backslash$ MHPCC-FR10N09 \FOpt $\backslash$ RB3LYP $\backslash 6-31 G(d) \backslash C 21 H 20 \backslash R A S M U S S E N \backslash 30-S e p-1998 \backslash 0$ <br>\#P B3LYP/6-31G* 5D FOPT=(NEWESTMFC,TIGHT) SCF=(VSHIFT, NOVARACC,DIREC T) GUESS=CHECK NAME=RASMUSSEN GEOM= (CHECK,NODISTANCE,NOANGLE,NODIHEDRA L) <br>Spiro[2.2]bioctaplane 5D D2h $\backslash \backslash 0,1 \backslash C, 0 ., 0 ., 0 . \backslash C, 0 ., 0.743178034,1.27$ $94820838 \backslash \mathrm{C}, 0 .,-0.743178034,1.2794820838 \backslash \mathrm{C}, 0 .,-0.743178034,-1.279482083$ $8 \backslash C, 0 ., 0.743178034,-1.2794820838 \backslash C, 1.4390933497,1.292669239,1.23105471$ $7 \backslash C,-1.4390933497,-1.292669239,1.231054717 \backslash C, 1.4390933497,-1.292669239$ ,-1.231054717\C,-1.4390933497,1.292669239,-1.231054717\C,-1.4390933497 ,1.292669239,1.231054717\C,1.4390933497,-1.292669239,1.231054717\C,-1. $4390933497,-1.292669239,-1.231054717 \backslash \mathrm{C}, 1.4390933497,1.292669239,-1.231$ 054717\C,1.6494510607,2.2218999229,0.\C,-1.6494510607,2.2218999229,0.\} C,1.6494510607,-2.2218999229,0.\C,-1.6494510607,-2.2218999229,0.\C,2.2 $351406534,0.0 .7959129535 \backslash \mathrm{C},-2.2351406534,0.0 .7959129535 \backslash \mathrm{C}, 2.23514065$ $34,0 .,-0.7959129535 \backslash \mathrm{C},-2.2351406534,0 .,-0.7959129535 \backslash \mathrm{H}, 1.811990483,1.7$ 508962772,2.1596826903\H,-1.811990483,-1.7508962772,2.1596826903\H,1.8 $11990483,-1.7508962772,-2.1596826903 \backslash$ Н, $-1.811990483,1.7508962772,-2.15$
$96826903 \backslash \mathrm{H}, 1.811990483,-1.7508962772,2.1596826903 \backslash \mathrm{H},-1.811990483,-1.75$ $08962772,-2.1596826903 \backslash \mathrm{H}, 1.811990483,1.7508962772,-2.1596826903 \backslash \mathrm{H},-1.8$ $11990483,1.7508962772,2.1596826903 \backslash \mathrm{H}, 2.6892469482,2.5728168382,0 . \backslash \mathrm{H},-2$ $.6892469482,2.5728168382,0 . \backslash H, 2.6892469482,-2.5728168382,0 . \backslash H,-2.68924$ $69482,-2.5728168382,0 . \backslash H, 1.016048925,3.1141346476,0 . \backslash \mathrm{H},-1.016048925,3$. $1141346476,0 . \backslash \mathrm{H}, 1.016048925,-3.1141346476,0 . \backslash \mathrm{H},-1.016048925,-3.1141346$ $476,0 . \backslash \mathrm{H}, 3.2550716576,0 ., 1.2143728321 \backslash \mathrm{H},-3.2550716576,0.11 .2143728321 \backslash$ H, 3.2550716576, 0., -1.2143728321 \H, -3.2550716576, 0., -1.2143728321 \VVers ion=IBM-RS6000-G94RevE. $2 \backslash$ State $=1-A G \backslash H F=-811.9547263 \backslash R M S D=9.808 e-09 \backslash R M S$ $\mathrm{F}=1.967 \mathrm{e}-06 \backslash \mathrm{Dipole}=0 ., 0 ., 0 . \backslash \mathrm{PG}=\mathrm{D} 02 \mathrm{H} \quad\left[\mathrm{O}(\mathrm{C} 1), \mathrm{SG}(\mathrm{C} 4), \mathrm{SG}{ }^{\prime}(\mathrm{C} 4 \mathrm{H} 4), \mathrm{SG}\right.$ (C4H8), X (C8H8) ] <br>@

## 4-28 spiro[2.2]octaplane $\boldsymbol{D}_{\mathbf{2}}$

$1 \backslash 1 \backslash$ MHPCC-FR12N15 $\backslash$ FOpt $\backslash R B 3 L Y P \backslash 6-31 G(d) \backslash C 21 H 24 \backslash R A S M U S S E N \backslash 30-S e p-1998 \backslash 0$ <br>\#P B3LYP/6-31G* 5D FOPT= (READFC, TIGHT) SCF= (VSHIFT, NOVARACC, DIRECT) GUESS=CHECK NAME=RASMUSSEN GEOM = (CHECK, NODISTANCE, NOANGLE, NODIHEDRAL) \} \Spiro[2.2]octaplane D2<br>0,1\C,0.,0., 0. \C, -0.7419801098,-1.2692492058, $-0.0887932013 \backslash C, 0.7419801098,-1.2692492058,0.0887932013 \backslash C, 0.7419801098$ , 1.2692492058,-0.0887932013\C,-0.7419801098,1.2692492058,0.0887932013\ $C,-1.3400598562,-1.2811786718,1.3634807266 \backslash C, 1.3400598562,-1.281178671$ $8,-1.3634807266 \backslash C, 1.3400598562,1.2811786718,1.3634807266 \backslash C,-1.34005985$ 62,1.2811786718,-1.3634807266\C, -1.2524991401, -1.394068245,-1. 50007422 $43 \backslash C, 1.2524991401,-1.394068245,1.5000742243 \backslash C, 1.2524991401,1.394068245$ , - $1.5000742243 \backslash \mathrm{C},-1.2524991401,1.394068245,1.5000742243 \backslash \mathrm{C},-2.017055759$ $9,0.0609465183,1.8172199242 \backslash C, 2.0170557599,0.0609465183,-1.8172199242 \backslash$ C, 2.0170557599,-0.0609465183,1.8172199242 \C, -2.0170557599,-0.060946518 $3,-1.8172199242 \backslash C, 0.0972551039,-1.6711818598,-2.2535722301 \backslash C, 0.0972551$ $039,1.6711818598,2.2535722301 \backslash C,-0.0972551039,1.6711818598,-2.25357223$ $01 \backslash \mathrm{C},-0.0972551039,-1.6711818598,2.2535722301 \backslash \mathrm{H},-2.1056674212,-2.06335$ $01188,1.4665584173 \backslash \mathrm{H}, 2.1056674212,-2.0633501188,-1.4665584173 \backslash \mathrm{H}, 2.1056$ $674212,2.0633501188,1.4665584173 \backslash \mathrm{H},-2.1056674212,2.0633501188$, -1.46655 $84173 \backslash \mathrm{H}, 1.9496728677,-2.2251586579,1.6947947245 \backslash \mathrm{H}, 1.9496728677,2.22515$ $86579,-1.6947947245 \backslash \mathrm{H},-1.9496728677,2.2251586579,1.6947947245 \backslash \mathrm{H},-1.949$ $6728677,-2.2251586579,-1.6947947245 \backslash \mathrm{H},-2.2142385953,-0.0061069081,2.89$ $60133009 \backslash \mathrm{H},-3.0048960774,0.1291891667,1.3379033886 \backslash \mathrm{H}, 2.2142385953,-0.0$ $061069081,-2.8960133009 \backslash \mathrm{H}, 3.0048960774,0.1291891667,-1.3379033886 \backslash \mathrm{H}, 2$. $2142385953,0.0061069081,2.8960133009 \backslash H, 3.0048960774,-0.1291891667,1.33$ $79033886 \backslash \mathrm{H},-2.2142385953,0.0061069081,-2.8960133009 \backslash \mathrm{H},-3.0048960774,-0$ $.1291891667,-1.3379033886 \backslash \mathrm{H}, 0.1418270749,-2.7488272955,-2.4532871632 \backslash \mathrm{H}$ , 0.1371885617,-1.1748861226, -3.2306184685 H , $0.1418270749,2.7488272955$, $2.4532871632 \backslash \mathrm{H}, 0.1371885617,1.1748861226,3.2306184685 \backslash \mathrm{H},-0.1418270749$, $2.7488272955,-2.4532871632 \backslash H,-0.1371885617,1.1748861226,-3.2306184685 \backslash$ H, - $0.1418270749,-2.7488272955,2.4532871632 \backslash \mathrm{H},-0.1371885617,-1.17488612$ $26,3.2306184685 \backslash \backslash V e r s i o n=I B M-R S 6000-G 94 R e v E .2 \backslash$ State=1-A $\backslash H F=-814.415406$ $1 \backslash \mathrm{RMSD}=9.529 \mathrm{e}-09 \backslash \mathrm{RMSF}=3.660 \mathrm{e}-06 \backslash \mathrm{Dipole}=0 ., 0 ., 0 . \backslash \mathrm{PG}=\mathrm{D} 02 \quad[\mathrm{O}(\mathrm{C} 1), \mathrm{X}(\mathrm{C} 20 \mathrm{H} 24$ )] <br>@

## 4-28 spiro[2.2]octaplane $\boldsymbol{D}_{\mathbf{2 h}}$

$1 \backslash 1 \backslash$ MHPCC-FR16N07\FOpt \RB3LYP\6-31G(d) \C21H24 \RASMUSSEN $\backslash 30-$ Sep-1998\0 <br>\#P B3LYP/6-31G* 5D FOPT=(NEWESTMFC,TIGHT) SCF= (VSHIFT,NOVARACC,DIREC T) GUESS=CHECK NAME=RASMUSSEN GEOM= (CHECK,NODISTANCE,NOANGLE,NODIHEDRA L) <br>Spiro[2.2]octaplane $D 2 h \backslash \backslash 0,1 \backslash C, 0 ., 0 ., 0 . \backslash C,-0.7399433506,-1.2751063$
$784,0 . \backslash C, 0.7399433506,-1.2751063784,0 . \backslash C, 0.7399433506,1.2751063784,0 . \$ C, - $0.7399433506,1.2751063784,0 . \backslash C,-1.2960538913,-1.337607283,1.4286163$ $514 \backslash C, 1.2960538913,-1.337607283,-1.4286163514 \backslash \mathrm{C}, 1.2960538913,1.3376072$ 83,1.4286163514\C,-1.2960538913,1.337607283,-1.4286163514\C,-1.2960538 913,-1.337607283,-1.4286163514\C,1.2960538913,-1.337607283,1.428616351 $4 \backslash C, 1.2960538913,1.337607283,-1.4286163514 \backslash C,-1.2960538913,1.337607283$ $, 1.4286163514 \backslash C,-2.0197880755,0 ., 1.8093146283 \backslash C,-2.0197880755,0 .,-1.80$ $93146283 \backslash C, 2.0197880755,0 ., 1.8093146283 \backslash C, 2.0197880755,0 .,-1.809314628$ $3 \backslash C, 0 .,-1.6652610053,2.2554091728 \backslash C, 0 .,-1.6652610053,-2.2554091728 \backslash C, 0$ ., 1.6652610053,2.2554091728\C,0., 1.6652610053,-2.2554091728\H,-2. 03036 $24498,-2.1453943042,1.5817603608 \backslash \mathrm{H}, 2.0303624498,-2.1453943042,-1.58176$ $03608 \backslash \mathrm{H}, 2.0303624498,2.1453943042,1.5817603608 \backslash \mathrm{H},-2.0303624498,2.14539$ 43042 , - $1.5817603608 \backslash \mathrm{H}, 2.0303624498,-2.1453943042,1.5817603608 \backslash \mathrm{H}, 2.0303$ $624498,2.1453943042,-1.5817603608 \backslash \mathrm{H},-2.0303624498,2.1453943042,1.58176$ $03608 \backslash \mathrm{H},-2.0303624498,-2.1453943042,-1.5817603608 \backslash \mathrm{H},-2.208352398,0 ., 2$. $8916875342 \backslash \mathrm{H},-3.0125974346,0 ., 1.3347906119 \backslash \mathrm{H},-2.208352398,0 .,-2.891687$ $5342 \backslash \mathrm{H},-3.0125974346,0 .,-1.3347906119 \backslash \mathrm{H}, 2.208352398,0 ., 2.8916875342 \backslash \mathrm{H}$, $3.0125974346,0 ., 1.3347906119 \backslash H, 2.208352398,0 .,-2.8916875342 \backslash \mathrm{H}, 3.012597$ $4346,0 .,-1.3347906119 \backslash H, 0 .,-1.157116576,3.2277666794 \backslash \mathrm{H}, 0 .,-2.741212155$ $1,2.4719012625 \backslash \mathrm{H}, 0 .,-1.157116576,-3.2277666794 \backslash \mathrm{H}, 0 .,-2.7412121551,-2.4$ $719012625 \backslash \mathrm{H}, 0 ., 1.157116576,3.2277666794 \backslash \mathrm{H}, 0 ., 2.7412121551,2.4719012625$ $\backslash \mathrm{H}, 0 ., 1.157116576,-3.2277666794 \backslash \mathrm{H}, 0 ., 2.7412121551,-2.4719012625 \backslash \backslash V e r s i$ on=IBM-RS6000-G94RevE. $2 \backslash$ State $=1-A G \backslash H F=-814.4088352 \backslash \mathrm{RMSD}=4.003 \mathrm{e}-09 \backslash \mathrm{RMSF}$ $=5.308 \mathrm{e}-07 \backslash \mathrm{Dipole}=0 ., 0 ., 0 . \backslash \mathrm{PG}=\mathrm{D} 02 \mathrm{H} \quad$ [O (C1) , SG (C4) , SG' (C4H8) , SG" (C4H8) , X (C8H8) ] <br>@

## 4-44 spiro[2.2]binonaplane $\boldsymbol{D}_{\mathbf{2}}$

$1 \backslash 1 \backslash$ MHPCC-FR16N07\FOpt \RB3LYP\6-31G(d) \C23H24\RASMUSSEN $\backslash 30-$ Sep-1998\0 <br>\#P B3LYP/6-31G* 5D FOPT=(READFC,TIGHT) SCF= (VSHIFT, NOVARACC,DIRECT) GUESS=CHECK NAME=RASMUSSEN GEOM= (CHECK,NODISTANCE,NOANGLE,NODIHEDRAL) \} \Spiro[2.2]binonaplane 5D D2<br>0,1\C,0.,0., 0. \C, -0.7398176679,-1.276350 $3991,0.0810693595 \backslash \mathrm{C}, 0.7398176679,-1.2763503991,-0.0810693595 \backslash \mathrm{C}, 0.73981$ $76679,1.2763503991,0.0810693595 \backslash C,-0.7398176679,1.2763503991,-0.081069$ $3595 \backslash \mathrm{C},-1.2810290829,-1.3472709276,1.4820023456 \backslash \mathrm{C}, 1.2810290829,-1.3472$ $709276,-1.4820023456 \backslash \mathrm{C}, 1.2810290829,1.3472709276,1.4820023456 \backslash \mathrm{C},-1.281$ 0290829, 1. $3472709276,-1.4820023456 \backslash C,-1.3361026077,-1.2347301681,-1.36$ $69418625 \backslash C, 1.3361026077,-1.2347301681,1.3669418625 \backslash C, 1.3361026077,1.23$ $47301681,-1.3669418625 \backslash C,-1.3361026077,1.2347301681,1.3669418625 \backslash C,-2$. $1607389768,-0.0615790492,1.6636065512 \backslash C, 2.1607389768,-0.0615790492,-1$. $6636065512 \backslash \mathrm{C}, 2.1607389768,0.0615790492,1.6636065512 \backslash \mathrm{C},-2.1607389768,0$. $0615790492,-1.6636065512 \backslash C,-0.0558236848,-1.2625699743,-2.3347334376 \backslash C$ , - 0.0558236848, 1.2625699743,2.3347334376\C, 0.0558236848,1.2625699743,$2.3347334376 \backslash C, 0.0558236848,-1.2625699743,2.3347334376 \backslash C, 0 ., 0 ., 3.22309$ $03162 \backslash \mathrm{C}, 0 ., 0 .,-3.2230903162 \backslash \mathrm{H},-1.870189293,-2.2393492756,1.750530688 \backslash \mathrm{H}$ , 1. $870189293,-2.2393492756,-1.750530688 \backslash H, 1.870189293,2.2393492756,1.7$ $50530688 \backslash \mathrm{H},-1.870189293,2.2393492756,-1.750530688 \backslash \mathrm{H}, 1.9739186494,-2.10$ $83272088,1.5647594393 \backslash \mathrm{H}, 1.9739186494,2.1083272088,-1.5647594393 \backslash \mathrm{H},-1.9$ $739186494,2.1083272088,1.5647594393 \backslash H,-1.9739186494,-2.1083272088,-1.5$ $647594393 \backslash \mathrm{H},-3.0413666301,-0.1197867825,1.0145856863 \backslash \mathrm{H}, 3.0413666301,-0$ $.1197867825,-1.0145856863 \backslash \mathrm{H}, 3.0413666301,0.1197867825,1.0145856863 \backslash \mathrm{H},-$ $3.0413666301,0.1197867825,-1.0145856863 \backslash \mathrm{H},-2.5556712975,-0.0089585184$, $2.6844828119 \backslash \mathrm{H}, 2.5556712975,-0.0089585184,-2.6844828119 \backslash \mathrm{H}, 2.5556712975$


#### Abstract

, 0.0089585184, 2. $6844828119 \backslash H,-2.5556712975,0.0089585184,-2.6844828119 \backslash$ H, - 0.1219626264, -2.14802116,-2.9785579984 \H, -0.1219626264, 2.14802116,2 $.9785579984 \backslash H, 0.1219626264,2.14802116,-2.9785579984 \backslash \mathrm{H}, 0.1219626264,-2$. $14802116,2.9785579984 \backslash H,-0.8687058475,-0.0519151124,3.8896908848 \backslash H, 0.8$ $687058475,0.0519151124,3.8896908848 \backslash \mathrm{H},-0.8687058475,0.0519151124,-3.88$ $96908848 \backslash \mathrm{H}, 0.8687058475,-0.0519151124,-3.8896908848 \backslash \backslash$ Version=IBM-RS600 $0-G 94$ RevE. $2 \backslash$ State $=1-A \backslash H F=-890.6169521 \backslash R M S D=8.735 e-09 \backslash R M S F=3.604 e-07 \backslash D i$ pole=0.,0.,0.\PG=D02 [O(C1), C2" (C1.C1), X(C20H24)]<br>@


## 4-44 spiro[2.2]binonaplane $\quad \boldsymbol{D}_{\mathbf{2 h}}$

$1 \backslash 1 \backslash$ MHPCC-FR11N05 $\backslash$ FOpt $\backslash R B 3 L Y P \backslash 6-31 G(d) \backslash C 23 H 24 \backslash R A S M U S S E N \backslash 30-S e p-1998 \backslash 0$ <br>\#P B3LYP/6-31G* 5D FOPT= (NEWESTMFC,TIGHT) SCF= (VSHIFT, NOVARACC, DIREC T) GUESS=CHECK NAME=RASMUSSEN GEOM = (CHECK, NODISTANCE, NOANGLE, NODIHEDRA L) <br>Spiro[2.2]binonaplane 5D D2h<br>0,1\C,0.,0.,0.\C,-0.7372555731,-1.28 $42137965,0 . \backslash C, 0.7372555731,-1.2842137965,0 . \backslash C, 0.7372555731,1.284213796$ $5,0 . \backslash C,-0.7372555731,1.2842137965,0 . \backslash C,-1.306398973,-1.2921465412,1.42$ $1714871 \backslash C, 1.306398973$, - 1.2921465412 , -1.421714871\C, 1.306398973, 1.29214 $65412,1.421714871 \backslash \mathrm{C},-1.306398973,1.2921465412,-1.421714871 \backslash \mathrm{C},-1.306398$ 973 ,-1.2921465412,-1.421714871\C, 1.306398973,-1.2921465412,1.421714871 $\backslash C, 1.306398973,1.2921465412,-1.421714871 \backslash \mathrm{C},-1.306398973,1.2921465412,1$ $.421714871 \backslash C,-2.1592928896,0 ., 1.6570725627 \backslash \mathrm{C},-2.1592928896,0 .,-1.65707$ $25627 \backslash \mathrm{C}, 2.1592928896,0 ., 1.6570725627 \backslash \mathrm{C}, 2.1592928896,0 .,-1.6570725627 \backslash \mathrm{C}$ , 0., -1. $2626759298,2.331566581 \backslash C, 0 .,-1.2626759298,-2.331566581 \backslash C, 0 ., 1.2$ $626759298,2.331566581 \backslash C, 0 ., 1.2626759298,-2.331566581 \backslash \mathrm{C}, 0 ., 0 ., 3.2213031$ $702 \backslash \mathrm{C}, 0 ., 0 .,-3.2213031702 \backslash \mathrm{H},-1.9266178184,-2.1724069575,1.6587384273 \backslash \mathrm{H}$ ,1.9266178184,-2.1724069575,-1.6587384273\H,1.9266178184,2.1724069575, $1.6587384273 \backslash \mathrm{H},-1.9266178184,2.1724069575,-1.6587384273 \backslash \mathrm{H}, 1.9266178184$ , - $2.1724069575,1.6587384273 \backslash \mathrm{H}, 1.9266178184,2.1724069575,-1.6587384273 \backslash$ H,-1.9266178184,2.1724069575,1.6587384273 \H, -1.9266178184, -2.172406957 $5,-1.6587384273 \backslash \mathrm{H},-2.54884706,0 ., 2.6809583334 \backslash \mathrm{H},-2.54884706,0 .,-2.6809$ $583334 \backslash \mathrm{H}, 2.54884706,0 ., 2.6809583334 \backslash \mathrm{H}, 2.54884706,0 .,-2.6809583334 \backslash \mathrm{H},-3$ $.0444708792,0 ., 1.0117136396 \backslash \mathrm{H},-3.0444708792,0 .,-1.0117136396 \backslash \mathrm{H}, 3.04447$ $08792,0 ., 1.0117136396 \backslash \mathrm{H}, 3.0444708792,0 .,-1.0117136396 \backslash \mathrm{H}, 0 .,-2.15009051$ , 2. $9777483649 \backslash \mathrm{H}, 0 .,-2.15009051$, - $2.9777483649 \backslash \mathrm{H}, 0 ., 2.15009051$, 2.9777483 $649 \backslash \mathrm{H}, 0 ., 2.15009051,-2.9777483649 \backslash \mathrm{H}, 0.8697403398,0 ., 3.8888331319 \backslash \mathrm{H},-0$. $8697403398,0 ., 3.8888331319 \backslash H, 0.8697403398,0 .,-3.8888331319 \backslash H,-0.869740$ $3398,0 .,-3.8888331319 \backslash \backslash V e r s i o n=I B M-R S 6000-G 94 R e v E .2 \backslash$ State=1-AG $\backslash H F=-890$ $.6114352 \backslash \mathrm{RMSD}=5.711 \mathrm{e}-09 \backslash \mathrm{RMSF}=3.050 \mathrm{e}-06 \backslash \mathrm{Dipole=0.,0.,0}. \mathrm{\backslash PG=D02H} \mathrm{\quad[O(C1)} \mathrm{}, \mathrm{}$, C2 (C1. C1) , SG (C4) , SG' (C4H4) , SG" (C4H12) , X (C8H8) ] <br>@

## Dimethanospiroalkaplanes

## 4-47 dimethanospiro[2.2]bioctaplane $\quad \boldsymbol{D}_{\mathbf{2}}$

$1 \backslash 1 \backslash$ MHPCC-FR34N07\FOpt \RB3LYP\6-31G(d) \C23H20\RASMUSSEN $\backslash 30-$ Sep-1998\0 <br>\#P B3LYP/6-31G* 5D FOPT=(READFC,TIGHT) SCF=(VSHIFT,NOVARACC,DIRECT) NAME=RASMUSSEN GUESS=CHECK GEOM=(CHECK,NODISTANCE,NOANGLE,NODIHEDRAL) \} \dimethanospiro[2.2]bioctaplane D2<br>0,1\C,0.,0.,0.\C,-0.7267949517,-1. $3101518635,0.0673929881 \backslash C, 0.7267949517,-1.3101518635,-0.0673929881 \backslash C, 0$ $.7267949517,1.3101518635,0.0673929881 \backslash \mathrm{C},-0.7267949517,1.3101518635,-0$. $0673929881 \backslash C,-1.2980563971,-1.2515632611,1.4495397777 \backslash \mathrm{C}, 1.2980563971,-$ $1.2515632611,-1.4495397777 \backslash \mathrm{C}, 1.2980563971,1.2515632611,1.4495397777 \backslash \mathrm{C}$, $-1.2980563971,1.2515632611,-1.4495397777 \backslash C,-1.3027267776,-1.2035805662$
, - $1.3580023705 \backslash \mathrm{C}, 1.3027267776,-1.2035805662,1.3580023705 \backslash \mathrm{C}, 1.302726777$ $6,1.2035805662,-1.3580023705 \backslash C,-1.3027267776,1.2035805662,1.3580023705$ $\backslash C,-2.2687409438,-0.0141645101,1.3378024216 \backslash C, 2.2687409438,-0.01416451$ $01,-1.3378024216 \backslash \mathrm{C}, 2.2687409438,0.0141645101,1.3378024216 \backslash \mathrm{C},-2.2687409$ $438,0.0141645101,-1.3378024216 \backslash C,-0.0171158947,-0.7868860744,-2.222688$ $6453 \backslash C,-0.0171158947,0.7868860744,2.2226886453 \backslash C, 0.0171158947,0.786886$ $0744,-2.2226886453 \backslash C, 0.0171158947,-0.7868860744,2.2226886453 \backslash C,-3.0985$ $863439,0 ., 0 . \backslash \mathrm{C}, 3.0985863439,0.0 . \backslash \mathrm{H},-1.7835278884,-2.1460327836,1.8729$ $898065 \backslash \mathrm{H}, 1.7835278884,-2.1460327836,-1.8729898065 \backslash \mathrm{H}, 1.7835278884,2.146$ $0327836,1.8729898065 \backslash \mathrm{H},-1.7835278884,2.1460327836,-1.8729898065 \backslash \mathrm{H}, 1.78$ $45412519,-2.1221420161,1.720301892 \backslash \mathrm{H}, 1.7845412519,2.1221420161,-1.7203$ $01892 \backslash \mathrm{H},-1.7845412519,2.1221420161,1.720301892 \backslash \mathrm{H},-1.7845412519,-2.1221$ $420161,-1.720301892 \backslash \mathrm{H},-2.9654546982,0.0136125964,2.1841990207 \backslash \mathrm{H}, 2.9654$ $546982,0.0136125964,-2.1841990207 \backslash \mathrm{H}, 2.9654546982,-0.0136125964,2.18419$ $90207 \backslash \mathrm{H},-2.9654546982,-0.0136125964,-2.1841990207 \backslash \mathrm{H},-0.0729121159,-1.2$ $073936411,-3.2388050682 \backslash \mathrm{H},-0.0729121159,1.2073936411,3.2388050682 \backslash \mathrm{H}, 0$. $0729121159,1.2073936411,-3.2388050682 \backslash \mathrm{H}, 0.0729121159,-1.2073936411,3.2$ $388050682 \backslash \mathrm{H},-3.7597738914,0.8776520242,0.0183499865 \backslash \mathrm{H},-3.7597738914,-0$ $.8776520242,-0.0183499865 \backslash \mathrm{H}, 3.7597738914,-0.8776520242,0.0183499865 \backslash \mathrm{H}$, 3.7597738914, 0.8776520242,-0.0183499865<br>Version=IBM-RS6000-G94RevE.2\ State=1-A $\backslash H F=-888.1575738 \backslash R M S D=8.853 e-09 \backslash R M S F=1.555 e-06 \backslash$ Dipole=0., 0., 0 $. \backslash \mathrm{PG}=\mathrm{D} 02$ [ $\mathrm{O}(\mathrm{C} 1), \mathrm{C} 2 \mathrm{l}(\mathrm{C} 1 . \mathrm{C} 1), \mathrm{X}(\mathrm{C} 2 \mathrm{OH} 20)] \backslash \backslash @$

## 4-47 dimethanospiro[2.2]bioctaplane $\quad \boldsymbol{D}_{\mathbf{2 h}}$

$1 \backslash 1 \backslash$ MHPCC-FR2 7N08 \FOpt \RB3LYP\6-31G(d) \C23H20\RASMUSSEN $\backslash 30-$ Sep-1998\0 <br>\#P B3LYP/6-31G* 5D FOPT= (NEWESTMFC, TIGHT) SCF= (VSHIFT, NOVARACC, DIREC T) NAME=RASMUSSEN GUESS=CHECK GEOM= (CHECK, NODISTANCE,NOANGLE,NODIHEDRA L) <br>dimethanospiro[2.2]bioctaplane $\mathrm{D} 2 \mathrm{~h} \backslash \backslash 0,1 \backslash \mathrm{C}, 0 ., 0 ., 0 . \backslash \mathrm{C},-0.7236170116$ , 0., 1.3176205035\C, 0.7236170116, 0., 1.3176205035\C, 0.7236170116,0., -1. 3 $176205035 \backslash \mathrm{C},-0.7236170116,0 .,-1.3176205035 \backslash \mathrm{C},-1.2969915968,1.402078730$ $9,1.2285224827 \backslash \mathrm{C}, 1.2969915968,-1.4020787309,1.2285224827 \backslash \mathrm{C}, 1.296991596$ 8, 1.4020787309,-1.2285224827\C, -1.2969915968, -1.4020787309,-1.22852248 $27 \backslash C,-1.2969915968,-1.4020787309,1.2285224827 \backslash \mathrm{C}, 1.2969915968,1.4020787$ 309,1.2285224827\C,1.2969915968,-1.4020787309,-1.2285224827\C,-1.29699 15968,1.4020787309,-1.2285224827\C, -2.2644619633,1.3348131912,0. \C, -2. $2644619633,-1.3348131912,0 . \backslash C, 2.2644619633,1.3348131912,0 . \backslash C, 2.2644619$ $633,-1.3348131912,0 . \backslash C, 0 ., 2.2211275254,0.7860704203 \backslash C, 0 .,-2.2211275254$ , 0.7860704203\C, 0., 2. 2211275254, -0.7860704203\C, 0., -2.2211275254, -0.78 $60704203 \backslash \mathrm{C},-3.0952957067,0 ., 0 . \backslash \mathrm{C}, 3.0952957067,0 ., 0 . \backslash \mathrm{H},-1.7874046688,1$. $7980658343,2.1322195727 \backslash \mathrm{H}, 1.7874046688,-1.7980658343,2.1322195727 \backslash \mathrm{H}, 1$. $7874046688,1.7980658343,-2.1322195727 \backslash \mathrm{H},-1.7874046688,-1.7980658343,-2$ $.1322195727 \backslash \mathrm{H}, 1.7874046688,1.7980658343,2.1322195727 \backslash \mathrm{H}, 1.7874046688$, -1 $.7980658343,-2.1322195727 \backslash \mathrm{H},-1.7874046688,1.7980658343,-2.1322195727 \backslash \mathrm{H}$ $,-1.7874046688,-1.7980658343,2.1322195727 \backslash \mathrm{H},-2.9591911208,2.1830955468$ , $0 . \backslash \mathrm{H},-2.9591911208,-2.1830955468,0 . \backslash \mathrm{H}, 2.9591911208,2.1830955468,0 . \backslash \mathrm{H}$, $2.9591911208,-2.1830955468,0 . \backslash \mathrm{H}, 0 ., 3.2384309216,1.2135884155 \backslash \mathrm{H}, 0 .,-3.2$ $384309216,1.2135884155 \backslash \mathrm{H}, 0 ., 3.2384309216,-1.2135884155 \backslash \mathrm{H}, 0 .,-3.2384309$ $216,-1.2135884155 \backslash \mathrm{H},-3.756321713,0 .,-0.8779149922 \backslash \mathrm{H},-3.756321713,0 ., 0$. $8779149922 \backslash \mathrm{H}, 3.756321713,0 ., 0.8779149922 \backslash \mathrm{H}, 3.756321713,0 .,-0.877914992$ $2 \backslash \backslash$ Version=IBM-RS6000-G94RevE. $2 \backslash$ State $=1-A G \backslash H F=-888.1540673 \backslash \mathrm{RMSD}=5.897 \mathrm{e}$ $-09 \backslash R M S F=5.623 e-06 \backslash D i p o l e=0 ., 0 ., 0 . \backslash P G=D 02 H \quad[O(C 1), C 2(C 1 . C 1), S G(C 4 H 4), S$ G'(C4H4),SG" (C4H4), X(C8H8)] <br>@

## 4-29 dimethanospiro[2.2]octaplane $\boldsymbol{D}_{\mathbf{2}}$

$1 \backslash 1 \backslash$ MHPCC-FR27N13\FOpt \RB3LYP\6-31G(d) \C23H24\RASMUSSEN $\backslash 30-$ Sep-1998\0 <br>\#P RB3LYP/6-31G* 5D FOPT=(READFC,TIGHT) SCF=(VSHIFT,NOVARACC,DIRECT) NAME=RASMUSSEN GUESS=CHECK GEOM=(CHECK,NODISTANCE,NOANGLE,NODIHEDRAL) $\backslash \backslash$ imethanospiro[2.2]octaplane $\mathrm{D} 2 \backslash \backslash 0,1 \backslash \mathrm{C}, 0.0 .0 .0 . \backslash \mathrm{C},-0.7191839521,-0.0$ $469287695,-1.3191144063 \backslash C, 0.7191839521,0.0469287695,-1.3191144063 \backslash C, 0$. 7191839521,-0.0469287695,1.3191144063\C,-0.7191839521,0.0469287695,1.3 $191144063 \backslash \mathrm{C},-1.3089729688,-1.4166741729,-1.3380523577 \backslash \mathrm{C}, 1.3089729688,1$ $.4166741729,-1.3380523577 \backslash \mathrm{C}, 1.3089729688,-1.4166741729,1.3380523577 \backslash \mathrm{C}$, $-1.3089729688,1.4166741729,1.3380523577 \backslash C,-1.3172568181,1.3519419981,-$ $1.3031776458 \backslash C, 1.3172568181,-1.3519419981,-1.3031776458 \backslash C, 1.3172568181$ ,1.3519419981,1.3031776458\C,-1.3172568181,-1.3519419981,1.3031776458\} C, $-2.1716483589,-1.3759029675,-0.0115655369 \backslash C, 2.1716483589,1.375902967$ $5,-0.0115655369 \backslash C, 2.1716483589,-1.3759029675,0.0115655369 \backslash \mathrm{C},-2.1716483$ $589,1.3759029675,0.0115655369 \backslash C,-0.028641231,2.267537116,-1.522052298 \backslash$ $C,-0.028641231,-2.267537116,1.522052298 \backslash C, 0.028641231,2.267537116,1.52$ $2052298 \backslash C, 0.028641231,-2.267537116,-1.522052298 \backslash C,-2.9979635374,0.0 . \backslash$ C, 2.9979635374,0., 0. \H, -1.99201834,-1.6414935319,-2.1767422262\H,1.992 01834,1.6414935319,-2.1767422262\H,1.99201834,-1.6414935319,2.17674222 $62 \backslash \mathrm{H},-1.99201834,1.6414935319,2.1767422262 \backslash \mathrm{H}, 2.0116041885,-1.524601081$ , $-2.141248613 \backslash \mathrm{H}, 2.0116041885,1.524601081,2.141248613 \backslash \mathrm{H},-2.0116041885,-$ $1.524601081,2.141248613 \backslash \mathrm{H},-2.0116041885,1.524601081,-2.141248613 \backslash \mathrm{H},-2$. $8963977218,-2.2002995987,0.0072837085 \backslash \mathrm{H}, 2.8963977218,2.2002995987,0.00$ $72837085 \backslash \mathrm{H}, 2.8963977218,-2.2002995987,-0.0072837085 \backslash \mathrm{H},-2.8963977218,2$. 2002995987,-0.0072837085\Н, -0.041977571, 2.5817512981,-2.5741924732\H,-$0.0534763635,3.1913968011,-0.9416585675 \backslash \mathrm{H},-0.041977571,-2.5817512981,2$ $.5741924732 \backslash \mathrm{H},-0.0534763635,-3.1913968011,0.9416585675 \backslash \mathrm{H}, 0.041977571,2$ . $5817512981,2.5741924732 \backslash \mathrm{H}, 0.0534763635,3.1913968011,0.9416585675 \backslash \mathrm{H}, 0$. $041977571,-2.5817512981,-2.5741924732 \backslash \mathrm{H}, 0.0534763635,-3.1913968011,-0$. $9416585675 \backslash \mathrm{H},-3.6571535514,-0.013391157,0.8785590834 \backslash \mathrm{H},-3.6571535514,0$ $.013391157,-0.8785590834 \backslash \mathrm{H}, 3.6571535514,-0.013391157,-0.8785590834 \backslash \mathrm{H}, 3$ .6571535514,0.013391157,0.8785590834 <br>Version=IBM-RS6000-G94RevE. $2 \backslash$ Sta $\mathrm{te}=1-\mathrm{A} \backslash \mathrm{HF}=-890.548503 \backslash \mathrm{RMSD}=9.112 \mathrm{e}-09 \backslash \mathrm{RMSF}=2.879 \mathrm{e}-06 \backslash \mathrm{Dipole=0.,0.,0}. \mathrm{\ PG}$ =D02 [O(C1), C2" (C1.C1), X(C20H24)] <br>@

## 4-29 dimethanospiro[2.2]octaplane $\quad D_{\text {2h }}$

$1 \backslash 1 \backslash$ MHPCC-FR21N11 \FOpt $\backslash$ RB3LYP $\backslash 6-31 G(d) \backslash C 23 H 24 \backslash R A S M U S S E N \backslash 30-S e p-1998 \backslash 0$ <br>\#P RB3LYP/6-31G* 5D FOPT=(NEWESTMFC,TIGHT) SCF=(VSHIFT,NOVARACC,DIRE CT) NAME=RASMUSSEN GUESS=CHECK GEOM=(CHECK,NODISTANCE,NOANGLE,NODIHEDR AL) <br>Dimethanospiro[2.2]octaplane D2h<br>0,1\C,0.,0.,0.\C,-0.7179973349, $-1.3223379228,0 . \backslash C, 0.7179973349,-1.3223379228,0 . \backslash C, 0.7179973349,1.3223$ $379228,0 . \backslash \mathrm{C},-0.7179973349,1.3223379228,0 . \backslash \mathrm{C},-1.3116097482,-1.320744704$ $8,1.3834032218 \backslash C, 1.3116097482,-1.3207447048,-1.3834032218 \backslash \mathrm{C}, 1.31160974$ $82,1.3207447048,1.3834032218 \backslash C,-1.3116097482,1.3207447048,-1.383403221$ $8 \backslash C,-1.3116097482,-1.3207447048,-1.3834032218 \backslash C, 1.3116097482,-1.320744$ $7048,1.3834032218 \backslash C, 1.3116097482,1.3207447048,-1.3834032218 \backslash C,-1.31160$ $97482,1.3207447048,1.3834032218 \backslash \mathrm{C},-2.1701697231,0 ., 1.3743173238 \backslash \mathrm{C},-2.1$ 701697231,0.,-1.3743173238\C,2.1701697231,0.,1.3743173238\C,2.17016972 31,0.,-1.3743173238\C,0.,-1.5228781491,2.2669882177\C,0.,-1.5228781491 ,-2.2669882177\C,0.,1.5228781491,2.2669882177\C,0.,1.5228781491,-2.266 9882177\C,-2.9970815389,0., 0. \C, 2.9970815389, 0., 0. \H, -2.0030677535,-2. 1579765959,1.5830968244 \H,2.0030677535,-2.1579765959,-1.5830968244 \H, 2
$.0030677535,2.1579765959,1.5830968244 \backslash \mathrm{H},-2.0030677535,2.1579765959,-1$. $5830968244 \backslash \mathrm{H}, 2.0030677535,-2.1579765959,1.5830968244 \backslash \mathrm{H}, 2.0030677535,2$. $1579765959,-1.5830968244 \backslash \mathrm{H},-2.0030677535,2.1579765959,1.5830968244 \backslash \mathrm{H}$, -$2.0030677535,-2.1579765959,-1.5830968244 \backslash H,-2.8939868282,0 ., 2.19966484$ $43 \backslash H,-2.8939868282,0 .,-2.1996648443 \backslash H, 2.8939868282,0 ., 2.1996648443 \backslash H, 2$ $.8939868282,0 .,-2.1996648443 \backslash \mathrm{H}, 0 .,-0.941246802,3.1905996928 \backslash \mathrm{H}, 0 .,-2.57$ $47862329,2.5837004284 \backslash \mathrm{H}, 0 .,-0.941246802,-3.1905996928 \backslash \mathrm{H}, 0 .,-2.57478623$ $29,-2.5837004284 \backslash \mathrm{H}, 0 ., 0.941246802,3.1905996928 \backslash \mathrm{H}, 0 ., 2.5747862329,2.583$ $7004284 \backslash \mathrm{H}, 0 ., 0.941246802,-3.1905996928 \backslash \mathrm{H}, 0 ., 2.5747862329,-2.5837004284$ $\backslash \mathrm{H},-3.6560508339,0.8787780648,0 . \backslash \mathrm{H},-3.6560508339,-0.8787780648,0 . \backslash \mathrm{H}, 3$. $6560508339,-0.8787780648,0 . \backslash H, 3.6560508339,0.8787780648,0 . \backslash \backslash V e r s i o n=I B$ M-RS6000-G94RevE. $2 \backslash$ State=1-AG $\backslash H F=-890.5477682 \backslash R M S D=5.620 e-09 \backslash R M S F=3.15$ 5e-06\Dipole=0., 0., 0. \PG=D02H [O(C1), C2 (C1.C1), SG (C4H8) , SG' (C4H4), SG" ( C4H4) , X (C8H8) ] <br>@

## 4-48 dimethanospiro[2.2]binonaplane $\quad \boldsymbol{D}_{\mathbf{2}}$

$1 \backslash 1 \backslash$ MHPCC-FR23N16\FOpt \RB3LYP\6-31G(d) \C25H24\RASMUSSEN $\backslash 30-$ Sep-1998\0 <br>\#P B3LYP/6-31G* 5D FOPT=(READFC,TIGHT) SCF=(VSHIFT,NOVARACC,DIRECT) NAME=RASMUSSEN GEOM=(CHECK,NODISTANCE,NOANGLE,NODIHEDRAL) GUESS=CHECK\} \dimethanospiro[2.2]binonaplane D2 5D<br>0,1\C,0.,0.,0.\C,-0.7205878413, $-1.3187770511,0.0439072374 \backslash C, 0.7205878413,-1.3187770511,-0.0439072374 \backslash$ C, 0.7205878413,1.3187770511,0.0439072374\C,-0.7205878413,1.3187770511, $-0.0439072374 \backslash C,-1.310918359,-1.3120778647,1.4143116958 \backslash C, 1.310918359$, $-1.3120778647,-1.4143116958 \backslash C, 1.310918359,1.3120778647,1.4143116958 \backslash C$, $-1.310918359,1.3120778647,-1.4143116958 \backslash \mathrm{C},-1.3111206887,-1.2707923081$, $-1.359405697 \backslash C, 1.3111206887,-1.2707923081,1.359405697 \backslash \mathrm{C}, 1.3111206887,1$ $.2707923081,-1.359405697 \backslash \mathrm{C},-1.3111206887,1.2707923081,1.359405697 \backslash \mathrm{C},-2$ $.2107004082,-0.0132434369,1.3543416055 \backslash C, 2.2107004082,-0.0132434369,-1$ $.3543416055 \backslash C, 2.2107004082,0.0132434369,1.3543416055 \backslash C,-2.2107004082,0$ $.0132434369,-1.3543416055 \backslash C,-0.0150046442,-1.2475574996,-2.3081722595 \backslash$ C, $-0.0150046442,1.2475574996,2.3081722595 \backslash C, 0.0150046442,1.2475574996$, $-2.3081722595 \backslash C, 0.0150046442,-1.2475574996,2.3081722595 \backslash C,-3.037483476$ 5, 0., 0. \C, 3.0374834765,0.,0.\C,0.,0.,3.1968844993\C,0.,0.,-3.196884499 $3 \backslash H,-1.9333946447,-2.1787589588,1.6982862889 \backslash \mathrm{H}, 1.9333946447,-2.1787589$ 588,-1.6982862889\H,1.9333946447,2.1787589588,1.6982862889\H,-1.933394 6447,2.1787589588,-1.6982862889\H,1.9393251372,-2.1434377429,1.5990808 $972 \backslash \mathrm{H}, 1.9393251372,2.1434377429,-1.5990808972 \backslash \mathrm{H},-1.9393251372,2.143437$ 7429,1.5990808972\H,-1.9393251372,-2.1434377429,-1.5990808972\H,-2.926 1421548, 0.0043048292,2.1860642632\H, 2.9261421548, 0.0043048292,-2.18606 $42632 \backslash \mathrm{H}, 2.9261421548,-0.0043048292,2.1860642632 \backslash \mathrm{H},-2.9261421548,-0.004$ $3048292,-2.1860642632 \backslash \mathrm{H},-0.0398676284,-2.1415523962,-2.9449483885 \backslash \mathrm{H},-0$ $.0398676284,2.1415523962,2.9449483885 \backslash$ Н, $0.0398676284,2.1415523962,-2.9$ $449483885 \backslash \mathrm{H}, 0.0398676284,-2.1415523962,2.9449483885 \backslash \mathrm{H},-3.6971325964,0$. $8789473301,0.013206949 \backslash \mathrm{H},-3.6971325964,-0.8789473301,-0.013206949 \backslash \mathrm{H}, 3$. 6971325964,-0.8789473301,0.013206949\H,3.6971325964,0.8789473301,-0.01 $3206949 \backslash \mathrm{H}, 0.8798204927,0.0165171955,3.8554465625 \backslash \mathrm{H},-0.8798204927,-0.01$ 65171955,3.8554465625\H, 0.8798204927,-0.0165171955,-3.8554465625\H,-0. 8798204927,0.0165171955,-3.8554465625<br>Version=IBM-RS6000-G94RevE.2\St ate $=1-A \backslash H F=-966.7997009 \backslash R M S D=6.731 e-09 \backslash R M S F=2.098 e-06 \backslash$ Dipole=0., 0., 0. $\backslash$ PG=D02 [O(C1), C2'(C1.C1), C2" (C1.C1), X(C20H24)]<br>@


#### Abstract

4-48 dimethanospiro[2.2]binonaplane $\quad \boldsymbol{D}_{\mathbf{2 h}}$ $1 \backslash 1 \backslash$ MHPCC-FR33N07\FOpt \RB3LYP\6-31G(d) \C25H24\RASMUSSEN\30-Sep-1998\0 <br>\#P B3LYP/6-31G* 5D FOPT=(NEWESTMFC,TIGHT) SCF=(VSHIFT,NOVARACC,DIREC T) NAME=RASMUSSEN GEOM=(CHECK,NODISTANCE,NOANGLE,NODIHEDRAL) GUESS=CHE $\mathrm{CK} \backslash$ \dimethanospiro[2.2]binonaplane D2h 5D $\backslash \backslash 0,1 \backslash \mathrm{C}, 0.0 .0 .0 . \backslash \mathrm{C},-0.7193339$ 675,-1.3222211115,0. \C,0.7193339675,-1.3222211115,0. \C, 0.7193339675,1. $322221115,0 . \backslash C,-0.7193339675,1.3222211115,0 . \backslash C,-1.3094859808,-1.29161$ $78499,1.3860921642 \backslash C, 1.3094859808,-1.2916178499,-1.3860921642 \backslash \mathrm{C}, 1.3094$ 859808,1.2916178499,1.3860921642\C,-1.3094859808,1.2916178499,-1.38609 $21642 \backslash \mathrm{C},-1.3094859808,-1.2916178499,-1.3860921642 \backslash \mathrm{C}, 1.3094859808,-1.29$ $16178499,1.3860921642 \backslash C, 1.3094859808,1.2916178499,-1.3860921642 \backslash C,-1.3$ $094859808,1.2916178499,1.3860921642 \backslash \mathrm{C},-2.2090736948,0 ., 1.3527971521 \backslash \mathrm{C}$, $-2.2090736948,0 .,-1.3527971521 \backslash C, 2.2090736948,0 ., 1.3527971521 \backslash \mathrm{C}, 2.2090$ $736948,0 .,-1.3527971521 \backslash C, 0 .,-1.2476253154,2.307008999 \backslash C, 0 .,-1.2476253$ 154,-2.307008999\C,0.,1.2476253154,2.307008999\C,0.,1.2476253154,-2.30 $7008999 \backslash C,-3.0364730304,0 ., 0 . \backslash C, 3.0364730304,0 ., 0 . \backslash C, 0 ., 0 ., 3.196009006$ $2 \backslash C, 0 ., 0 .,-3.1960090062 \backslash H,-1.9378333299,-2.159838477,1.6492355347 \backslash \mathrm{H}, 1$. 9378333299,-2.159838477,-1.6492355347\H,1.9378333299,2.159838477,1.649 $2355347 \backslash \mathrm{H},-1.9378333299,2.159838477,-1.6492355347 \backslash \mathrm{H}, 1.9378333299,-2.15$ 9838477,1.6492355347\H,1.9378333299,2.159838477,-1.6492355347\H,-1.937 8333299,2.159838477,1.6492355347\H,-1.9378333299,-2.159838477,-1.64923 $55347 \backslash \mathrm{H},-2.9235620971,0 ., 2.1854165507 \backslash \mathrm{H},-2.9235620971,0 .,-2.1854165507$ \H, 2.9235620971, 0., 2.1854165507 $\mathrm{H}, 2.9235620971,0 .,-2.1854165507 \backslash \mathrm{H}, 0 .,-$ $2.1415903527,2.9451461403 \backslash \mathrm{H}, 0 .,-2.1415903527,-2.9451461403 \backslash \mathrm{H}, 0 ., 2.1415$ 903527,2.9451461403\H,0.,2.1415903527,-2.9451461403\н,-3.695977718,0.8 $791227768,0 . \backslash$ Н, $-3.695977718,-0.8791227768,0 . \backslash \mathrm{H}, 3.695977718,-0.87912277$ $68,0 . \backslash \mathrm{H}, 3.695977718,0.8791227768,0 . \backslash \mathrm{H}, 0.8798896866,0.3 .854798189 \backslash \mathrm{H},-0$ $.8798896866,0 ., 3.854798189 \backslash H, 0.8798896866,0 .,-3.854798189 \backslash H,-0.8798896$ 866,0.,-3.854798189<br>Version=IBM-RS6000-G94RevE. $2 \backslash$ State=1-AG\HF=-966.7 $990251 \backslash \mathrm{RMSD}=7.180 \mathrm{e}-09 \backslash \mathrm{RMSF}=1.473 \mathrm{e}-06 \backslash \mathrm{Dipole=0.,0.,0}. \mathrm{\backslash PG=D02H} \mathrm{\quad[O(C1),C2}$ (C1.C1), C2'(C1.C1), SG(C4H4), SG'(C4H4), SG" (C4H8), X(C8H8)] <br>@


Table C-23. Guassian archive files for the HF/6-31G(d) optimized alkaplanes in Chapter 4.

## Alkaplanes

## 4-30 bihexaplane $\boldsymbol{D}_{\mathbf{2}}$

$1 \backslash 1 \backslash G I N C-V P P 01 \backslash S P \backslash R M P 2-F C \backslash 6-311+G(2 d, p) \backslash C 17 H 16 \backslash R A S M U S S E N \backslash 02-A p r-2000 \backslash 0$ <br>\#P MP2/6-311+G(2D, P) 5D MAXDISK=1980000000 NAME=RASMUSSEN <br>Bihexapla ne $\mathrm{D} 2 \backslash \backslash 0,1 \backslash \mathrm{C}, 0,0 ., 0.0 . \backslash \mathrm{C}, 0,-1.1169218004,-0.1913900441,-1.0976883799 \backslash$ C, 0, -1.1169218004, 0.1913900441,1.0976883799\C,0,1.1169218004, 0.1913900 $441,-1.0976883799 \backslash C, 0,1.1169218004,-0.1913900441,1.0976883799 \backslash \mathrm{C}, 0,-0.7$ 648023637,2.2606425076,0.0778803093\C,0,-0.7648023637,-2.2606425076,-0 $.0778803093 \backslash C, 0,0.7648023637,-2.2606425076,0.0778803093 \backslash C, 0,0.76480236$ $37,2.2606425076,-0.0778803093 \backslash C, 0,-0.8965087458,1.3799555252,-1.349132$ $063 \backslash C, 0,-0.8965087458,-1.3799555252,1.349132063 \backslash C, 0,0.8965087458,-1.37$ $99555252,-1.349132063 \backslash C, 0,0.8965087458,1.3799555252,1.349132063 \backslash \mathrm{C}, 0,-0$ $.6342936612,-1.5474703101,-1.51434929 \backslash C, 0,-0.6342936612,1.5474703101,1$ $.51434929 \backslash C, 0,0.6342936612,1.5474703101,-1.51434929 \backslash C, 0,0.6342936612,-$ $1.5474703101,1.51434929 \backslash \mathrm{H}, 0,1.0260197609,-2.0833783525,2.3764890602 \backslash \mathrm{H}$, $0,1.0260197609,2.0833783525,-2.3764890602 \backslash \mathrm{H}, 0,-1.0260197609,2.08337835$
$25,2.3764890602 \backslash \mathrm{H}, 0,-1.0260197609,-2.0833783525,-2.3764890602 \backslash \mathrm{H}, 0,1.55$ $5995143,1.8455880639,2.0730818386 \backslash \mathrm{H}, 0,1.555995143,-1.8455880639,-2.073$ $0818386 \backslash \mathrm{H}, 0,-1.555995143,-1.8455880639,2.0730818386 \backslash \mathrm{H}, 0,-1.555995143,1$ $.8455880639,-2.0730818386 \backslash H, 0,-2.1362570694,-0.3204435805,-0.792057544$ $7 \backslash \mathrm{H}, 0,-2.1362570694,0.3204435805,0.7920575447 \backslash \mathrm{H}, 0,2.1362570694,0.32044$ $35805,-0.7920575447 \backslash \mathrm{H}, 0,2.1362570694,-0.3204435805,0.7920575447 \backslash \mathrm{H}, 0,-1$ $.3055572945,3.2006314753,0.0209602142 \backslash \mathrm{H}, 0,-1.3055572945,-3.2006314753$, $-0.0209602142 \backslash \mathrm{H}, 0,1.3055572945,-3.2006314753,0.0209602142 \backslash \mathrm{H}, 0,1.305557$ 2945, 3.2006314753,-0.0209602142 <br>Version=Fujitsu-VP-Unix-G98RevA.7\Sta te=1-A $\backslash \mathrm{HF}=-652.5396576 \backslash \mathrm{MP} 2=-655.1665063 \backslash \mathrm{RMSD}=9.494 \mathrm{e}-09 \backslash \mathrm{PG}=\mathrm{D} 02 \quad[\mathrm{O}(\mathrm{C} 1), \mathrm{X}$ (C16H16)] <br>@

## 4-30 bihexaplane $\boldsymbol{D}_{\mathbf{2 h}}$

$1 \backslash 1 \backslash G I N C-V P P 05 \backslash S P \backslash R M P 2-F C \backslash 6-311+G(2 d, p) \backslash C 17 H 16 \backslash R A S M U S S E N \backslash 02-A p r-2000 \backslash 0$ <br>\#P MP2/6-311+G(2D,P) 5D MAXDISK=1980000000 NAME=RASMUSSEN <br>Bihexapla ne $\mathrm{D} 2 \mathrm{~h} \backslash \backslash 0,1 \backslash \mathrm{C}, 0,0 ., 0 ., 0 . \backslash \mathrm{C}, 0,0 ., 1.1068869634,1.1492091539 \backslash \mathrm{C}, 0,0 .,-1.10$ $68869634,-1.1492091539 \backslash \mathrm{C}, 0,0 ., 1.1068869634,-1.1492091539 \backslash \mathrm{C}, 0,0 .,-1.106$ $8869634,1.1492091539 \backslash C, 0,1.4542050264,1.4209758569,0.7705060747 \backslash C, 0,-1$ $.4542050264,-1.4209758569,-0.7705060747 \backslash \mathrm{C}, 0,1.4542050264,1.4209758569$, $-0.7705060747 \backslash C, 0,-1.4542050264,1.4209758569,-0.7705060747 \backslash C, 0,1.45420$ 50264,-1.4209758569, -0.7705060747\C, 0, -1.4542050264,1.4209758569, 0.770 $5060747 \backslash \mathrm{C}, 0,1.4542050264,-1.4209758569,0.7705060747 \backslash \mathrm{C}, 0,-1.4542050264$, $-1.4209758569,0.7705060747 \backslash \mathrm{C}, 0,2.2409963733,0 ., 0.772833763 \backslash \mathrm{C}, 0,-2.2409$ $963733,0 .,-0.772833763 \backslash C, 0,2.2409963733,0 .,-0.772833763 \backslash C, 0,-2.2409963$ $733,0.0 .772833763 \backslash \mathrm{H}, 0,-3.1926451551,0 .,-1.3034672223 \backslash \mathrm{H}, 0,3.1926451551$ , 0., 1. $3034672223 \backslash \mathrm{H}, 0,-3.1926451551,0 ., 1.3034672223 \backslash \mathrm{H}, 0,3.1926451551,0$. ,-1.3034672223 \H, 0,1.9757055763,2.2314796916,1.2853991632\H,0,-1.97570 $55763,-2.2314796916,-1.2853991632 \backslash \mathrm{H}, 0,1.9757055763,2.2314796916,-1.285$ $3991632 \backslash \mathrm{H}, 0,-1.9757055763,2.2314796916,-1.2853991632 \backslash \mathrm{H}, 0,1.9757055763$, $-2.2314796916,-1.2853991632 \backslash \mathrm{H}, 0,-1.9757055763,2.2314796916,1.285399163$ $2 \backslash \mathrm{H}, 0,1.9757055763,-2.2314796916,1.2853991632 \backslash \mathrm{H}, 0,-1.9757055763,-2.231$ $4796916,1.2853991632 \backslash \mathrm{H}, 0,0 ., 0.8474546833,2.1891059097 \backslash \mathrm{H}, 0,0 .,-0.847454$ $6833,-2.1891059097 \backslash \mathrm{H}, 0,0.0 .8474546833,-2.1891059097 \backslash \mathrm{H}, 0,0 .,-0.8474546$ 833,2.1891059097<br>Version=Fujitsu-VP-Unix-G98RevA. 7 \State=1-AG\HF=-652 $.4880451 \backslash \mathrm{MP} 2=-655.1424045 \backslash \mathrm{RMSD}=3.115 \mathrm{e}-09 \backslash \mathrm{PG}=\mathrm{D} 02 \mathrm{H} \quad\left[\mathrm{O}(\mathrm{C} 1), \mathrm{SG}(\mathrm{C} 4 \mathrm{H} 4), \mathrm{SG}{ }^{\prime}(\mathrm{C}\right.$ 4H4) , X (C8H8) ] <br>@

## 4-31 hexaplane $\boldsymbol{D}_{\mathbf{2}}$

$1 \backslash 1 \backslash G I N C-V P P 03 \backslash S P \backslash R M P 2-F C \backslash 6-311+G(2 d, p) \backslash C 17 H 20 \backslash R A S M U S S E N \backslash 27-J u n-1999 \backslash 0$ <br>\#P RMP2/6-311+G(2D,P) 5D SCF=DIRECT NAME=RASMUSSEN GEOM= (CHECK,NODIS TANCE, NOANGLE, NODIHEDRAL) GUESS=CHECK MAXDISK=1800000000<br>hexaplane 5D $\mathrm{D} 2 \backslash \backslash 0,1 \backslash \mathrm{C} \backslash \mathrm{X}, 1,0.5 \backslash \mathrm{X}, 1,0.5,2,90 . \backslash \mathrm{X}, 1,0.5,2,90 ., 3,-90 ., 0 \backslash \mathrm{X}, 1,0.5,3,90 .$, $2,180 ., 0 \backslash X, 1,0.5,2,90 ., 3,180 ., 0 \backslash X, 1,0.5,2,90 ., 4,180 ., 0 \backslash C, 1,1.57437116$, $2,84.29816596,7,44.98709994,0 \backslash C, 1,1.57437116,5,84.29816596,7,44.987099$ $94,0 \backslash C, 1,1.57437116,2,84.29816596,4,44.98709994,0 \backslash C, 1,1.57437116,5,84$. $29816596,4,44.98709994,0 \backslash C, 8,1.51372486,1,92.0262113,2,18.89635042,0 \backslash C$ , $9,1.51372486,1,92.0262113,5,18.89635042,0 \backslash C, 10,1.51372486,1,92.026211$ $3,2,18.89635042,0 \backslash C, 11,1.51372486,1,92.0262113,5,18.89635042,0 \backslash C, 8,1.6$ $3232972,1,83.09318934,5,-12.08672559,0 \backslash C, 9,1.63232972,1,83.09318934,2$, $-12.08672559,0 \backslash C, 10,1.63232972,1,83.09318934,5,-12.08672559,0 \backslash C, 11,1.6$ $3232972,1,83.09318934,2,-12.08672559,0 \backslash C, 13,1.61540188,9,95.00711984,1$ $,-73.12035643,0 \backslash C, 14,1.61540188,10,95.00711984,1,-73.12035643,0 \backslash C, 15,1$
$.61540188,11,95.00711984,1,-73.12035643,0 \backslash C, 12,1.61540188,8,95.0071198$ $4,1,-73.12035643,0 \backslash H, 8,1.07261729,1,120.65508398,2,-92.01433365,0 \backslash H, 9$, $1.07261729,1,120.65508398,5,-92.01433365,0 \backslash \mathrm{H}, 10,1.07261729,1,120.65508$ $398,2,-92.01433365,0 \backslash H, 11,1.07261729,1,120.65508398,5,-92.01433365,0 \backslash H$ , 12, 1.0928235, 8, 122.80326112,1,168.84844519, 0\H,13,1.0928235,9,122.803 $26112,1,168.84844519,0 \backslash \mathrm{H}, 14,1.0928235,10,122.80326112,1,168.84844519,0$ $\backslash \mathrm{H}, 15,1.0928235,11,122.80326112,1,168.84844519,0 \backslash \mathrm{H}, 17,1.08678516,9,114$ $.48275905,1,186.25301415,0 \backslash H, 18,1.08678516,10,114.48275905,1,186.25301$ $415,0 \backslash \mathrm{H}, 19,1.08678516,11,114.48275905,1,186.25301415,0 \backslash \mathrm{H}, 16,1.08678516$ , 8, 114.48275905, 1, 186.25301415,0\H,20,1.08649164,13,107.64014877,9,290 $.03442105,0 \backslash \mathrm{H}, 21,1.08649164,14,107.64014877,10,290.03442105,0 \backslash \mathrm{H}, 22,1.0$ $8649164,15,107.64014877,11,290.03442105,0 \backslash H, 23,1.08649164,12,107.64014$ $877,8,290.03442105,0 \backslash \mathrm{H}, 20,1.08617912,13,111.56858956,9,174.5612924,0 \backslash \mathrm{H}$ , 21, 1.08617912, 14,111.56858956,10,174.5612924,0\H,22,1.08617912,15,111 $.56858956,11,174.5612924,0 \backslash \mathrm{H}, 23,1.08617912,12,111.56858956,8,174.56129$ 24, 0<br>Version=Fujitsu-VP-Unix-G98RevA. 6\State=1-A\HF=-654.9471412\MP2= $-657.6334885 \backslash \mathrm{RMSD}=5.814 \mathrm{e}-09 \backslash \mathrm{PG}=\mathrm{D} 02$ [O(C1),X(C16H20)]<br>@

## 4-31 hexaplane $D_{\mathbf{2 h}}$

$1 \backslash 1 \backslash G I N C-V P P 03 \backslash S P \backslash R M P 2-F C \backslash 6-311+G(2 d, p) \backslash C 17 H 20 \backslash R A S M U S S E N \backslash 27-J u n-1999 \backslash 0$ <br>\#P RMP2/6-311+G(2D,P) 5D SCF=DIRECT NAME=RASMUSSEN GEOM=(CHECK,NODIS TANCE, NOANGLE,NODIHEDRAL) GUESS=CHECK MAXDISK=1800000000<br>hexaplane 5D $\mathrm{D} 2 \mathrm{~h} \backslash \backslash 0,1 \backslash \mathrm{C}, 0 ., 0 ., 0 . \backslash \mathrm{C},-1.1028812014,-1.1258345697,0 . \backslash \mathrm{C}, 1.1028812014,-$ $1.1258345697,0 . \backslash C, 1.1028812014,1.1258345697,0 . \backslash C,-1.1028812014,1.12583$ 45697,0. \C, -1.345289051,-0.7704647923,1.4989453739\C,1.345289051,-0.77 $04647923,-1.4989453739 \backslash C, 1.345289051,0.7704647923,1.4989453739 \backslash \mathrm{C},-1.34$ 5289051,0.7704647923,-1.4989453739\C,-1.345289051,-0.7704647923,-1.498 $9453739 \backslash C, 1.345289051,-0.7704647923,1.4989453739 \backslash C, 1.345289051,0.77046$ 47923,-1.4989453739\C,-1.345289051,0.7704647923,1.4989453739\C,0.,-1.3 $290477792,2.1668973766 \backslash C, 0 .,-1.3290477792,-2.1668973766 \backslash \mathrm{C}, 0 ., 1.3290477$ 792,2.1668973766\C,0.,1.3290477792,-2.1668973766\H,-0.8740814542,-2.17 56275111,0. \H, 0.8740814542,-2.1756275111,0. \H, 0.8740814542,2.175627511 1,0. \H,-0.8740814542,2.1756275111,0. \H,-2.2060481738,-1.2221340811,2.0 $084141438 \backslash \mathrm{H}, 2.2060481738,-1.2221340811,-2.0084141438 \backslash \mathrm{H}, 2.2060481738$, 1. 2221340811,2.0084141438\H,-2.2060481738,1.2221340811,-2.0084141438\H,2 . $2060481738,-1.2221340811,2.0084141438 \backslash \mathrm{H}, 2.2060481738,1.2221340811,-2$. $0084141438 \backslash$ н, $-2.2060481738,1.2221340811,2.0084141438 \backslash$ Н, -2.2060481738 , $1.2221340811,-2.0084141438 \backslash H, 0 .,-2.4162861519,2.1111927504 \backslash H, 0 .,-2.416$ 2861519,-2.1111927504 \Н, 0., 2.4162861519,2.1111927504 \Н, 0., 2.4162861519 ,-2.1111927504 \H, 0.,-1.0960545377,3.2274380869\H, 0.,-1.0960545377,-3.2 $274380869 \backslash \mathrm{H}, 0.1 .0960545377,3.2274380869 \backslash \mathrm{H}, 0.1 .0960545377,-3.22743808$ $69 \backslash$ Version=Fujitsu-VP-Unix-G98RevA. $6 \backslash$ State $=1-A G \backslash H F=-654.9079887 \backslash M P 2=-$ $657.6192908 \backslash \mathrm{RMSD}=6.141 \mathrm{e}-09 \backslash \mathrm{PG}=\mathrm{D} 02 \mathrm{H}$ [O(C1), SG(C4H4), SG"(C4H8), X(C8H8)]\} \@

## 4-32 biheptaplane $\boldsymbol{D}_{\mathbf{2}}$

$1 \backslash 1 \backslash G I N C-V P P 05 \backslash S P \backslash R M P 2-F C \backslash 6-311+G(2 d, p) \backslash C 19 H 20 \backslash R A S M U S S E N \backslash 03-A p r-2000 \backslash 0$ <br>\#P MP2/6-311+G(2D,P) 5D MAXDISK=1980000000 NAME=RASMUSSEN <br>Biheptapl ane C19H20 RHF/6-31G* 5D OPT D2 <br>0,1\C\X,1,0.5\X,1,0.5,2,90. \X,1,0.5,2 , $90 ., 3,-90 ., 0 \backslash X, 1,0.5,3,90 ., 2,180 ., 0 \backslash X, 1,0.5,2,90 ., 3,180 ., 0 \backslash X, 1,0.5,2$, $90 ., 4,180 ., 0 \backslash C, 1,1.57015259,2,84.20975239,7,44.49425156,0 \backslash C, 1,1.570152$ $59,5,84.20975239,7,44.49425156,0 \backslash C, 1,1.57015259,2,84.20975239,4,44.494$
$25156,0 \backslash C, 1,1.57015259,5,84.20975239,4,44.49425156,0 \backslash C, 8,1.50302557,1$, $92.82460395,2,22.00271427,0 \backslash C, 9,1.50302557,1,92.82460395,5,22.00271427$ , $0 \backslash \mathrm{C}, 10,1.50302557,1,92.82460395,2,22.00271427,0 \backslash C, 11,1.50302557,1,92$. $82460395,5,22.00271427,0 \backslash C, 8,1.6206111,1,83.36750595,5,-11.84935517,0 \backslash$ $\mathrm{C}, 9,1.6206111,1,83.36750595,2,-11.84935517,0 \backslash \mathrm{C}, 10,1.6206111,1,83.36750$ $595,5,-11.84935517,0 \backslash C, 11,1.6206111,1,83.36750595,2,-11.84935517,0 \backslash C, 1$ $3,1.61307541,9,98.37725803,1,-69.15792203,0 \backslash C, 14,1.61307541,10,98.3772$ $5803,1,-69.15792203,0 \backslash C, 15,1.61307541,11,98.37725803,1,-69.15792203,0 \backslash$ $\mathrm{C}, 12,1.61307541,8,98.37725803,1,-69.15792203,0 \backslash \mathrm{C}, 1,3.32719114,3,90 ., 5$, $180 ., 0 \backslash \mathrm{C}, 1,3.32719114,6,90 ., 2,180 ., 0 \backslash H, 8,1.07274332,1,120.51895228,2$, $88.58165685,0 \backslash H, 9,1.07274332,1,120.51895228,5,-88.58165685,0 \backslash \mathrm{H}, 10,1.07$ $274332,1,120.51895228,2,-88.58165685,0 \backslash H, 11,1.07274332,1,120.51895228$, $5,-88.58165685,0 \backslash \mathrm{H}, 12,1.09205535,8,122.99527435,1,168.80979851,0 \backslash \mathrm{H}, 13$, $1.09205535,9,122.99527435,1,168.80979851,0 \backslash \mathrm{H}, 14,1.09205535,10,122.9952$ $7435,1,168.80979851,0 \backslash H, 15,1.09205535,11,122.99527435,1,168.80979851,0$ $\backslash \mathrm{H}, 17,1.08635181,9,115.08477548,1,182.67145711,0 \backslash \mathrm{H}, 18,1.08635181,10,11$ $5.08477548,1,182.67145711,0 \backslash \mathrm{H}, 19,1.08635181,11,115.08477548,1,182.6714$ $5711,0 \backslash \mathrm{H}, 16,1.08635181,8,115.08477548,1,182.67145711,0 \backslash \mathrm{H}, 20,1.08485558$ , 13, 112. $4627486,9,269.00587516,0 \backslash H, 21,1.08485558,14,112.4627486,10,269$ $.00587516,0 \backslash \mathrm{H}, 22,1.08485558,15,112.4627486,11,269.00587516,0 \backslash \mathrm{H}, 23,1.08$ $485558,12,112.4627486,8,269.00587516,0 \backslash H, 24,1.08605373,1,125.80024641$, $3,-2.9038485,0 \backslash \mathrm{H}, 24,1.08605373,1,125.80024641,6,-2.9038485,0 \backslash \mathrm{H}, 25,1.08$ $605373,1,125.80024641,3,-2.9038485,0 \backslash \mathrm{H}, 25,1.08605373,1,125.80024641,6$, $-2.9038485,0 \backslash \backslash V e r s i o n=F u j i t s u-V P-U n i x-G 98 R e v A .7 \backslash$ State=1-A\HF=-730.7038 $956 \backslash \mathrm{MP} 2=-733.6696169 \backslash \mathrm{RMSD}=4.414 \mathrm{e}-09 \backslash \mathrm{PG}=\mathrm{D} 02 \quad[\mathrm{O}(\mathrm{C} 1), \mathrm{C} 2(\mathrm{C} 1 . \mathrm{C} 1), \mathrm{X}(\mathrm{C} 16 \mathrm{H} 20)]$ $\backslash \backslash @$

## 4-32 biheptaplane $\quad \boldsymbol{D}_{\mathbf{2 h}}$

$1 \backslash 1 \backslash G I N C-V P P 03 \backslash S P \backslash R M P 2-F C \backslash 6-311+G(2 d, p) \backslash C 19 H 20 \backslash R A S M U S S E N \backslash 06-A p r-2000 \backslash 0$ <br>\#P MP2/6-311+G(2D,P) 5D MAXDISK=1980000000 NAME=RASMUSSEN SCF=RESTAR $T \backslash \backslash$ Biheptaplane C19H20 RHF/6-31G* 5D OPT D2h $\backslash \backslash 0,1 \backslash C \backslash X, 1,0.5 \backslash X, 1,0.5,2$, 90. \X, 1, 0.5, 2, 90., 3,-90., 0\X,1,0.5,3,90.,2,180., 0\X,1,0.5,2,90.,3,180. , $0 \backslash \mathrm{X}, 1,0.5,2,90.4,180 ., 0 \backslash \mathrm{C}, 1,1.68558641,2,90 ., 7,45.61236375,0 \backslash \mathrm{C}, 1,1.6$ 8558641,5,90.,7,45.61236375,0\C,1,1.68558641,2,90.,4,45.61236375,0\C,1 , 1.68558641,5,90.,4,45.61236375,0\C, 8,1.52841974,1,84.51707377,2,16.02 $97512,0 \backslash C, 9,1.52841974,1,84.51707377,5,16.0297512,0 \backslash C, 10,1.52841974,1$, $84.51707377,2,16.0297512,0 \backslash C, 11,1.52841974,1,84.51707377,5,16.0297512$, $0 \backslash C, 8,1.52841974,1,84.51707377,5,-16.0297512,0 \backslash C, 9,1.52841974,1,84.517$ 07377,2,-16.0297512, 0\C,10,1.52841974,1,84.51707377,5,-16.0297512,0\C, $11,1.52841974,1,84.51707377,2,-16.0297512,0 \backslash C, 1,2.51040365,2,26.718416$ $68,4,180 ., 0 \backslash C, 1,2.51040365,5,26.71841668,4,180 ., 0 \backslash C, 1,2.51040365,2,26$. $71841668,7,180 ., 0 \backslash C, 1,2.51040365,5,26.71841668,7,180 ., 0 \backslash C, 1,3.2746044$, $3,90.5,180 ., 0 \backslash \mathrm{C}, 1,3.2746044,6,90 ., 2,180 ., 0 \backslash \mathrm{H}, 8,1.07025221,1,114.74257$ $984,5,90 ., 0 \backslash \mathrm{H}, 9,1.07025221,1,114.74257984,2,90 ., 0 \backslash \mathrm{H}, 10,1.07025221,1,11$ $4.74257984,5,90 ., 0 \backslash \mathrm{H}, 11,1.07025221,1,114.74257984,2,90.0 \backslash \mathrm{H}, 12,1.08572$ $696,8,118.54728829,1,173.97825369,0 \backslash \mathrm{H}, 13,1.08572696,9,118.54728829,1,1$ $73.97825369,0 \backslash \mathrm{H}, 14,1.08572696,10,118.54728829,1,173.97825369,0 \backslash \mathrm{H}, 15,1$. $08572696,11,118.54728829,1,173.97825369,0 \backslash H, 17,1.08572696,9,118.547288$ $29,1,-173.97825369,0 \backslash \mathrm{H}, 18,1.08572696,10,118.54728829,1,-173.97825369,0$ $\backslash H, 19,1.08572696,11,118.54728829,1,-173.97825369,0 \backslash \mathrm{H}, 16,1.08572696,8,1$ $18.54728829,1,-173.97825369,0 \backslash \mathrm{H}, 20,1.08314808,1,137.18070881,2,180 ., 0 \backslash$ H, 21, 1.08314808,1,137.18070881,5,180., 0\H,22,1.08314808,1,137.18070881
$, 2,180 ., 0 \backslash \mathrm{H}, 23,1.08314808,1,137.18070881,5,180 ., 0 \backslash \mathrm{H}, 24,1.08614418,1,12$ $5.74299668,3,0 ., 0 \backslash H, 24,1.08614418,1,125.74299668,6,0.0 \backslash H, 25,1.0861441$ $8,1,125.74299668,3,0 ., 0 \backslash H, 25,1.08614418,1,125.74299668,6,0 ., 0 \backslash \backslash V e r s i o n$ $=$ Fujitsu-VP-Unix-G98RevA. $7 \backslash$ State $=1-A G \backslash H F=-730.6308507 \backslash M P 2=-733.6321348$ $\backslash \mathrm{RMSD}=7.442 \mathrm{e}-10 \backslash \mathrm{PG}=\mathrm{D} 02 \mathrm{H} \quad\left[\mathrm{O}(\mathrm{C} 1), \mathrm{C} 2(\mathrm{C} 1 . \mathrm{C} 1), \mathrm{SG}(\mathrm{C} 4 \mathrm{H} 4), \mathrm{SG} \mathrm{I}^{\prime}(\mathrm{C} 4 \mathrm{H} 4), \mathrm{SG}\right.$ ( H 4$), \mathrm{X}($ C8H8) ] <br>@

## 4-33 heptaplane $\boldsymbol{C}_{\mathbf{2}}$

$1 \backslash 1 \backslash G I N C-P C \backslash S P \backslash R M P 2-F C \backslash 6-311+G(2 d, p) \backslash C 19 H 24 \backslash R A S M U S S E N \backslash 03-J u l-1999 \backslash 0 \backslash \backslash \#$ P RMP2/6-311+G(2D,P) 5D SCF= (DIRECT) NAME=RASMUSSEN TEST GUESS=CHECK G $E O M=(C H E C K, N O D I S T A N C E, N O A N G L E, N O D I H E D R A L) ~ M A X D I S K=1800000000 \backslash \backslash H e p t a p l a$ ne $5 \mathrm{D} C 2 \backslash \backslash 0,1 \backslash \mathrm{C}, 0,0 ., 0 ., 0 . \backslash \mathrm{X}, 1,0.5 \backslash \mathrm{X}, 1,0.5,2,90 . \backslash \mathrm{X}, 1,0.5,2,90 ., 3,-90 .$, $0 \backslash X, 1,0.5,3,90 ., 2,180 ., 0 \backslash X, 1,0.5,2,90 ., 3,180 ., 0 \backslash X, 1,0.5,2,90 ., 4,180 ., 0$ $\backslash C, 1,1.61655996,2,101.21347008,7,41.92503949,0 \backslash C, 1,1.61655996,5,101.21$ $347008,7,41.92503949,0 \backslash C, 1,1.54795155,2,90 ., 4,46.12392838,0 \backslash C, 1,1.5479$ $5155,5,90 ., 4,46.12392838,0 \backslash C, 8,1.54746938,1,92.30173755,2,-12.19225597$ , $0 \backslash \mathrm{C}, 9,1.54746938,1,92.30173755,5,-12.19225597,0 \backslash C, 8,1.4838598,1,97.80$ $706327,5,31.99148952,0 \backslash C, 9,1.4838598,1,97.80706327,2,31.99148952,0 \backslash C, 1$ $0,1.75397812,1,83.4994442,2,0.87528201,0 \backslash C, 11,1.75397812,1,83.4994442$, $5,0.87528201,0 \backslash C, 10,1.54939966,1,100.34594221,5,-21.15458935,0 \backslash C, 11,1$. $54939966,1,100.34594221,2,-21.15458935,0 \backslash C, 1,2.70800632,2,25.20270518$, $3,25.74154459,0 \backslash C, 1,2.75828538,5,48.01395382,3,-17.03609685,0 \backslash C, 1,2.75$ $828538,2,48.01395382,6,-17.03609685,0 \backslash C, 1,2.70800632,5,25.20270518,6,2$ $5.74154459,0 \backslash C, 1,2.65435695,2,36.28177946,7,164.08820307,0 \backslash C, 1,2.65435$ $695,5,36.28177946,7,164.08820307,0 \backslash \mathrm{H}, 8,1.07832873,1,114.57382565,2,96$. $0991694,0 \backslash \mathrm{H}, 9,1.07832873,1,114.57382565,5,96.0991694,0 \backslash \mathrm{H}, 10,1.07398359$ , 1, 120.05801347, 2, -91. $60409107,0 \backslash H, 11,1.07398359,1,120.05801347,5,-91$. $60409107,0 \backslash \mathrm{H}, 12,1.08678549,8,113.74250803,1,194.13740117,0 \backslash \mathrm{H}, 13,1.0867$ $8549,9,113.74250803,1,194.13740117,0 \backslash H, 14,1.09010276,8,119.71433349,1$, $-193.87871595,0 \backslash \mathrm{H}, 15,1.09010276,9,119.71433349,1,-193.87871595,0 \backslash H, 16$, $1.08811686,10,108.78823781,1,177.17808795,0 \backslash \mathrm{H}, 17,1.08811686,11,108.788$ $23781,1,177.17808795,0 \backslash \mathrm{H}, 18,1.09023416,10,116.86162296,1,-176.31382542$ , $0 \backslash \mathrm{H}, 19,1.09023416,11,116.86162296,1,-176.31382542,0 \backslash \mathrm{H}, 20,1.08669709,1$ $5,106.1057025,9,-80.23367551,0 \backslash H, 20,1.0850553,15,113.09035003,9,164.19$ $791881,0 \backslash H, 21,1.0872992,13,107.13578726,9,76.57567983,0 \backslash H, 21,1.0868653$ $3,13,110.93390899,9,-168.11953017,0 \backslash \mathrm{H}, 22,1.0872992,12,107.13578726,8,7$ $6.57567983,0 \backslash \mathrm{H}, 22,1.08686533,12,110.93390899,8,-168.11953017,0 \backslash \mathrm{H}, 23,1$. $08669709,14,106.1057025,8,-80.23367551,0 \backslash H, 23,1.0850553,14,113.0903500$ $3,8,164.19791881,0 \backslash H, 25,1.08627689,18,107.90668321,10,71.52551091,0 \backslash H$, $25,1.08649326,18,109.4845975,10,-174.12611138,0 \backslash H, 24,1.08627689,19,107$ $.90668321,11,71.52551091,0 \backslash H, 24,1.08649326,19,109.4845975,11,-174.1261$ 1138, $0 \backslash \backslash$ Version=SGI-G98RevA. $6 \backslash$ State $=1-A \backslash H F=-733.1138631 \backslash M P 2=-736.11227$ $21 \backslash \mathrm{RMSD}=6.182 \mathrm{e}-09 \backslash \mathrm{PG}=\mathrm{C} 02 \quad[\mathrm{C} 2(\mathrm{C} 1), \mathrm{X}(\mathrm{C} 18 \mathrm{H} 24)] \backslash \backslash$

## 4-33 heptaplane $\boldsymbol{C}_{2 \mathrm{v}}$

$1 \backslash 1 \backslash$ GINC-PC $\backslash \mathrm{SP} \backslash \mathrm{RMP} 2-\mathrm{FC} \backslash 6-311+\mathrm{G}(2 \mathrm{~d}, \mathrm{p}) \backslash \mathrm{C} 19 \mathrm{H} 24 \backslash$ RASMUSSEN $\backslash 02-\mathrm{Jul-1999} \mathrm{\backslash 0} \mathrm{\backslash} \mathrm{\backslash} \mathrm{\#}$ P RMP2/6-311+G(2D,P) 5D SCF=(DIRECT) NAME=RASMUSSEN TEST GUESS=CHECK G EOM $=(C H E C K, N O D I S T A N C E, N O A N G L E, N O D I H E D R A L) ~ M A X D I S K=1800000000 \backslash \backslash H e p t a p l a$ ne 5D $C 2 v \backslash \backslash 0,1 \backslash C \backslash X, 1,0.5 \backslash X, 1,0.5,2,90 . \backslash X, 1,0.5,2,90 ., 3,-90 ., 0 \backslash X, 1,0.5$, $3,90.2,180 ., 0 \backslash X, 1,0.5,2,90 ., 3,180 ., 0 \backslash X, 1,0.5,2,90 ., 4,180 ., 0 \backslash C, 1,1.701$ 94552,2,90., 7, 36.72878585,0\C,1,1.70194552,5,90.,7,36.72878585,0\C,1,1 $.50205578,2,90.4,47.48545511,0 \backslash C, 1,1.50205578,5,90 ., 4,47.48545511,0 \backslash C$


#### Abstract

, 8, 1. $5946114,1,88.56909714,2,13.78871383,0 \backslash C, 9,1.5946114,1,88.56909714$ $, 5,13.78871383,0 \backslash C, 10,1.52809327,1,93.38852007,2,-22.20134426,0 \backslash C, 11,1$ $.52809327,1,93.38852007,5,-22.20134426,0 \backslash C, 8,1.5946114,1,88.56909714,5$ $,-13.78871383,0 \backslash C, 9,1.5946114,1,88.56909714,2,-13.78871383,0 \backslash C, 10,1.52$ $809327,1,93.38852007,5,22.20134426,0 \backslash C, 11,1.52809327,1,93.38852007,2,2$ $2.20134426,0 \backslash C, 1,2.65602964,2,35.64473191,3,-12.45568585,0 \backslash C, 1,2.65602$ $964,5,35.64473191,3,12.45568585,0 \backslash C, 1,2.65602964,2,35.64473191,6,12.45$ $568585,0 \backslash C, 1,2.65602964,5,35.64473191,6,-12.45568585,0 \backslash C, 1,2.76219361$, $2,38.78075377,4,180 ., 0 \backslash C, 1,2.76219361,5,38.78075377,4,180 ., 0 \backslash H, 8,1.076$ $03768,1,136.43115835,2,-90 ., 0 \backslash H, 9,1.07603768,1,136.43115835,2,90 ., 0 \backslash H$, $10,1.07906935,1,118.13811578,2,90.0 \backslash \mathrm{H}, 11,1.07906935,1,118.13811578,2$, $-90 ., 0 \backslash \mathrm{H}, 12,1.09481314,8,109.49197891,1,168.2510894,0 \backslash \mathrm{H}, 13,1.09481314$, 9, 109.49197891, 1, 168.2510894, 0\H,16,1.09481314, 8, 109.49197891,1,-168.2 $510894,0 \backslash \mathrm{H}, 17,1.09481314,9,109.49197891,1,-168.2510894,0 \backslash \mathrm{H}, 14,1.093411$ $76,10,119.16318368,1,195.73482876,0 \backslash H, 15,1.09341176,11,119.16318368,1$, $195.73482876,0 \backslash \mathrm{H}, 18,1.09341176,10,119.16318368,1,-195.73482876,0 \backslash \mathrm{H}, 19$, $1.09341176,11,119.16318368,1,-195.73482876,0 \backslash \mathrm{H}, 20,1.08650319,1,128.977$ $94482,2,-0.28037778,0 \backslash H, 20,1.08805265,1,125.50175604,2,179.82038374,0 \backslash$ $\mathrm{H}, 21,1.08650319,1,128.97794482,5,0.28037778,0 \backslash \mathrm{H}, 21,1.08805265,1,125.50$ $175604,5,-179.82038374,0 \backslash H, 22,1.08650319,1,128.97794482,2,0.28037778,0$ $\backslash \mathrm{H}, 22,1.08805265,1,125.50175604,2,-179.82038374,0 \backslash \mathrm{H}, 23,1.08650319,1,12$ $8.97794482,5,-0.28037778,0 \backslash H, 23,1.08805265,1,125.50175604,5,179.820383$ $74,0 \backslash H, 24,1.08370525,1,133.92146243,2,0 ., 0 \backslash H, 24,1.08872572,1,120.22067$ $405,2,180 ., 0 \backslash \mathrm{H}, 25,1.08370525,1,133.92146243,5,0 ., 0 \backslash \mathrm{H}, 25,1.08872572,1,1$ $20.22067405,5,180 ., 0 \backslash \backslash V e r s i o n=S G I-G 98 R e v A .6 \backslash$ State $=1-A 1 \backslash H F=-733.0823567$ $\backslash \mathrm{MP} 2=-736.0849754 \backslash \mathrm{RMSD}=4.024 \mathrm{e}-09 \backslash \mathrm{PG}=\mathrm{C} 02 \mathrm{~V} \quad\left[\mathrm{C} 2(\mathrm{C} 1), \mathrm{SGV}(\mathrm{C} 4 \mathrm{H} 4), \mathrm{SGV} \mathrm{I}^{\prime}(\mathrm{C} 2 \mathrm{H} 4)\right.$, X (C12H16) ] <br>@


## 4-34 bioctaplane $\boldsymbol{D}_{\mathbf{2}}$

$1 \backslash 1 \backslash G I N C-V P P 02 \backslash S P \backslash R M P 2-F C \backslash 6-311+G(2 d, p) \backslash C 21 H 24 \backslash R A S M U S S E N \backslash 02-A p r-2000 \backslash 0$ <br>\#P MP2/6-311+G(2D, P) 5D MAXDISK=1980000000 NAME=RASMUSSEN <br>Bioctapla ne $\mathrm{D} 2 \backslash \backslash 0,1 \backslash \mathrm{C}, 0,0 ., 0 ., 0 . \backslash \mathrm{C}, 0,0.7802544987,-2.2265246671,-0.0500082031 \backslash \mathrm{C}$ , 0, 0.7802544987,2.2265246671, 0.0500082031 \C, 0, - 0.7802544987, 2. 22652466 $71,-0.0500082031 \backslash \mathrm{C}, 0,-0.7802544987,-2.2265246671,0.0500082031 \backslash \mathrm{C}, 0,-0.2$ $68912062,-1.9313407894,-2.2958793505 \backslash \mathrm{C}, 0,-0.268912062,1.9313407894,2.2$ $958793505 \backslash \mathrm{C}, 0,0.268912062,1.9313407894,-2.2958793505 \backslash \mathrm{C}, 0,0.268912062$, $1.9313407894,2.2958793505 \backslash C, 0,1.0203661377,-1.6782214729,-1.5458860707$ $\backslash C, 0,1.0203661377,1.6782214729,1.5458860707 \backslash C, 0,-1.0203661377,1.678221$ $4729,-1.5458860707 \backslash \mathrm{C}, 0,-1.0203661377,-1.6782214729,1.5458860707 \backslash \mathrm{C}, 0,1$. $2720220568,1.3678652774,-1.3088655735 \backslash C, 0,1.2720220568,-1.3678652774,1$ $.3088655735 \backslash C, 0,-1.2720220568,-1.3678652774,-1.3088655735 \backslash C, 0,-1.27202$ $20568,1.3678652774,1.3088655735 \backslash \mathrm{C}, 0,1.1641731588,-0.2461523524,-1.0584$ $806421 \backslash C, 0,1.1641731588,0.2461523524,1.0584806421 \backslash \mathrm{C}, 0,-1.1641731588,0$. $2461523524,-1.0584806421 \backslash C, 0,-1.1641731588,-0.2461523524,1.0584806421 \backslash$ $\mathrm{H}, 0,1.1832581321,-3.2297220681,0.086844028 \backslash \mathrm{H}, 0,1.1832581321,3.22972206$ $81,-0.086844028 \backslash \mathrm{H}, 0,-1.1832581321,3.2297220681,0.086844028 \backslash \mathrm{H}, 0,-1.1832$ $581321,-3.2297220681,-0.086844028 \backslash \mathrm{H}, 0,-0.4405297118,-2.9913553597,-2.4$ $716884942 \backslash \mathrm{H}, 0,-0.4405297118,2.9913553597,2.4716884942 \backslash \mathrm{H}, 0,0.4405297118$ , 2. $9913553597,-2.4716884942 \backslash \mathrm{H}, 0,0.4405297118,-2.9913553597,2.471688494$ $2 \backslash H, O,-0.2853736328,-1.4256976122,-3.2566285269 \backslash \mathrm{H}, 0,-0.2853736328,1.42$ $56976122,3.2566285269 \backslash \mathrm{H}, 0,0.2853736328,1.4256976122,-3.2566285269 \backslash \mathrm{H}, 0$, $0.2853736328,-1.4256976122,3.2566285269 \backslash \mathrm{H}, 0,1.9067961923,-2.078276573$,
$-2.028210598 \backslash H, 0,1.9067961923,2.078276573,2.028210598 \backslash H, 0,-1.906796192$ $3,2.078276573,-2.028210598 \backslash H, 0,-1.9067961923,-2.078276573,2.028210598 \backslash$ H, 0, 2. $2980185163,1.6175489903,-1.5568031974 \backslash \mathrm{H}, 0,2.2980185163,-1.617548$ $9903,1.5568031974 \backslash \mathrm{H}, 0,-2.2980185163,-1.6175489903,-1.5568031974 \backslash \mathrm{H}, 0,-2$ $.2980185163,1.6175489903,1.5568031974 \backslash \mathrm{H}, 0,2.1279481869,-0.4090684099$, $0.6397243637 \backslash \mathrm{H}, 0,2.1279481869,0.4090684099,0.6397243637 \backslash \mathrm{H}, 0,-2.1279481$ $869,0.4090684099,-0.6397243637 \backslash \mathrm{H}, 0,-2.1279481869,-0.4090684099,0.63972$ $43637 \backslash \backslash$ Version=Fujitsu-VP-Unix-G98RevA. 7 \State=1-A $\backslash \mathrm{HF}=-808.8084607 \backslash \mathrm{MP2}$ $=-812.0946901 \backslash \mathrm{RMSD}=2.700 \mathrm{e}-09 \backslash \mathrm{PG}=\mathrm{D} 02 \quad[\mathrm{O}(\mathrm{C} 1), \mathrm{X}(\mathrm{C} 20 \mathrm{H} 24)] \backslash \backslash @$

## 4-34 bioctaplane $\boldsymbol{D}_{\mathbf{2 h}}$

$1 \backslash 1 \backslash G I N C-V P P 01 \backslash S P \backslash R M P 2-F C \backslash 6-311+G(2 d, p) \backslash C 21 H 24 \backslash R A S M U S S E N \backslash 02-A p r-2000 \backslash 0$ <br>\#P MP2/6-311+G(2D,P) 5D MAXDISK=1980000000 NAME=RASMUSSEN <br>Bioctapla ne $D 2 h \backslash \backslash 0,1 \backslash C, 0,0 ., 0 ., 0 . \backslash C, 0,1.0821798327,-1.2200107026,0 . \backslash C, 0,-1.0821$ 798327,-1.2200107026,0.\C,0,1.0821798327,1.2200107026,0. \C,0,-1.082179 8327,1.2200107026,0.\C,0,-1.4217658708,-1.1670724836,1.5153953957\C,0, $1.4217658708,1.1670724836,-1.5153953957 \backslash \mathrm{C}, 0,-1.4217658708,-1.167072483$ $6,-1.5153953957 \backslash C, 0,1.4217658708,-1.1670724836,-1.5153953957 \backslash C, 0,-1.42$ $17658708,1.1670724836,-1.5153953957 \backslash C, 0,1.4217658708,-1.1670724836,1.5$ $153953957 \backslash \mathrm{C}, 0,-1.4217658708,1.1670724836,1.5153953957 \backslash \mathrm{C}, 0,1.4217658708$ , 1.1670724836,1.5153953957\C,0,-2.2877922008,0.,1.9313931391\C, 0, 2.287 $7922008,0 .,-1.9313931391 \backslash C, 0,-2.2877922008,0 .,-1.9313931391 \backslash C, 0,2.2877$ 922008,0.,1.9313931391\C,0,0.,-0.7881679069,2.1923566647\C,0,0.,0.7881 679069,-2.1923566647\C,0,0.,-0.7881679069,-2.1923566647\C,0,0.,0.78816 79069,2.1923566647\H, 0, -0.7293969297,2.2194759897, 0. \H, 0, 0.7293969297, $2.2194759897,0 . \backslash \mathrm{H}, 0,-0.7293969297,-2.2194759897,0 . \backslash \mathrm{H}, 0,0.7293969297,-2$ $.2194759897,0 . \backslash H, 0,-1.8088442085,-2.1204522455,1.8703038839 \backslash \mathrm{H}, 0,1.8088$ 442085,2.1204522455,-1.8703038839\H, 0,-1.8088442085,-2.1204522455,-1.8 $703038839 \backslash \mathrm{H}, 0,1.8088442085,-2.1204522455,-1.8703038839 \backslash \mathrm{H}, 0,-1.80884420$ 85,2.1204522455,-1.8703038839\H, 0,1.8088442085,-2.1204522455,1.8703038 $839 \backslash \mathrm{H}, 0,-1.8088442085,2.1204522455,1.8703038839 \backslash \mathrm{H}, 0,1.8088442085,2.120$ 4522455,1.8703038839\H,0,-2.448355427,0.,3.007958724 \H, 0, 2.448355427,0 ., -3.007958724 \H, 0,-2.448355427,0.,-3.007958724 \H, 0, 2.448355427, 0., 3. 0 $07958724 \backslash \mathrm{H}, 0,-3.2592065888,0 ., 1.4460593687 \backslash \mathrm{H}, 0,3.2592065888,0 .,-1.4460$ $593687 \backslash \mathrm{H}, 0,-3.2592065888,0 .,-1.4460593687 \backslash \mathrm{H}, 0,3.2592065888,0 ., 1.446059$ $3687 \backslash \mathrm{H}, 0,0 ., 1.1848732685,-3.2156063522 \backslash \mathrm{H}, 0,0 .,-1.1848732685,3.21560635$ $22 \backslash \mathrm{H}, 0,0 ., 1.1848732685,3.2156063522 \backslash \mathrm{H}, 0,0 .,-1.1848732685,-3.2156063522$ <br>Version=Fujitsu-VP-Unix-G98RevA. 7 \State=1-AG $\backslash \mathrm{HF}=-808.7267193 \backslash \mathrm{MP} 2=-81$ $2.0430898 \backslash \mathrm{RMSD}=4.907 \mathrm{e}-09 \backslash \mathrm{PG}=\mathrm{D} 02 \mathrm{H} \quad\left[\mathrm{O}(\mathrm{C} 1), \mathrm{SG}(\mathrm{C} 4 \mathrm{H} 4), \mathrm{SG}{ }^{\prime}(\mathrm{C} 4 \mathrm{H} 4)\right.$, $\mathrm{SG} \mathrm{Cl}^{(\mathrm{C} 4 \mathrm{H} 8)}$ ) X (C8H8)] <br>@

## 4-27 octaplane (A-type) $\quad \boldsymbol{S}_{4}$

$1 \backslash 1 \backslash G I N C-P C \backslash S P \backslash R M P 2-F C \backslash 6-311+G(2 d, p) \backslash C 21 H 28 \backslash R A S M U S S E N \backslash 22-S e p-1998 \backslash 0 \backslash \backslash \#$ P RMP2/6-311+G(2D,P) 5D TEST SCF=(RESTART,DIRECT) NAME=RASMUSSEN GEOM= (NODISTANCE,NOANGLE,NODIHEDRAL) MAXDISK=1900000000<br>Octaplane 5D S4<br>0 , $1 \backslash \mathrm{C} \backslash \mathrm{X}, 1,0.5 \backslash \mathrm{X}, 1,0.5,2,90 . \backslash \mathrm{X}, 1,0.5,2,90 ., 3,-90 ., 0 \backslash \mathrm{X}, 1,0.5,3,90 ., 2,180$. , $0 \backslash \mathrm{X}, 1,0.5,2,90 ., 3,180 ., 0 \backslash \mathrm{X}, 1,0.5,2,90.4,180 ., 0 \backslash \mathrm{C}, 1,1.58297526,2,84.3$ $8253808,3,0 ., 0 \backslash C, 1,1.58297526,5,84.38253808,4,0 ., 0 \backslash C, 1,1.58297526,2,84$ $.38253808,6,0 ., 0 \backslash C, 1,1.58297526,5,84.38253808,7,0 ., 0 \backslash C, 8,1.51198778,1$, 105.92147099,2,-16.1735458,0\C,9,1.51198778,1,105.92147099,5,16.173545 $8,0 \backslash C, 10,1.51198778,1,105.92147099,2,-16.1735458,0 \backslash C, 11,1.51198778,1,1$ $05.92147099,5,16.1735458,0 \backslash C, 8,1.61543088,1,94.07709075,5,11.95412161$,
$0 \backslash C, 9,1.61543088,1,94.07709075,2,-11.95412161,0 \backslash C, 10,1.61543088,1,94.0$ $7709075,5,11.95412161,0 \backslash C, 11,1.61543088,1,94.07709075,2,-11.95412161,0$ $\backslash C, 12,1.58150608,8,94.41235136,1,74.65306988,0 \backslash C, 13,1.58150608,9,94.41$ $235136,1,-74.65306988,0 \backslash C, 14,1.58150608,10,94.41235136,1,74.65306988,0$ $\backslash C, 15,1.58150608,11,94.41235136,1,-74.65306988,0 \backslash C, 13,1.54320849,9,114$ $.16556437,1,48.10155878,0 \backslash C, 14,1.54320849,10,114.16556437,1,-48.101558$ $78,0 \backslash C, 15,1.54320849,11,114.16556437,1,48.10155878,0 \backslash C, 12,1.54320849,8$ , 114.16556437, 1, -48.10155878, 0\H, 8, 1.07743674, 1, 112.42134288, 2, 92. 8171 $8919,0 \backslash \mathrm{H}, 9,1.07743674,1,112.42134288,5,-92.81718919,0 \backslash \mathrm{H}, 10,1.07743674$, $1,112.42134288,2,92.81718919,0 \backslash \mathrm{H}, 11,1.07743674,1,112.42134288,5,-92.81$ $718919,0 \backslash \mathrm{H}, 12,1.08967705,8,115.37472862,1,186.16682845,0 \backslash \mathrm{H}, 13,1.089677$ $05,9,115.37472862,1,-186.16682845,0 \backslash H, 14,1.08967705,10,115.37472862,1$, $186.16682845,0 \backslash \mathrm{H}, 15,1.08967705,11,115.37472862,1,-186.16682845,0 \backslash \mathrm{H}, 17$, $1.08814833,9,109.79745283,1,191.88387526,0 \backslash \mathrm{H}, 18,1.08814833,10,109.7974$ $5283,1,-191.88387526,0 \backslash H, 19,1.08814833,11,109.79745283,1,191.88387526$, $0 \backslash \mathrm{H}, 16,1.08814833,8,109.79745283,1,-191.88387526,0 \backslash \mathrm{H}, 20,1.08601504,12$, $111.07809123,8,206.1334016,0 \backslash H, 20,1.08651431,12,105.87100785,8,91.7874$ $3151,0 \backslash H, 21,1.08601504,13,111.07809123,9,-206.1334016,0 \backslash H, 21,1.0865143$ $1,13,105.87100785,9,-91.78743151,0 \backslash \mathrm{H}, 22,1.08601504,14,111.07809123,10$, $206.1334016,0 \backslash H, 22,1.08651431,14,105.87100785,10,91.78743151,0 \backslash H, 23,1$. $08601504,15,111.07809123,11,-206.1334016,0 \backslash \mathrm{H}, 23,1.08651431,15,105.8710$ $0785,11,-91.78743151,0 \backslash \mathrm{H}, 24,1.08674761,13,109.69835679,9,202.92905426$, $0 \backslash \mathrm{H}, 24,1.08790442,13,107.39814613,9,88.5095412,0 \backslash \mathrm{H}, 25,1.08674761,14,10$ $9.69835679,10,-202.92905426,0 \backslash H, 25,1.08790442,14,107.39814613,10,-88.5$ $095412,0 \backslash \mathrm{H}, 26,1.08674761,15,109.69835679,11,202.92905426,0 \backslash \mathrm{H}, 26,1.0879$ $0442,15,107.39814613,11,88.5095412,0 \backslash H, 27,1.08674761,12,109.69835679$, 8 , - 202. $92905426,0 \backslash \mathrm{H}, 27,1.08790442,12,107.39814613,8,-88.5095412,0 \backslash \backslash \operatorname{Vers}$ ion=SGI-G94RevE. $2 \backslash \mathrm{HF}=-811.2490442 \backslash \mathrm{MP} 2=-814.5618261 \backslash \mathrm{RMSD}=5.859 \mathrm{e}-09 \backslash \mathrm{PG}=\mathrm{S}$ 04 [O (C1) , X (C2OH28) ] <br>@

## 4-27 octaplane (A-type) $\quad \boldsymbol{C}_{4 \mathrm{~h}}$

$1 \backslash 1 \backslash G I N C-P C \backslash S P \backslash R M P 2-F C \backslash 6-311+G(2 d, p) \backslash C 21 H 28 \backslash R A S M U S S E N \backslash 20-S e p-1998 \backslash 0 \backslash \backslash \#$ P RMP2/6-311+G(2D,P) 5D SCF= (RESTART,DIRECT) NAME=RASMUSSEN TEST GEOM= (NODISTANCE, NOANGLE, NODIHEDRAL) MAXDISK=1900000000<br>Octaplane 5D C4h<br> $0,1 \backslash C \backslash X, 1,1 . \backslash X, 1,1 ., 2,90 . \backslash X, 1,1 ., 2,90 ., 3,180 ., 0 \backslash X, 1,1 ., 2,90 ., 3,90 ., 0 \backslash X$ $, 1,1 ., 2,90 ., 5,180 ., 0 \backslash X, 1,1 ., 3,90 ., 2,180 ., 0 \backslash C, 1,1.58331455,2,90 ., 4,180$. , $0 \backslash \mathrm{C}, 1,1.58331455,2,90 ., 3,-180 ., 0 \backslash C, 1,1.58331455,7,90 ., 6,-180 ., 0 \backslash C, 1,1$ $.58331455,7,90 ., 5,180 ., 0 \backslash C, 8,1.54912035,1,99.8930019,11,103.52096619,0$ $\backslash C, 9,1.54912035,1,99.8930019,10,103.52096619,0 \backslash C, 10,1.54912035,1,99.89$ $30019,8,-103.52096619,0 \backslash C, 11,1.54912035,1,99.8930019,9,-103.52096619,0$ $\backslash C, 8,1.54912035,1,99.8930019,11,-103.52096619,0 \backslash C, 9,1.54912035,1,99.89$ $30019,10,-103.52096619,0 \backslash \mathrm{C}, 10,1.54912035,1,99.8930019,8,103.52096619,0$ $\backslash \mathrm{C}, 11,1.54912035,1,99.8930019,9,103.52096619,0 \backslash \mathrm{C}, 13,1.5676745,9,98.264$ $41313,1,-76.58639551,0 \backslash C, 14,1.5676745,10,98.26441313,1,76.58639551,0 \backslash C$ , 12, 1. $5676745,8,98.26441313,1,-76.58639551,0 \backslash C, 15,1.5676745,11,98.2644$ $1313,1,76.58639551,0 \backslash C, 18,1.5676745,10,98.26441313,1,-76.58639551,0 \backslash C$, $16,1.5676745,8,98.26441313,1,76.58639551,0 \backslash C, 19,1.5676745,11,98.264413$ $13,1,-76.58639551,0 \backslash \mathrm{C}, 17,1.5676745,9,98.26441313,1,76.58639551,0 \backslash \mathrm{H}, 8,1$ $.07685577,1,111.03704203,2,-90 ., 0 \backslash H, 9,1.07685577,1,111.03704203,2,-90$. , $0 \backslash \mathrm{H}, 10,1.07685577,1,111.03704203,7,90 ., 0 \backslash H, 11,1.07685577,1,111.037042$ $03,7,90 ., 0 \backslash H, 19,1.09228066,11,112.50786654,1,171.89274442,0 \backslash H, 17,1.092$ $28066,9,112.50786654,1,-171.89274442,0 \backslash H, 18,1.09228066,10,112.50786654$
, 1, 171. $89274442,0 \backslash \mathrm{H}, 16,1.09228066,8,112.50786654,1,-171.89274442,0 \backslash \mathrm{H}, 1$ $2,1.09228066,8,112.50786654,1,171.89274442,0 \backslash H, 13,1.09228066,9,112.507$ $86654,1,171.89274442,0 \backslash H, 15,1.09228066,11,112.50786654,1,-171.89274442$ , $0 \backslash \mathrm{H}, 14,1.09228066,10,112.50786654,1,-171.89274442,0 \backslash \mathrm{H}, 27,1.08832891,1$ $4,108.05731582,10,-94.03905881,0 \backslash H, 24,1.08832891,12,108.05731582,8,94$. $03905881,0 \backslash \mathrm{H}, 25,1.08832891,15,108.05731582,11,-94.03905881,0 \backslash \mathrm{H}, 26,1.08$ $832891,13,108.05731582,9,94.03905881,0 \backslash H, 20,1.08832891,18,108.05731582$ $, 10,94.03905881,0 \backslash \mathrm{H}, 21,1.08832891,16,108.05731582,8,-94.03905881,0 \backslash \mathrm{H}, 2$ $2,1.08832891,19,108.05731582,11,94.03905881,0 \backslash \mathrm{H}, 23,1.08832891,17,108.0$ $5731582,9,-94.03905881,0 \backslash \mathrm{H}, 20,1.08676959,13,110.50582985,9,162.0228694$ $2,0 \backslash \mathrm{H}, 21,1.08676959,14,110.50582985,10,-162.02286942,0 \backslash \mathrm{H}, 22,1.08676959$ , 12, 110.50582985, 8, 162.02286942, 0\H,23,1.08676959,15,110.50582985,11,$162.02286942,0 \backslash \mathrm{H}, 24,1.08676959,18,110.50582985,10,162.02286942,0 \backslash \mathrm{H}, 27$, $1.08676959,17,110.50582985,9,-162.02286942,0 \backslash H, 25,1.08676959,16,110.50$ $582985,8,-162.02286942,0 \backslash H, 26,1.08676959,19,110.50582985,11,162.022869$ $42,0 \backslash \backslash V e r s i o n=S G I-G 94 R e v E .2 \backslash H F=-811.2101014 \backslash M P 2=-814.5397715 \backslash \mathrm{RMSD}=2.02$ $5 \mathrm{e}-09 \backslash \mathrm{PG}=\mathrm{C} 04 \mathrm{H} \quad[\mathrm{O}(\mathrm{C} 1), \mathrm{SGH}(\mathrm{C} 4 \mathrm{H} 4), \mathrm{X}(\mathrm{C} 16 \mathrm{H} 24)] \backslash \backslash @$

## 4-35 octaplane (B-type) $\boldsymbol{D}_{\mathbf{2}}$

$1 \backslash 1 \backslash G I N C-V P P 02 \backslash S P \backslash R M P 2-F C \backslash 6-311+G(2 d, p) \backslash C 21 H 28 \backslash R A S M U S S E N \backslash 01-A p r-2000 \backslash 0$ <br>\#P MP2/6-311+G(2D, P) 5D MAXDISK=1980000000 NAME=RASMUSSEN <br>Octaplane C21H28 RHF/6-31G* 5D D2 OPT $\backslash \backslash 0,1 \backslash C \backslash X, 1,0.5 \backslash X, 1,0.5,2,90 . \backslash \mathrm{X}, 1,0.5,2,90$ $., 3,-90 ., 0 \backslash X, 1,0.5,3,90 ., 2,180 ., 0 \backslash X, 1,0.5,2,90 ., 3,180 ., 0 \backslash X, 1,0.5,2,90$. , 4, 180., 0\C, 1, 1.60961856, 2, 82.94178422, 7,47.70047117, 0\C, 1, 1.60961856, $5,82.94178422,7,47.70047117,0 \backslash C, 1,1.60961856,2,82.94178422,4,47.700471$ $17,0 \backslash C, 1,1.60961856,5,82.94178422,4,47.70047117,0 \backslash C, 8,1.51253751,1,107$ $.56460244,2,-12.625793,0 \backslash C, 9,1.51253751,1,107.56460244,5,-12.625793,0 \backslash$ $C, 10,1.51253751,1,107.56460244,2,-12.625793,0 \backslash C, 11,1.51253751,1,107.56$ $460244,5,-12.625793,0 \backslash C, 8,1.61749146,1,93.22044212,5,5.13197343,0 \backslash C, 9$, $1.61749146,1,93.22044212,2,5.13197343,0 \backslash C, 10,1.61749146,1,93.22044212$, $5,5.13197343,0 \backslash C, 11,1.61749146,1,93.22044212,2,5.13197343,0 \backslash C, 12,1.621$ $04312,8,94.54348222,1,65.18047885,0 \backslash C, 13,1.62104312,9,94.54348222,1,65$ $.18047885,0 \backslash C, 14,1.62104312,10,94.54348222,1,65.18047885,0 \backslash C, 15,1.6210$ $4312,11,94.54348222,1,65.18047885,0 \backslash C, 13,1.51078427,9,111.67851499,1,-$ $59.54743329,0 \backslash C, 14,1.51078427,10,111.67851499,1,-59.54743329,0 \backslash C, 15,1$. $51078427,11,111.67851499,1,-59.54743329,0 \backslash C, 12,1.51078427,8,111.678514$ $99,1,-59.54743329,0 \backslash H, 8,1.06158875,1,116.08409954,2,90.43948275,0 \backslash \mathrm{H}, 9$, $1.06158875,1,116.08409954,5,90.43948275,0 \backslash H, 10,1.06158875,1,116.084099$ $54,2,90.43948275,0 \backslash \mathrm{H}, 11,1.06158875,1,116.08409954,5,90.43948275,0 \backslash \mathrm{H}, 12$ , 1.08952346, 8, 114.5383927,1,175.24318316, 0 \H, 13, 1. $08952346,9,114.53839$ $27,1,175.24318316,0 \backslash \mathrm{H}, 14,1.08952346,10,114.5383927,1,175.24318316,0 \backslash \mathrm{H}$, $15,1.08952346,11,114.5383927,1,175.24318316,0 \backslash \mathrm{H}, 17,1.0871152,9,107.100$ $22125,1,190.98398914,0 \backslash \mathrm{H}, 18,1.0871152,10,107.10022125,1,190.98398914,0$ $\backslash \mathrm{H}, 19,1.0871152,11,107.10022125,1,190.98398914,0 \backslash \mathrm{H}, 16,1.0871152,8,107$. $10022125,1,190.98398914,0 \backslash \mathrm{H}, 20,1.08517073,12,110.35776429,8,208.448204$ $32,0 \backslash \mathrm{H}, 20,1.08683651,12,104.44560649,8,95.56525093,0 \backslash \mathrm{H}, 21,1.08517073,1$ $3,110.35776429,9,208.44820432,0 \backslash H, 21,1.08683651,13,104.44560649,9,95.5$ $6525093,0 \backslash \mathrm{H}, 22,1.08517073,14,110.35776429,10,208.44820432,0 \backslash \mathrm{H}, 22,1.086$ $83651,14,104.44560649,10,95.56525093,0 \backslash \mathrm{H}, 23,1.08517073,15,110.35776429$ $, 11,208.44820432,0 \backslash H, 23,1.08683651,15,104.44560649,11,95.56525093,0 \backslash \mathrm{H}$, $24,1.08816769,13,112.4419168,9,162.50144699,0 \backslash H, 24,1.08853325,13,107.3$ $8119406,9,-80.50891127,0 \backslash H, 25,1.08816769,14,112.4419168,10,162.5014469$
$9,0 \backslash \mathrm{H}, 25,1.08853325,14,107.38119406,10,-80.50891127,0 \backslash \mathrm{H}, 26,1.08816769$, $15,112.4419168,11,162.50144699,0 \backslash \mathrm{H}, 26,1.08853325,15,107.38119406,11,-8$ $0.50891127,0 \backslash \mathrm{H}, 27,1.08816769,12,112.4419168,8,162.50144699,0 \backslash \mathrm{H}, 27,1.08$ 853325,12,107.38119406, 8, -80.50891127, 0<br>Version=Fujitsu-VP-Unix-G98Re vA. $7 \backslash$ State $=1-A \backslash H F=-811.1251994 \backslash \mathrm{MP} 2=-814.4468527 \backslash \mathrm{RMSD}=5.036 \mathrm{e}-09 \backslash \mathrm{PG}=\mathrm{D} 02$ [O (C1) , X (C2OH28) ] <br>@

## 4-35 octaplane (B-type) $\boldsymbol{D}_{\mathbf{2 h}}$

$1 \backslash 1 \backslash G I N C-V P P 01 \backslash S P \backslash R M P 2-F C \backslash 6-311+G(2 d, p) \backslash C 21 H 28 \backslash R A S M U S S E N \backslash 01-A p r-2000 \backslash 0$ <br>\#P MP2/6-311+G(2D, P) 5D MAXDISK=1980000000 NAME=RASMUSSEN <br>Octaplane C21H28 RHF/6-31G* 5D D2h OPT $\backslash \backslash, 1 \backslash C \backslash X, 1,0.5 \backslash X, 1,0.5,2,90 . \backslash X, 1,0.5,2,9$ $0 ., 3,-90 ., 0 \backslash X, 1,0.5,3,90 ., 2,180 ., 0 \backslash X, 1,0.5,2,90 ., 3,180 ., 0 \backslash X, 1,0.5,2,90$ $., 4,180 ., 0 \backslash C, 1,1.63505159,2,90 ., 7,48.5357606,0 \backslash C, 1,1.63505159,5,90 ., 7$, $48.5357606,0 \backslash C, 1,1.63505159,2,90 ., 4,48.5357606,0 \backslash C, 1,1.63505159,5,90 .$, $4,48.5357606,0 \backslash C, 8,1.54294657,1,99.16313133,2,-8.7970349,0 \backslash C, 9,1.54294$ $657,1,99.16313133,5,-8.7970349,0 \backslash C, 10,1.54294657,1,99.16313133,2,-8.79$ $70349,0 \backslash C, 11,1.54294657,1,99.16313133,5,-8.7970349,0 \backslash C, 8,1.54294657,1$, $99.16313133,5,8.7970349,0 \backslash C, 9,1.54294657,1,99.16313133,2,8.7970349,0 \backslash C$ , 10, 1. $54294657,1,99.16313133,5,8.7970349,0 \backslash C, 11,1.54294657,1,99.163131$ $33,2,8.7970349,0 \backslash C, 1,2.72322632,2,37.28043612,3,180 ., 0 \backslash C, 1,2.72322632$, $5,37.28043612,3,180 ., 0 \backslash C, 1,2.72322632,2,37.28043612,6,180 ., 0 \backslash C, 1,2.723$ $22632,5,37.28043612,6,180 ., 0 \backslash C, 1,2.91066933,2,45.0832956,4,180 ., 0 \backslash C, 1$, $2.91066933,5,45.0832956,4,180 ., 0 \backslash C, 1,2.91066933,2,45.0832956,7,180 ., 0 \backslash$ $\mathrm{C}, 1,2.91066933,5,45.0832956,7,180 ., 0 \backslash H, 8,1.06352752,1,119.05828378,2,9$ $0 ., 0 \backslash \mathrm{H}, 9,1.06352752,1,119.05828378,5,90.0 \backslash \mathrm{H}, 10,1.06352752,1,119.05828$ $378,2,90 ., 0 \backslash H, 11,1.06352752,1,119.05828378,5,90.0 \backslash H, 12,1.09295791,8,1$ $10.55211045,1,174.55527636,0 \backslash \mathrm{H}, 13,1.09295791,9,110.55211045,1,174.5552$ $7636,0 \backslash \mathrm{H}, 14,1.09295791,10,110.55211045,1,174.55527636,0 \backslash \mathrm{H}, 15,1.0929579$ $1,11,110.55211045,1,174.55527636,0 \backslash \mathrm{H}, 17,1.09295791,9,110.55211045,1,-1$ $74.55527636,0 \backslash \mathrm{H}, 18,1.09295791,10,110.55211045,1,-174.55527636,0 \backslash \mathrm{H}, 19,1$ $.09295791,11,110.55211045,1,-174.55527636,0 \backslash \mathrm{H}, 16,1.09295791,8,110.5521$ $1045,1,-174.55527636,0 \backslash \mathrm{H}, 20,1.08614757,1,123.63570832,2,0 ., 0 \backslash \mathrm{H}, 20,1.08$ $934385,1,131.16777341,2,180 ., 0 \backslash \mathrm{H}, 21,1.08614757,1,123.63570832,5,0 ., 0 \backslash \mathrm{H}$ , 21, 1.08934385, 1, 131.16777341,5,180., 0\H, 22, 1.08614757,1, 123.63570832, $2,0 ., 0 \backslash H, 22,1.08934385,1,131.16777341,2,180 ., 0 \backslash H, 23,1.08614757,1,123.6$ $3570832,5,0 ., 0 \backslash H, 23,1.08934385,1,131.16777341,5,180 ., 0 \backslash H, 24,1.08868731$ , 1, 133. $64612102,2,0 ., 0 \backslash H, 24,1.08882291,1,119.87969864,2,180 ., 0 \backslash H, 25,1$. $08868731,1,133.64612102,5,0 ., 0 \backslash H, 25,1.08882291,1,119.87969864,5,180 ., 0$ $\backslash H, 26,1.08868731,1,133.64612102,2,0 ., 0 \backslash H, 26,1.08882291,1,119.87969864$, $2,180 ., 0 \backslash H, 27,1.08868731,1,133.64612102,5,0 ., 0 \backslash H, 27,1.08882291,1,119.8$ $7969864,5,180 ., 0 \backslash \backslash V e r s i o n=F u j i t s u-V P-U n i x-G 98 R e v A .7 \backslash$ State=1-AG H (HF=-811 $.0832306 \backslash \mathrm{MP} 2=-814.4241284 \backslash \mathrm{RMSD}=6.676 \mathrm{e}-09 \backslash \mathrm{PG}=\mathrm{D} 02 \mathrm{H} \quad\left[\mathrm{O}(\mathrm{C} 1), \mathrm{SG}(\mathrm{C} 4 \mathrm{H} 4), \mathrm{SG} \mathrm{I}^{\prime}(\mathrm{C}\right.$ $4 \mathrm{H} 8), \mathrm{SG}$ ( C 4 H 8 ) , X (C8H8) ] <br>@

## 4-36 binonaplane $\boldsymbol{D}_{\mathbf{2}}$

$1 \backslash 1 \backslash G I N C-V P P 06 \backslash S P \backslash R M P 2-F C \backslash 6-311+G(2 d, p) \backslash C 23 H 28 \backslash R A S M U S S E N \backslash 04-A p r-2000 \backslash 0$ <br>\#P MP2/6-311+G(2D, P) 5D MAXDISK=1980000000 NAME=RASMUSSEN SCF=RESTAR $T \backslash \backslash$ Binonaplane $D 2 \backslash \backslash 0,1 \backslash C, 0,0.0 .0 . \backslash C, 0,1.182858225,0.2228741585,-1.05$ $03885319 \backslash \mathrm{C}, 0,1.182858225,-0.2228741585,1.0503885319 \backslash \mathrm{C}, 0,-1.182858225,-$ $0.2228741585,-1.0503885319 \backslash C, 0,-1.182858225,0.2228741585,1.0503885319 \backslash$ $C, 0,1.2192354699,-2.3277563096,0.0943359466 \backslash C, 0,1.2192354699,2.3277563$ $096,-0.0943359466 \backslash C, 0,-1.2192354699,2.3277563096,0.0943359466 \backslash C, 0,-1.2$
$192354699,-2.3277563096,-0.0943359466 \backslash \mathrm{C}, 0,0.2360852128,-1.8849031227,-$ $2.2724932733 \backslash C, 0,0.2360852128,1.8849031227,2.2724932733 \backslash C, 0,-0.2360852$ 128, 1.8849031227,-2.2724932733\C, 0, -0.2360852128, -1.8849031227, 2.27249 $32733 \backslash \mathrm{C}, 0,1.3105759199,-1.3724196491,-1.3287144309 \backslash \mathrm{C}, 0,1.3105759199,1$. $3724196491,1.3287144309 \backslash \mathrm{C}, 0,-1.3105759199,1.3724196491,-1.3287144309 \backslash \mathrm{C}$ , 0, -1. $3105759199,-1.3724196491,1.3287144309 \backslash \mathrm{C}, 0,1.0885673126,1.6313515$ $112,-1.5751690575 \backslash C, 0,1.0885673126,-1.6313515112,1.5751690575 \backslash C, 0,-1.0$ $885673126,-1.6313515112,-1.5751690575 \backslash \mathrm{C}, 0,-1.0885673126,1.6313515112,1$ $.5751690575 \backslash \mathrm{C}, 0,0 ., 3.246421914,0 . \backslash \mathrm{C}, 0,0 .,-3.246421914,0 . \backslash \mathrm{H}, 0,0.0304085$ $848,-3.9057926744,-0.8580182781 \backslash H, 0,0.0304085848,3.9057926744,0.858018$ $2781 \backslash \mathrm{H}, 0,-0.0304085848,3.9057926744,-0.8580182781 \backslash \mathrm{H}, 0,-0.0304085848,-3$ $.9057926744,0.8580182781 \backslash H, 0,2.1319522709,-2.9166867231,0.0861763145 \backslash \mathrm{H}$ , 0, 2. 1319522709, 2. $9166867231,-0.0861763145 \backslash \mathrm{H}, 0,-2.1319522709,2.9166867$ $231,0.0861763145 \backslash \mathrm{H}, 0,-2.1319522709,-2.9166867231,-0.0861763145 \backslash \mathrm{H}, 0,0.3$ $909945759,-2.9217761435,-2.5493000416 \backslash \mathrm{H}, 0,0.3909945759,2.9217761435,2$. $5493000416 \backslash \mathrm{H}, 0,-0.3909945759,2.9217761435,-2.5493000416 \backslash \mathrm{H}, 0,-0.3909945$ $759,-2.9217761435,2.5493000416 \backslash \mathrm{H}, 0,0.2549756266,-1.3173256018,-3.19971$ $97593 \backslash \mathrm{H}, 0,0.2549756266,1.3173256018,3.1997197593 \backslash \mathrm{H}, 0,-0.2549756266,1.3$ $173256018,-3.1997197593 \backslash \mathrm{H}, 0,-0.2549756266,-1.3173256018,3.1997197593 \backslash \mathrm{H}$ , 0, 2. $2967644258,-1.5565376652$, -1. $7445660233 \backslash \mathrm{H}, 0,2.2967644258,1.5565376$ $652,1.7445660233 \backslash \mathrm{H}, 0,-2.2967644258,1.5565376652,-1.7445660233 \backslash \mathrm{H}, 0,-2.2$ $967644258,-1.5565376652,1.7445660233 \backslash H, 0,1.9308455201,1.9409792283,-2$. $1905012161 \backslash \mathrm{H}, 0,1.9308455201,-1.9409792283,2.1905012161 \backslash \mathrm{H}, 0,-1.93084552$ 01, -1.9409792283,-2.1905012161 \H, 0, -1.9308455201,1.9409792283, 2. 190501 $2161 \backslash \mathrm{H}, 0,2.1498042232,0.370948378,-0.6392474134 \backslash \mathrm{H}, 0,2.1498042232,-0.37$ $0948378,0.6392474134 \backslash \mathrm{H}, 0,-2.1498042232,-0.370948378,-0.6392474134 \backslash \mathrm{H}, 0$, -2.1498042232,0.370948378,0.6392474134 <br>Version=Fujitsu-VP-Unix-G98Rev A. $7 \backslash$ State $=1-A \backslash H F=-886.8660116 \backslash \mathrm{MP} 2=-890.4813737 \backslash \mathrm{RMSD}=7.599 \mathrm{e}-09 \backslash \mathrm{PG}=\mathrm{D} 02 \quad$ [ $\mathrm{O}(\mathrm{C} 1), \mathrm{C} 2(\mathrm{C} 1 . \mathrm{C} 1), \mathrm{X}(\mathrm{C} 20 \mathrm{H} 28)] \backslash \backslash @$

## 4-36 binonaplane $\boldsymbol{D}_{\mathbf{2 h}}$

$1 \backslash 1 \backslash G I N C-V P P 02 \backslash S P \backslash R M P 2-F C \backslash 6-311+G(2 d, p) \backslash C 23 H 28 \backslash R A S M U S S E N \backslash 01-A p r-2000 \backslash 0$ <br>\#P MP2/6-311+G(2D,P) 5D MAXDISK=1980000000 NAME=RASMUSSEN <br>Binonapla ne $\mathrm{D} 2 \mathrm{~h} \backslash \backslash 0,1 \backslash \mathrm{C}, 0,0.0 .0 .0 \mathrm{C}, 0,1.2444502664,0.1 .0664501355 \backslash \mathrm{C}, 0,1.244450$ $2664,0 .,-1.0664501355 \backslash C, 0,-1.2444502664,0 ., 1.0664501355 \backslash C, 0,-1.2444502$ $664,0 .,-1.0664501355 \backslash C, 0,1.2223864773,1.4889580121,1.4444458078 \backslash C, 0,-1$ $.2223864773,-1.4889580121,-1.4444458078 \backslash C, 0,1.2223864773,-1.4889580121$ , 1. $4444458078 \backslash C, 0,1.2223864773,-1.4889580121,-1.4444458078 \backslash C, 0,-1.2223$ $864773,-1.4889580121,1.4444458078 \backslash C, 0,1.2223864773,1.4889580121,-1.444$ $4458078 \backslash C, 0,-1.2223864773,1.4889580121,1.4444458078 \backslash C, 0,-1.2223864773$, $1.4889580121,-1.4444458078 \backslash \mathrm{C}, 0,0 ., 1.8623942268,2.2637460041 \backslash \mathrm{C}, 0,0 .,-1$. $8623942268,-2.2637460041 \backslash C, 0,0 .,-1.8623942268,2.2637460041 \backslash C, 0,0 ., 1.86$ $23942268,-2.2637460041 \backslash C, 0,1.2397993312,2.2870097828,0 . \backslash C, 0,-1.2397993$ $312,-2.2870097828,0 . \backslash C, 0,1.2397993312,-2.2870097828,0 . \backslash C, 0,-1.23979933$ $12,2.2870097828,0 . \backslash \mathrm{C}, 0,0 .,-3.1952300946,0 . \backslash \mathrm{C}, 0,0 ., 3.1952300946,0 . \backslash \mathrm{H}, 0$, $2.1279367767,1.7634569445,1.9888635946 \backslash \mathrm{H}, 0,-2.1279367767,-1.7634569445$ , - 1. $9888635946 \backslash \mathrm{H}, 0,2.1279367767,-1.7634569445,1.9888635946 \backslash \mathrm{H}, 0,2.12793$ $67767,-1.7634569445,-1.9888635946 \backslash \mathrm{H}, 0,-2.1279367767,-1.7634569445,1.98$ $88635946 \backslash \mathrm{H}, 0,2.1279367767,1.7634569445,-1.9888635946 \backslash \mathrm{H}, 0,-2.1279367767$ $, 1.7634569445,1.9888635946 \backslash \mathrm{H}, 0,-2.1279367767,1.7634569445,-1.988863594$ $6 \backslash \mathrm{H}, 0,0 ., 1.2880954866,3.1867556589 \backslash \mathrm{H}, 0,0 \ldots,-1.2880954866,-3.1867556589 \backslash$ $\mathrm{H}, 0,0 .,-1.2880954866,3.1867556589 \backslash \mathrm{H}, 0,0 ., 1.2880954866,-3.1867556589 \backslash \mathrm{H}$,

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0,0., 2. 9039452952,2.5623277391\H,0,0.,-2.9039452952,-2.5623277391\H,0,
0., -2.9039452952,2.5623277391\H,0,0.,2.9039452952,-2. 5623277391\H,0,-2
.1314327933,-2.9125646491, O.\H, 0, 2.1314327933,2.9125646491,0.\H, 0, -2. . I
314327933,2.9125646491, O.\H, 0, 2.1314327933,-2.9125646491,0.\H,0,0.,3.8
581832293,0.8547429737\H,0,0.,-3.8581832293,-0.8547429737\H,0,0.,-3.85
81832293,0.8547429737\H,0,0.,3.8581832293,-0.8547429737\H,0,-2.2453816
183,0.,-0.7178009526\H,0,-2.2453816183,0.,0.7178009526\H,0,2.245381618
3,0.,-0.7178009526\H,0,2.2453816183,0.,0.7178009526\\Version=Fujitsu-V
P-Unix-G98RevA.7\State=1-AG\HF=-886.8058435\MP2=-890.4440272\RMSD=8.54
2e-09\PG=D02H [O(C1),C2(C1.C1),SG(C4H4),SG'(C4H4),SG"(C4H12),X(C8H8)]\
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Table C-24. Guassian archive files for the MP2(fc)/6-311+G(2d,p)(red) optimized alkaplanes in Chapter 4.

## Alkaplanes

## 4-31 hexaplane $\boldsymbol{D}_{\mathbf{2}}$

$1 \backslash 1 \backslash G I N C-P C \backslash F O p t \backslash R M P 2-F C \backslash G e n \backslash C 17 H 20 \backslash R A S M U S S E N \backslash 01-N O v-1996 \backslash 0 \backslash \ \# P R M P 2 / G$ EN 5D OPT=NEWESTMFC SCF=DIRECT NAME=RASMUSSEN TEST GEOM=(NODISTANCE,NO ANGLE,NODIHEDRAL) GUESS=CHECK $\backslash$ Hexaplane $D 2 \backslash \backslash 0,1 \backslash C, 0 ., 0 ., 0 . \backslash C,-1.12903$ 18369,-1.1331313219,0.1270137794\C,1.1290318369,-1.1331313219,-0.12701 $37794 \backslash C, 1.1290318369,1.1331313219,0.1270137794 \backslash C,-1.1290318369,1.13313$ 13219,-0.1270137794\C,-1.3740033432,-0.7191320781,1.5676269593\C,1.374 $0033432,-0.7191320781,-1.5676269593 \backslash C, 1.3740033432,0.7191320781,1.5676$ $269593 \backslash C,-1.3740033432,0.7191320781,-1.5676269593 \backslash C,-1.313748355,-0.82$ 00297533,-1.4403020277\C,1.313748355,-0.8200297533,1.4403020277\C,1.31 $3748355,0.8200297533,-1.4403020277 \backslash \mathrm{C},-1.313748355,0.8200297533,1.44030$ $20277 \backslash \mathrm{C}, 0.0181483979,-1.3267988155,-2.1655855498 \backslash \mathrm{C}, 0.0181483979,1.3267$ 988155,2.1655855498\C,-0.0181483979,1.3267988155,-2.1655855498\C,-0.01 81483979,-1.3267988155,2.1655855498\H,-0.8669996319,-2.1964154148,0.12 $91941454 \backslash \mathrm{H}, 0.8669996319,-2.1964154148,-0.1291941454 \backslash \mathrm{H}, 0.8669996319,2.1$ 964154148, 0.1291941454\H,-0.8669996319,2.1964154148,-0.1291941454 \H, -2 . $2467719511,-1.0960112841,2.1433874675 \backslash \mathrm{H}, 2.2467719511,-1.0960112841,-2$ $.1433874675 \backslash \mathrm{H}, 2.2467719511,1.0960112841,2.1433874675 \backslash \mathrm{H},-2.2467719511,1$ $.0960112841,-2.1433874675 \backslash \mathrm{H}, 2.1781621706,-1.3367855967,1.8924753778 \backslash \mathrm{H}$, $2.1781621706,1.3367855967,-1.8924753778 \backslash \mathrm{H},-2.1781621706,1.3367855967,1$ $.8924753778 \backslash \mathrm{H},-2.1781621706,-1.3367855967,-1.8924753778 \backslash \mathrm{H}, 0.0809160296$ ,-2.4222361024,-2.0956618393\H, 0.0809160296,2.4222361024,2.0956618393\} H, -0.0809160296, 2.4222361024,-2.0956618393\H,-0.0809160296,-2.42223610 24,2.0956618393\H,-0.0836430051,-1.0957999577,-3.2354381555\H, -0.08364 30051,1.0957999577,3.2354381555\H,0.0836430051,1.0957999577,-3.2354381 555\H, 0.0836430051,-1.0957999577,3.2354381555<br>Version=SGI-G94RevD.4 \S tate $=1-A \backslash H F=-654.8200575 \backslash \mathrm{MP} 2=-657.1961785 \backslash \mathrm{RMSD}=6.777 \mathrm{e}-09 \backslash \mathrm{RMSF}=2.564 \mathrm{e}-0$ $5 \backslash$ Dipole=0.,0.,0.\PG=D02 [O(C1), X(C16H20)]<br>@

## 4-31 hexaplane $\boldsymbol{D}_{\mathbf{2 h}}$

$1 \backslash 1 \backslash G I N C-P C \backslash F O p t \backslash R M P 2-F C \backslash G e n \backslash C 17 H 20 \backslash R A S M U S S E N \backslash 29-O c t-1996 \backslash 0 \backslash \backslash \#$ RMP2/G EN 5D OPT=NEWESTMFC SCF=DIRECT NAME=RASMUSSEN TEST GEOM=(NODISTANCE,NO ANGLE, NODIHEDRAL) GUESS=CHECK<br>Hexaplane D2h<br>0,1\C,0.,0.,0.\C,-1.1111 295599,-1.1413872751,0.\C,1.1111295599,-1.1413872751,0.\C,1.1111295599
, 1.1413872751, 0. \C, -1.1111295599,1.1413872751,0. \C,-1.3319954622,-0.76 $85607203,1.4894130892 \backslash C, 1.3319954622,-0.7685607203,-1.4894130892 \backslash C, 1.3$ $319954622,0.7685607203,1.4894130892 \backslash C,-1.3319954622,0.7685607203,-1.48$ $94130892 \backslash C,-1.3319954622,-0.7685607203,-1.4894130892 \backslash C, 1.3319954622,-0$ $.7685607203,1.4894130892 \backslash C, 1.3319954622,0.7685607203,-1.4894130892 \backslash C$, $1.3319954622,0.7685607203,1.4894130892 \backslash C, 0 .,-1.3328453668,2.1551407036$ $\backslash C, 0 .,-1.3328453668,-2.1551407036 \backslash C, 0 ., 1.3328453668,2.1551407036 \backslash C, 0 .$, $1.3328453668,-2.1551407036 \backslash \mathrm{H},-0.8904325876,-2.216472958,0 . \backslash \mathrm{H}, 0.8904325$ $876,-2.216472958,0 . \backslash H, 0.8904325876,2.216472958,0 . \backslash H,-0.8904325876,2.21$ $6472958,0 . \backslash \mathrm{H},-2.2099967312,-1.2246353779,2.0089046314 \backslash \mathrm{H}, 2.2099967312$, -$1.2246353779,-2.0089046314 \backslash \mathrm{H}, 2.2099967312,1.2246353779,2.0089046314 \backslash \mathrm{H}$, $-2.2099967312,1.2246353779,-2.0089046314 \backslash H, 2.2099967312$, -1.2246353779, $2.0089046314 \backslash \mathrm{H}, 2.2099967312,1.2246353779,-2.0089046314 \backslash \mathrm{H},-2.2099967312$ , 1. $2246353779,2.0089046314 \backslash \mathrm{H},-2.2099967312,-1.2246353779$, -2.0089046314 $\backslash \mathrm{H}, \mathrm{O},-2.4316541225,2.0834328328 \backslash \mathrm{H}, 0 .,-2.4316541225,-2.0834328328 \backslash \mathrm{H}, \mathrm{O}$. , 2. $4316541225,2.0834328328 \backslash \mathrm{H}, 0 ., 2.4316541225,-2.0834328328 \backslash \mathrm{H}, 0 .,-1.099$ $1798163,3.2283958843 \backslash \mathrm{H}, 0 .,-1.0991798163,-3.2283958843 \backslash \mathrm{H}, 0 ., 1.099179816$ $3,3.2283958843 \backslash \mathrm{H}, 0 ., 1.0991798163,-3.2283958843 \backslash \backslash V e r s i o n=S G I-G 94 R e v D .4 \backslash$ State=1-AG $\backslash \mathrm{HF}=-654.7817264 \backslash \mathrm{MP} 2=-657.1747648 \backslash \mathrm{RMSD}=4.241 \mathrm{e}-09 \backslash \mathrm{RMSF}=2.869 \mathrm{e}$ -05\Dipole=0.,0.,0.\PG=D02H [O(C1), SG(C4H4), SG" (C4H8) , X (C8H8)] <br>@

## 4-33 heptaplane $\boldsymbol{C}_{\mathbf{2}}$

$1 \backslash 1 \backslash$ GINC-PC $\backslash$ FOpt $\backslash$ RMP2-FC $\backslash$ Gen $\backslash \mathrm{C} 19 \mathrm{H} 24 \backslash$ RASMUSSEN $\backslash 18$-Jul-1999\0<br>\#P RMP2/G EN 5D OPT=NEWESTMFC SCF=DIRECT NAME=RASMUSSEN TEST GEOM=(CHECK,NODISTA NCE,NOANGLE,NODIHEDRAL) GUESS=CHECK MAXDISK=1600000000<br>Heptaplane C2 \} $\backslash 0,1 \backslash C, 0 ., 0.0985813703,0 . \backslash C,-1.0766168239,-1.0911463008,-0.2989166607 \backslash$ C,1.0766168239,-1.0911463008,0.2989166607\C,1.1270195842,1.1901787064, $0.0248371017 \backslash C,-1.1270195842,1.1901787064,-0.0248371017 \backslash \mathrm{C},-1.045755513$ 6,-1.5597290269,1.1633403935\C,1.0457555136,-1.5597290269,-1.163340393 $5 \backslash \mathrm{C},-0.4588133044,-1.5663375937,-1.5665678773 \backslash \mathrm{C}, 0.4588133044,-1.566337$ 5937,1.5665678773\C,0.9699243279,1.0030649638,1.7412529009\C,-0.969924 3279,1.0030649638,-1.7412529009\C,1.6905819018,0.9741491722,-1.4039668 $108 \backslash C,-1.6905819018,0.9741491722,1.4039668108 \backslash C, 1.0304509019,-0.402675$ 8992,2.4445518161\C,1.9439688586,-0.4881127283,-1.8457911209\C,-1.9439 688586,-0.4881127283,1.8457911209\C,-1.0304509019,-0.4026758992,-2.444 $5518161 \backslash \mathrm{C},-0.4324618811,1.6178483985,2.1169351647 \backslash \mathrm{C}, 0.4324618811,1.617$ 8483985,-2.1169351647\Н,-2.0943285597,-0.7199677392,-0.4899498774 \H, 2. $0943285597,-0.7199677392,0.4899498774 \backslash \mathrm{H}, 0.8851064269,2.2624749589,0.01$ $68039534 \backslash$ Н, $-0.8851064269,2.2624749589,-0.0168039534 \backslash \mathrm{H},-1.5027525001,-2$ . 5502386733,1.3159246212 \H,1.5027525001,-2.5502386733,-1.3159246212 \H, $-0.7755591575,-2.5380996965,-1.9884374841 \backslash \mathrm{H}, 0.7755591575,-2.5380996965$ , 1.9884374841 \H,1.7378024535,1.6555509248, 2.1960729784\H,-1.7378024535 ,1.6555509248,-2.1960729784 \H, 2.5746264272,1.5819547236,-1.678382769\H , $-2.5746264272,1.5819547236,1.678382769 \backslash \mathrm{H}, 2.0730583526,-0.6673825737,2$ $.6704572407 \backslash \mathrm{H}, 0.5205476909,-0.3135350808,3.4127513351 \backslash \mathrm{H}, 2.984667364,-0$ $.7427219424,-1.6004068587 \backslash \mathrm{H}, 1.8643478954,-0.5452794103,-2.9402595655 \backslash \mathrm{H}$ , $-2.984667364,-0.7427219424,1.6004068587 \backslash \mathrm{H},-1.8643478954,-0.5452794103$ , $2.9402595655 \backslash \mathrm{H},-2.0730583526,-0.6673825737,-2.6704572407 \backslash \mathrm{H},-0.5205476$ 909,-0.3135350808,-3.4127513351 \H, 0.4327127595, 2.6971492884,-1.9087545 $609 \backslash \mathrm{H}, 0.5475522977,1.5209129564,-3.2062303847 \backslash \mathrm{H},-0.4327127595,2.697149$ 2884,1.9087545609\H,-0.5475522977,1.5209129564,3.2062303847<br>Version=S GI-G98RevA. $6 \backslash$ State $=1-A \backslash H F=-732.9676394 \backslash M P 2=-735.597152 \backslash$ RMSD $=1.949 e-09 \backslash$

RMSF=6.359e-05\Dipole=0.,0.2385169,0.\PG=C02 [C2 (C1), X(C18H24)] <br>@

## 4-33 heptaplane $\boldsymbol{C}_{2 \mathrm{v}}$

$1 \backslash 1 \backslash G I N C-P C \backslash F O p t \backslash R M P 2-F C \backslash G e n \backslash C 19 H 24 \backslash R A S M U S S E N \backslash 12-J u l-1999 \backslash 0 \backslash \ \# P R M P 2 / G$ EN 5D OPT=NEWESTMFC SCF=DIRECT NAME=RASMUSSEN TEST GEOM=(CHECK,NODISTA NCE, NOANGLE,NODIHEDRAL) GUESS=CHECK MAXDISK=1600000000<br>Heptaplane C2v $\backslash \backslash 0,1 \backslash C, 0.0 .0107190341,0 . \backslash C,-1.0742293371,-1.2176958886,0 . \backslash C, 1.074229$ 3371,-1.2176958886, 0. \C,1.0977781524,1.1025388476, 0. \C, -1.0977781524, 1 $.1025388476,0 . \backslash C,-1.3144204334,-0.9917957327,1.5528100939 \backslash C, 1.31442043$ $34,-0.9917957327,-1.5528100939 \backslash C, 0.777231355,1.5809975877,1.4061329477$ $\backslash C,-0.777231355,1.5809975877,-1.4061329477 \backslash C,-1.3144204334,-0.99179573$ 27,-1.5528100939\C,1.3144204334,-0.9917957327,1.5528100939\C,0.7772313 $55,1.5809975877,-1.4061329477 \backslash C,-0.777231355,1.5809975877,1.4061329477$ $\backslash C, 1.5139928681,0.4327952563,2.1656139491 \backslash C, 1.5139928681,0.4327952563$, $-2.1656139491 \backslash C,-1.5139928681,0.4327952563,2.1656139491 \backslash C,-1.513992868$ $1,0.4327952563,-2.1656139491 \backslash C, 0 .,-1.6263466488,2.1249029095 \backslash C, 0 .,-1.6$ 263466488,-2.1249029095\H,-0.8821042526,-2.3021701273,0. \H, 0.882104252 $6,-2.3021701273,0 . \backslash \mathrm{H}, 2.1274977483,0.7137812353,0 . \backslash \mathrm{H},-2.1274977483,0.71$ 37812353,0. \H, -2.1496562042,-1.6376378432,1.9131424818\H,2.1496562042, $-1.6376378432,-1.9131424818 \backslash \mathrm{H},-2.1496562042,-1.6376378432,-1.913142481$ $8 \backslash \mathrm{H}, 2.1496562042,-1.6376378432,1.9131424818 \backslash \mathrm{H}, 1.2038030836,2.553064063$ $6,1.7276721367 \backslash \mathrm{H},-1.2038030836,2.5530640636,-1.7276721367 \backslash \mathrm{H}, 1.20380308$ $36,2.5530640636,-1.7276721367 \backslash \mathrm{H},-1.2038030836,2.5530640636,1.727672136$ $7 \backslash \mathrm{H}, 1.2122184437,0.3785273143,3.2203269123 \backslash \mathrm{H}, 2.5854487192,0.6854009424$ , 2. 1686452343\H,1.2122184437,0.3785273143,-3.2203269123\H,2.5854487192 , 0.6854009424,-2.1686452343\H,-1.2122184437,0.3785273143,3.2203269123\} H, $-2.5854487192,0.6854009424,2.1686452343 \backslash \mathrm{H},-1.2122184437,0.3785273143$ ,-3.2203269123\H,-2.5854487192,0.6854009424,-2.1686452343\H,0.,-1.5059 $688472,3.2154735466 \backslash \mathrm{H}, 0 .,-2.7114515148,1.936429327 \backslash \mathrm{H}, 0 .,-1.5059688472$, $-3.2154735466 \backslash \mathrm{H}, 0 .,-2.7114515148,-1.936429327 \backslash$ Version=SGI-G98RevA. $6 \backslash \mathrm{~S}$ tate=1-A1 $\backslash H F=-732.9319078 \backslash \mathrm{MP} 2=-735.5691002 \backslash \mathrm{RMSD}=4.527 \mathrm{e}-09 \backslash \mathrm{RMSF}=4.319 \mathrm{e}-$ 05\Dipole=0.,-0.7242204,0. \PG=C02V [C2 (C1) ,SGV (C4H4), SGV' (C2H4) , X (C12H 16)]<br>@

## 4-27 octaplane (A-type) $\quad \boldsymbol{S}_{\mathbf{4}}$

$1 \backslash 1 \backslash$ GINC-PC $\backslash$ FOpt $\backslash$ RMP2-FC $\backslash$ Gen $\backslash \mathrm{C} 21 \mathrm{H} 28 \backslash$ RASMUSSEN $\backslash 04$-Dec-1996\0<br>\#P RMP2/G EN 5D OPT=(READFC) IOP (1/19=9) IOP(1/8=25) NAME=RASMUSSEN MAXDISK=1800 000000 GUESS=CHECK GEOM=(CHECK,NODISTANCE,NOANGLE,NODIHEDRAL) <br>Octapla ne $S 4 \backslash \backslash 0,1 \backslash C, 0 ., 0 ., 0 . \backslash C, 1.5829410884,0.0032190317,0.1399557932 \backslash \mathrm{C},-0.00$ 32190317,1.5829410884,-0.1399557932\C,-1.5829410884,-0.0032190317,0.13 $99557932 \backslash C, 0.0032190317,-1.5829410884,-0.1399557932 \backslash C, 1.8476752014,0.4$ 0855226,1.5721947281\C,-0.40855226,1.8476752014,-1.5721947281\C,-1.847 6752014,-0.40855226,1.5721947281\C, 0.40855226,-1.8476752014,-1.5721947 $281 \backslash C, 1.8321431227,0.3325361416,-1.4100718371 \backslash C,-0.3325361416,1.832143$ 1227,1.4100718371\C,-1.8321431227,-0.3325361416,-1.4100718371\C,0.3325 361416,-1.8321431227,1.4100718371\C,1.4103765803,-0.9767665185,2.19044 $04194 \backslash C, 0.9767665185,1.4103765803,-2.1904404194 \backslash C,-1.4103765803,0.9767$ 665185,2.1904404194\C,-0.9767665185,-1.4103765803,-2.1904404194\C,-1.6 528673292,1.076307557,-2.0428813679\C,-1.076307557,-1.6528673292,2.042 $8813679 \backslash C, 1.6528673292,-1.076307557,-2.0428813679 \backslash C, 1.076307557,1.6528$ $673292,2.0428813679 \backslash \mathrm{H}, 1.9983469492,-1.0187491442,0.1366380451 \backslash \mathrm{H}, 1.0187$ $491442,1.9983469492,-0.1366380451 \backslash \mathrm{H},-1.9983469492,1.0187491442,0.13663$
$80451 \backslash \mathrm{H},-1.0187491442,-1.9983469492,-0.1366380451 \backslash \mathrm{H}, 2.9149010986,0.555$ $4213943,1.8203247561 \backslash \mathrm{H},-0.5554213943,2.9149010986,-1.8203247561 \backslash \mathrm{H},-2.9$ $149010986,-0.5554213943,1.8203247561 \backslash H, 0.5554213943,-2.9149010986,-1.8$ $203247561 \backslash \mathrm{H},-0.6084299052,2.8916407652,1.5487005999 \backslash \mathrm{H},-2.8916407652,-0$ $.6084299052,-1.5487005999 \backslash \mathrm{H}, 0.6084299052,-2.8916407652,1.5487005999 \backslash \mathrm{H}$, $2.8916407652,0.6084299052,-1.5487005999 \backslash H, 1.0477349934,-0.8387048625,3$ $.2185533445 \backslash \mathrm{H}, 2.3269692657,-1.5774543511,2.2709311203 \backslash \mathrm{H}, 0.8387048625$, 1 $.0477349934,-3.2185533445 \backslash \mathrm{H}, 1.5774543511,2.3269692657,-2.2709311203 \backslash \mathrm{H}$, $-1.0477349934,0.8387048625,3.2185533445 \backslash \mathrm{H},-2.3269692657,1.5774543511,2$ $.2709311203 \backslash \mathrm{H},-0.8387048625,-1.0477349934,-3.2185533445 \backslash \mathrm{H},-1.577454351$ $1,-2.3269692657,-2.2709311203 \backslash \mathrm{H},-1.6453482676,1.002971558,-3.139596674$ $5 \backslash \mathrm{H},-2.5376960764,1.6770132088,-1.7863004899 \backslash \mathrm{H},-1.002971558,-1.6453482$ $676,3.1395966745 \backslash \mathrm{H},-1.6770132088,-2.5376960764,1.7863004899 \backslash \mathrm{H}, 1.645348$ $2676,-1.002971558,-3.1395966745 \backslash \mathrm{H}, 2.5376960764,-1.6770132088,-1.786300$ $4899 \backslash \mathrm{H}, 1.002971558,1.6453482676,3.1395966745 \backslash \mathrm{H}, 1.6770132088,2.53769607$ $64,1.7863004899 \backslash$ VVersion=SGI-G94RevD. $4 \backslash \mathrm{HF}=-811.0825753 \backslash \mathrm{MP} 2=-813.967335$ $1 \backslash \mathrm{RMSD}=1.178 \mathrm{e}-09 \backslash \mathrm{RMSF}=1.921 \mathrm{e}-05 \backslash \mathrm{Dipole}=0 ., 0 ., 0 . \backslash \mathrm{PG}=\mathrm{SO} 4 \quad[\mathrm{O}(\mathrm{C} 1)$, X (C20H28 )] <br>@

## 4-27 octaplane (A-type) $\quad \boldsymbol{C}_{4 \mathrm{~h}}$

$1 \backslash 1 \backslash G I N C-P C \backslash F O p t \backslash R M P 2-F C \backslash G e n \backslash C 21 H 28 \backslash R A S M U S S E N \backslash 30-N o v-1996 \backslash 0 \backslash \ \# P R M P 2 / G$ EN 5D OPT=(READFC) IOP(1/19=9) IOP(1/8=25) NAME=RASMUSSEN MAXDISK=2000 000000 GUESS=CHECK GEOM=(CHECK,NODISTANCE,NOANGLE,NODIHEDRAL) <br>Octapla ne C4h <br>0,1\C,0.,0.,0.\C,1.5830051578,-0.0032842892,0.\C,-1.5830051578 $, 0.0032842892,0 . \backslash C,-0.0032842892,-1.5830051578,0 . \backslash C, 0.0032842892,1.583$ $0051578,0 . \backslash C, 1.8394163631,-0.3576112294,1.4817692257 \backslash \mathrm{C},-1.8394163631,0$ $.3576112294,1.4817692257 \backslash \mathrm{C},-0.3576112294,-1.8394163631,-1.4817692257 \backslash \mathrm{C}$ , 0.3576112294,1.8394163631,-1.4817692257\C,1.8394163631,-0.3576112294, $-1.4817692257 \backslash \mathrm{C},-1.8394163631,0.3576112294,-1.4817692257 \backslash \mathrm{C},-0.35761122$ 94,-1.8394163631,1.4817692257\C,0.3576112294,1.8394163631,1.4817692257 \C,-1.5307574447,-1.0420884035,2.1099580501 \C,1.0420884035,-1.53075744 $47,-2.1099580501 \backslash C, 1.5307574447,1.0420884035,2.1099580501 \backslash C,-1.0420884$ 035,1.5307574447,-2.1099580501\C,1.0420884035,-1.5307574447,2.10995805 $01 \backslash C, 1.5307574447,1.0420884035,-2.1099580501 \backslash C,-1.0420884035,1.5307574$ 447,2.1099580501 \C, -1.5307574447,-1.0420884035,-2.1099580501 \H, 1.97727 15272,1.0271026366,0. \H,-1.9772715272,-1.0271026366,0. \H,1.0271026366, $-1.9772715272,0 . \backslash$ Н, -1.0271026366,1.9772715272,0. \H, 0.5520662408, 2.9130 648755,1.6772137032 \H, $-2.9130648755,0.5520662408,-1.6772137032 \backslash \mathrm{H},-0.55$ 20662408,-2.9130648755,1.6772137032\H,2.9130648755,-0.5520662408,-1.67 $72137032 \backslash$ Н, $2.9130648755,-0.5520662408,1.6772137032 \backslash \mathrm{H},-2.9130648755,0.5$ $520662408,1.6772137032 \backslash \mathrm{H}, 0.5520662408,2.9130648755,-1.6772137032 \backslash \mathrm{H},-0$. $5520662408,-2.9130648755,-1.6772137032 \backslash \mathrm{H},-2.4481546771,-1.643611549,-2$ $.0220800627 \backslash \mathrm{H}, 1.643611549,-2.4481546771,2.0220800627 \backslash \mathrm{H}, 2.4481546771,1$. 643611549,-2.0220800627\H,-1.643611549,2.4481546771,2.0220800627\H,-2. $4481546771,-1.643611549,2.0220800627 \backslash \mathrm{H}, 1.643611549,-2.4481546771,-2.02$ $20800627 \backslash \mathrm{H}, 2.4481546771,1.643611549,2.0220800627 \backslash \mathrm{H},-1.643611549,2.4481$ $546771,-2.0220800627 \backslash \mathrm{H},-1.3393182722,-0.9405922682,3.1877958309 \backslash \mathrm{H}, 0.94$ $05922682,-1.3393182722,-3.1877958309 \backslash н, 1.3393182722,0.9405922682,3.187$ $7958309 \backslash \mathrm{H},-0.9405922682,1.3393182722,-3.1877958309 \backslash \mathrm{H}, 0.9405922682,-1.3$ $393182722,3.1877958309 \backslash \mathrm{H},-1.3393182722,-0.9405922682,-3.1877958309 \backslash \mathrm{H}, 1$ $.3393182722,0.9405922682,-3.1877958309 \backslash \mathrm{H},-0.9405922682,1.3393182722,3$. $1877958309 \backslash$ VVersion=SGI-G94RevD. $4 \backslash \mathrm{HF}=-811.0436117 \backslash \mathrm{MP} 2=-813.9438268 \backslash$ RMS
$D=6.353 e-09 \backslash R M S F=1.674 e-04 \backslash D i p o l e=0 ., 0 ., 0 . \backslash P G=C 04 H \quad[O(C 1), S G H(C 4 H 4), X($ C16H24)]<br>@

## Spiroalkaplanes

## 4-39 spiro[2.2]hexaplane $\quad \boldsymbol{D}_{\mathbf{2}}$

$1 \backslash 1 \backslash G I N C-R S C Q C 2 \backslash F O p t \backslash R M P 2-F C \backslash G e n \backslash C 17 H 16 \backslash R A S M U S S E N \backslash 04-S e p-1996 \backslash 0 \backslash \backslash \# P ~ R M$ P2/GEN 5D FOPT= (NEWESTMFC) SCF=DIRECT NAME=RASMUSSEN MAXDISK=750000000 GEOM = (NODISTANCE, NOANGLE,NODIHEDRAL) OPTCYC=2<br>Spiro[2.2]hexaplane D2 $\backslash \backslash 0,1 \backslash C, 0 ., 0 ., 0 . \backslash C,-0.098071,1.268125,0.729105 \backslash \mathrm{C}, 0.098071,1.268125,-0$. $729105 \backslash C,-0.098071,-1.268125,-0.729105 \backslash C, 0.098071,-1.268125,0.729105 \backslash C$ , - $1.628843,1.32674,0.741139 \backslash C, 1.628843,1.32674,-0.741139 \backslash C,-1.628843$, -$1.32674,-0.741139 \backslash C, 1.628843,-1.32674,0.741139 \backslash C, 1.530455,1.257651,0.8$ $7734 \backslash C,-1.530455,1.257651,-0.87734 \backslash C, 1.530455,-1.257651,-0.87734 \backslash C,-1$. $530455,-1.257651,0.87734 \backslash C,-2.177758,0.042483,1.422767 \backslash C, 2.177758,0.04$ $2483,-1.422767 \backslash C,-2.177758,-0.042483,-1.422767 \backslash C, 2.177758,-0.042483,1$. $422767 \backslash \mathrm{H},-2.15705,2.230869,1.102097 \backslash \mathrm{H}, 2.15705,2.230869,-1.102097 \backslash \mathrm{H},-2$. 15705,-2.230869,-1.102097 \H, 2.15705,-2.230869,1.102097\H,-1.957871,2.1 $47444,-1.368493 \backslash \mathrm{H}, 1.957871,-2.147444,-1.368493 \backslash \mathrm{H},-1.957871,-2.147444,1$ $.368493 \backslash \mathrm{H}, 1.957871,2.147444,1.368493 \backslash \mathrm{H},-3.265965,-0.036248,1.270958 \backslash \mathrm{H}$, $-2.019251,0.119917,2.509545 \backslash \mathrm{H}, 3.265965,-0.036248,-1.270958 \backslash \mathrm{H}, 2.019251$, $0.119917,-2.509545 \backslash \mathrm{H},-3.265965,0.036248,-1.270958 \backslash \mathrm{H},-2.019251,-0.11991$ $7,-2.509545 \backslash \mathrm{H}, 3.265965,0.036248,1.270958 \backslash \mathrm{H}, 2.019251,-0.119917,2.509545$ $\backslash$ Version=IBM-RS6000-G94RevD.1 \State=1-A\HF=-652.5118802 \MP2=-654.8353 $459 \backslash \mathrm{RMSD}=2.653 \mathrm{e}-09 \backslash \mathrm{RMSF}=4.772 \mathrm{e}-05 \backslash \mathrm{Dipole=0.,0.,0}. \mathrm{\backslash PG=D02} \mathrm{\quad[O(C1),X(C16H}$ 16)]<br>@

## 4-39 spiro[2.2]hexaplane $\quad \boldsymbol{D}_{\mathbf{2 h}}$

$1 \backslash 1 \backslash G I N C-R S C Q C 2 \backslash F O p t \backslash R M P 2-F C \backslash G e n \backslash C 17 H 16 \backslash R A S M U S S E N \backslash 23-A u g-1996 \backslash 1 \backslash \backslash \# \mathrm{RM}$ P2/GEN 5D FOPT= (READFC, Z-MATRIX) SCF=DIRECT NAME=RASMUSSEN MAXDISK=750 000000 GEOM = (CHECK, NODISTANCE, NOANGLE, NODIHEDRAL) GUESS=CHECK $\backslash$ Spiro [2 .2]hexaplane $D 2 h \backslash \backslash 0,1 \backslash C \backslash X, 1,0.5 \backslash X, 1,0.5,2,90 . \backslash X, 1,0.5,2,90 ., 3,-90 ., 0 \backslash X$ $, 1,0.5,3,90 ., 2,180 ., 0 \backslash X, 1,0.5,2,90 ., 3,180 ., 0 \backslash X, 1,0.5,2,90 ., 4,180 ., 0 \backslash C$, $1, \mathrm{cc} 1,2,90 ., 7, \mathrm{ccxx} 1,0 \backslash \mathrm{C}, 1, \mathrm{cc} 1,5,90 ., 7, \mathrm{ccxx} 1,0 \backslash \mathrm{C}, 1, \mathrm{cc} 1,2,90 ., 4, \mathrm{ccxx} 1,0 \backslash$ $\mathrm{C}, 1, \mathrm{Cc} 1,5,90 ., 4, \operatorname{ccxx} 1,0 \backslash \mathrm{C}, 8, \mathrm{cc} 2,1, \operatorname{ccc} 2,2, \operatorname{cccx} 2,0 \backslash \mathrm{C}, 9, \mathrm{Cc} 2,1, \mathrm{Ccc} 2,5, \mathrm{Cccx}$ $2,0 \backslash C, 10, \operatorname{cc} 2,1, \operatorname{ccc} 2,2, \operatorname{cccx} 2,0 \backslash C, 11, \operatorname{cc} 2,1, \operatorname{ccc} 2,5, \operatorname{cccx} 2,0 \backslash C, 8, \operatorname{cc} 2,1, \mathrm{Ccc} 2$ $, 5,-\operatorname{cccx} 2,0 \backslash C, 9, \operatorname{cc} 2,1, \operatorname{ccc} 2,2,-\operatorname{cccx} 2,0 \backslash C, 10, \operatorname{cc} 2,1, \operatorname{ccc} 2,5,-\operatorname{cccx} 2,0 \backslash C, 11$, $\mathrm{cc} 2,1, \operatorname{ccc} 2,2,-\operatorname{cccx} 2,0 \backslash \mathrm{C}, 1, \mathrm{cl} 3,2, \mathrm{clx} 3,3,180 ., 0 \backslash \mathrm{C}, 1, \mathrm{cl} 3,5, \mathrm{clx} 3,3,180 ., 0 \backslash$ $\mathrm{C}, 1, \mathrm{cl} 3,2, \mathrm{clx} 3,6,180 ., 0 \backslash \mathrm{C}, 1, \mathrm{cl} 3,5, \mathrm{clx} 3,6,180 ., 0 \backslash \mathrm{H}, 12, \mathrm{hc} 2,8, \mathrm{hcc} 2,1, \mathrm{hccc}$ $2,0 \backslash H, 13, h c 2,9, h c c 2,1, h c c c 2,0 \backslash H, 14, h c 2,10, h c c 2,1, h c c c 2,0 \backslash H, 15, h c 2,11, h$ $\mathrm{cc} 2,1, \mathrm{hccc} 2,0 \backslash \mathrm{H}, 17, \mathrm{hc} 2,9, \mathrm{hcc} 2,1,-\mathrm{hccc} 2,0 \backslash \mathrm{H}, 18, \mathrm{hc} 2,10, \mathrm{hcc} 2,1,-\mathrm{hccc} 2,0 \backslash \mathrm{H}$ , 19, hc2, 11, hcc2, 1, -hccc $2,0 \backslash H, 16, h c 2,8, h c c 2,1,-h c c c 2,0 \backslash H, 20, h c 3,1, h c c 3$, $2,0 ., 0 \backslash H, 20, h c 4,1, h c c 4,2,180 ., 0 \backslash H, 21, h c 3,1, h c c 3,5,0 ., 0 \backslash H, 21, h c 4,1, h c c 4$ $, 5,180 ., 0 \backslash H, 22, h c 3,1, h c c 3,2,0 ., 0 \backslash H, 22, h c 4,1, h c c 4,2,180 ., 0 \backslash H, 23, h c 3,1, h$ $\mathrm{Cc} 3,5,0 ., 0 \backslash \mathrm{H}, 23, \mathrm{hc} 4,1, \mathrm{hcc} 4,5,180 ., 0 \backslash \backslash \mathrm{Cc} 1=1.46544651 \backslash \mathrm{CC} 2=1.57598469 \backslash \mathrm{cl} 3$ $=2.59583871 \backslash h c 2=1.10905855 \backslash h c 3=1.10123908 \backslash h c 4=1.10162245 \backslash c c c 2=92.14840$ $323 \backslash \mathrm{clx} 3=33.34171677 \backslash \mathrm{hcc} 2=117.97109252 \backslash \mathrm{hcc} 3=138.49197339 \backslash \mathrm{hcc} 4=115.1639$ $3256 \backslash \mathrm{ccxx}=29.82779092 \backslash \mathrm{cccx} 2=2.11909281 \backslash \mathrm{hccc} 2=185.30837416 \backslash \backslash$ Version=IB M-RS6000-G94RevD.1 \State=1-AG $\backslash \mathrm{HF}=-652.4988 \backslash \mathrm{MP} 2=-654.8291904 \backslash \mathrm{RMSD}=2.040$
 C8H8) ] <br>@

## 4-40 spiro[2.2]biheptaplane $\boldsymbol{D}_{\mathbf{2}}$

$1 \backslash 1 \backslash G I N C-P C \backslash F O p t \backslash R M P 2-F C \backslash G e n \backslash C 19 H 16 \backslash R A S M U S S E N \backslash 12-J u l-1999 \backslash 0 \backslash \ \# P R M P 2 / G$ EN 5D OPT=NEWESTMFC SCF=DIRECT NAME=RASMUSSEN TEST GEOM=(CHECK,NODISTA NCE, NOANGLE,NODIHEDRAL) GUESS=CHECK MAXDISK=1600000000<br>spiro[2.2]bihe ptaplane $\mathrm{D} 2 \backslash \backslash 0,1 \backslash \mathrm{C}, 0.0 .0 .0 . \backslash \mathrm{C},-0.0882563313,1.2546370465,0.733518755 \backslash \mathrm{C}$ $, 0.0882563313,1.2546370465,-0.733518755 \backslash C,-0.0882563313,-1.2546370465$, $-0.733518755 \backslash C, 0.0882563313,-1.2546370465,0.733518755 \backslash C,-1.6152829497$, $1.356760153,0.7542959987 \backslash \mathrm{C}, 1.6152829497,1.356760153,-0.7542959987 \backslash \mathrm{C},-1$ $.6152829497,-1.356760153,-0.7542959987 \backslash C, 1.6152829497,-1.356760153,0.7$ $542959987 \backslash \mathrm{C}, 1.5471331608,1.2714630105,0.8599068108 \backslash \mathrm{C},-1.5471331608,1.2$ $714630105,-0.8599068108 \backslash C, 1.5471331608,-1.2714630105,-0.8599068108 \backslash C,-$ $1.5471331608,-1.2714630105,0.8599068108 \backslash C,-2.3538382507,0.0452056768,1$ $.1597319848 \backslash C, 2.3538382507,0.0452056768,-1.1597319848 \backslash C,-2.3538382507$, $-0.0452056768,-1.1597319848 \backslash C, 2.3538382507,-0.0452056768,1.1597319848 \backslash$ C, $-3.3855829609,0 ., 0 . \backslash C, 3.3855829609,0.0 . \backslash H,-4.0275446554,-0.89032363$ $69,0.0179499788 \backslash \mathrm{H},-4.0275446554,0.8903236369,-0.0179499788 \backslash \mathrm{H}, 4.0275446$ 554,-0.8903236369,-0.0179499788\H, 4.0275446554,0.8903236369,0.01794997 $88 \backslash \mathrm{H},-2.1283556034,2.251720037,1.1544217762 \backslash \mathrm{H}, 2.1283556034,2.251720037$ , $-1.1544217762 \backslash \mathrm{H},-2.1283556034,-2.251720037,-1.1544217762 \backslash \mathrm{H}, 2.12835560$ $34,-2.251720037,1.1544217762 \backslash \mathrm{H},-1.9852777967,2.1354006087,-1.385645552$ $1 \backslash H, 1.9852777967,-2.1354006087,-1.3856455521 \backslash H,-1.9852777967,-2.135400$ 6087,1.3856455521 \H, 1.9852777967,2.1354006087,1.3856455521\H,-2.790712 1108, 0.0731844754,2.1662807121 \H, 2.7907121108, 0.0731844754, -2.16628071 $21 \backslash \mathrm{H},-2.7907121108,-0.0731844754,-2.1662807121 \backslash \mathrm{H}, 2.7907121108,-0.07318$ 44754,2.1662807121 <br>Version=SGI-G98RevA. $6 \backslash$ State $=1-A \backslash H F=-728.2143676 \backslash M P$ $2=-730.7989672 \backslash \mathrm{RMSD}=7.629 \mathrm{e}-09 \backslash \mathrm{RMSF}=8.852 \mathrm{e}-05 \backslash \mathrm{Dipole}=0 ., 0 ., 0 . \backslash \mathrm{PG}=\mathrm{D} 02 \quad$ [O (C1), C2 (C1.C1), X(C16H16)] <br>@

## 4-40 spiro[2.2]biheptaplane $\quad \boldsymbol{D}_{\mathbf{2 h}}$

$1 \backslash 1 \backslash G I N C-P C \backslash F O p t \backslash R M P 2-F C \backslash G e n \backslash C 19 H 16 \backslash R A S M U S S E N \backslash 11-J u l-1999 \backslash 0 \backslash \backslash \#$ RMP2/G EN 5D OPT=NEWESTMFC SCF=DIRECT NAME=RASMUSSEN TEST GEOM=(CHECK,NODISTA NCE, NOANGLE,NODIHEDRAL) GUESS=CHECK MAXDISK=1600000000<br>spiro[2.2]bihe ptaplane $\mathrm{D} 2 \mathrm{~h} \backslash \backslash 0,1 \backslash \mathrm{C}, 0.0 .0 . \backslash \mathrm{C}, 0 ., 1.2535035095,0.7332268442 \backslash \mathrm{C}, 0 ., 1.253$ 5035095,-0.7332268442\C,0.,-1.2535035095,-0.7332268442\C,0.,-1.2535035 $095,0.7332268442 \backslash C,-1.5750849989,1.3152462213,0.8073971513 \backslash C, 1.5750849$ $989,1.3152462213,-0.8073971513 \backslash C,-1.5750849989,-1.3152462213,-0.807397$ $1513 \backslash C, 1.5750849989,-1.3152462213,0.8073971513 \backslash C, 1.5750849989,1.315246$ 2213, 0.8073971513\C,-1.5750849989,1.3152462213,-0.8073971513\C,1.57508 49989,-1.3152462213,-0.8073971513\C,-1.5750849989,-1.3152462213,0.8073 $971513 \backslash C,-2.3439831568,0 ., 1.1629561913 \backslash C, 2.3439831568,0 ., 1.1629561913 \backslash$ C, $-2.3439831568,0 .,-1.1629561913 \backslash C, 2.3439831568,0 .,-1.1629561913 \backslash C,-3$. $374170326,0 ., 0 . \backslash \mathrm{C}, 3.374170326,0 ., 0 . \backslash \mathrm{H},-4.0156904216,-0.890695366,0 . \backslash \mathrm{H}$, $-4.0156904216,0.890695366,0 . \backslash H, 4.0156904216,0.890695366,0 . \backslash \mathrm{H}, 4.0156904$ 216,-0.890695366, 0. \H,-2.0595442948,2.1954127127,1.2730970271\H, 2. 0595 442948,2.1954127127,-1.2730970271\H,-2.0595442948,-2.1954127127,-1.273 $0970271 \backslash \mathrm{H}, 2.0595442948,-2.1954127127,1.2730970271 \backslash \mathrm{H},-2.0595442948,2.19$ 54127127,-1.2730970271\H,2.0595442948,-2.1954127127,-1.2730970271\H,-2 $.0595442948,-2.1954127127,1.2730970271$ \H, $2.0595442948,2.1954127127,1.2$ $730970271 \backslash \mathrm{H},-2.7866814097,0.2 .1680700651 \backslash \mathrm{H}, 2.7866814097,0 ., 2.16807006$ $51 \backslash \mathrm{H},-2.7866814097,0 .,-2.1680700651 \backslash \mathrm{H}, 2.7866814097,0 .,-2.1680700651 \backslash \backslash \mathrm{~V}$ ersion=SGI-G98RevA.6\State=1-AG $\backslash H F=-728.2027786 \backslash \mathrm{MP2}=-730.7948805 \backslash \mathrm{RMSD}=$ $4.946 \mathrm{e}-09 \backslash \mathrm{RMSF}=7.896 \mathrm{e}-05 \backslash \mathrm{Dipole}=0 ., 0.0 . \backslash \mathrm{PG}=\mathrm{D} 02 \mathrm{H} \quad[\mathrm{O}(\mathrm{C} 1), \mathrm{C} 2(\mathrm{C} 1 . \mathrm{C} 1), \mathrm{SG}(\mathrm{C}$
4),SG'(C4H4),SG" (H4), X(C8H8)] <br>@

## 4-41 spiro[2.2]heptaplane $\boldsymbol{C}_{\mathbf{2}}$

$1 \backslash 1 \backslash G I N C-P C \backslash F O p t \backslash R M P 2-F C \backslash G e n \backslash C 19 H 20 \backslash R A S M U S S E N \backslash 21-J u l-1999 \backslash 0 \backslash \ \# P R M P 2 / G$ EN 5D OPT=NEWESTMFC SCF=DIRECT NAME=RASMUSSEN TEST GEOM=(CHECK,NODISTA NCE, NOANGLE,NODIHEDRAL) GUESS=CHECK MAXDISK=1980000000<br>spiro[2.2]hept aplane $C 2 \backslash \backslash 0,1 \backslash C, 0 ., 0 ., 0.217175893 \backslash C,-0.6649977253,0.2876032453,1.5126$ $06194 \backslash C, 0.6649977253,-0.2876032453,1.512606194 \backslash C, 0.6117848192,-0.46990$ 50278,-1.0094105391 \C,-0.6117848192,0.4699050278,-1.0094105391\C,0.009 1492304,1.7539093727,1.4745977393\C, -0.0091492304,-1.7539093727,1.4745 $977393 \backslash C,-1.4711520456,-1.0007261491,1.5369005933 \backslash C, 1.4711520456,1.000$ $7261491,1.5369005933 \backslash C, 1.8314049299,0.5256548807,-1.053796082 \backslash C,-1.831$ 4049299,-0.5256548807,-1.053796082\C,0.2517886418,-1.9350739238,-1.163 $3764158 \backslash C,-0.2517886418,1.9350739238,-1.1633764158 \backslash C, 2.4474130946,0.93$ $08108217,0.3302641467 \backslash C, 0.355426018,-2.6211063148,0.2391017193 \backslash C,-0.35$ $5426018,2.6211063148,0.2391017193 \backslash C,-2.4474130946,-0.9308108217,0.3302$ $641467 \backslash \mathrm{C}, 1.1898354264,1.7785971323,-1.706576275 \backslash \mathrm{C},-1.1898354264,-1.778$ 5971323,-1.706576275 \Н, -0.1582353292, 2.3446874777, 2.3924744142\H, 0.158 2353292,-2.3446874777,2.3924744142\H,-2.0282858625,-1.2878920548, 2.454 $2792229 \backslash \mathrm{H}, 2.0282858625,1.2878920548,2.4542792229 \backslash \mathrm{H}, 2.6454645698,0.1457$ 372405,-1.6915370496\H,-2.6454645698,-0.1457372405,-1.6915370496\H, 0. 8 581129953,-2.5100237687,-1.8834637284 \H,-0.8581129953,2.5100237687,-1. $8834637284 \backslash \mathrm{H}, 3.2135948615,0.1947477736,0.6225648006 \backslash \mathrm{H}, 2.9802231076,1.8$ 817256149, 0.18915026\H,1.3901445196,-2.9674508248, 0.3918134255\H,-0.27 28292921,-3.5251264816,0.2442489941 \H,-1.3901445196,2.9674508248, 0.391 $8134255 \backslash \mathrm{H}, 0.2728292921,3.5251264816,0.2442489941 \backslash \mathrm{H},-3.2135948615,-0.19$ $47477736,0.6225648006 \backslash \mathrm{H},-2.9802231076,-1.8817256149,0.18915026 \backslash \mathrm{H},-1.11$ 86246241,-1.6188239477,-2.7911218795\H,-1.8000769175,-2.6777896905,-1. $5418026235 \backslash \mathrm{H}, 1.1186246241,1.6188239477,-2.7911218795 \backslash \mathrm{H}, 1.8000769175,2$. 6777896905,-1.5418026235<br>Version=SGI-G98RevA. $6 \backslash$ State $=1-A \backslash H F=-730.7070$ $594 \backslash \mathrm{MP} 2=-733.2899243 \backslash \mathrm{RMSD}=6.158 \mathrm{e}-09 \backslash \mathrm{RMSF}=5.177 \mathrm{e}-05 \backslash \mathrm{Dipole=0.,0.,-0.116}$ $4871 \backslash \mathrm{PG}=\mathrm{C0} 2$ [C2 (C1), X(C18H20)] <br>@

## 4-41 spiro[2.2]heptaplane $\quad \boldsymbol{C}_{2 \mathrm{v}}$

$1 \backslash 1 \backslash G I N C-P C \backslash F O p t \backslash R M P 2-F C \backslash G e n \backslash C 19 H 20 \backslash R A S M U S S E N \backslash 13-J u l-1999 \backslash 0 \backslash \ \# P R M P 2 / G$ EN 5D OPT=NEWESTMFC SCF=DIRECT NAME=RASMUSSEN TEST GEOM=(CHECK,NODISTA NCE, NOANGLE, NODIHEDRAL) GUESS=CHECK MAXDISK=1600000000<br>spiro[2.2]hept aplane $\mathrm{C} 2 \mathrm{v} \backslash \backslash 0,1 \backslash \mathrm{C}, 0.0 .0 .2105234966 \backslash \mathrm{C}, 0.7659550272,0 .,-1.0155681417 \backslash \mathrm{C}$ $,-0.7659550272,0 .,-1.0155681417 \backslash C,-0.7173296358,0 ., 1.5098086593 \backslash C, 0.71$ 73296358,0.,1.5098086593\C,1.2596581952,1.4604678219,-1.1097212819\C,-$1.2596581952,-1.4604678219,-1.1097212819 \backslash \mathrm{C},-0.8194402516,1.5552469329$, $1.5042553561 \backslash C, 0.8194402516,-1.5552469329,1.5042553561 \backslash C, 1.2596581952$, $-1.4604678219,-1.1097212819 \backslash C,-1.2596581952,1.4604678219,-1.1097212819$ $\backslash C,-0.8194402516,-1.5552469329,1.5042553561 \backslash C, 0.8194402516,1.555246932$ $9,1.5042553561 \backslash C,-1.6435435152,2.0520438538,0.2852685544 \backslash C,-1.64354351$ $52,-2.0520438538,0.2852685544 \backslash C, 1.6435435152,2.0520438538,0.2852685544$ $\backslash C, 1.6435435152,-2.0520438538,0.2852685544 \backslash C, 0 ., 2.1450290858,-1.696887$ 1358\C,0.,-2.1450290858,-1.6968871358\H,2.1141254629,1.6041757866,-1.7 $938349897 \backslash \mathrm{H},-2.1141254629,-1.6041757866,-1.7938349897 \backslash \mathrm{H}, 2.1141254629$, -$1.6041757866,-1.7938349897 \backslash H,-2.1141254629,1.6041757866,-1.7938349897 \backslash$ H, -1.2177915028, 2.0347844799,2.4252990145 $\mathrm{H}, 1.2177915028,-2.0347844799$ , $2.4252990145 \backslash \mathrm{H},-1.2177915028,-2.0347844799,2.4252990145 \backslash \mathrm{H}, 1.217791502$

8, 2. $0347844799,2.4252990145 \backslash \mathrm{H},-1.5862927706,3.1483228014,0.2188528158 \backslash$ $\mathrm{H},-2.6966034404,1.8167165997,0.5116890928 \backslash \mathrm{H},-1.5862927706,-3.148322801$ $4,0.2188528158 \backslash \mathrm{H},-2.6966034404,-1.8167165997,0.5116890928 \backslash \mathrm{H}, 1.58629277$ $06,3.1483228014,0.2188528158 \backslash \mathrm{H}, 2.6966034404,1.8167165997,0.5116890928 \backslash$ H, 1. $5862927706,-3.1483228014,0.2188528158 \backslash \mathrm{H}, 2.6966034404,-1.8167165997$ $, 0.5116890928 \backslash \mathrm{H}, 0 ., 3.2288291468,-1.5118081075 \backslash \mathrm{H}, 0 ., 1.9950394981,-2.785$ $5260821 \backslash \mathrm{H}, 0 .,-3.2288291468,-1.5118081075 \backslash \mathrm{H}, 0 .,-1.9950394981,-2.7855260$ $821 \backslash$ Version=SGI-G98RevA. $6 \backslash$ State $=1-A 1 \backslash H F=-730.6948866 \backslash M P 2=-733.2840025$ $\backslash \mathrm{RMSD}=9.912 \mathrm{e}-09 \backslash \mathrm{RMSF}=3.897 \mathrm{e}-05 \backslash \mathrm{Dipole=0.,0.,-0.106713} \mathrm{\backslash PG=C02V} \mathrm{\quad} \mathrm{[C2} \mathrm{(C1)}$, SGV (C2H4) ,SGV' (C4) , X (C12H16) ] <br>@

## 4-42 spiro[2.2]heptaplane $\boldsymbol{C}_{\mathbf{2}}$

$1 \backslash 1 \backslash G I N C-P C \backslash F O p t \backslash R M P 2-F C \backslash G e n \backslash C 19 H 20 \backslash R A S M U S S E N \backslash 09-N o v-1996 \backslash 1 \backslash \backslash \#$ RMP2/G EN 5D FOPT=(READFC,Z-MATRIX) $S C F=(R E S T A R T, D I R E C T)$ NAME=RASMUSSEN GEOM= (CHECK, NODISTANCE, NOANGLE, NODIHEDRAL) GUESS=CHECK MAXDISK=1500000000<br> spiro[2.2]heptaplane (orient b) $C 2 \backslash \backslash 0,1 \backslash C \backslash X, 1,0.5 \backslash X, 1,0.5,2,90 . \backslash X, 1,0$. $5,2,90 ., 3,-90 ., 0 \backslash X, 1,0.5,3,90 ., 2,180 ., 0 \backslash X, 1,0.5,2,90 ., 3,180 ., 0 \backslash X, 1,0.5$ $, 2,90 ., 4,180 ., 0 \backslash c, 1, c c 1 a, 2, c c x 1,7, c c x x 1 a, 0 \backslash c, 1, c c 1 a, 5, c c x 1,7, c c x x 1 a, 0 \backslash$ $\mathrm{C}, 1, \mathrm{cc} 1 \mathrm{~b}, 2,90 ., 4, \mathrm{ccxx} 1 \mathrm{~b}, 0 \backslash \mathrm{C}, 1, \mathrm{cc} 1 \mathrm{~b}, 5,90 ., 4, \mathrm{ccxx} 1 \mathrm{~b}, 0 \backslash \mathrm{C}, 8, \mathrm{cc} 2 \mathrm{a}, 1, \mathrm{ccc} 2 \mathrm{aa}$ $, 2, \operatorname{cccx} 2 \mathrm{aa}, 0 \backslash \mathrm{c}, 9, \operatorname{c} 2 \mathrm{aa}, 1, \operatorname{ccc} 2 \mathrm{aa}, 5, \operatorname{cccx} 2 \mathrm{aa}, 0 \backslash \mathrm{c}, 8, \mathrm{cc} 2 \mathrm{ab}, 1, \mathrm{ccc} 2 \mathrm{ab}, 5,-\mathrm{cccx}$ $2 \mathrm{ab}, 0 \backslash \mathrm{C}, 9, \mathrm{cc} 2 \mathrm{ab}, 1, \mathrm{ccc} 2 \mathrm{ab}, 2,-\mathrm{ccc} 2 \mathrm{ab}, 0 \backslash \mathrm{c}, 10, \mathrm{cc} 2 \mathrm{ba}, 1, \mathrm{ccc} 2 \mathrm{ba}, 2, \mathrm{cccx} 2 \mathrm{ba}, 0 \backslash$ $\mathrm{C}, 11, \mathrm{cc} 2 \mathrm{ba}, 1, \operatorname{ccc} 2 \mathrm{ba}, 5, \operatorname{ccc} 2 \mathrm{ba}, 0 \backslash \mathrm{C}, 10, \mathrm{cc} 2 \mathrm{bb}, 1, \mathrm{ccc} 2 \mathrm{bb}, 5,-\mathrm{cccx} 2 \mathrm{bb}, 0 \backslash \mathrm{c}, 11$, cc2bb, $1, ~ c c c 2 b b, 2,-c c c x 2 b b, 0 \backslash c, 1, c l 3 a, 2, c l x 3 a, 3, c l x x 3 a, 0 \backslash c, 1, c l 3 b, 5, c l x$ $3 b, 3,-c l x x 3 b, 0 \backslash c, 1, c l 3 b, 2, c l x 3 b, 6,-c l x x 3 b, 0 \backslash c, 1, c l 3 a, 5, c l x 3 a, 6, c l x x 3 a$, $0 \backslash C, 1, c l 4 a, 2, c l x 4 a, 7, c l x x 4 a, 0 \backslash C, 1, c l 4 a, 5, c l x 4 a, 7, c l x x 4 a, 0 \backslash H, 12, h c 2 a a, 8$ , hcc $2 \mathrm{aa}, 1, \operatorname{hcc} 2 \mathrm{aa}, 0 \backslash \mathrm{H}, 13, \mathrm{hc} 2 \mathrm{aa}, 9, \mathrm{hcc} 2 \mathrm{aa}, 1, \mathrm{hccc} 2 \mathrm{aa}, 0 \backslash \mathrm{H}, 14, \mathrm{hc} 2 \mathrm{ab}, 8$, hcc2a $\mathrm{b}, 1$, -hccc $2 \mathrm{ab}, 0 \backslash \mathrm{H}, 15, \mathrm{hc} 2 \mathrm{ab}, 9, \operatorname{hcc} 2 \mathrm{ab}, 1,-\operatorname{hccc} 2 \mathrm{ab}, 0 \backslash \mathrm{H}, 16, \mathrm{hc} 2 \mathrm{ba}, 10, \mathrm{hcc} 2 \mathrm{ba}, 1$ , hccc2ba, $0 \backslash \mathrm{H}, 17$, hc2ba, $11, h c c 2 \mathrm{ba}, 1, \operatorname{hccc} 2 \mathrm{ba}, 0 \backslash \mathrm{H}, 18, \mathrm{hc} 2 \mathrm{bb}, 10, \mathrm{hcc} 2 \mathrm{bb}, 1$, -hc cc2bb, $0 \backslash H, 19, h c 2 b b, 11, h c c 2 b b, 1,-h c c c 2 b b, 0 \backslash H, 20, h c 3 a a, 15, h c c 3 a a, 9, h c c c 3$ aa, $0 \backslash \mathrm{H}, 20$, hc3ba, 15, hcc3ba, 9 , hccc3ba, $0 \backslash \mathrm{H}, 21, \mathrm{hc} 3 \mathrm{ab}, 13$, hcc3ab, 9 , hccc3ab, 0 $\backslash H, 21, h c 3 b b, 13, h c c 3 b b, 9, h c c c 3 b b, 0 \backslash H, 22, h c 3 a b, 12, h c c 3 a b, 8, h c c c 3 a b, 0 \backslash H, 2$ 2 , hc3bb, 12 , hcc3bb, 8 , hccc3bb, $0 \backslash H, 23$, hc3aa, $14, \operatorname{hcc} 3 a \mathrm{a}, 8$, hccc3aa, $0 \backslash \mathrm{H}, 23$, hc $3 \mathrm{ba}, 14, \mathrm{hcc} 3 \mathrm{ba}, 8, \operatorname{hccc} 3 \mathrm{ba}, 0 \backslash \mathrm{H}, 25, \mathrm{hc} 4 \mathrm{ab}, 18, \mathrm{hcc} 4 \mathrm{ab}, 10, \mathrm{hccc} 4 \mathrm{ab}, 0 \backslash \mathrm{H}, 25$, hc4bb $, 18, h c c 4 b b, 10, h c c c 4 b b, 0 \backslash H, 24, h c 4 a b, 19, h c c 4 a b, 11, h c c c 4 a b, 0 \backslash H, 24, h c 4 b b, 1$ $9, h c c 4 b b, 11, h c c c 4 b b, 0 \backslash \backslash c c 1 a=1.50472927 \backslash c c 1 b=1.42877216 \backslash c c 2 a a=1.5790856$ $8 \backslash c c 2 a b=1.5207282 \backslash c c 2 b a=1.58343709 \backslash c c 2 b b=1.5154454 \backslash c l 3 a=2.66180317 \backslash c l 3$ $\mathrm{b}=2.72681257 \backslash \mathrm{cl} 4 \mathrm{a}=2.54334938 \backslash \mathrm{hc} 2 \mathrm{aa}=1.10355077 \backslash \mathrm{hc} 2 \mathrm{ab}=1.10676724 \backslash \mathrm{hc} 2 \mathrm{ba}=1$ $.10412782 \backslash h c 2 b b=1.10570192 \backslash c c x 1=95.55707388 \backslash c c c 2 a a=90.52197006 \backslash c c c 2 a b=$ $93.24089391 \backslash \mathrm{ccc} 2 \mathrm{ba}=92.04822704 \backslash \mathrm{ccc} 2 \mathrm{bb}=103.04855701 \backslash \mathrm{clx} 3 \mathrm{a}=28.74370494 \backslash \mathrm{c}$ $\operatorname{lx} 3 \mathrm{~b}=38.5528581 \backslash \mathrm{clx} 4 \mathrm{a}=45.82096371 \backslash \mathrm{hcc} 2 \mathrm{aa}=114.55741012 \backslash \mathrm{hcc} 2 \mathrm{ab}=118.04828$ $856 \backslash h c c 2 b a=111.78930172 \backslash h c c 2 b b=117.65120429 \backslash c c x x 1 a=49.17955152 \backslash c c x x 1 b=$ $67.52196076 \backslash c l x x 3 a=9.75466869 \backslash c l x x 3 b=13.09207941 \backslash c l x x 4 a=173.57393967 \backslash c$ $\mathrm{ccx} 2 \mathrm{aa}=-19.9071213 \backslash \mathrm{cccx} 2 \mathrm{ab}=-24.61343855 \backslash \mathrm{cccx} 2 \mathrm{ba}=-20.89897786 \backslash \mathrm{cccx} 2 \mathrm{bb}=-$ $13.93889483 \backslash$ hccc2aa=199.25026658 \hccc2ab=196.64165749 \hccc2ba=191.7403 $9996 \backslash h c c c 2 b b=190.30152398 \backslash h c 3 a a=1.09844321 \backslash h c 3 b a=1.09684122 \backslash h c c 3 a a=107$ $.28549578 \backslash h c c 3 b a=112.82393796 \backslash$ hccc3aa $=-83.9782319 \backslash$ hccc3ba=158. 50797292 $\backslash h c 3 a b=1.09821396 \backslash h c 3 b b=1.09687198 \backslash h c c 3 a b=107.35390054 \backslash h c c 3 b b=112.4135$ $3939 \backslash h \operatorname{hcc} 3 \mathrm{ab}=81.25462017 \backslash \mathrm{hccc} 3 \mathrm{bb}=-161.27103387 \backslash \mathrm{hc} 4 \mathrm{ab}=1.10108745 \backslash \mathrm{hc} 4 \mathrm{bb}=$ $1.10009715 \backslash \mathrm{hcc} 4 \mathrm{ab}=108.13662122 \backslash \mathrm{hcc} 4 \mathrm{bb}=109.54528992 \backslash \mathrm{hccc} 4 \mathrm{ab}=71.52474035$ $\backslash h c c c 4 b b=-173.24683181 \backslash \backslash V e r s i o n=S G I-G 94 R e v D .4 \backslash$ State $=1-A \backslash H F=-730.744942$ $9 \backslash M P 2=-733.3395333 \backslash R M S D=5.859 e-09 \backslash R M S F=2.619 e-05 \backslash D i p o l e=0 ., 0.2843531,0$ $. \backslash \mathrm{PG}=\mathrm{C0} 2$ [C2 (C1), X(C18H20)]<br>@

## 4-42 spiro[2.2]heptaplane $\quad \boldsymbol{C}_{2 \mathrm{v}}$

$1 \backslash 1 \backslash G I N C-R S C Q C 9 \backslash F O p t \backslash R M P 2-F C \backslash G e n \backslash C 19 H 20 \backslash R A S M U S S E N \backslash 04-N o v-1996 \backslash 0 \backslash \ \# P R M$ P2/GEN 5D FOPT=(NEWESTMFC,Z-MATRIX) SCF=DIRECT NAME=RASMUSSEN MAXDISK= 100000000 GEOM=(NODISTANCE,NOANGLE,NODIHEDRAL) OPTCYC=1 IOP(1/8=1) <br>s piro[2.2]heptaplane (orient b) C2v<br>0,1\C,0.,0.,0.006925398\C,1.338390 8098,0.,-0.5185492589\C,-1.3383908098,0.,-0.5185492589\C,-1.0933067704 , 0., 0.9836745482\C,1.0933067704,0., 0.9836745482\C,1.3336817668,1.46310 31404,-1.0206451117\C,-1.3336817668,-1.4631031404,-1.0206451117\C,-0.7 $914887344,1.4419799023,1.4869195584 \backslash C, 0.7914887344,-1.4419799023,1.486$ $9195584 \backslash C, 1.3336817668,-1.4631031404,-1.0206451117 \backslash \mathrm{C},-1.3336817668,1.4$ 631031404,-1.0206451117\C,-0.7914887344,-1.4419799023,1.4869195584 \C, 0 $.7914887344,1.4419799023,1.4869195584 \backslash C,-1.4626713381,2.2426833735,0.3$ $267689364 \backslash C,-1.4626713381,-2.2426833735,0.3267689364 \backslash C, 1.4626713381,2$. $2426833735,0.3267689364 \backslash C, 1.4626713381,-2.2426833735,0.3267689364 \backslash C, 0$. , 1.7762429723,-1.7839212135\C,0.,-1.7762429723,-1.7839212135\H, 2.17879 47245,1.7372999894,-1.6825641793\H,-2.1787947245,-1.7372999894,-1.6825 $641793 \backslash \mathrm{H}, 2.1787947245,-1.7372999894,-1.6825641793 \backslash \mathrm{H},-2.1787947245,1.73$ 72999894,-1.6825641793\H,-1.2341839323,1.7459992226,2.4563959746\H,1.2 341839323,-1.7459992226,2.4563959746\H,-1.2341839323,-1.7459992226,2.4 563959746\H,1.2341839323,1.7459992226,2.4563959746\H,-1.0639775639,3.2 608135206,0.2372740253\H,-2.5312531742,2.3387996182,0.5670243826\H,-1. $0639775639,-3.2608135206,0.2372740253 \backslash \mathrm{H},-2.5312531742,-2.3387996182,0$. 5670243826\H,1.0639775639,3.2608135206,0.2372740253\H, 2.5312531742, 2.3 387996182,0.5670243826\H,1.0639775639,-3.2608135206,0.2372740253\H, 2.5 $312531742,-2.3387996182,0.5670243826 \backslash \mathrm{H}, 0 ., 2.847277566,-2.0356183505 \backslash \mathrm{H}$, $0 ., 1.2382438086,-2.7451633027 \backslash \mathrm{H}, 0 .,-2.847277566,-2.0356183505 \backslash \mathrm{H}, 0 .,-1$. 2382438086,-2.7451633027<br>Version=IBM-RS6000-G94RevD.4\State=1-A1 \HF=$730.7373888 \backslash \mathrm{MP} 2=-733.3320181 \backslash \mathrm{RMSD}=6.640 \mathrm{e}-09 \backslash \mathrm{RMSF}=2.554 \mathrm{e}-05 \backslash \mathrm{Dipole}=0 ., 0$ .,-0.1632911 \PG=C02V [C2 (C1), SGV(C2H4), SGV' (C4) , X(C12H16)] <br>@

## 4-43 spiro[2.2]bioctaplane $\quad \boldsymbol{D}_{\mathbf{2}}$

$1 \backslash 1 \backslash G I N C-V P P 08 \backslash F O p t \backslash R M P 2-F C \backslash G e n \backslash C 21 H 20 \backslash R A S M U S S E N \backslash 23-S e p-1998 \backslash 0 \backslash \backslash \# P$ MP2 /GEN 5D OPT=READFC SCF=DIRECT NAME=RASMUSSEN GEOM=(CHECK,NODISTANCE,NO ANGLE, NODIHEDRAL) GUESS=CHECK MAXDISK=1900000000 <br>Spiro[2.2]bioctaplan e 5D D2 <br>0,1\C,0.,0.,0.\C, -0.7517544693,-1.2724157251,0.0881173844\C,0 . $7517544693,-1.2724157251,-0.0881173844 \backslash \mathrm{C}, 0.7517544693,1.2724157251,0$. $0881173844 \backslash C,-0.7517544693,1.2724157251,-0.0881173844 \backslash C,-1.2598616235$, $-1.2765929645,1.5016019017 \backslash C, 1.2598616235,-1.2765929645,-1.5016019017 \backslash$ C,1.2598616235,1.2765929645,1.5016019017\C,-1.2598616235,1.2765929645, $-1.5016019017 \backslash C,-1.3188701688,-1.1675253736,-1.361834487 \backslash \mathrm{C}, 1.318870168$ 8,-1.1675253736,1.361834487\C,1.3188701688,1.1675253736,-1.361834487\C ,-1.3188701688,1.1675253736,1.361834487\C,-2.2147482435,-0.0642037626, $1.6417299611 \backslash C, 2.2147482435,-0.0642037626,-1.6417299611 \backslash C, 2.2147482435$ , 0.0642037626,1.6417299611\C,-2.2147482435,0.0642037626,-1.6417299611\} C, -0.0426841094,-0.7891397054,-2.2146315759\C,-0.0426841094, 0.78913970 54,2.2146315759\C,0.0426841094,0.7891397054,-2.2146315759\C, 0.04268410 94,-0.7891397054,2.2146315759\H,-1.6830509306,-2.2098972168,1.90834035 $12 \backslash \mathrm{H}, 1.6830509306,-2.2098972168,-1.9083403512 \backslash \mathrm{H}, 1.6830509306,2.2098972$ 168,1.9083403512\H,-1.6830509306,2.2098972168,-1.9083403512\H,1.787244 9159,-2.1038481126,1.7015461655\H,1.7872449159,2.1038481126,-1.7015461 655\H,-1.7872449159,2.1038481126,1.7015461655\H,-1.7872449159,-2.10384 $81126,-1.7015461655 \backslash \mathrm{H},-3.1008714395,-0.1381648542,1.0040458589 \backslash \mathrm{H}, 3.100$
$8714395,-0.1381648542,-1.0040458589 \backslash H, 3.1008714395,0.1381648542,1.0040$ $458589 \backslash \mathrm{H},-3.1008714395,0.1381648542,-1.0040458589 \backslash \mathrm{H},-2.570126593,0.000$ $877122,2.6794652012 \backslash \mathrm{H}, 2.570126593,0.000877122,-2.6794652012 \backslash \mathrm{H}, 2.570126$ $593,-0.000877122,2.6794652012 \backslash \mathrm{H},-2.570126593,-0.000877122,-2.679465201$ $2 \backslash H,-0.1326757288,-1.1928701594,-3.2375307368 \backslash \mathrm{H},-0.1326757288,1.192870$ 1594, 3. $2375307368 \backslash \mathrm{H}, 0.1326757288,1.1928701594,-3.2375307368 \backslash \mathrm{H}, 0.132675$ 7288,-1.1928701594, 3.2375307368<br>Version=Fujitsu-VP-Unix-G94RevE. $2 \backslash$ Sta $t e=1-A \backslash H F=-806.5791782 \backslash M P 2=-809.4191608 \backslash R M S D=2.930 e-09 \backslash R M S F=1.940 e-04 \backslash$ Dipole=0.,0., 0. \PG=D02 [O(C1), X(C20H20)] <br>@

## 4-43 spiro[2.2]bioctaplane $\boldsymbol{D}_{\mathbf{2 h}}$

$1 \backslash 1 \backslash G I N C-V P P 10 \backslash F O p t \backslash R M P 2-F C \backslash G e n \backslash C 21 H 20 \backslash R A S M U S S E N \backslash 22-S e p-1998 \backslash 0 \backslash \backslash \# P$ MP2 /GEN 5D OPT=READFC SCF=DIRECT NAME=RASMUSSEN GEOM= (CHECK,NODISTANCE,NO ANGLE, NODIHEDRAL) GUESS=CHECK MAXDISK=1900000000<br>Spiro[2.2]bioctaplan e 5D D2h <br>0,1\C,0.,0.,0. \C, -0.7482117958,-1.2782593977,0. \C, 0.74821179 $58,-1.2782593977,0 . \backslash C, 0.7482117958,1.2782593977,0 . \backslash C,-0.7482117958,1.2$ $782593977,0 . \backslash C,-1.2867627673,-1.2246455558,1.4286796441 \backslash C, 1.2867627673$ , - $1.2246455558,-1.4286796441 \backslash C, 1.2867627673,1.2246455558,1.4286796441 \backslash$ C, -1. $2867627673,1.2246455558,-1.4286796441 \backslash \mathrm{C},-1.2867627673,-1.22464555$ $58,-1.4286796441 \backslash C, 1.2867627673,-1.2246455558,1.4286796441 \backslash C, 1.2867627$ $673,1.2246455558$, $-1.4286796441 \backslash C,-1.2867627673,1.2246455558,1.42867964$ $41 \backslash \mathrm{C},-2.2111476938,0 ., 1.6361186933 \backslash \mathrm{C},-2.2111476938,0 .,-1.6361186933 \backslash \mathrm{C}$, $2.2111476938,0 ., 1.6361186933 \backslash C, 2.2111476938,0 .,-1.6361186933 \backslash C, 0 .,-0.7$ $884217411,2.2128388779 \backslash C, 0 .,-0.7884217411,-2.2128388779 \backslash C, 0 ., 0.7884217$ $411,2.2128388779 \backslash \mathrm{C}, 0.0 .7884217411,-2.2128388779 \backslash \mathrm{H},-1.7410961002,-2.15$ $71337176,1.8046994797 \backslash H, 1.7410961002,-2.1571337176,-1.8046994797 \backslash H, 1.7$ $410961002,2.1571337176,1.8046994797 \backslash \mathrm{H},-1.7410961002,2.1571337176,-1.80$ $46994797 \backslash \mathrm{H}, 1.7410961002,-2.1571337176,1.8046994797 \backslash \mathrm{H}, 1.7410961002,2.15$ $71337176,-1.8046994797 \backslash \mathrm{H},-1.7410961002,2.1571337176,1.8046994797 \backslash \mathrm{H},-1$. $7410961002,-2.1571337176,-1.8046994797 \backslash \mathrm{H},-2.5585567549,0 ., 2.6781927471$ $\backslash \mathrm{H},-2.5585567549,0 .,-2.6781927471 \backslash \mathrm{H}, 2.5585567549,0 ., 2.6781927471 \backslash \mathrm{H}, 2.5$ $585567549,0 .,-2.6781927471 \backslash \mathrm{H},-3.1031456548,0 ., 1.0026274038 \backslash \mathrm{H},-3.103145$ $6548,0 .,-1.0026274038 \backslash H, 3.1031456548,0 ., 1.0026274038 \backslash \mathrm{H}, 3.1031456548,0$. , - $1.0026274038 \backslash \mathrm{H}, 0 .,-1.2065603949,3.2372717655 \backslash \mathrm{H}, 0 .,-1.2065603949$, -3.2 $372717655 \backslash \mathrm{H}, 0 ., 1.2065603949,3.2372717655 \backslash \mathrm{H}, 0 ., 1.2065603949$, -3.23727176 $55 \backslash \backslash V e r s i o n=F u j i t s u-V P-U n i x-G 94 R e v E .2 \backslash$ State=1-AG\HF=-806.5651503\MP2=$809.4122348 \backslash \mathrm{RMSD}=3.485 \mathrm{e}-09 \backslash \mathrm{RMSF}=2.316 \mathrm{e}-04 \backslash \mathrm{Dipole=0.,0.,0}. \mathrm{\backslash PG=D02H} \mathrm{\quad[O(C}$ 1) ,SG(C4) ,SG' (C4H4) ,SG" (C4H8) , X (C8H8) ] <br>@

## 4-28 spiro[2.2]octaplane $\boldsymbol{D}_{\mathbf{2}}$

$1 \backslash 1 \backslash A N U-P C \backslash F O p t \backslash R M P 2-F C \backslash G e n \backslash C 21 H 24 \backslash R A S M U S S E N \backslash 10-J u l-1996 \backslash 0 \backslash \ \# P R M P 2 / G$ EN 5D FOPT=(READFC) IOP (1/19=9) IOP (1/8=25) NAME=RASMUSSEN MAXDISK=120 0000000 OPTCYC=2 GEOM=(CHECK,NODISTANCE,NOANGLE,NODIHEDRAL) SCF=DIRECT <br>Spiro[2.2]octaplane D2<br>0,1\C,0.,0.,0.\C,1.2697414256,0.0804151012,$0.7463344451 \backslash C, 1.2697414256,-0.0804151012,0.7463344451 \backslash C,-1.2697414256$ , 0.0804151012,0.7463344451\C,-1.2697414256,-0.0804151012,-0.7463344451 \C,1.2711004887,-1.3564055647,-1.3309755408\C,1.2711004887,1.356405564 7,1.3309755408\C,-1.2711004887,-1.3564055647,1.3309755408\C,-1.2711004 887,1.3564055647,-1.3309755408\C,1.3781554636,1.4867570761,-1.25281449 $66 \backslash C, 1.3781554636,-1.4867570761,1.2528144966 \backslash C,-1.3781554636,1.4867570$ $761,1.2528144966 \backslash \mathrm{C},-1.3781554636,-1.4867570761,-1.2528144966 \backslash \mathrm{C},-0.0583$ 591594,-1.7842122306,-2.0219562455\C,-0.0583591594,1.7842122306,2.0219
$562455 \backslash \mathrm{C}, 0.0583591594,-1.7842122306,2.0219562455 \backslash \mathrm{C}, 0.0583591594,1.7842$ $122306,-2.0219562455 \backslash C, 1.6337620142,2.2429787146,0.0891347004 \backslash C,-1.633$ $7620142,-2.2429787146,0.0891347004 \backslash C,-1.6337620142,2.2429787146,-0.089$ $1347004 \backslash \mathrm{C}, 1.6337620142,-2.2429787146,-0.0891347004 \backslash \mathrm{H}, 2.0668354443,-1.4$ $624803146,-2.0882635839 \backslash \mathrm{H}, 2.0668354443,1.4624803146,2.0882635839 \backslash \mathrm{H},-2$. $0668354443,-1.4624803146,2.0882635839 \backslash H,-2.0668354443,1.4624803146,-2$. $0882635839 \backslash \mathrm{H}, 2.2188042505,-1.6759290727,1.9453868386 \backslash \mathrm{H},-2.2188042505,1$ $.6759290727,1.9453868386 \backslash \mathrm{H},-2.2188042505,-1.6759290727,-1.9453868386 \backslash \mathrm{H}$ , 2. $2188042505,1.6759290727,-1.9453868386 \backslash \mathrm{H}, 0.0072601739,-2.8589513163$, $-2.2474780792 \backslash \mathrm{H},-0.1238897769,-1.2751669928,-2.9963785083 \backslash \mathrm{H}, 0.00726017$ $39,2.8589513163,2.2474780792 \backslash H,-0.1238897769,1.2751669928,2.9963785083$ $\backslash \mathrm{H},-0.0072601739,-2.8589513163,2.2474780792 \backslash \mathrm{H}, 0.1238897769,-1.27516699$ $28,2.9963785083 \backslash \mathrm{H},-0.0072601739,2.8589513163,-2.2474780792 \backslash \mathrm{H}, 0.1238897$ $769,1.2751669928,-2.9963785083 \backslash \mathrm{H}, 2.7075629727,2.4685452838,0.132667408$ $8 \backslash H, 1.1134908769,3.2086651266,0.1260059364 \backslash \mathrm{H},-2.7075629727,-2.46854528$ $38,0.1326674088 \backslash \mathrm{H},-1.1134908769,-3.2086651266,0.1260059364 \backslash \mathrm{H},-2.707562$ $9727,2.4685452838,-0.1326674088 \backslash \mathrm{H},-1.1134908769,3.2086651266,-0.126005$ $9364 \backslash \mathrm{H}, 2.7075629727,-2.4685452838,-0.1326674088 \backslash \mathrm{H}, 1.1134908769,-3.2086$ 651266,-0.1260059364<br>Version=SGI-G94RevD. $2 \backslash$ State=1-A\HF=-808.9456238\} MP2 $=-811.7838705 \backslash \mathrm{RMSD}=1.600 \mathrm{e}-09 \backslash \mathrm{RMSF}=1.245 \mathrm{e}-04 \backslash \mathrm{Dipole=0.,0.,0}. \mathrm{\ PG=D02}$ [ $\mathrm{O}(\mathrm{C} 1), \mathrm{X}(\mathrm{C} 20 \mathrm{H} 24)] \backslash \backslash @$

## 4-28 spiro[2.2]octaplane $\quad \boldsymbol{D}_{\mathbf{2 h}}$

$1 \backslash 1 \backslash$ ANU-PC $\backslash$ FOpt $\backslash$ RMP2-FC $\backslash G e n \backslash C 21 H 24 \backslash R A S M U S S E N \backslash 05-J u l-1996 \backslash 0 \backslash \ \# P R M P 2 / G$ EN 5D FOPT=(READFC) SCF=(DIRECT) IOP (1/19=9) GUESS=CHECK NAME=RASMUSSE N GEOM=(CHECK,NODISTANCE,NOANGLE,NODIHEDRAL) IOP (1/8=5) OPTCYC=3<br>Spir o[2.2]octaplane D2h <br>0,1\C,0.,0.,0.\C,0.,0.7445751725,1.2711808434\C,0 ., -0.7445751725,1.2711808434\C,0.,-0.7445751725,-1.2711808434\C,0.,0.7 $445751725,-1.2711808434 \backslash \mathrm{C}, 1.4192105164,1.2915739332,1.3240829488 \backslash \mathrm{C},-1$. $4192105164,-1.2915739332,1.3240829488 \backslash C, 1.4192105164,-1.2915739332,-1$. $3240829488 \backslash \mathrm{C},-1.4192105164,1.2915739332,-1.3240829488 \backslash \mathrm{C},-1.4192105164$, $1.2915739332,1.3240829488 \backslash C, 1.4192105164,-1.2915739332,1.3240829488 \backslash C$, $-1.4192105164,-1.2915739332,-1.3240829488 \backslash C, 1.4192105164,1.2915739332$, $-1.3240829488 \backslash C, 1.7790174491,2.0244410159,0 . \backslash C,-1.7790174491,2.0244410$ 159,0.\C,1.7790174491,-2.0244410159,0.\C,-1.7790174491,-2.0244410159,0 . \C, 2.2438985685,0.,1.628397999\C,-2.2438985685,0.,1.628397999\C, 2.243 8985685,0.,-1.628397999\C,-2.2438985685,0.,-1.628397999\H,1.5692984298 , 2.0189489435,2.1436599556\H,-1.5692984298,-2.0189489435,2.1436599556\} H,1.5692984298,-2.0189489435,-2.1436599556\H,-1.5692984298,2.018948943 $5,-2.1436599556 \backslash \mathrm{H}, 1.5692984298,-2.0189489435,2.1436599556 \backslash \mathrm{H},-1.5692984$ 298,-2.0189489435,-2.1436599556 \H, 1.5692984298, 2.0189489435,-2.1436599 $556 \backslash \mathrm{H},-1.5692984298,2.0189489435,2.1436599556 \backslash \mathrm{H}, 2.8575664232,2.2411401$ $443,0 . \backslash \mathrm{H}, 1.2749373378,3.0039209586,0 . \backslash \mathrm{H},-2.8575664232,2.2411401443,0 . \backslash$ H, $-1.2749373378,3.0039209586,0 . \backslash \mathrm{H}, 2.8575664232,-2.2411401443,0 . \backslash \mathrm{H}, 1.27$ $49373378,-3.0039209586,0 . \backslash H,-2.8575664232,-2.2411401443,0 . \backslash H,-1.274937$ $3378,-3.0039209586,0 . \backslash \mathrm{H}, 3.2064566031,0 ., 1.100074062 \backslash \mathrm{H}, 2.4823415107,0 .$, $2.7009930119 \backslash \mathrm{H},-3.2064566031,0 ., 1.100074062 \backslash \mathrm{H},-2.4823415107,0 ., 2.70099$ $30119 \backslash$ Н, $3.2064566031,0 .,-1.100074062 \backslash \mathrm{H}, 2.4823415107,0 .,-2.7009930119 \backslash \mathrm{H}$ ,-3.2064566031,0.,-1.100074062\H,-2.4823415107,0.,-2.7009930119<br>Versi on=SGI-G94RevD. $2 \backslash$ State $=1-\mathrm{AG} \backslash \mathrm{HF}=-808.935232 \backslash \mathrm{MP} 2=-811.7801327 \backslash$ RMSD $=2.331$ e-09 " (C4H8) , X (C8H8) ] <br>@

## 4-44 spiro[2.2]binonaplane $\boldsymbol{D}_{\mathbf{2}}$

$1 \backslash 1 \backslash G I N C-V P P 08 \backslash F O p t \backslash R M P 2-F C \backslash G e n \backslash C 23 H 24 \backslash R A S M U S S E N \backslash 24-S e p-1998 \backslash 0 \backslash \backslash \# P$ MP2 /GEN 5D OPT=READFC SCF=DIRECT NAME=RASMUSSEN GEOM= (CHECK,NODISTANCE,NO ANGLE, NODIHEDRAL) GUESS=CHECK MAXDISK=1900000000<br>Spiro[2.2]binonaplan e 5D D2 <br>0,1\C,0.,0.,0.\C, -0.743715378, -1.2773338828, 0.0701967799\C, 0. $743715378,-1.2773338828,-0.0701967799 \backslash \mathrm{C}, 0.743715378,1.2773338828,0.070$ $1967799 \backslash \mathrm{C},-0.743715378,1.2773338828,-0.0701967799 \backslash \mathrm{C},-1.2785823941,-1.3$ $326470023,1.4677459745 \backslash C, 1.2785823941,-1.3326470023,-1.4677459745 \backslash C, 1$. $2785823941,1.3326470023,1.4677459745 \backslash C,-1.2785823941,1.3326470023,-1.4$ $677459745 \backslash C,-1.3256697563,-1.2316391108,-1.3625492693 \backslash C, 1.3256697563$, $1.2316391108,1.3625492693 \backslash C, 1.3256697563,1.2316391108,-1.3625492693 \backslash C$, $-1.3256697563,1.2316391108,1.3625492693 \backslash \mathrm{C},-2.1498913036,-0.0556914298$, $1.6470539711 \backslash C, 2.1498913036,-0.0556914298,-1.6470539711 \backslash C, 2.1498913036$ , 0.0556914298,1.6470539711 \C, -2.1498913036, 0.0556914298, -1.6470539711 \} $C,-0.050644317,-1.2533551598,-2.3113814188 \backslash C,-0.050644317,1.2533551598$ , 2. $3113814188 \backslash C, 0.050644317,1.2533551598,-2.3113814188 \backslash C, 0.050644317,-$ $1.2533551598,2.3113814188 \backslash \mathrm{C}, 0 ., 0 ., 3.1981049076 \backslash \mathrm{C}, 0 ., 0 .,-3.1981049076 \backslash \mathrm{H}$ , - $1.869907458,-2.2278946328,1.7322890594 \backslash \mathrm{H}, 1.869907458,-2.2278946328$, $1.7322890594 \backslash \mathrm{H}, 1.869907458,2.2278946328,1.7322890594 \backslash \mathrm{H},-1.869907458,2$. $2278946328,-1.7322890594 \backslash \mathrm{H}, 1.9623586395,-2.1103921534,1.5625978898 \backslash \mathrm{H}, 1$ $.9623586395,2.1103921534,-1.5625978898 \backslash \mathrm{H},-1.9623586395,2.1103921534,1$. $5625978898 \backslash \mathrm{H},-1.9623586395,-2.1103921534,-1.5625978898 \backslash \mathrm{H},-3.0264132756$ , - 0. $1099159989,0.992049942 \backslash \mathrm{H}, 3.0264132756,-0.1099159989,-0.992049942 \backslash \mathrm{H}$ , 3.0264132756, 0.1099159989, 0.992049942 \H, -3.0264132756, 0.1099159989, -0 $.992049942 \backslash \mathrm{H},-2.5512977797,-0.0063722734,2.6670358678 \backslash \mathrm{H}, 2.5512977797$, -$0.0063722734,-2.6670358678 \backslash \mathrm{H}, 2.5512977797,0.0063722734,2.6670358678 \backslash \mathrm{H}$, $-2.5512977797,0.0063722734,-2.6670358678 \backslash \mathrm{H},-0.1102006462,-2.1436715653$ , - $2.9539778303 \backslash \mathrm{H},-0.1102006462,2.1436715653,2.9539778303 \backslash \mathrm{H}, 0.110200646$ $2,2.1436715653,-2.9539778303 \backslash \mathrm{H}, 0.1102006462,-2.1436715653,2.9539778303$ $\backslash \mathrm{H},-0.8701162549,-0.0484312695,3.8639148244 \backslash \mathrm{H}, 0.8701162549,0.048431269$ $5,3.8639148244 \backslash \mathrm{H},-0.8701162549,0.0484312695,-3.8639148244 \backslash \mathrm{H}, 0.87011625$ $49,-0.0484312695,-3.8639148244 \backslash \backslash V e r s i o n=F u j i t s u-V P-U n i x-G 94 R e v E .2 \backslash$ Stat $\mathrm{e}=1-\mathrm{A} \backslash \mathrm{HF}=-884.6738629 \backslash \mathrm{MP} 2=-887.7745627 \backslash \mathrm{RMSD}=9.561 \mathrm{e}-09 \backslash \mathrm{RMSF}=5.305 \mathrm{e}-05 \backslash \mathrm{D}$ ipole=0.,0.,0.\PG=D02 [O(C1), C2" (C1.C1), X (C2OH24)] <br>@

## 4-44 spiro[2.2]binonaplane $\quad \boldsymbol{D}_{\mathbf{2 h}}$

$1 \backslash 1 \backslash G I N C-V P P 09 \backslash F O p t \backslash R M P 2-F C \backslash G e n \backslash C 23 H 24 \backslash R A S M U S S E N \backslash 24-S e p-1998 \backslash 0 \backslash \backslash \# P$ MP2 /GEN 5D OPT=READFC SCF=DIRECT NAME=RASMUSSEN GEOM= (CHECK,NODISTANCE,NO ANGLE, NODIHEDRAL) GUESS=CHECK MAXDISK=1900000000<br>Spiro[2.2]binonaplan e 5D D2h <br>0,1\C,0.,0.,0.\C,0., 0.7420507006,1.2813988012\C,0., -0.742050 $7006,1.2813988012 \backslash C, 0 .,-0.7420507006,-1.2813988012 \backslash C, 0 ., 0.7420507006$, $1.2813988012 \backslash C, 1.4129171803,1.3010032979,1.2827619913 \backslash C,-1.4129171803$, $-1.3010032979,1.2827619913 \backslash C, 1.4129171803,-1.3010032979,-1.2827619913 \backslash$ C, -1.4129171803, 1.3010032979, -1. $2827619913 \backslash \mathrm{C},-1.4129171803,1.301003297$ $9,1.2827619913 \backslash C, 1.4129171803,-1.3010032979,1.2827619913 \backslash C,-1.41291718$ $03,-1.3010032979,-1.2827619913 \backslash C, 1.4129171803,1.3010032979,-1.28276199$ $13 \backslash C, 1.6425054526,2.1490883646,0 . \backslash C,-1.6425054526,2.1490883646,0 . \backslash C, 1$. $6425054526,-2.1490883646,0 . \backslash C,-1.6425054526,-2.1490883646,0 . \backslash C, 2.30924$ $42341,0 ., 1.2534405673 \backslash \mathrm{C},-2.3092442341,0.1 .2534405673 \backslash \mathrm{C}, 2.3092442341,0$ ., -1. $2534405673 \backslash \mathrm{C},-2.3092442341,0 .,-1.2534405673 \backslash \mathrm{C}, 3.1973603752,0$. 0. C, $-3.1973603752,0 ., 0 . \backslash H, 1.6472799958,1.9203231585,2.1681205218 \backslash \mathrm{H},-1.64$ $72799958,-1.9203231585,2.1681205218 \backslash \mathrm{H}, 1.6472799958,-1.9203231585,-2.16$
$81205218 \backslash \mathrm{H},-1.6472799958,1.9203231585,-2.1681205218 \backslash \mathrm{H}, 1.6472799958,-1$. $9203231585,2.1681205218 \backslash \mathrm{H},-1.6472799958,-1.9203231585,-2.1681205218 \backslash \mathrm{H}$, $1.6472799958,1.9203231585,-2.1681205218 \backslash \mathrm{H},-1.6472799958,1.9203231585,2$ $.1681205218 \backslash \mathrm{H}, 2.6653737591,2.5453401639,0 . \backslash \mathrm{H},-2.6653737591,2.545340163$ $9,0 . \backslash H, 2.6653737591,-2.5453401639,0 . \backslash H,-2.6653737591,-2.5453401639,0 . \$ $\mathrm{H}, 0.9908972627,3.0297400895,0 . \backslash \mathrm{H},-0.9908972627,3.0297400895,0 . \backslash \mathrm{H}, 0.990$ 8972627,-3.0297400895, 0. \H, -0.9908972627,-3.0297400895, 0. \H, 2. 95330050 81, 0., 2. $1457613231 \backslash \mathrm{H},-2.9533005081,0 ., 2.1457613231 \backslash \mathrm{H}, 2.9533005081,0 .,-$ $2.1457613231 \backslash \mathrm{H},-2.9533005081,0 .,-2.1457613231 \backslash \mathrm{H}, 3.8638721118,-0.871091$ 3119, 0. \H, 3.8638721118, 0.8710913119, 0. \H, -3.8638721118, -0.8710913119,0 $. \backslash H,-3.8638721118,0.8710913119,0 . \backslash \backslash V e r s i o n=F u j i t s u-V P-U n i x-G 94 R e v E .2 \backslash S$ tate=1-AG $\backslash \mathrm{HF}=-884.6658922 \backslash \mathrm{MP} 2=-887.7718614 \backslash \mathrm{RMSD}=7.516 \mathrm{e}-09 \backslash \mathrm{RMSF}=4.661 \mathrm{e}-$ $05 \backslash$ Dipole=0., 0., 0. \PG=D02H [O (C1) , C2 (C1.C1) , SG (C4) , SG' (C4H4) , SG" (C4H12 ) , X(C8H8)] <br>@

## Dimethanospiroalkaplanes

## 4-47 dimethanospiro[2.2]bioctaplane $\quad \boldsymbol{D}_{\mathbf{2}}$

$1 \backslash 1 \backslash G I N C-V P P 08 \backslash F O p t \backslash R M P 2-F C \backslash G e n \backslash C 23 H 20 \backslash R A S M U S S E N \backslash 06-O c t-1998 \backslash 0 \backslash \backslash \# P$ MP2 /GEN 5D OPT=READFC SCF=DIRECT NAME=RASMUSSEN GEOM=(CHECK,NODISTANCE,NO ANGLE,NODIHEDRAL) GUESS=CHECK MAXDISK=1900000000<br>Dimethanospiro[2.2]b ioctaplane D2 5D <br>0,1\C,0.,0.,0.\C,-0.7300236831,-1.3155091044,0.05697 $88089 \backslash C, 0.7300236831,-1.3155091044,-0.0569788089 \backslash C, 0.7300236831,1.3155$ $091044,0.0569788089 \backslash C,-0.7300236831,1.3155091044,-0.0569788089 \backslash C,-1.29$ 17295248,-1.2419758676,1.436159607\C,1.2917295248,-1.2419758676,-1.436 $159607 \backslash C, 1.2917295248,1.2419758676,1.436159607 \backslash C,-1.2917295248,1.24197$ 58676,-1.436159607\C,-1.2936830431,-1.2006176742,-1.3561659499\C,1.293 6830431,-1.2006176742,1.3561659499\C,1.2936830431,1.2006176742,-1.3561 $659499 \backslash C,-1.2936830431,1.2006176742,1.3561659499 \backslash C,-2.250679585,-0.012$ 8530704,1.3277945053\C,2.250679585,-0.0128530704,-1.3277945053\C, 2. 250 679585,0.0128530704,1.3277945053\C,-2.250679585,0.0128530704,-1.327794 $5053 \backslash C,-0.0150522952,-0.7810991014,-2.2017498641 \backslash C,-0.0150522952,0.781$ 0991014,2.2017498641\C,0.0150522952,0.7810991014,-2.2017498641\C, 0.015 0522952,-0.7810991014,2.2017498641\C,-3.0761314824,0.,0.\C,3.076131482 $4,0 ., 0 . \backslash H,-1.7786314821,-2.1393886686,1.860007725 \backslash \mathrm{H}, 1.7786314821,-2.13$ 93886686,-1.860007725\H,1.7786314821,2.1393886686,1.860007725\H,-1.778 6314821,2.1393886686,-1.860007725\H,1.7782172461,-2.1192565655,1.72577 $85054 \backslash \mathrm{H}, 1.7782172461,2.1192565655,-1.7257785054 \backslash \mathrm{H},-1.7782172461,2.1192$ 565655,1.7257785054 \H,-1.7782172461,-2.1192565655,-1.7257785054 \H,-2.9 $469407384,0.0121748228,2.1783556497 \backslash \mathrm{H}, 2.9469407384,0.0121748228,-2.178$ 3556497\H,2.9469407384,-0.0121748228,2.1783556497\H,-2.9469407384,-0.0 121748228,-2.1783556497\H,-0.0645324934,-1.2027499148,-3.2226238278\H, $-0.0645324934,1.2027499148,3.2226238278 \backslash \mathrm{H}, 0.0645324934,1.2027499148,-3$ $.2226238278 \backslash$ Н, $0.0645324934,-1.2027499148,3.2226238278 \backslash \mathrm{H},-3.7371162733$, $0.8793168236,0.0166427067 \backslash \mathrm{H},-3.7371162733,-0.8793168236,-0.0166427067 \backslash$ H,3.7371162733,-0.8793168236,0.0166427067\H,3.7371162733,0.8793168236, $-0.0166427067 \backslash \backslash$ Version=Fujitsu-VP-Unix-G94RevE. $2 \backslash$ State=1-A $\backslash H F=-882.301$ $1745 \backslash$ MP2 $=-885.4068207 \backslash$ RMSD $=4.992 \mathrm{e}-09 \backslash \mathrm{RMSF}=1.572 \mathrm{e}-04 \backslash \mathrm{Dipole}=0 ., 0 ., 0 . \backslash \mathrm{PG}$ =D02 [O(C1), C2" (C1.C1), X(C20H2O)]<br>@

## 4-47 dimethanospiro[2.2]bioctaplane $\quad \boldsymbol{D}_{\mathbf{2 h}}$

$1 \backslash 1 \backslash G I N C-V P P 09 \backslash F O p t \backslash R M P 2-F C \backslash G e n \backslash C 23 H 20 \backslash R A S M U S S E N \backslash 05-O c t-1998 \backslash 0 \backslash \backslash \# P$ MP2
/GEN 5D OPT=READFC SCF=DIRECT NAME=RASMUSSEN GEOM=(CHECK,NODISTANCE,NO ANGLE, NODIHEDRAL) GUESS=CHECK MAXDISK=1900000000<br>Dimethanospiro[2.2]b ioctaplane D2h 5D<br>0,1\C,0.,0.,0.\C,-0.7277377137,-1.318699668,0.\C,0. 7277377137,-1.318699668,0.\C,0.7277377137,1.318699668,0. \C, -0.72773771 $37,1.318699668,0 . \backslash C,-1.290072493,-1.2220195953,1.3950359058 \backslash \mathrm{C}, 1.290072$ 493,-1.2220195953,-1.3950359058\C,1.290072493,1.2220195953,1.395035905 $8 \backslash C,-1.290072493,1.2220195953,-1.3950359058 \backslash C,-1.290072493,-1.22201959$ 53,-1.3950359058\C,1.290072493,-1.2220195953,1.3950359058\C,1.29007249 3,1.2220195953,-1.3950359058\C,-1.290072493,1.2220195953,1.3950359058\} C, $-2.2478801746,0 ., 1.3259991001 \backslash C,-2.2478801746,0 .,-1.3259991001 \backslash C, 2.2$ $478801746,0 ., 1.3259991001 \backslash C, 2.2478801746,0 .,-1.3259991001 \backslash \mathrm{C}, 0 .,-0.7802$ 046605,2.2010327438\C,0.,-0.7802046605,-2.2010327438\C,0.,0.7802046605 , 2. $2010327438 \backslash \mathrm{C}, 0 ., 0.7802046605,-2.2010327438 \backslash \mathrm{C},-3.0739494442,0 ., 0 . \backslash \mathrm{C}$, $3.0739494442,0.0 . \backslash H,-1.7809487337,-2.1282883215,1.7929973371$ H, 1.7809 487337,-2.1282883215,-1.7929973371\H,1.7809487337,2.1282883215,1.79299 $73371 \backslash \mathrm{H},-1.7809487337,2.1282883215,-1.7929973371 \backslash \mathrm{H}, 1.7809487337,-2.128$ 2883215,1.7929973371 \H,1.7809487337,2.1282883215,-1.7929973371\H,-1.78 09487337,2.1282883215,1.7929973371\H,-1.7809487337,-2.1282883215,-1.79 $29973371 \backslash \mathrm{H},-2.9427226175,0 ., 2.1777295656 \backslash \mathrm{H},-2.9427226175,0 .,-2.1777295$ $656 \backslash \mathrm{H}, 2.9427226175,0.2 .1777295656 \backslash \mathrm{H}, 2.9427226175,0 .,-2.1777295656 \backslash \mathrm{H}, 0$ .,-1.2077190865,3.2227163057\H,0.,-1.2077190865,-3.2227163057\H,0.,1.2 077190865,3.2227163057\H,0.,1.2077190865,-3.2227163057\H,-3.734738666, $0.8795245114,0 . \backslash \mathrm{H},-3.734738666,-0.8795245114,0 . \backslash \mathrm{H}, 3.734738666,-0.87952$ 45114, 0. \H, 3.734738666,0.8795245114,0. <br>Version=Fujitsu-VP-Unix-G94Rev E. $2 \backslash$ State $=1-\mathrm{AG} \backslash \mathrm{HF}=-882.2969199 \backslash \mathrm{MP2} 2=-885.4051496 \backslash \mathrm{RMSD}=9.076 \mathrm{e}-09 \backslash \mathrm{RMSF}=1$. 999e-04\Dipole=0., 0., 0. \PG=D02H [O(C1), C2 (C1.C1), SG(C4H4), SG' (C4H4), SG " (C4H4) , X(C8H8)] <br>@

## 4-29 dimethanospiro[2.2]octaplane $\boldsymbol{D}_{\mathbf{2 h}}$

$1 \backslash 1 \backslash A N U-P C \backslash F O p t \backslash R M P 2-F C \backslash G e n \backslash C 23 H 24 \backslash R A S M U S S E N \backslash 23-M a y-1996 \backslash 0 \backslash \ \# P ~ R M P 2 / G$ EN 5D FOPT IOP(1/19=9) SCF=(DIRECT) NAME=RASMUSSEN MAXDISK=1500000000 GEOM= (NODISTANCE, NOANGLE, NODIHEDRAL) IOP (1/8=1) <br>Dimethanospiro[2.2] oc taplane $D 2 h \backslash \backslash 0,1 \backslash C, 0.0 ., 0 . \backslash C,-0.72225,0 .,-1.319325 \backslash C, 0.72225,0 .,-1.31$ $9325 \backslash C, 0.72225,0 ., 1.319325 \backslash C,-0.72225,0 ., 1.319325 \backslash C,-1.304752,-1.37881$ $1,-1.309498 \backslash C, 1.304752,1.378811,-1.309498 \backslash C, 1.304752,-1.378811,1.30949$ $8 \backslash C,-1.304752,1.378811,1.309498 \backslash C,-1.304752,1.378811,-1.309498 \backslash C, 1.304$ 752,-1.378811,-1.309498\C,1.304752,1.378811,1.309498\C,-1.304752,-1.37 $8811,1.309498 \backslash C,-2.155586,-1.364456,0 . \backslash C,-2.155586,1.364456,0 . \backslash C, 2.155$ $586,-1.364456,0 . \backslash C, 2.155586,1.364456,0 . \backslash C, 0 .,-2.251095,-1.507105 \backslash C, 0 .$, $2.251095,-1.507105 \backslash C, 0 .,-2.251095,1.507105 \backslash C, 0 ., 2.251095,1.507105 \backslash C,-2$ .973545,0., 0. \C, 2.973545,0.,0. \H,-1.998132,-1.572494,-2.151994 \H, 1.998 132,1.572494,-2.151994\H,1.998132,-1.572494,2.151994 \н,-1.998132,1.572 $494,2.151994 \backslash$ Н, 1.998132, -1.572494, -2.151994 \H, 1.998132, 1.572494, 2.1519 $94 \backslash H,-1.998132,-1.572494,2.151994 \backslash \mathrm{H},-1.998132,1.572494,-2.151994 \backslash \mathrm{H},-2$. 883005,-2.191116,0. \H,-2.883005,2.191116, 0. \H, 2.883005,-2.191116,0. \H, $2.883005,2.191116,0 . \backslash \mathrm{H}, 0 .,-3.178994,-0.930633 \backslash \mathrm{H}, 0 .,-2.562334,-2.562596$ $\backslash H, 0 ., 3.178994,-0.930633 \backslash H, 0 ., 2.562334,-2.562596 \backslash H, 0 .,-3.178994,0.9306$ $33 \backslash \mathrm{H}, 0 .,-2.562334,2.562596 \backslash \mathrm{H}, 0 ., 3.178994,0.930633 \backslash \mathrm{H}, 0 ., 2.562334,2.5625$ $96 \backslash \mathrm{H},-3.633519,0.0 .881098 \backslash \mathrm{H},-3.633519,0 .,-0.881098 \backslash \mathrm{H}, 3.633519,0 .,-0.8$ $81098 \backslash \mathrm{H}, 3.633519,0 ., 0.881098 \backslash \backslash$ Version=SGI-G94RevD. $2 \backslash$ State=1-AG $\backslash \mathrm{HF}=-884$ $.5990242 \backslash \mathrm{MP} 2=-887.7193533 \backslash \mathrm{RMSD}=3.314 \mathrm{e}-09 \backslash \mathrm{RMSF}=1.282 \mathrm{e}-04 \backslash \mathrm{Dipole}=0 ., 0 ., 0$ $. \backslash \mathrm{PG}=\mathrm{D} 02 \mathrm{H}$ [O(C1), C2 (C1.C1), SG(C4H8), SG'(C4H4), SG" (C4H4), X(C8H8)] <br>@

## 4-48 dimethanospiro[2.2]binonaplane $\boldsymbol{D}_{\mathbf{2 h}}$

$1 \backslash 1 \backslash G I N C-V P P 08 \backslash F O p t \backslash R M P 2-F C \backslash G e n \backslash C 25 H 24 \backslash R A S M U S S E N \backslash 06-O c t-1998 \backslash 0 \backslash \backslash \# P$ MP2 /GEN 5D OPT=READFC SCF=DIRECT NAME=RASMUSSEN GEOM=(CHECK,NODISTANCE,NO ANGLE,NODIHEDRAL) GUESS=CHECK MAXDISK=1900000000<br>Dimethanospiro[2.2]b inonaplane $D 2 h$ 5D $\backslash \backslash 0,1 \backslash C, 0 ., 0 ., 0 . \backslash C,-0.7234540639,-1.3196189126,0 . \backslash C, 0$ $.7234540639,-1.3196189126,0 . \backslash C, 0.7234540639,1.3196189126,0 . \backslash C,-0.72345$ 40639,1.3196189126,0.\C,-1.3022774891,-1.2825138059,1.3802310184\C,1.3 022774891,-1.2825138059,-1.3802310184\C,1.3022774891,1.2825138059,1.38 $02310184 \backslash \mathrm{C},-1.3022774891,1.2825138059,-1.3802310184 \backslash \mathrm{C},-1.3022774891,-1$ . $2825138059,-1.3802310184 \backslash \mathrm{C}, 1.3022774891,-1.2825138059,1.3802310184 \backslash \mathrm{C}$, $1.3022774891,1.2825138059,-1.3802310184 \backslash \mathrm{C},-1.3022774891,1.2825138059,1$ $.3802310184 \backslash C,-2.1929242611,0 ., 1.3442990025 \backslash C,-2.1929242611,0 .,-1.3442$ $990025 \backslash C, 2.1929242611,0 ., 1.3442990025 \backslash C, 2.1929242611,0 .,-1.3442990025 \backslash$ $C, 0 .,-1.2393181272,2.2859733017 \backslash C, 0 .,-1.2393181272,-2.2859733017 \backslash C, 0 .$, $1.2393181272,2.2859733017 \backslash C, 0 ., 1.2393181272,-2.2859733017 \backslash C,-3.0133357$ 572,0.,0.\C,3.0133357572,0.,0.\C,0.,0.,3.175018257\C,0.,0.,-3.17501825 $7 \backslash \mathrm{H},-1.9334369211,-2.1539964911,1.640211109 \backslash \mathrm{H}, 1.9334369211,-2.15399649$ 11,-1.640211109\H,1.9334369211,2.1539964911,1.640211109\Н,-1.933436921 $1,2.1539964911,-1.640211109 \backslash \mathrm{H}, 1.9334369211,-2.1539964911,1.640211109 \backslash \mathrm{H}$ ,1.9334369211,2.1539964911,-1.640211109\H,-1.9334369211,2.1539964911,1 $.640211109 \backslash \mathrm{H},-1.9334369211,-2.1539964911,-1.640211109 \backslash \mathrm{H},-2.9098263806$, $0 ., 2.1791134731 \backslash H,-2.9098263806,0 .,-2.1791134731 \backslash H, 2.9098263806,0 ., 2.1$ $791134731 \backslash \mathrm{H}, 2.9098263806,0 .,-2.1791134731 \backslash \mathrm{H}, 0 .,-2.1376837077,2.9225103$ $635 \backslash \mathrm{H}, 0 .,-2.1376837077,-2.9225103635 \backslash \mathrm{H}, 0.2 .1376837077,2.9225103635 \backslash \mathrm{H}$, $0 ., 2.1376837077,-2.9225103635 \backslash \mathrm{H},-3.6727117196,0.8812009834,0 . \backslash \mathrm{H},-3.672$ 7117196,-0.8812009834,0.\H,3.6727117196,-0.8812009834,0.\H,3.672711719 $6,0.8812009834,0 . \backslash H, 0.8818726966,0 ., 3.8322019371 \backslash H,-0.8818726966,0 ., 3$. $8322019371 \backslash \mathrm{H}, 0.8818726966,0 .,-3.8322019371 \backslash \mathrm{H},-0.8818726966,0 .,-3.83220$ $19371 \backslash$ VVersion=Fujitsu-VP-Unix-G94RevE. $2 \backslash$ State=1-AG $\backslash H F=-960.3859279 \backslash \mathrm{MP}$ $2=-963.7563016 \backslash \mathrm{RMSD}=5.368 \mathrm{e}-09 \backslash \mathrm{RMSF}=1.515 \mathrm{e}-04 \backslash \mathrm{Dipole}=0 ., 0 ., 0 . \backslash \mathrm{PG}=\mathrm{D} 02 \mathrm{H} \quad[$ O(C1), C2 (C1.C1), C2' (C1.C1), SG(C4H4), SG' (C4H4) ,SG" (C4H8) , X(C8H8)] <br>@

## C.2.3.2 Other Neutral Species

Table C-25. Guassian archive files for the B3-LYP/6-31G(d) optimized neutral species in Chapter 4 other than the alkaplanes.

## Small Molecules

## ${ }^{3} \mathrm{CH}_{2} \quad C_{2 v}$

$1 \backslash 1 \backslash$ GINC-RSCQC2 \FOpt \UB3LYP\6-31G(d) \C1H2 (3) \RASMUSSEN $\backslash 28-M a r-2000 \backslash 0 \backslash \backslash$ \#P B3LYP/6-31G(D) 5D OPT=(TIGHT) FREQ=NORAMAN NAME=RASMUSSEN MAXDISK=5 $24288000 \backslash$ \methylene C2v singlet $\backslash \backslash 0,3 \backslash \mathrm{H},-0.3911394152,0 .,-0.9679965146 \backslash$ C, $-0.0823284961,0.0 .0690489376 \backslash \mathrm{H}, 0.8851103917,0 ., 0.5537028888 \backslash$ VVersio $\mathrm{n}=$ IBM-RS6000-G98RevA. $6 \backslash$ State $=3-\mathrm{B} 1 \backslash \mathrm{HF}=-39.1491202 \backslash \mathrm{~S} 2=2.005228 \backslash \mathrm{~S} 2-1=0 . \backslash \mathrm{S}$ $2 \mathrm{~A}=2.000007 \backslash \mathrm{RMSD}=9.702 \mathrm{e}-09 \backslash \mathrm{RMSF}=5.926 \mathrm{e}-08 \backslash \mathrm{Dipole}=0.1942974,0 .,-0.16295$ $73 \backslash \mathrm{PG}=\mathrm{CO} 2 \mathrm{~V}$ [C2 (C1), SGV (H2)] <br>@

## $\mathrm{CH}_{4} \quad \boldsymbol{T}_{\mathrm{d}}$

$1 \backslash 1 \backslash G I N C-R S C Q C 2 \backslash F O p t \backslash R B 3 L Y P \backslash 6-31 G(d) \backslash C 1 H 4 \backslash R A S M U S S E N \backslash 04-J u l-1999 \backslash 0 \backslash \ \# P$ B3LYP/6-31G(D) 5D OPT FREQ=NORAMAN NAME=RASMUSSEN MAXDISK=262144000<br>M
ethane Td singlet $\backslash \backslash 0,1 \backslash C, 0 ., 0 ., 0 . \backslash H,-0.0000000002,0.0000000001,1.09346$ $18907 \backslash \mathrm{H}, 1.0309257573,0 .,-0.3644872967 \backslash \mathrm{H},-0.5154628786,0.8928078951,-0$. $3644872971 \backslash \mathrm{H},-0.5154628785,-0.8928078952,-0.3644872969 \backslash$ VVersion=IBM-RS 6000-G98RevA. $6 \backslash$ State $=1-\mathrm{A} \backslash \backslash \mathrm{HF}=-40.5176632 \backslash \mathrm{RMSD}=6.889 \mathrm{e}-10 \backslash \mathrm{RMSF}=3.305 \mathrm{e}-05$ $\backslash$ Dipole=0.,0.,0.\PG=TD [O(C1),4C3(H1)]<br>@

## $\mathrm{NH}_{3} \quad \boldsymbol{C}_{3 \mathrm{v}}$

$1 \backslash 1 \backslash G I N C-P C \backslash F O p t \backslash R B 3 L Y P \backslash 6-31 G(d) \backslash H 3 N 1 \backslash R A S M U S S E N \backslash 04-J u l-1999 \backslash 0 \backslash \ \# P$ B3LY P/6-31G(D) 5D OPT FREQ=NORAMAN NAME=RASMUSSEN MAXDISK=2097152000<br>ammo nia $\mathrm{C} 3 \mathrm{v} \backslash \backslash 0,1 \backslash \mathrm{H}, 0.0 .2768182775,0.9392671756 \backslash \mathrm{H}, 0.8134292351,0.276818277$ 5,-0.4696335878\H,-0.8134292351,0.2768182775,-0.4696335878\N, 0.,-0.118 6364046, 0. <br>Version=SGI-G98RevA.6\State=1-A1 \HF=-56.5466884 \RMSD=1.614 $\mathrm{e}-09 \backslash \mathrm{RMSF}=2.459 \mathrm{e}-05 \backslash \mathrm{Dipole}=0 ., 0.7455619,0 . \backslash \mathrm{PG}=\mathrm{CO} \mathrm{V}$ [C3(N1),3SGV(H1)]<br> @

## $\mathrm{H}_{2} \mathrm{O} \quad \boldsymbol{C}_{2 v}$

$1 \backslash 1 \backslash G I N C-P C \backslash F O p t \backslash R B 3 L Y P \backslash 6-31 G(d) \backslash H 2 O 1 \backslash R A S M U S S E N \backslash 04-J u l-1999 \backslash 0 \backslash \ \# P$ B3LY P/6-31G(D) 5D OPT FREQ=NORAMAN NAME=RASMUSSEN MAXDISK=2097152000<br>wate r $\mathrm{C} 2 \mathrm{v} \backslash \backslash 0,1 \backslash \mathrm{H},-0.1236611385,0 .,-0.8912467159 \backslash 0,-0.0915552862,0.0 .07678$ $74496 \backslash \mathrm{H}, 0.8561034278,0.0 .2769471188 \backslash \backslash$ Version=SGI-G98RevA. $6 \backslash$ State $=1-A 1$ $\backslash \mathrm{HF}=-76.4070235 \backslash \mathrm{RMSD}=3.940 \mathrm{e}-09 \backslash \mathrm{RMSF}=6.779 \mathrm{e}-05 \backslash \mathrm{Dipole}=0.6293277,0 .,-0.5$ $278173 \backslash \mathrm{PG}=\mathrm{CO} 2 \mathrm{~V}$ [C2(O1),SGV(H2)]<br>@

## Unstrained Hydrocarbons

## ethane $\quad D_{2 d}$

$1 \backslash 1 \backslash G I N C-V P P 07 \backslash F O p t \backslash R B 3 L Y P \backslash 6-31 G(d) \backslash C 2 H 6 \backslash R A S M U S S E N \backslash 04-J u l-1999 \backslash 0 \backslash \backslash \# P$ B 3LYP/6-31G(D) 5D OPT FREQ=NORAMAN NAME=RASMUSSEN MAXDISK=131072000<br>Et hane D3d<br>0,1\C,0.,0.,-0.7655664258\C,0.,0.,0.7655664258\H,1.021112508 $1,-0.000000001,-1.1643694313 \backslash \mathrm{H}, 0.5105562541,0.8843093721,1.1643694313$ \H, -0.510556254,0.8843093722,-1.1643694313\H,-1.0211125081,0.000000000 $1,1.1643694313 \backslash \mathrm{H},-0.5105562541,-0.8843093721,-1.1643694313 \backslash \mathrm{H}, 0.5105562$ 54,-0.8843093722,1.1643694313<br>Version=Fujitsu-VP-Unix-G98RevA.6\State $=1-\mathrm{AlG} \backslash \mathrm{HF}=-79.8290131 \backslash \mathrm{RMSD}=4.818 \mathrm{e}-10 \backslash \mathrm{RMSF}=4.469 \mathrm{e}-05 \backslash \mathrm{Dipole}=0 ., 0 ., 0 . \backslash \mathrm{PG}$ =D03D [C3(C1.C1),3SGD (H2)] <br>@

## propane $\quad C_{2 \mathrm{v}}$

1 \1 \GINC-VPP07\FOpt \RB3LYP\6-31G(d) \C3H8\RASMUSSEN $\backslash 04-J u l-1999 \backslash 0 \backslash \backslash \# P$ B 3LYP/6-31G(D) 5D OPT FREQ=NORAMAN NAME=RASMUSSEN MAXDISK=131072000<br>Pr opane $\mathrm{C} 2 \mathrm{v} \backslash \backslash 0,1 \backslash \mathrm{C},-0.4890415316,0 .,-0.3248967091 \backslash \mathrm{C},-0.4900434616,0 ., 1.2$ $077190512 \backslash \mathrm{C}, 0.923395561,0 .,-0.9198198405 \backslash \mathrm{H},-1.0392707211,0.8777572702$, $-0.6904436849 \backslash \mathrm{H},-1.0392707211,-0.8777572702,-0.6904436849 \backslash \mathrm{H}, 0.02470498$ $46,0.884759783,1.6029808433 \backslash \mathrm{H}, 0.0247049846,-0.884759783,1.6029808433 \backslash \mathrm{H}$ ,-1.5099107649,0.,1.6096592802\H,1.4872656798,-0.884759783,-0.59849704 $93 \backslash \mathrm{H}, 1.4872656798,0.884759783,-0.5984970493 \backslash \mathrm{H}, 0.8986474717,0 .,-2.01575$ $45083 \backslash \backslash$ Version=Fujitsu-VP-Unix-G98RevA. $6 \backslash$ State $=1-A 1 \backslash H F=-119.14216 \backslash$ RMSD $=6.306 \mathrm{e}-09 \backslash \mathrm{RMSF}=2.886 \mathrm{e}-05 \backslash \mathrm{Dipole}=-0.0182717,0 .,-0.0121389 \backslash \mathrm{PG}=\mathrm{CO} 2 \mathrm{~V} \quad[\mathrm{C} 2($ C1) , SGV (C2H2) , SGV' (H2) , X (H4) ] <br>@
isobutane $\quad C_{3 v}$
$1 \backslash 1 \backslash G I N C-V P P 06 \backslash F O p t \backslash R B 3 L Y P \backslash 6-31 G(d) \backslash C 4 H 10 \backslash R A S M U S S E N \backslash 04-J u l-1999 \backslash 0 \backslash \ \# P$

B3LYP/6-31G(D) 5D OPT FREQ=NORAMAN NAME=RASMUSSEN MAXDISK=2097152000<br> isobutane C3v <br>0,1\C,0.,0.,0.3735092858\H,0.,0.,1.4741342348\C,1.46217 $08651,0 .,-0.0959984468 \backslash C,-0.7310854326,-1.2662771139,-0.0959984468 \backslash C,-$ $0.7310854326,1.2662771139,-0.0959984468 \backslash \mathrm{H}, 1.9976770071,-0.8863539373,0$ . $2651237172 \backslash \mathrm{H}, 1.9976770071,0.8863539373,0.2651237172 \backslash \mathrm{H}, 1.520545451,0 .$, $-1.1926534036 \backslash \mathrm{H},-1.76644353,-1.2868620681,0.2651237172 \backslash \mathrm{H},-0.2312334771$ , $-2.1732160054,0.2651237172 \backslash \mathrm{H},-0.7602727255,-1.3168309881,-1.192653403$ $6 \backslash \mathrm{H},-0.2312334771,2.1732160054,0.2651237172 \backslash \mathrm{H},-1.76644353,1.2868620681$ , 0.2651237172\H,-0.7602727255,1.3168309881,-1.1926534036<br>Version=Fuji tsu-VP-Unix-G98RevA. $6 \backslash$ State $=1-A 1 \backslash H F=-158.4560426 \backslash$ RMSD $=4.160 e-09 \backslash R M S F=3$ .344e-05\Dipole=0.,0.,0.0335783\PG=C03V [C3 (C1H1), 3SGV(C1H1), X(H6)] <br>@

## neopentane $T_{d}$

$1 \backslash 1 \backslash G I N C-V P P 02 \backslash F O p t \backslash R B 3 L Y P \backslash 6-31 G(d) \backslash C 5 H 12 \backslash R A S M U S S E N \backslash 04-J u l-1999 \backslash 0 \backslash \ \# P$ B3LYP/6-31G(D) 5D OPT FREQ=NORAMAN NAME=RASMUSSEN MAXDISK=2097152000<br> Neopentane 5D Td <br>0,1\C,0.,0.,0.\C,0.,0.,1.5404645355\C,1.4523638923,0 ., -0. $5134881785 \backslash C,-0.7261819461,1.2577840262,-0.5134881785 \backslash C,-0.726181$ $9461,-1.2577840262,-0.5134881785 \backslash$ Н, $0.5115788515,-0.886080563,1.9367416$ $389 \backslash \mathrm{H},-1.0231577031,0 ., 1.9367416389 \backslash \mathrm{H}, 0.5115788515,0.886080563,1.93674$ $16389 \backslash \mathrm{H}, 1.9965038122,0.886080563,-0.1632593796 \backslash \mathrm{H}, 1.4849249607,0 .,-1.61$ $02228797 \backslash \mathrm{H}, 1.9965038122,-0.886080563,-0.1632593796 \backslash \mathrm{H},-0.7424624803,1.2$ 859827386,-1.6102228798\H,-0.2308836288,2.1720633016,-0.1632593796\H, -$1.7656201834,1.2859827386,-0.1632593796 \backslash \mathrm{H},-1.7656201834,-1.2859827387$, $-0.1632593796 \backslash \mathrm{H},-0.2308836288,-2.1720633016,-0.1632593796 \backslash \mathrm{H},-0.7424624$ 803,-1.2859827387,-1.6102228798<br>Version=Fujitsu-VP-Unix-G98RevA.6\HF= $-197.769659 \backslash \mathrm{RMSD}=3.946 \mathrm{e}-10 \backslash \mathrm{RMSF}=6.883 \mathrm{e}-06 \backslash \mathrm{Dipole=0.,0.,0}. \mathrm{\backslash PG=TD} \mathrm{\quad[O(C1)}$ , 4C3 (C1) , 6SGD (H2)] <br>@

## Simple Alicyclic Hydrocarbons

## 4-49 cyclopropane $\boldsymbol{D}_{\mathbf{3 h}}$

$1 \backslash 1 \backslash G I N C-R S C Q C 9 \backslash F O p t \backslash R B 3 L Y P \backslash 6-31 G(d) \backslash C 3 H 6 \backslash R A S M U S S E N \backslash 12-O c t-1999 \backslash 0 \backslash \ \# P$ B3LYP/6-31G(D) 5D OPT FREQ=NORAMAN NAME=RASMUSSEN MAXDISK=917504000<br>C yclopropane D3h 5D <br>0,1\C,0.4355146522,0.0000000001,0.754333505\C,0.43 55146522,0., -0.754333505\C,-0.8710293044,0., 0. \H,-1.4636995, 0.91098603 75,-0.0000000001 \H,-1.4636994999,-0.9109860376,0. \H, 0.73184975,-0.9109 860375,1.2676009506\H, 0.7318497499, 0.9109860377,1.2676009504 \H, 0.73184 $975,0.9109860375,-1.2676009505 \backslash \mathrm{H}, 0.73184975,-0.9109860376,-1.267600950$ $4 \backslash \backslash$ Version=IBM-RS6000-G98RevA. 6\State=1-A1' $\backslash \mathrm{HF}=-117.8931613 \backslash$ RMSD $=1.591$ e-09\RMSF=7.393e-05\Dipole=0.,0.,0.\PG=D03H [3C2(C1),3SGV (H2)] <br>@

4-50 cyclobutane $\boldsymbol{C}_{\mathbf{2 v}}$

$1 \backslash 1 \backslash G I N C-R S C Q C 2 \backslash F O p t \backslash R B 3 L Y P \backslash 6-31 G(d) \backslash C 4 H 8 \backslash R A S M U S S E N \backslash 06-O c t-1999 \backslash 0 \backslash \ \# P$ B3LYP/6-31G* 5D OPT FREQ=NORAMAN NAME=RASMUSSEN MAXDISK=524288000 GEOM $=($ NODISTANCE,NOANGLE,NODIHEDRAL) SYMM=LOOSE <br>cyclobutane C9H14 C2v $\backslash$ \0, $1 \backslash \mathrm{C}, 1.0843616596,0.0 .1246890222 \backslash \mathrm{H}, 1.4229567686,0 ., 1.1667669018 \backslash \mathrm{C},-1.0$ $843616596,0.0 .1246890222 \backslash \mathrm{H}, 0 .,-1.4229174339,-1.1667734356 \backslash \mathrm{H}, 0 ., 1.4229$ 174339,-1.1667734356\C,0.,1.0843567499,-0.1246823855\H,0.,1.9656739837 , $0.5252363824 \backslash \mathrm{H}, 1.9656485967,0 .,-0.5252696688 \backslash \mathrm{H},-1.4229567686,0 ., 1.166$ $7669018 \backslash \mathrm{C}, 0 .,-1.0843567499,-0.1246823855 \backslash \mathrm{H}, 0 .,-1.9656739837,0.52523638$ $24 \backslash H,-1.9656485967,0 .,-0.5252696688 \backslash \backslash$ Version=IBM-RS6000-G98RevA.6\Stat $e=1-A 1 \backslash H F=-157.2104584 \backslash$ RMSD $=5.393 e-09 \backslash \mathrm{RMSF}=2.274 \mathrm{e}-06 \backslash \mathrm{Dipole=0.,0.,-0.0}$

000059 \PG=C02V [SGV (C2H4), SGV'(C2H4)] <br>@

## 4-51 cyclopentane $\boldsymbol{C}_{\mathbf{1}}$

$1 \backslash 1 \backslash G I N C-P C \backslash F O p t \backslash R B 3 L Y P \backslash 6-31 G(d) \backslash C 5 H 10 \backslash R A S M U S S E N \backslash 04-N O v-1999 \backslash 0 \backslash \ \# P$ B3L YP/6-31G(D) 5D OPT=(STEEP,TIGHT) NAME=RASMUSSEN GUESS=CHECK MAXDISK=20 97152000 GEOM=CHECK $\operatorname{IOP}(1 / 8=5) \backslash \backslash$ Cyclopentane $C 1 \backslash \backslash 0,1 \backslash \mathrm{H}, 1.8187328711,-1$ $.3612841462,-0.1742175538 \backslash C, 1.0193945202,-0.742955832,0.2496824554 \backslash \mathrm{C}, 1$ $.0428834052,0.7109442167,-0.2469706582 \backslash C,-0.353206239,1.2414757472,0.1$ $37176315 \backslash \mathrm{C},-1.3085701151,0.0191688392,0.0029500419 \backslash \mathrm{C},-0.3900305522,-1$. $2290835906,-0.1428575961 \backslash \mathrm{H}, 1.1358835619,-0.7617295525,1.3421669887 \backslash \mathrm{H}, 1$ $.1664069213,0.7254538884,-1.3387166655 \backslash \mathrm{H}, 1.8584731522,1.3046100376,0.1$ $811744975 \backslash \mathrm{H},-0.3372353414,1.5922955252,1.1766790419 \backslash \mathrm{H},-0.6662629027,2$. $0912764964,-0.4789216132 \backslash \mathrm{H},-1.9692585606,0.1206016632,-0.8649113084 \backslash \mathrm{H}$, $-1.9586539577,-0.0642791567,0.8807268645 \backslash \mathrm{H},-0.3811535571,-1.5679600138$ ,-1.1864939539\H,-0.7297583014,-2.0762810241,0.4626303544<br>Version=SGI -G98RevA. $6 \backslash \mathrm{HF}=-196.5537338 \backslash \mathrm{RMSD}=4.584 \mathrm{e}-09 \backslash \mathrm{RMSF}=1.422 \mathrm{e}-05 \backslash \mathrm{Dipole}=-0.002$ 3576,0.0001155,0.0000339\PG=C01 [X(C5H10)] <br>@

## C-4-52 cyclohexane (chair) <br> $D_{3 \mathrm{~d}}$

$1 \backslash 1 \backslash G I N C-P C \backslash$ Freq $\backslash$ RB3LYP $\backslash 6-31 G(d) \backslash C 6 H 12 \backslash R A S M U S S E N \backslash 04-J u l-1999 \backslash 0 \backslash \ \# P$ GEO M=ALLCHECK GUESS=TCHECK RB3LYP/6-31G(D) FREQ <br>Cyclohexane D3d<br>0,1\C,1 . $2706641196,-0.7336182715,0.2295115541 \backslash C,-1.2706641196,-0.7336182715,0$ $.2295115541 \backslash C, 0 ., 1.467236543,0.2295115541 \backslash C, 1.2706641196,0.7336182715$, $-0.2295115541 \backslash C, 0 .,-1.467236543,-0.2295115541 \backslash C,-1.2706641196,0.733618$ 2715,-0.2295115541 \H, 1.3292500466,-0.7674428722,1.3279036092\H,-1.3292 500466,-0.7674428722,1.3279036092\H,0.,1.5348857445,1.3279036092\H,1.3 $292500466,0.7674428722,-1.3279036092 \backslash$ Н, $0 .,-1.5348857445,-1.3279036092 \backslash$ H, -1.3292500466,0.7674428722,-1.3279036092\H,2.1640007648,-1.249386424 $1,-0.1459703661 \backslash \mathrm{H},-2.1640007648,-1.2493864241,-0.1459703661 \backslash \mathrm{H}, 0 ., 2.498$ $7728481,-0.1459703661 \backslash \mathrm{H}, 2.1640007648,1.2493864241,0.1459703661 \backslash \mathrm{H}, 0 .,-2$ $.4987728481,0.1459703661 \backslash \mathrm{H},-2.1640007648,1.2493864241,0.1459703661 \backslash \mathrm{Ve}$ rsion=SGI-G98RevA. $6 \backslash$ State $=1-A 1 G \backslash H F=-235.8764069 \backslash$ RMSD $=1.345 e-10 \backslash$ RMSF $=5$. 609e-06\Dipole=0.,0.,0.\PG=D03D [3SGD (C2H4)]<br>@

## BC-4-53 cyclooctane (boat-chair) $\boldsymbol{C}_{\mathrm{s}}$

$1 \backslash 1 \backslash G I N C-V P P 11 \backslash F O p t \backslash R B 3 L Y P \backslash 6-31 G(d) \backslash C 8 H 16 \backslash R A S M U S S E N \backslash 28-O c t-1999 \backslash 0 \backslash \ \# P$ B3LYP/6-31G* 5D OPT NAME=RASMUSSEN GUESS=CHECK MAXDISK=2097152000 GEOM $=C H E C K \backslash \backslash$ cyclooctane Cs chair <br>0,1\H,0.8487459518,1.5587440049,2.131912 $9907 \backslash \mathrm{C},-0.6324581345,0.0826697654,1.615221169 \backslash \mathrm{H}, 1.2197348297,-1.053536$ 9744,-1.3912709338\H,1.4845215076,2.4054231138,0. \H, -0.9088891096, 0.10
 9088891096,0.1099692051,-2.6773878583\H,0.3006915741,-2.9098357299,0. \} H,-1.2824814304,-2.1554131399,0. \C, 0.1332463223,1.3892217754,1.3143631 $424 \backslash \mathrm{C},-0.2043488958,-1.9335276676,0 . \backslash \mathrm{H},-0.5740494006,2.2301544675,-1.3$ $572221425 \backslash \mathrm{H},-0.5740494006,2.2301544675,1.3572221425 \backslash \mathrm{C}, 0.1332463223,1.3$ $892217754,-1.3143631424 \backslash C, 0.1364638752,-1.2299609284,-1.3288229143 \backslash C, 0$ $.1364638752,-1.2299609284,1.3288229143 \backslash \mathrm{H},-1.5842109791,0.0676251238,1$. $0708399865 \backslash \mathrm{H}, 0.8487459518,1.5587440049,-2.1319129907 \backslash \mathrm{H},-0.087762615,-1$ $.9474726398,-2.129041867 \backslash H,-0.087762615,-1.9474726398,2.129041867 \backslash \mathrm{C}, 0$. 926090285,1.4589459538,0.\C,-0.6324581345,0.0826697654,-1.615221169 \H, $1.2197348297,-1.0535369744,1.3912709338 \backslash \mathrm{H}, 1.6926579034,0.6731823157,0$. <br>Version=Fujitsu-VP-Unix-G98RevA.6\State=1-A'\HF=-314.485\RMSD=6.477e
$-09 \backslash \mathrm{RMSF}=2.117 \mathrm{e}-05 \backslash \mathrm{Dipole}=0.0045143,-0.0177618,0 . \backslash \mathrm{PG}=\mathrm{CS} \quad[\mathrm{SG}(\mathrm{C} 2 \mathrm{H} 4), \mathrm{X}(\mathrm{C} 6$ H12)]<br>@

## CC-4-54 bicyclo[3.3.1]nonane (chair-chair) $\boldsymbol{C}_{2 \mathrm{v}}$

$1 \backslash 1 \backslash G I N C-V P P 09 \backslash F O p t \backslash R B 3 L Y P \backslash 6-31 G(d) \backslash C 9 H 16 \backslash R A S M U S S E N \backslash 30-O c t-1999 \backslash 0 \backslash \ \# P$ B3LYP/6-31G(D) 5D OPT NAME=RASMUSSEN GUESS=CHECK MAXDISK=2097152000 GE OM=CHECK $\backslash \backslash$ bicyclononane $C 2 v$ (chair-chair) $\backslash \backslash 0,1 \backslash \mathrm{H}, 0 .,-0.8827652788,-2.1$ $946187569 \backslash \mathrm{H}, 2.1489160919,0 .,-1.2844552236 \backslash \mathrm{H},-2.1489160919,0 .,-1.284455$ $2236 \backslash \mathrm{C},-1.2538480054,0 .,-0.6463614232 \backslash \mathrm{H}, 0 .,-2.6322138286,1.3168767481 \backslash$ C, 0.,0.,-1.5396986866\H,0.,-0.9883030591,1.9035523586\H,-1.4476194712, $-2.1352894645,-0.5232279382 \backslash \mathrm{C}, 0 .,-1.5851112288,0.9860848026 \backslash \mathrm{H}, 0.0 .082$ 7652788,-2.1946187569\C,0.,1.5851112288,0.9860848026\H,-2.1532505068, 1 $.305104376,0.8560765794 \backslash H, 0.0 .9883030591,1.9035523586 \backslash \mathrm{C},-1.2864374982$ ,-1.3059321012,0.1811419479\C,1.2864374982,-1.3059321012,0.1811419479\} C,1.2864374982,1.3059321012,0.1811419479\C,-1.2864374982,1.3059321012, $0.1811419479 \backslash \mathrm{H},-2.1532505068,-1.305104376,0.8560765794 \backslash \mathrm{H}, 2.1532505068$, $-1.305104376,0.8560765794 \backslash \mathrm{H}, 1.4476194712,2.1352894645,-0.5232279382 \backslash \mathrm{H}$, $-1.4476194712,2.1352894645,-0.5232279382 \backslash H, 1.4476194712,-2.1352894645$, $-0.5232279382 \backslash \mathrm{C}, 1.2538480054,0 .,-0.6463614232 \backslash \mathrm{H}, 2.1532505068,1.3051043$ 76,0.8560765794\H,0.,2.6322138286,1.3168767481<br>Version=Fujitsu-VP-Uni x -G98RevA. $6 \backslash$ State $=1-\mathrm{A} 1 \backslash \mathrm{HF}=-352.6020631 \backslash \mathrm{RMSD}=9.300 \mathrm{e}-09 \backslash \mathrm{RMSF}=8.619 \mathrm{e}-06 \backslash \mathrm{D}$ ipole=0.,0.,0.0023168\PG=C02V [C2 (C1), SGV (C2H6), SGV' (C2H2), X(C4H8)] <br>@

## Strained Hydrocarbons

## 4-55 tetrahedrane $\boldsymbol{T}_{\mathrm{d}}$

$1 \backslash 1 \backslash G I N C-R S C Q C 2 \backslash F O p t \backslash R B 3 L Y P \backslash 6-31 G(d) \backslash C 4 H 4 \backslash R A S M U S S E N \backslash 22-O c t-1999 \backslash 0 \backslash \ \# P$ B3LYP/6-31G(D) 5D OPT FREQ=NORAMAN NAME=RASMUSSEN SYMM=LOOSE MAXDISK=5 24288000 IOP (3/32=2) <br>tetrahedrane Td 5D <br>0,1\C,0.7393943451,0., 0.5228 $307554 \backslash C,-0.5950186186,0.6037129548,0.3186526449 \backslash C,-0.3740443406,-0.82$ $46872328,0.006147824 \backslash \mathrm{C}, 0.2296686142,0.220974278,-0.8476312244 \backslash \mathrm{H},-1.300$ 0299944,1.3190258668,0.6962101406\H, -0.817233019,-1.8018228422,0.01343 $21102 \backslash \mathrm{H}, 0.5017928479,0.4827969754,-1.8519521597 \backslash \mathrm{H}, 1.6154701654,0 ., 1.14$ $23099089 \backslash \backslash$ Version=IBM-RS6000-G98RevA. $6 \backslash \mathrm{HF}=-154.6340841 \backslash$ RMSD $=1.958 \mathrm{e}-09 \backslash$ RMSF=2.004e-04\Dipole=0.,0.,0.\PG=TD [4C3(.C1H1)]<br>@

## 4-56 pyramidane $\boldsymbol{C}_{4 \mathrm{v}}$

$1 \backslash 1 \backslash G I N C-P C \backslash F O p t \backslash R B 3 L Y P \backslash 6-31 G(d) \backslash C 5 H 4 \backslash R A S M U S S E N \backslash 04-J u l-1999 \backslash 0 \backslash \ \# P$ B3LY P/6-31G(D) 5D OPT FREQ=NORAMAN NAME=RASMUSSEN MAXDISK=2097152000<br>PYra midane ([3.3.3.3]fenestrane) $\mathrm{C} 4 \mathrm{v} \backslash \backslash 0,1 \backslash \mathrm{C}, 0 ., 0 ., 1.0546612837 \backslash \mathrm{C}, 0 .,-1.024$ $2154553,-0.2476446964 \backslash C, 1.0242154553,0 .,-0.2476446964 \backslash C, 0 ., 1.024215455$ $3,-0.2476446964 \backslash \mathrm{C},-1.0242154553,0 .,-0.2476446964 \backslash \mathrm{H}, 0 .,-2.0932691227,-0$ $.0961237473 \backslash \mathrm{H}, 2.0932691227,0 .,-0.0961237473 \backslash \mathrm{H}, 0 ., 2.0932691227,-0.09612$ $37473 \backslash \mathrm{H},-2.0932691227,0 .,-0.0961237473 \backslash \backslash$ Version=SGI-G98RevA. $6 \backslash$ State $=1-$ $\mathrm{A} 1 \backslash \mathrm{HF}=-192.7260181 \backslash \mathrm{RMSD}=3.615 \mathrm{e}-09 \backslash \mathrm{RMSF}=1.134 \mathrm{e}-04 \backslash \mathrm{Dipole=0.,0.,-0.65356}$ $43 \backslash \mathrm{PG}=\mathrm{C0} 4 \mathrm{~V}$ [C4 (C1), 2SGV (C2H2)] <br>@

## 4-57 [1.1.1]propellane $\boldsymbol{D}_{3}$

$1 \backslash 1$ \GINC-VPP07\FOpt \RB3LYP\6-31G(d) \C5H6\RASMUSSEN $\backslash 02$-Nov-1999\0<br>\#P B 3LYP/6-31G(D) 5D OPT FREQ=NORAMAN NAME=RASMUSSEN GUESS=CHECK MAXDISK=2 097152000 GEOM=CHECK SYMM=LOOSE <br>propellane C1 <br>0,1\C,1.2527557924,0.3 $366966804,0 . \backslash \mathrm{C}, 0 ., 0 ., 0.7895950502 \backslash \mathrm{H}, 1.582406964,1.3735838206,0 . \backslash \mathrm{C},-0.3$
$347900176,-1.2532666811,0 . \backslash \mathrm{C},-0.9179657748,0.9165700008,0 . \backslash \mathrm{H},-0.686625$ 9816, 1.9797194431, 0. \C, 0., 0., - 0.7895950502 \H, -1.9807619649, 0.683612719 $6,0 . \backslash \mathrm{H}, 2.0578003209,-0.3952241785,0 . \backslash \mathrm{H}, 0.3983550009,-2.0571965402,0 . \backslash \mathrm{H}$ ,-1.3711743392,-1.5844952645,0. <br>Version=Fujitsu-VP-Unix-G98RevA.6\Sta te=1-A1' $\backslash \mathrm{HF}=-194.0055446 \backslash \mathrm{RMSD}=2.580 \mathrm{e}-09 \backslash \mathrm{RMSF}=4.071 e-05 \backslash \mathrm{Dipole=0.,0.,0}$. $\backslash \mathrm{PG}=\mathrm{D} 03 \mathrm{H} \quad[\mathrm{C} 3(\mathrm{C} 1 . \mathrm{C} 1), 3 \mathrm{C} 2(\mathrm{C} 1), \mathrm{SGH}(\mathrm{H} 6)] \backslash \backslash @$

## 4-58 spiropentane $\boldsymbol{D}_{\mathbf{2 d}}$

$1 \backslash 1 \backslash G I N C-V P P 07 \backslash F O p t \backslash R B 3 L Y P \backslash 6-31 G(d) \backslash C 5 H 8 \backslash R A S M U S S E N \backslash 04-J u l-1999 \backslash 0 \backslash \backslash \# P$ B 3LYP/6-31G(D) 5D OPT FREQ=NORAMAN NAME=RASMUSSEN MAXDISK=131072000<br>Sp iropentane $D 2 d 5 D \backslash \backslash 0,1 \backslash C, 0.0 .0 . \backslash C,-0.5408506919,-1.2730959398,-0.540$ $8506919 \backslash C, 0.5408506919,-1.2730959398,0.5408506919 \backslash C,-0.5408506919,1.27$ $30959398,0.5408506919 \backslash \mathrm{C}, 0.5408506919,1.2730959398,-0.5408506919 \backslash \mathrm{H},-1.5$ $450570167,-1.57759691,-0.2526151656 \backslash \mathrm{H}, 1.5450570167,-1.57759691,0.25261$ $51656 \backslash \mathrm{H},-1.5450570167,1.57759691,0.2526151656 \backslash \mathrm{H}, 1.5450570167,1.5775969$ $1,-0.2526151656 \backslash \mathrm{H},-0.2526151656,-1.57759691,-1.5450570167 \backslash \mathrm{H}, 0.25261516$ $56,-1.57759691,1.5450570167 \backslash \mathrm{H},-0.2526151656,1.57759691,1.5450570167 \backslash \mathrm{H}$, $0.2526151656,1.57759691,-1.5450570167 \backslash \backslash V e r s i o n=F u j i t s u-V P-U n i x-G 98 R e v A$ $.6 \backslash$ State $=1-A 1 \backslash H F=-195.2681523 \backslash R M S D=1.937 e-09 \backslash R M S F=6.970 e-05 \backslash D i p o l e=0 .$, 0., 0. \PG=D02D [O (C1), 2SGD (C2) , X (H8)] <br>

## 4-59 prismane $\boldsymbol{D}_{3 \mathrm{~h}}$

$1 \backslash 1 \backslash G I N C-P C \backslash F O p t \backslash R B 3 L Y P \backslash 6-31 G(d) \backslash C 6 H 6 \backslash R A S M U S S E N \backslash 04-J u l-1999 \backslash 0 \backslash \backslash \# P$ B3LY P/6-31G(D) 5D OPT FREQ=NORAMAN NAME=RASMUSSEN MAXDISK=2097152000<br>Pris mane $\mathrm{D} 3 \mathrm{~h} \backslash \backslash 0,1 \backslash \mathrm{C},-0.4392492784,0.7608020749,0.7792210646 \backslash \mathrm{C},-0.439249284$ $9,-0.7608020712,-0.7792210646 \backslash C,-0.4392492784,0.7608020749,-0.77922106$ $46 \backslash \mathrm{C},-0.4392492849,-0.7608020712,0.7792210646 \backslash \mathrm{C}, 0.8784985633,-0.000000$ $0038,0.7792210646 \backslash \mathrm{C}, 0.8784985633,-0.0000000038,-0.7792210646 \backslash \mathrm{H},-0.8380$ $167187,1.4514875489,1.5148145405 \backslash \mathrm{H},-0.8380167312,-1.4514875417,1.51481$ $45405 \backslash \mathrm{H},-0.8380167187,1.4514875489,-1.5148145405 \backslash \mathrm{H},-0.8380167312,-1.45$ $14875417,-1.5148145405 \backslash \mathrm{H}, 1.67603345,-0.0000000072,1.5148145405 \backslash \mathrm{H}, 1.676$ 03345,-0.0000000072,-1.5148145405<br>Version=SGI-G98RevA. 6\State=1-A1'\H $\mathrm{F}=-232.051228 \backslash \mathrm{RMSD}=4.045 \mathrm{e}-09 \backslash \mathrm{RMSF}=9.790 \mathrm{e}-05 \backslash \mathrm{Dipole}=0 ., 0 ., 0 . \backslash \mathrm{PG}=\mathrm{D} 03 \mathrm{H} \quad[3$ SGV (C2H2)] <br>@

## 4-60 cubane $\boldsymbol{O}_{\mathbf{h}}$

$1 \backslash 1 \backslash G I N C-R S C Q C 2 \backslash F O p t \backslash R B 3 L Y P \backslash 6-31 G(d) \backslash C 8 H 8 \backslash R A S M U S S E N \backslash 04-J u l-1999 \backslash 0 \backslash \backslash \# P$ B3LYP/6-31G(D) 5D OPT FREQ=NORAMAN NAME=RASMUSSEN MAXDISK=262144000<br>C ubane Oh <br>0, 1\C,0.7851623106,0.7851623106,0.7851623106\C,0.7851623106, $0.7851623106,-0.7851623106 \backslash C,-0.7851623106,0.7851623106,-0.7851623106 \backslash$ $C,-0.7851623106,0.7851623106,0.7851623106 \backslash C, 0.7851623106,-0.7851623106$ , $0.7851623106 \backslash \mathrm{C}, 0.7851623106,-0.7851623106,-0.7851623106 \backslash \mathrm{C},-0.78516231$ $06,-0.7851623106,-0.7851623106 \backslash \mathrm{C},-0.7851623106,-0.7851623106,0.7851623$ $106 \backslash \mathrm{H}, 1.4156434145,1.4156434145,1.4156434145 \backslash \mathrm{H}, 1.4156434145,1.41564341$ $45,-1.4156434145 \backslash \mathrm{H},-1.4156434145,1.4156434145,-1.4156434145 \backslash \mathrm{H},-1.41564$ $34145,1.4156434145,1.4156434145 \backslash \mathrm{H}, 1.4156434145,-1.4156434145,1.4156434$ $145 \backslash \mathrm{H}, 1.4156434145,-1.4156434145,-1.4156434145 \backslash \mathrm{H},-1.4156434145,-1.4156$ $434145,-1.4156434145 \backslash \mathrm{H},-1.4156434145,-1.4156434145,1.4156434145 \backslash \backslash V e r s i$ on=IBM-RS6000-G98RevA. $6 \backslash \mathrm{HF}=-309.4557307 \backslash \mathrm{RMSD}=6.445 e-09 \backslash \mathrm{RMSF}=7.218 \mathrm{e}-05 \backslash$ Dipole=0.,0.,0.\PG=OH [4C3(H1C1.C1H1)] <br>@

## 4-61 tetramethyltetrahedrane $\boldsymbol{T}_{\mathrm{d}}$

$1 \backslash 1 \backslash G I N C-V P P 11 \backslash F O p t \backslash R B 3 L Y P \backslash 6-31 G(d) \backslash C 8 H 12 \backslash R A S M U S S E N \backslash 21-O c t-1999 \backslash 0 \backslash \ \# P$ B3LYP/6-31G(D) 5D OPT FREQ=NORAMAN NAME=RASMUSSEN SYMM=LOOSE MAXDISK=2 097152000 GEOM=CHECK GUESS=CHECK IOP (3/32=2) <br>tetramethyltetrahedrane Td 5D<br>0,1\C,0.5257935001,0.5257935001,0.5257935001\C, -0.5257935001,-0 $.5257935001,0.5257935001 \backslash C, 0.5257935001,-0.5257935001,-0.5257935001 \backslash C$, $-0.5257935001,0.5257935001,-0.5257935001 \backslash C,-1.3824451307,-1.3824451307$ ,1.3824451307\C,1.3824451307,-1.3824451307,-1.3824451307\C,-1.38244513 $07,1.3824451307,-1.3824451307 \backslash C, 1.3824451307,1.3824451307,1.3824451307$ $\backslash \mathrm{H}, 2.0310778422,2.0310778422,0.7792453518 \backslash \mathrm{H}, 2.0310778422,0.7792453518$, $2.0310778422 \backslash \mathrm{H}, 0.7792453518,2.0310778422,2.0310778422 \backslash \mathrm{H},-2.0310778422$, $-2.0310778422,0.7792453518 \backslash \mathrm{H},-2.0310778422,-0.7792453518,2.0310778422 \backslash$ H, - 0.7792453518, -2.0310778422,2.0310778422 \H, 0.7792453518, -2.031077842 $2,-2.0310778422 \backslash$ Н, $2.0310778422,-2.0310778422,-0.7792453518 \backslash \mathrm{H}, 2.0310778$ 422,-0.7792453518,-2.0310778422 \Н, -2.0310778422, 0.7792453518,-2.031077 $8422 \backslash \mathrm{H},-0.7792453518,2.0310778422,-2.0310778422 \backslash \mathrm{H},-2.0310778422,2.0310$ 778422,-0.7792453518<br>Version=Fujitsu-VP-Unix-G98RevA.6\HF=-311.916659 $\backslash$ RMSD $=3.515 \mathrm{e}-10 \backslash \mathrm{RMSF}=3.261 \mathrm{e}-05 \backslash \mathrm{Dipole}=0 ., 0 ., 0 . \backslash \mathrm{PG}=\mathrm{TD} \quad[4 \mathrm{C} 3(. \mathrm{C} 1 \mathrm{C} 1), 6 \mathrm{SGD}($ H2) ] <br>@

## 4-62 tetra-tert-butyltetrahedrane $\boldsymbol{T}$

$1 \backslash 1 \backslash G I N C-P C \backslash F O p t \backslash R B 3 L Y P \backslash 6-31 G(d) \backslash C 20 H 36 \backslash R A S M U S S E N \backslash 20-O c t-1999 \backslash 0 \backslash \ \# P$ B3 LYP/6-31G(D) 5D OPT FREQ=NORAMAN NAME=RASMUSSEN SYMM=LOOSE MAXDISK=209 $7152000 \operatorname{IOP}(3 / 32=2) \backslash$ tetrahedrane $T d 5 D \backslash \backslash 0,1 \backslash C,-1.9758364536,-0.000367$ 2513,1.3969946448\C,-2.4689023978,-1.4475793734,1.6176443949\C,1.63999 00027,2.4851801144,1.3935749246\C,0.999106906,2.2038687011,0.016492498 $2 \backslash C,-0.6135019482,-0.5905665871,-2.2650320814 \backslash C, 2.0915333129,2.2989238$ 707,-1.0715297095\C,1.5902314958,-1.6129348627,0.8515449384\C, -0.74670 42227,-0.0001387909, 0.5279494658\C,-1.6551564138, 0.6326286241,2.769111 $1842 \backslash C, 1.7848778816,-1.4142567509,2.3710392808 \backslash C,-0.0774638306,3.27616$ 19207,-0.2617267757 \C,-3.1022188677,0.8136075918, 0.7225090064\C,1.0778 802361,-3.0478488095,0.5971015925\C,2.9532365926,-1.4369227602,0.14623 $64175 \backslash C, 0.6547400082,-0.8609417353,-3.104486001 \backslash C,-1.4075087967,0.5629$ $122536,-2.9171539662 \backslash C,-1.4910077277,-1.861864946,-2.2623203485 \backslash C, 0.60$ $09771562,-0.6095571679,0.3218141867 \backslash C, 0.377580515,0.8328817207,0.00623$ $28124 \backslash \mathrm{C},-0.2318534484,-0.2231857619,-0.855996465 \backslash \mathrm{H},-1.7317403739,0.282$ 5170498,-3.9271568176\H,-0.7939058033,1.4666859601,-2.9989759059\H,-2. $3000624071,0.8126962904,-2.3333108811 \backslash \mathrm{H}, 1.3250566372,0.0054255781,-3.1$ $047218033 \backslash$ Н, $0.3862116658,-1.0809105398,-4.1453316188 \backslash \mathrm{H}, 1.2117754836,-1$ $.718538757,-2.7117402774 \backslash \mathrm{H},-1.7318854642,-2.1639736063,-3.2892388551 \backslash \mathrm{H}$ $,-2.4338097994,-1.6887227456,-1.7320785095 \backslash \mathrm{H},-0.9788568033,-2.69894059$ 27,-1.77557344\H,1.663502806,2.1715522273,-2.0718180307\H,2.8602180237 ,1.5308945325,-0.9330684821 \H, 2.5830626856,3.2792631017,-1.0370737427\} H, 0.3769641883,4.2739016923,-0.3048993286\H,-0.8371827735,3.2857675977 , $0.5274153121 \backslash \mathrm{H},-0.5841300158,3.0944787678,-1.2157694211 \backslash \mathrm{H}, 2.051637329$ 3,3.5017581688,1.4247018186\H,2.4567008301,1.78449472,1.5985963342\H,0 .9058376503,2.3934415282,2.2013627159\H, 0.9908961103,-3.2506874352, - 0. $4758851873 \backslash \mathrm{H}, 0.0938061934,-3.2063795291,1.0513956051 \backslash \mathrm{H}, 1.7701705058,-3$ $.7838867351,1.0246945067 \backslash \mathrm{H}, 2.8556089275,-1.5350114125,-0.9403933335 \backslash \mathrm{H}$, $3.6649944441,-2.1971194418,0.4917145089 \backslash$ Н, $3.3826455465,-0.4518503019,0$ .3589582506\H,2.1151063716,-0.395435552,2.6009724654 \H, 2.5416653713,-2 .1097075044,2.7550630958\H, 0.8518883203,-1.5974944942,2.9150657359\H,-


#### Abstract

$2.7825897745,1.8405104769,0.5146040576 \backslash \mathrm{H},-3.9847463092,0.8593348793,1$. $3728225276 \backslash \mathrm{H},-3.4055365771,0.3560783275,-0.2254760754 \backslash \mathrm{H},-2.6752619882$, $-1.9481552709,0.6654068979 \backslash H,-3.392987683,-1.4520726471,2.2091674645 \backslash \mathrm{H}$ , - $1.7214853231,-2.0407436933,2.1557282006 \backslash \mathrm{H},-1.3654888204,1.6834585945$ $, 2.6602101526 \backslash \mathrm{H},-0.8347328148,0.1064751832,3.2690956193 \backslash \mathrm{H},-2.533346359$ $9,0.5908955825,3.4255364408 \backslash \backslash V e r s i o n=S G I-G 98 R e v A .6 \backslash H F=-783.67012 \backslash \mathrm{RMSD}=$ $7.142 \mathrm{e}-09 \backslash \mathrm{RMSF}=5.148 \mathrm{e}-06 \backslash \mathrm{Dipole}=0 ., 0 ., 0 . \backslash \mathrm{PG}=\mathrm{T} \quad[4 \mathrm{C} 3(. \mathrm{C} 1 \mathrm{C} 1), \mathrm{X}(\mathrm{C} 12 \mathrm{H} 36)] \backslash \backslash$ @


## 4-63 pagodane $\boldsymbol{D}_{\mathbf{2 h}}$

$1 \backslash 1 \backslash G I N C-P A L O \backslash F O p t \backslash R B 3 L Y P \backslash 6-31 G(d) \backslash C 20 H 20 \backslash R A S M U S S E N \backslash 21-O c t-1999 \backslash 0 \backslash \ \# P$ B3LYP/6-31G(D) 5D OPT FREQ=NORAMAN NAME=RASMUSSEN SYMM=LOOSE <br>pagodane $\mathrm{D} 2 \mathrm{~h} \backslash \backslash 0,1 \backslash \mathrm{C},-0.7773829579,-0.7877176329,0 . \backslash \mathrm{C}, 0.7773829579,-0.787717632$ $9,0 . \backslash C,-0.7773829579,0.7877176329,0 . \backslash C, 0.7773829579,0.7877176329,0 . \backslash C$, $1.2791971266,-1.1487579197,1.4072011584 \backslash C, 1.2791971266,1.1487579197,-1$ $.4072011584 \backslash C, 1.2791971266,-1.1487579197,-1.4072011584 \backslash C,-1.2791971266$ ,-1.1487579197,1.4072011584\C,-1.2791971266,-1.1487579197,-1.407201158 $4 \backslash \mathrm{C},-1.2791971266,1.1487579197,1.4072011584 \backslash \mathrm{C},-1.2791971266,1.14875791$ 97,-1.4072011584\C,1.2791971266,1.1487579197,1.4072011584\C,-2.2493205 955, 0., 1.7704171003\C,2.2493205955,0.,1.7704171003\C,-2.2493205955,0., $-1.7704171003 \backslash C, 2.2493205955,0 .,-1.7704171003 \backslash C, 0 .,-0.7976327697,2.232$ $0646706 \backslash \mathrm{C}, 0 ., 0.7976327697,2.2320646706 \backslash \mathrm{C}, 0 ., 0.7976327697,-2.2320646706$ \C,0.,-0.7976327697,-2.2320646706\H,0.,-1.2158704021,-3.2437027576\H,0 ., 1.2158704021,-3.2437027576\H,0.,-1.2158704021,3.2437027576\H,0.,1.21 58704021,3.2437027576\H,-1.65336782,-2.1675152449,-1.5497043472\H,-1.6 5336782,2.1675152449,-1.5497043472\H,1.65336782,2.1675152449,-1.549704 $3472 \backslash \mathrm{H}, 1.65336782,-2.1675152449,-1.5497043472 \backslash \mathrm{H},-1.65336782,-2.1675152$ 449,1.5497043472\H,-1.65336782,2.1675152449,1.5497043472\H,1.65336782, $-2.1675152449,1.5497043472 \backslash \mathrm{H}, 1.65336782,2.1675152449,1.5497043472 \backslash \mathrm{H}, 2$. $5340332739,0 .,-2.8303095354 \backslash \mathrm{H},-2.5340332739,0 .,-2.8303095354 \backslash \mathrm{H},-2.5340$ 332739,0.,2.8303095354 \H, 2.5340332739,0., 2.8303095354 \H, -3.1673532247, 0.,-1.1710399936\H,-3.1673532247,0.,1.1710399936\H,3.1673532247,0.,-1. 1710399936\H,3.1673532247,0.,1.1710399936<br>Version=Sun-SVR4-Unix-G98Re vA. $7 \backslash$ State=1-AG $\backslash H F=-774.1082975 \backslash \mathrm{RMSD}=4.751 \mathrm{e}-09 \backslash \mathrm{RMSF}=8.685 \mathrm{e}-06 \backslash \mathrm{Dipole}=0$ ., 0., 0. \PG=D02H [SG(C4), SG' (C4H4), SG" (C4H8) , X (C8H8) ] <br>@

## 4-64 dodecahedrane $\quad I_{\mathrm{h}}$

$1 \backslash 1 \backslash G I N C-P C \backslash F O p t \backslash R B 3 L Y P \backslash 6-31 G(d) \backslash C 20 H 20 \backslash R A S M U S S E N \backslash 02-N o v-1999 \backslash 0 \backslash \backslash \# P$ B3 LYP/6-31G(D) 5D OPT NAME=RASMUSSEN SYMM=LOOSE MAXDISK=2097152000<br>dode cahedrane Ih <br>0,1\C,0.,1.3234975676,1.732480808\C,-1.258720986,0.40898 32404,1.732480808\C,-0.7779323517,-1.0707320242,1.732480808\C,0.777932 3517,-1.0707320242,1.732480808\C,1.258720986,0.4089832404,1.732480808\} C, 2.0366533376,0.6617487838,0.4089832404\C,1.258720986,1.732480808,-0. $4089832404 \backslash \mathrm{C}, 0 ., 2.1414640484,0.4089832404 \backslash \mathrm{C},-1.258720986,1.732480808$, $0.4089832404 \backslash C,-2.0366533376,0.6617487838,0.4089832404 \backslash C,-2.0366533376$ ,-0.6617487838,-0.4089832404\C,-1.258720986,-1.732480808,0.4089832404\} C, 0.,-2.1414640484,-0.4089832404 \C,1.258720986,-1.732480808, 0.40898324 $04 \backslash C, 2.0366533376,-0.6617487838,-0.4089832404 \backslash C, 1.258720986,-0.4089832$ $404,-1.732480808 \backslash C, 0.7779323517,1.0707320242,-1.732480808 \backslash C,-0.7779323$ 517,1.0707320242,-1.732480808\C,-1.258720986,-0.4089832404,-1.73248080 $8 \backslash \mathrm{C}, 0 .,-1.3234975676,-1.732480808 \backslash \mathrm{H}, 0.1 .9881921778,2.6025773488 \backslash \mathrm{H},-1$. 8908831264,0.614385171,2.6025773488\H,-1.1686300408,-1.6084812599,2.60
$25773488 \backslash \mathrm{H}, 1.1686300408,-1.6084812599,2.6025773488 \backslash \mathrm{H}, 1.8908831264,0.61$ $4385171,2.6025773488 \backslash \mathrm{H}, 3.0595131672,0.9940960889,0.614385171 \backslash \mathrm{H}, 1.89088$ $31264,2.6025773488,-0.614385171 \backslash \mathrm{H}, 0 ., 3.2169625199,0.614385171 \backslash \mathrm{H},-1.890$ $8831264,2.6025773488,-0.614385171 \backslash \mathrm{H},-3.0595131672,0.9940960889,0.61438$ $5171 \backslash \mathrm{H},-3.0595131672,-0.9940960889,-0.614385171 \backslash \mathrm{H},-1.8908831264,-2.602$ $5773488,0.614385171 \backslash \mathrm{H}, 0 .,-3.2169625199,-0.614385171 \backslash \mathrm{H}, 1.8908831264,-2$. $6025773488,0.614385171 \backslash \mathrm{H}, 3.0595131672,-0.9940960889,-0.614385171 \backslash \mathrm{H}, 1.8$ $908831264,-0.614385171,-2.6025773488 \backslash H, 1.1686300408,1.6084812599,-2.60$ $25773488 \backslash \mathrm{H},-1.1686300408,1.6084812599,-2.6025773488 \backslash \mathrm{H},-1.8908831264,-0$ $.614385171,-2.6025773488 \backslash \mathrm{H}, 0 .,-1.9881921778,-2.6025773488 \backslash$ VVersion=SGI -G98RevA. $6 \backslash$ State $=1-A G \backslash H F=-774.1730002 \backslash \mathrm{RMSD}=7.290 \mathrm{e}-09 \backslash \mathrm{RMSF}=4.536 \mathrm{e}-06 \backslash \mathrm{Di}$ pole=0.,0.,0. \PG=IH [10C3 (H1C1.C1H1)] <br>@

## Capping Hydrocarbons

## 4-65 bicyclo[2.2.0]hexane $\boldsymbol{C}_{\mathbf{2}}$

$1 \backslash 1 \backslash G I N C-V P P 10 \backslash F O p t \backslash R B 3 L Y P \backslash 6-31 G(d) \backslash C 6 H 10 \backslash R A S M U S S E N \backslash 07-O c t-1999 \backslash 0 \backslash \backslash \# P$ B3LYP/6-31G* 5D OPT=TIGHT FREQ=NORAMAN NAME=RASMUSSEN MAXDISK=20971520 00 GEOM = (CHECK, NODISTANCE, NOANGLE, NODIHEDRAL) GUESS=CHECK <br>bicyclohexa ne $\mathrm{C} 2 \backslash \backslash 0,1 \backslash \mathrm{H},-2.4441359235,-0.4514109433,0.2488085326 \backslash \mathrm{H},-0.8993043219$, $1.0580336958,1.492799176 \backslash \mathrm{H}, 2.4441359235,0.4514109433,0.2488085326 \backslash \mathrm{C},-1$ $.4994445186,-0.2418600554,-0.2634082119 \backslash H, 0.8993043219,-1.0580336958,1$ $.492799176 \backslash \mathrm{C},-0.5053787603,0.6028787473,0.5794953454 \backslash \mathrm{H}, 0.1420181313,1$. $788492794,-1.2195330434 \backslash \mathrm{H}, 0.8929526974,2.3132049674,0.2976236362 \backslash \mathrm{H}, 1.7$ $356323045,-0.1705828355,-1.2513314354 \backslash \mathrm{H},-0.8929526974,-2.3132049674,0$. $2976236362 \backslash \mathrm{H},-0.1420181313,-1.788492794,-1.2195330434 \backslash \mathrm{C}, 0.5053787603$, $0.6028787473,0.5794953454 \backslash \mathrm{H},-1.7356323045,0.1705828355,-1.2513314354 \backslash \mathrm{C}$ , 0. 5053787603,1.4441954783,-0.2441482778\C,1.4994445186, 0.2418600554, $0.2634082119 \backslash C,-0.5053787603,-1.4441954783,-0.2441482778 \backslash$ VVersion=Fuji tsu-VP-Unix-G98RevA. $6 \backslash$ State $=1-A \backslash H F=-234.5941715 \backslash$ RMSD $=2.960 e-10 \backslash \mathrm{RMSF}=1$. $117 e-06 \backslash$ Dipole=0.,0.,0.0522987\PG=C02 [X(C6H10)] <br>@

## TB-4-52 cyclohexane (twistboat) <br> $C_{2}$

$1 \backslash 1 \backslash G I N C-R S C Q C 9 \backslash F O p t \backslash R B 3 L Y P \backslash 6-31 G(d) \backslash C 6 H 12 \backslash R A S M U S S E N \backslash 09-O c t-1999 \backslash 0 \backslash \backslash \# P$ B3LYP/6-31G* 5D OPT=CALCFC NAME=RASMUSSEN MAXDISK=917504000 GEOM=(CH ECK, NODISTANCE,NOANGLE,NODIHEDRAL) GUESS=CHECK<br>cyclohexane C2 twist<br> $0,1 \backslash \mathrm{H}, 0.4509797272,-1.2156974455,-1.4603209804 \backslash \mathrm{C}, 0.6621170381,-1.22989$ $22507,-0.3820168923 \backslash \mathrm{H},-1.2282907369,-2.1506273973,0.192757875 \backslash \mathrm{H}, 1.2282$ $847748,2.1506377881,0.1926793853 \backslash \mathrm{C},-0.6621060499,1.2298717825,-0.38210$ $04436 \backslash \mathrm{H},-0.4509371527,1.2156206696,-1.4603975376 \backslash \mathrm{H}, 2.1866365881,-0.261$ $1050922,0.8402298211 \backslash \mathrm{H},-2.1886278525,-0.2482848642,-0.8395552683 \backslash \mathrm{H}, 0.4$ $579446953,1.2135816377,1.4601796783 \backslash \mathrm{H},-1.2157991148,2.1576537123,-0.19$ $32636659 \backslash \mathrm{H},-2.186660851,0.2611484717,0.8401527333 \backslash \mathrm{H}, 1.2158045414,-2.15$ $76643724,-0.1931154576 \backslash \mathrm{H},-0.4579865037,-1.2135038481,1.4602299692 \backslash \mathrm{C}, 1$. $528556813,-0.0044479678,0.0001727632 \backslash C, 0.6692114555,1.2261626662,0.381$ $8797406 \backslash C,-1.5285565789,0.0044478735,0.0001281205 \backslash C,-0.6692227197,-1.2$ $261422104,0.3819247431 \backslash \mathrm{H}, 2.1886521362,0.2482413803,-0.8395047416 \backslash \backslash V e r s$ ion=IBM-RS6000-G98RevA. $6 \backslash H F=-235.8660513 \backslash \mathrm{RMSD}=4.879 e-09 \backslash \mathrm{RMSF}=8.537 \mathrm{e}-07$ \Dipole=0.,0.,-0.0000126\PG=C01 [X(C6H12)] <br>@

## 4-66 cycloheptane $\boldsymbol{C}_{\mathbf{1}}$

$1 \backslash 1 \backslash G I N C-P A L O \backslash F O p t \backslash R B 3 L Y P \backslash 6-31 G(d) \backslash C 7 H 14 \backslash D R R 501 \backslash 04-A p r-2000 \backslash 0 \backslash \backslash \# P$ B3LY

P/6-31G(D) 5D OPT FREQ=NORAMAN $\backslash \backslash$ cycloheptane $C 1 \backslash \backslash 0,1 \backslash C, 0.5590326618,-0$ $.3080971746,-0.820500652 \backslash \mathrm{H},-1.4377475666,1.7294000603,1.331022492 \backslash \mathrm{C},-0$ $.323927877,1.7890931316,-0.5255459693 \backslash \mathrm{H}, 1.309543479,1.4630217413,-2.01$ $15260868 \backslash \mathrm{C}, 0.3950855486,0.9524188047,-1.6886136193 \backslash \mathrm{H}, 0.9595739913,0.21$ $23138066,0.0423625372 \backslash \mathrm{H},-0.5080557851,-0.4611810436,-0.7047302367 \backslash \mathrm{C}, 0$. 9627130237,-1.7012847204,-0.3053203196\C,0.0125789835,-1.617277206,0.9 $831940793 \backslash \mathrm{H}, 2.0216441457,-1.7904533506,-0.0355913944 \backslash \mathrm{H}, 0.6873280964,-2$ . $5644650592,-0.9221048432 \backslash \mathrm{H}, 0.438323937,-2.1709264515,1.8305606372 \backslash \mathrm{H},-$ $0.9257736046,-2.1246307744,0.7203002479 \backslash C,-0.3788447645,-0.1587816738$, $1.5247967957 \backslash \mathrm{C},-1.0837398808,0.9652813728,0.6222431971 \backslash \mathrm{H}, 0.5109009243$, $0.2913188133,1.989733802 \backslash \mathrm{H},-1.0749032502,-0.3441203286,2.357100731 \backslash \mathrm{H}, 0$ $.4573616174,2.3825282082,-0.031099414 \backslash \mathrm{H},-1.9970171392,0.5282398221,0.1$ $917322134 \backslash \mathrm{H},-0.2528823786,0.8138023574,-2.5620830727 \backslash \mathrm{H},-1.0456826388,2$ $.5070369937,-0.9371986841 \backslash$ VVersion=Sun-SVR4-Unix-G98RevA. $7 \backslash \mathrm{HF}=-275.045$ $1835 \backslash \mathrm{RMSD}=3.957 \mathrm{e}-09 \backslash \mathrm{RMSF}=3.916 \mathrm{e}-05 \backslash \mathrm{Dipole}=-0.1017681,0.056031,0.149206$ $1 \backslash \mathrm{PG}=\mathrm{C} 01$ [X(C7H14)]<br>@

## 4-67 norbornane $\boldsymbol{C}_{\mathbf{2 v}}$

$1 \backslash 1 \backslash G I N C-P C \backslash F O p t \backslash R B 3 L Y P \backslash 6-31 G(d) \backslash C 7 H 12 \backslash R A S M U S S E N \backslash 06-O c t-1999 \backslash 0 \backslash \backslash \# P$ B3L YP/6-31G* 5D OPT FREQ=NORAMAN NAME=RASMUSSEN MAXDISK=2097152000 GEOM=( NODISTANCE,NOANGLE,NODIHEDRAL) SYMM=LOOSE<br>bicycloheptane C2v <br>0,1\H,0 . 89124767,0.,2.0286307551 \H, -0.89124767,0., 2.0286307551 \H, 0., -2. 155550 1936,0.731703749\H,-2.1615393906,-1.176766414,-0.0182607583\H, 0., 2. 155 5501936,0.731703749\C,0.,0.,1.3892799937\H,1.209269343,1.2063930968,-1 $.5035338543 \backslash \mathrm{H},-2.1615393906,1.176766414,-0.0182607583 \backslash \mathrm{H}, 1.209269343,-1$ $.2063930968,-1.5035338543 \backslash \mathrm{C}, 0 .,-1.1336730196,0.3401203297 \backslash \mathrm{H},-1.2092693$ 43,-1.2063930968,-1.5035338543\C,0.,1.1336730196,0.3401203297\H,-1.209 269343,1.2063930968,-1.5035338543\C,1.2556694209,0.7829984181,-0.49377 $56032 \backslash \mathrm{C}, 1.2556694209,-0.7829984181,-0.4937756032 \backslash \mathrm{C},-1.2556694209,-0.78$ 29984181,-0.4937756032\C,-1.2556694209,0.7829984181,-0.4937756032\H, 2. $1615393906,1.176766414,-0.0182607583 \backslash \mathrm{H}, 2.1615393906,-1.176766414,-0.01$ $82607583 \backslash \backslash$ Version=SGI-G98RevA. 6\State=1-A1 \HF=-273.9639734\RMSD=7.084e $-09 \backslash \mathrm{RMSF}=5.235 \mathrm{e}-05 \backslash \mathrm{Dipole}=0 ., 0.0 .0236245 \backslash \mathrm{PG}=\mathrm{CO} 2 \mathrm{~V} \quad[\mathrm{C} 2(\mathrm{C} 1), \mathrm{SGV}(\mathrm{C} 2 \mathrm{H} 2)$, SG $\left.\mathrm{V}^{\prime}(\mathrm{H} 2), \mathrm{X}(\mathrm{C} 4 \mathrm{H} 8)\right] \backslash \backslash$

## 4-68 cis-bicyclo[3.3.0]octane $\quad \boldsymbol{C}_{2 \mathrm{v}}$

$1 \backslash 1 \backslash G I N C-P C \backslash F O p t \backslash R B 3 L Y P \backslash 6-31 G(d) \backslash C 8 H 14 \backslash R A S M U S S E N \backslash 06-O c t-1999 \backslash 0 \backslash \ \# P$ B3L YP/6-31G* 5D OPT FREQ=NORAMAN NAME=RASMUSSEN MAXDISK=2097152000 GEOM=( NODISTANCE,NOANGLE,NODIHEDRAL) SYMM=LOOSE<br>bicyclooctane C2v <br>0,1\H,0. , 2.653972206,-1.0200676768\C,0.7883279884,0.,-0.47661414\H,0.,-3.11752 01911,0.6849926321\C,-0.7883279884,0.,-0.47661414\H,-1.148498892,0.,-1 $.512944598 \backslash \mathrm{H}, 0.3 .1175201911,0.6849926321 \backslash \mathrm{H}, 1.3604887418,1.1548171911$, $1.2829303738 \backslash \mathrm{C}, 0 .,-2.2574215456,0.004818018 \backslash \mathrm{H},-1.3604887418,1.15481719$ 11,1.2829303738\H, 0.,-2.653972206,-1.0200676768\H,-1.3604887418,-1.154 8171911,1.2829303738\H,1.148498892,0.,-1.512944598\H,1.3604887418,-1.1 548171911,1.2829303738\С,1.2067058416,1.3223416119,0.2075309631\C,-1.2 $067058416,1.3223416119,0.2075309631 \backslash \mathrm{C},-1.2067058416,-1.3223416119,0.20$ $75309631 \backslash \mathrm{C}, 1.2067058416,-1.3223416119,0.2075309631 \backslash \mathrm{H}, 2.141496567,1.735$ 2086914,-0.1887179651 \H,-2.141496567,1.7352086914,-0.1887179651 \H,-2.1 41496567,-1.7352086914,-0.1887179651 \Н, $2.141496567,-1.7352086914,-0.18$ $87179651 \backslash \mathrm{C}, 0.2 .2574215456,0.004818018 \backslash \backslash$ Version=SGI-G98RevA. $6 \backslash$ State=1$A 1 \backslash H F=-313.2839567 \backslash R M S D=9.909 e-09 \backslash R M S F=6.120 e-05 \backslash D i p o l e=0 ., 0 .,-0.04961$
$25 \backslash \mathrm{PG}=\mathrm{CO} 2 \mathrm{~V}$ [SGV(C2H4),SGV'(C2H2),X(C4H8)]<br>@

## Cr-4-53 cyclooctane (crown) $\quad \boldsymbol{C}_{4 \mathrm{v}}$

$1 \backslash 1 \backslash G I N C-P C \backslash F O p t \backslash R B 3 L Y P \backslash 6-31 G(d) \backslash C 8 H 16 \backslash R A S M U S S E N \backslash 06-O c t-1999 \backslash 0 \backslash \ \# P$ B3L YP/6-31G* 5D OPT FREQ=NORAMAN NAME=RASMUSSEN MAXDISK=2097152000 GEOM=( NODISTANCE, NOANGLE,NODIHEDRAL) SYMM=LOOSE <br>cyclooctane C2v crown <br>0,1\} H, 2.0884183234, 2.0883264804,-0.0906237867\C,-1.3234551482,-1.323485268 $5,-0.2825893268 \backslash \mathrm{H}, 1.2504069793,1.2502280916,-1.3784110848 \backslash \mathrm{H},-1.2504069$ 793,-1.2502280916,-1.3784110848\H,-1.2504069793,1.2502280916,-1.378411 $0848 \backslash \mathrm{H}, 2.0884183234,-2.0883264804,-0.0906237867 \backslash \mathrm{H}, 1.2504069793,-1.2502$ 280916,-1.3784110848\Н, -2.0884183234,-2.0883264804,-0.0906237867\Н,1.7 676852161,0.,1.3785194502\H,-2.0884183234,2.0883264804,-0.0906237867\H , 0.,1.7685619083,1.378246401 \H, 0., -1.7685619083,1.378246401 \H, -1.76768 52161,0.,1.3785194502\C,0.,-1.8717164024,0.2824271181\C,1.8713352941,0 ., 0.2827412411\C,0.,1.8717164024,0.2824271181\C,-1.8713352941,0.,0. 282 $7412411 \backslash \mathrm{H}, 0 .,-2.9534014389,0.0901747759 \backslash \mathrm{H}, 2.953152391,0.0 .091190882 \backslash \mathrm{H}$ , 0., 2. $9534014389,0.0901747759 \backslash H,-2.953152391,0 ., 0.091190882 \backslash \mathrm{C}, 1.323455$ $1482,-1.3234852685,-0.2825893268 \backslash C, 1.3234551482,1.3234852685,-0.282589$ $3268 \backslash C,-1.3234551482,1.3234852685,-0.2825893268 \backslash$ VVersion=SGI-G98RevA. 6 \State=1-A1 \HF=-314.4843963\RMSD=3.045e-09\RMSF=8.625e-06\Dipole=0., 0. ,-0.0000416\PG=C02V [SGV (C2H4), SGV' (C2H4), X(C4H8)] <br>@

## TBTB-4-54 bicyclo[3.3.1]nonane (twistboat-twistboat) $\boldsymbol{C}_{\mathbf{2}}$

$1 \backslash 1 \backslash G I N C-V P P 10 \backslash F O p t \backslash R B 3 L Y P \backslash 6-31 G(d) \backslash C 9 H 16 \backslash R A S M U S S E N \backslash 08-O c t-1999 \backslash 0 \backslash \ \# P$ B3LYP/6-31G* 5D OPT FREQ=NORAMAN NAME=RASMUSSEN MAXDISK=2097152000 GEO M= (CHECK,NODISTANCE,NOANGLE,NODIHEDRAL) GUESS=CHECK <br>bicyclononane C1 \} $\backslash 0,1 \backslash \mathrm{H}, 0.8768876518,-0.053154862,2.0408447162 \backslash \mathrm{H}, 0.0430778491,-2.145987$ $1824,1.0752805844 \backslash \mathrm{H},-0.0418922727,2.1456955782,1.0759174094 \backslash \mathrm{H}, 2.861601$ 6462,-0.1521103805,-1.1259799457\H,-2.862621168, 0.1522883372,-1.123413 $6321 \backslash \mathrm{C}, 0.0009032729,-0.0001996236,1.3827171211 \backslash \mathrm{H}, 1.4811584864,1.788560$ 4887,-1.121196821 \H, 2.6419360284,-0.4394439198, 0.5871970222\H, 0.576698 0715,-0.9814232157,-1.6003066853\H, -0.8740638626, 0.0525519385,2.042192 $0318 \backslash \mathrm{H},-1.4825821779,-1.7884605494,-1.1199359104 \backslash \mathrm{H},-2.6416700948,0.439$ $3551401,0.5896198118 \backslash \mathrm{H},-0.5783752556,0.981967586,-1.5994910733 \backslash \mathrm{C}, 1.519$ 5288226,1.2723784409,-0.1529561227\C,1.0235100027,-1.1987775536,-0.621 $6568424 \backslash \mathrm{C},-1.5197891976,-1.2723102304,-0.1516327461 \backslash \mathrm{C},-1.0241897522,1$. 1989457642,-0.6203033499\H, 2.1940646446,1.8619002606,0.481376497\H,1.4 83472232,-2.1899789437,-0.7203607064 \H,-2.1937064084,-1.8617879768, 0.4 $834021209 \backslash \mathrm{H},-1.4842986675,2.1901557766,-0.7182181314 \backslash \mathrm{C}, 2.1088782473,-0$ $.1498433874,-0.3279601018 \backslash C,-0.096590148,-1.2409592991,0.4715215456 \backslash \mathrm{C}$, $-2.1092820714,0.1499132972,-0.3259704864 \backslash \mathrm{C}, 0.09708304,1.2408312459,0.4$ $717531012 \backslash \backslash V e r s i o n=F u j i t s u-V P-U n i x-G 98 R e v A .6 \backslash H F=-352.5878101 \backslash$ RMSD $=3.32$ $2 \mathrm{e}-09 \backslash \mathrm{RMSF}=9.878 \mathrm{e}-06 \backslash \mathrm{Dipole}=0.0000056,-0.000002,0.0274632 \backslash \mathrm{PG}=\mathrm{C01} \quad[\mathrm{X}(\mathrm{C} 9$ H16)] <br>@

## Bridged Spiropentanes

## 4-26 [3.3.3]fenestrane $\quad \boldsymbol{C}_{\mathbf{1}}$

$1 \backslash 1 \backslash$ GINC-RSCQC9 ${ }^{\text {FOpt } \backslash \text { RB3LYP } \backslash 6-31 G(d) \backslash C 5 H 6 \backslash R A S M U S S E N \backslash 30-M a r-2000 \backslash 0 \backslash \ \# P ~}$ B3LYP/6-31G(D) 5D OPT FREQ=NORAMAN NAME=RASMUSSEN MAXDISK=917504000<br>[ 3.3.3]fenestrane $\mathrm{C} 1 \backslash \backslash 0,1 \backslash \mathrm{H}, 1.7155044296,-0.894308902,-1.3579264922 \backslash \mathrm{C}, 1$ $.413980406,-0.2822587271,-0.5056957528 \backslash C, 0.0470214629,0.2987284717,-0$.
$4977452693 \backslash \mathrm{C}, 0.3551976636,-0.863241701,0.4236230129 \backslash \mathrm{H}, 2.2281486969,0.3$ $179016956,-0.0921915928 \backslash C,-1.4053300422,0.5063086667,-0.2431402078 \backslash C,-$ $0.3778456243,0.3612667108,0.8938621089 \backslash \mathrm{H},-0.1105675828,-1.8292368228,0$ $.2367567861 \backslash \mathrm{H},-0.100330403,1.0934251864,1.6484110167 \backslash \mathrm{H},-1.8184700799$, 1 $.4967410698,-0.4456478812 \backslash \mathrm{H},-2.112428257,-0.3093427532,-0.4148251878 \backslash \backslash$ Version=IBM-RS6000-G98RevA. $6 \backslash \mathrm{HF}=-193.9541773 \backslash \mathrm{RMSD}=8.441 \mathrm{e}-09 \backslash \mathrm{RMSF}=1.158$ e-05\Dipole $=-0.0007864,0.0807396,-0.2485692 \backslash \mathrm{PG}=\mathrm{CO} \quad[\mathrm{X}(\mathrm{C} 5 \mathrm{H} 6)] \backslash \backslash @$

## 4-25 [3.4.3]fenestrane $\boldsymbol{C}_{\mathbf{2}}$

$1 \backslash 1 \backslash G I N C-P C \backslash F O p t \backslash R B 3 L Y P \backslash 6-31 G(d) \backslash C 6 H 8 \backslash R A S M U S S E N \backslash 30-M a r-2000 \backslash 0 \backslash \backslash \# P$ B3LY P/6-31G(D) 5D OPT FREQ=NORAMAN NAME=RASMUSSEN MAXDISK=2097152000<br>[3.4 .3]fenestrane $\mathrm{C} 2 \backslash \backslash 0,1 \backslash \mathrm{C}, 0.0 .,-0.7279955703 \backslash \mathrm{C}, 0 ., 0 ., 1.4374075063 \backslash \mathrm{C}, 1.4$ $701936672,-0.0025618829,-0.7603538466 \backslash \mathrm{C},-1.4701936672,0.0025618829,-0$. $7603538466 \backslash C,-0.7405858867,0.7883524604,0.3414588882 \backslash C, 0.7405858867,-0$ $.7883524604,0.3414588882 \backslash \mathrm{H},-0.8416709049,1.8727093846,0.3349187987 \backslash \mathrm{H}, 0$ $.8416709049,-1.8727093846,0.3349187987 \backslash H, 1.9721262441,-0.6520799873$, -1 $.4771873888 \backslash \mathrm{H},-2.0103867221,-0.922342714,-0.5538627905 \backslash \mathrm{H}, 2.0103867221$, $0.922342714,-0.5538627905 \backslash \mathrm{H},-1.9721262441,0.6520799873,-1.4771873888 \backslash \mathrm{H}$ , 0.6259398472, 0.6309627659, 2.0812653226\H,-0.6259398472,-0.6309627659, $2.0812653226 \backslash \backslash$ Version=SGI-G98RevA. $6 \backslash$ State $=1-A \backslash H F=-233.3017787 \backslash R M S D=1.8$ $03 \mathrm{e}-09 \backslash \mathrm{RMSF}=4.819 \mathrm{e}-05 \backslash \mathrm{Dipole}=0 ., 0 .,-0.03346 \backslash \mathrm{PG}=\mathrm{C0} 2 \quad[\mathrm{C} 2(\mathrm{C} 1 \mathrm{C} 1), \mathrm{X}(\mathrm{C} 4 \mathrm{H} 8)] \backslash$ \@

## 4-45 [3.5.3]fenestrane $\quad \boldsymbol{C}_{\mathbf{2}}$

$1 \backslash 1 \backslash G I N C-P C \backslash F O p t \backslash R B 3 L Y P \backslash 6-31 G(d) \backslash C 7 H 10 \backslash R A S M U S S E N \backslash 30-M a r-2000 \backslash 0 \backslash \backslash \# P$ B3L YP/6-31G(D) 5D OPT FREQ=NORAMAN NAME=RASMUSSEN MAXDISK=2097152000<br>[3. 5.3]fenestrane 7a C2 <br>0,1\C,0.,0.,0.857146396\C,1.4554473352,-0.015494 $6651,1.1326315593 \backslash C,-1.4554473352,0.0154946651,1.1326315593 \backslash C,-0.86898$ 2542,-0.8549667909,0.0060619834 \C, 0.868982542, 0.8549667909, 0.006061983 $4 \backslash \mathrm{C},-0.7077623042,-0.3299775959,-1.4326075004 \backslash \mathrm{C}, 0.7077623042,0.3299775$ 959,-1.4326075004 \H, -0.9130057032,-1.9322652154, 0.1602395947\H, 0.91300 57032,1.9322652154,0.1602395947\H,1.8389782186,0.5161015336,2.00309319 $7 \backslash H,-2.023646102,0.9085584863,0.8740842881 \backslash H, 2.023646102,-0.9085584863$ , 0.8740842881 \H,-1.8389782186,-0.5161015336,2.003093197\H,-1.474072558 9,0.422144407,-1.6647360715\H,1.4740725589,-0.422144407,-1.6647360715\} H, -0.8067477085,-1.1253120927,-2.18063645\H, 0.8067477085,1.1253120927, $-2.18063645 \backslash \backslash$ Version=SGI-G98RevA. $6 \backslash$ State $=1-A \backslash H F=-272.6675955 \backslash$ RMSD $=9.78$ $3 \mathrm{e}-09 \backslash \mathrm{RMSF}=4.360 \mathrm{e}-05 \backslash \mathrm{Dipole=0.,0.,-0.055789} \mathrm{\backslash PG=CO2} \mathrm{\quad[C2(C1),X(C6H10)]} \mathrm{\backslash} \mathrm{\backslash}$ @

## 4-46 tetracyclo-[3.3.1.0 $\left.0^{2,4} .0^{2,8}\right]$ nonane $\quad C_{1}$

$1 \backslash 1 \backslash G I N C-P C \backslash F O p t \backslash R B 3 L Y P \backslash 6-31 G(d) \backslash C 9 H 12 \backslash R A S M U S S E N \backslash 14-S e p-1999 \backslash 0 \backslash \backslash \# P$ B3L YP/6-31G(D) 5D OPT NAME=RASMUSSEN<br>Baird Molecule C1<br>0,1\C,0.10739050 $6,-1.3144655154,0.4503640932 \backslash C, 1.2940038302,-0.3765449898,0.6825188491$ $\backslash C, 1.7432849521,0.4642304891,-0.5218020706 \backslash \mathrm{H}, 0.1040960741,-2.240999018$ $6,1.0230367412 \backslash \mathrm{H}, 2.0898789716,-0.7356923189,1.3361364523 \backslash \mathrm{H},-0.28989933$ $41,-1.7539536877,-1.6995109139 \backslash C,-0.8782421908,0.9117375495,0.34447147$ $01 \backslash \mathrm{C},-0.0662275896,-0.026525218,1.1889766014 \backslash \mathrm{H},-1.4267838354,1.2549871$ 902,2.4615996434\H,2.161011246,1.4108836633,-0.1563388579\H, 2.56868670 33,-0.0582390421,-1.021150774 \H,-2.1462528863,-0.2997173638,1.83847633 $41 \backslash \mathrm{C}, 0.596371828,0.7501791548,-1.5560072939 \backslash \mathrm{H},-0.5572989336,1.95521937$ 58,0.3668276128\C,-1.3720572709,0.4573490881,1.7212037435\C,-0.8077044
$573,0.2864184103,-1.0540744438 \backslash \mathrm{H}, 0.5661091179,1.8230613963,-1.78010578$ $81 \backslash \mathrm{H}, 0.8116572209,0.2408042778,-2.5034717885 \backslash \mathrm{H},-1.7053501233,-1.673815$ $2233,-0.6429192275 \backslash \mathrm{C},-0.7156634219,-1.235267874,-0.8303216902 \backslash \mathrm{H},-1.582$ 791337,0.5747941829,-1.7745549869<br>Version=SGI-G98RevA. $6 \backslash H F=-350.06395$ $25 \backslash \mathrm{RMSD}=3.624 \mathrm{e}-09 \backslash \mathrm{RMSF}=1.728 \mathrm{e}-05 \backslash \mathrm{Dipole}=0.0539787,-0.0007308,-0.093120$ $5 \backslash \mathrm{PG}=\mathrm{CO1}[\mathrm{X}(\mathrm{C} 9 \mathrm{H} 12)] \backslash \backslash @$

## Fenestranes

## $\boldsymbol{C}_{\mathrm{s}}$-4-18 trans,cis,cis,cis-[4.4.4.4]fenestrane $\quad \boldsymbol{C}_{\mathrm{s}}$

$1 \backslash 1 \backslash G I N C-P C \backslash F O p t \backslash R B 3 L Y P \backslash 6-31 G(d) \backslash C 9 H 12 \backslash R A S M U S S E N \backslash 04-J u l-1999 \backslash 0 \backslash \backslash \# P$ B3L YP/6-31G(D) 5D OPT FREQ=NORAMAN NAME=RASMUSSEN MAXDISK=2097152000<br>[4. 4.4.4]fenestrane $C s 5 D \backslash \backslash 0,1 \backslash C,-0.5681578553,0 .,-0.0681393291 \backslash C,-0.5654$ $036774,0 ., 1.3878691367 \backslash \mathrm{C}, 0.8836611905,0 .,-0.7063187439 \backslash \mathrm{C},-0.0638546012$ , 1. 5154202235,1.2653051144\C, -0.0638546012,-1.5154202235,1.2653051144\ C, - 0. $5411441499,-1.5532835345,-0.2808158809 \backslash C,-0.5411441499,1.55328353$ $45,-0.2808158809 \backslash C, 0.6066068233,-1.4056409214,-1.3100478438 \backslash C, 0.606606$ $8233,1.4056409214,-1.3100478438 \backslash \mathrm{H},-1.5677532121,0 ., 1.8347708843 \backslash \mathrm{H}, 1.73$ $4277867,0 .,-0.0196334474 \backslash \mathrm{H},-0.605956383,2.2074366305,1.9165817497 \backslash \mathrm{H},-0$ $.605956383,-2.2074366305,1.9165817497 \backslash \mathrm{H}, 1.0087598817,1.6910882496,1.38$ $16659239 \backslash \mathrm{H}, 1.0087598817,-1.6910882496,1.3816659239 \backslash \mathrm{H},-1.3917495605,-2$. $2140100419,-0.482742189 \backslash \mathrm{H},-1.3917495605,2.2140100419,-0.482742189 \backslash \mathrm{H}, 0$. $2174837913,-1.3662421431,-2.3346949691 \backslash H, 0.2174837913,1.3662421431,-2$. $3346949691 \backslash \mathrm{H}, 1.4282525364,-2.1316961588,-1.2752607635 \backslash \mathrm{H}, 1.4282525364,2$ $.1316961588,-1.2752607635 \backslash \backslash V e r s i o n=S G I-G 98 R e v A .6 \backslash$ State=1-A' $\backslash H F=-349.97$ $17593 \backslash \mathrm{RMSD}=7.492 \mathrm{e}-09 \backslash \mathrm{RMSF}=6.328 \mathrm{e}-05 \backslash \mathrm{Dipole}=0.0452043,0 ., 0.0089296 \backslash \mathrm{PG}=\mathrm{C}$ S [SG(C3H2),X(C6H10)]<br>@

## $D_{\text {2d }}$-4-18 all-cis-[4.4.4.4]fenestrane $\quad D_{2 d}$

$1 \backslash 1 \backslash G I N C-P C \backslash F O p t \backslash R B 3 L Y P \backslash 6-31 G(d) \backslash C 9 H 12 \backslash R A S M U S S E N \backslash 04-J u l-1999 \backslash 0 \backslash \backslash \# P$ B3L YP/6-31G(D) 5D OPT FREQ=NORAMAN NAME=RASMUSSEN MAXDISK=2097152000<br>[4. 4.4.4]fenestrane $\mathrm{D} 2 \mathrm{~d} 5 \mathrm{D} \backslash \backslash 0,1 \backslash \mathrm{C}, 0 ., 0 ., 0 . \backslash \mathrm{C}, 0 .,-1.3568486208,0.624984505$ $9 \backslash C, 0 ., 1.3568486208,0.6249845059 \backslash C, 1.3568486208,0 .,-0.6249845059 \backslash C,-1$. $3568486208,0 .,-0.6249845059 \backslash C,-1.4758170859,-1.4758170859,0 . \backslash C, 1.47581$ $70859,-1.4758170859,0 . \backslash C, 1.4758170859,1.4758170859,0 . \backslash C,-1.4758170859$, $1.4758170859,0 . \backslash \mathrm{H}, 0 .,-1.4614401443,1.7132433357 \backslash \mathrm{H}, 0 ., 1.4614401443,1.71$ $32433357 \backslash \mathrm{H}, 1.4614401443,0 .,-1.7132433357 \backslash \mathrm{H},-1.4614401443,0 .,-1.7132433$ $357 \backslash \mathrm{H},-2.222053265,-1.6394971005,0.7855659151 \backslash \mathrm{H},-1.6394971005,-2.22205$ $3265,-0.7855659151 \backslash \mathrm{H}, 2.222053265,-1.6394971005,0.7855659151 \backslash \mathrm{H}, 1.639497$ 1005,-2.222053265,-0.7855659151 \H, 2. $222053265,1.6394971005,0.785565915$ $1 \backslash \mathrm{H}, 1.6394971005,2.222053265,-0.7855659151 \backslash \mathrm{H},-2.222053265,1.6394971005$ , 0.7855659151 \H,-1.6394971005,2.222053265,-0.7855659151 <br>Version=SGI-G 98RevA. $6 \backslash$ State $=1-\mathrm{A} 1 \backslash \mathrm{HF}=-349.9597123 \backslash \mathrm{RMSD}=1.437 \mathrm{e}-09 \backslash \mathrm{RMSF}=1.499 \mathrm{e}-04 \backslash \mathrm{Dipo}$ le=0., 0., 0. \PG=D02D [O(C1), 2SGD (C2H2), X(C4H8)]<br>@

## $\boldsymbol{C}_{\mathbf{2 v}}$-4-18 all-trans-[4.4.4.4]fenestrane $\quad \boldsymbol{C}_{\mathbf{2 v}}$

$1 \backslash 1 \backslash G I N C-R S C Q C 9 \backslash F O p t \backslash R B 3 L Y P \backslash 6-31 G(d) \backslash C 9 H 12 \backslash R A S M U S S E N \backslash 04-J u l-1999 \backslash 0 \backslash \backslash \# P$ B3LYP/6-31G(D) 5D OPT FREQ=NORAMAN NAME=RASMUSSEN MAXDISK=524288000<br> [4.4.4.4]fenestrane $\mathrm{C} 2 \mathrm{~V} 5 \mathrm{D} \backslash \backslash 0,1 \backslash \mathrm{C}, 0.0 .0 .0 .7599170491 \backslash \mathrm{C}, 0 .,-1.746008543$ $9,0.4657803821 \backslash C, 0 ., 1.7460085439,0.4657803821 \backslash C, 1.3242654338,0 ., 0.1028$ $461973 \backslash C,-1.3242654338,0 ., 0.1028461973 \backslash C,-1.2730417945,-1.4810377617$, $0.3869901487 \backslash C, 1.2730417945,-1.4810377617,-0.3869901487 \backslash C, 1.2730417945$
, 1.4810377617,-0.3869901487\C,-1.2730417945,1.4810377617,-0.3869901487 $\backslash \mathrm{H}, 0 .,-2.5884869101,1.1611746009 \backslash \mathrm{H}, 0 ., 2.5884869101,1.1611746009 \backslash \mathrm{H}, 2.04$ $89203256,0 ., 0.9279846519 \backslash \mathrm{H},-2.0489203256,0.0 .9279846519 \backslash \mathrm{H},-1.08939216$ $47,-1.6230074485,-1.4567759811 \backslash \mathrm{H},-2.1555526417,-2.067259546,-0.1116180$ $651 \backslash \mathrm{H}, 1.0893921647,-1.6230074485,-1.4567759811 \backslash \mathrm{H}, 2.1555526417,-2.06725$ $9546,-0.1116180651 \backslash \mathrm{H}, 1.0893921647,1.6230074485,-1.4567759811 \backslash \mathrm{H}, 2.15555$ 26417,2.067259546,-0.1116180651 \H, -1.0893921647,1.6230074485,-1.456775 $9811 \backslash \mathrm{H},-2.1555526417,2.067259546,-0.1116180651 \backslash$ Version=IBM-RS6000-G98 RevA. $6 \backslash$ State $=1-\mathrm{Al} \backslash \mathrm{HF}=-349.9431204 \backslash \mathrm{RMSD}=2.558 \mathrm{e}-09 \backslash \mathrm{RMSF}=1.233 \mathrm{e}-05 \backslash \mathrm{Dipole}$ =0., 0., - 0.1935512 \PG=C02V [C2 (C1), SGV (C2H2) ,SGV' (C2H2) , X (C4H8)] <br>@

## $\boldsymbol{C}_{\mathbf{2}} \mathbf{- 4 - 1 8} \quad$ trans,cis,trans,cis-[4.4.4.4]fenestrane $\boldsymbol{C}_{\mathbf{2}}$

$1 \backslash 1 \backslash G I N C-P C \backslash F O p t \backslash R B 3 L Y P \backslash 6-31 G(d) \backslash C 9 H 12 \backslash R A S M U S S E N \backslash 06-J u l-1999 \backslash 0 \backslash \backslash \# P B 3 L$ YP/6-31G(D) 5D OPT FREQ=NORAMAN NAME=RASMUSSEN MAXDISK=2097152000<br>[4. 4.4.4]fenestrane 5D C2 <br>0,1\C,-0.1447160884,0., 0. \C, -1.0946533441,-1.0 $610542736,-0.3345749939 \backslash C, 0.9926638998,-1.0455348906,0.3034968361 \backslash C,-1$ $.0946533441,1.0610542736,0.3345749939 \backslash C, 0.9926638998,1.0455348906,-0.3$ $034968361 \backslash C, 0.2191444657,-1.8545630759,-0.8820722624 \backslash C, 0.2191444657,1$. $8545630759,0.8820722624 \backslash \mathrm{C}, 2.100984575,0 ., 0 . \backslash \mathrm{C},-2.3395335127,0 ., 0 . \backslash \mathrm{H},-1$ $.1699386895,-1.5952516116,0.6242932189 \backslash \mathrm{H}, 1.0556948781,-1.6415660043,1$. $2227558165 \backslash \mathrm{H},-1.1699386895,1.5952516116,-0.6242932189 \backslash \mathrm{H}, 1.0556948781,1$ $.6415660043,-1.2227558165 \backslash \mathrm{H}, 0.5563063815,-1.5309006632,-1.8700921728 \backslash \mathrm{H}$ , 0.2246741238, -2.9481615374, -0.8159180892 \H, 0.5563063815, 1.5309006632, $1.8700921728 \backslash \mathrm{H}, 0.2246741238,2.9481615374,0.8159180892 \backslash \mathrm{H}, 2.7452350758$, 0 $.2184919514,0.8594531074 \backslash \mathrm{H}, 2.7452350758,-0.2184919514,-0.8594531074 \backslash \mathrm{H}$, $-2.9651068203,-0.4244482707,0.7868346512 \backslash \mathrm{H},-2.9651068203,0.4244482707$, $-0.7868346512 \backslash \backslash V e r s i o n=S G I-G 98 R e v A .6 \backslash$ State=1-A\HF=-349.8269479\RMSD=9. 257e-09 $\mathrm{RMSF}=1.506 \mathrm{e}-05 \backslash \mathrm{Dipole}=0.2401515,0 ., 0 . \backslash \mathrm{PG}=\mathrm{C} 02 \quad[\mathrm{C} 2(\mathrm{C} 1 \mathrm{C} 1 \mathrm{C} 1), \mathrm{X}(\mathrm{C} 6 \mathrm{H}$ 12) ] <br>@

## all-cis-4-19 [5.5.5.5]fenestrane $\boldsymbol{D}_{\mathbf{2}}$

$1 \backslash 1 \backslash G I N C-P C \backslash F O p t \backslash R B 3 L Y P \backslash 6-31 G(d) \backslash C 13 H 20 \backslash R A S M U S S E N \backslash 05-J u l-1999 \backslash 0 \backslash \backslash \# P$ B3 LYP/6-31G(D) 5D OPT FREQ=NORAMAN NAME=RASMUSSEN MAXDISK=2097152000<br>al l-cis-[5.5.5.5]fenestrane D2 5D $\backslash \backslash 0,1 \backslash C, 0 ., 0 ., 0 . \backslash C, 0.9395918309,-0.9427$ 098837,-0.824631176\C,0.9395918309, 0.9427098837, 0.824631176\C, -0.93959 18309,0.9427098837,-0.824631176\C,-0.9395918309,-0.9427098837,0.824631 $176 \backslash C, 2.3409504058,-0.7388749567,-0.2083875909 \backslash C, 2.3409504058,0.738874$ 9567, 0.2083875909\C, 0.3456357942,2.3589213613, 0.6889653624\C, -0.345635 $7942,2.3589213613,-0.6889653624 \backslash C,-2.3409504058,0.7388749567,-0.208387$ $5909 \backslash \mathrm{C},-2.3409504058,-0.7388749567,0.2083875909 \backslash \mathrm{C},-0.3456357942,-2.358$ 9213613,0.6889653624\C,0.3456357942,-2.3589213613,-0.6889653624 \H, 0.97 54612777,-0.6303082757,-1.8767561162 \H, 0.9754612777,0.6303082757,1.876 7561162 \H, -0.9754612777,0.6303082757,-1.8767561162 \H,-0.9754612777,-0. 6303082757,1.8767561162\H,2.460728686,-1.3740137615,0.681011353\H,3.14 99307006,-0.9993344114,-0.9012219747\Н, -1.09975659, 3.1491992442,-0.787 $4805062 \backslash \mathrm{H}, 0.3978185175,2.5291263447,-1.4787660462 \backslash \mathrm{H},-2.460728686,1.374$ $0137615,0.681011353 \backslash \mathrm{H},-3.1499307006,0.9993344114,-0.9012219747 \backslash \mathrm{H}, 1.099$ 75659,-3.1491992442,-0.7874805062\H,-0.3978185175,-2.5291263447,-1.478 $7660462 \backslash \mathrm{H}, 3.1499307006,0.9993344114,0.9012219747 \backslash \mathrm{H}, 2.460728686,1.37401$ 37615,-0.681011353\H,-0.3978185175,2.5291263447,1.4787660462\Н, 1.09975 659,3.1491992442,0.7874805062\H,-3.1499307006,-0.9993344114,0.90122197 $47 \backslash \mathrm{H},-2.460728686,-1.3740137615,-0.681011353 \backslash$ Н, $0.3978185175,-2.5291263$
$447,1.4787660462 \backslash \mathrm{H},-1.09975659,-3.1491992442,0.7874805062 \backslash \backslash \mathrm{Version=SGI}$ -G98RevA. $6 \backslash$ State $=1-A \backslash H F=-507.4366706 \backslash R M S D=3.960 e-09 \backslash R M S F=2.573 e-05 \backslash D i p$ ole=0., 0., 0. \PG=D02 [O(C1), X (C12H20)] <br>@

## all-trans-4-19 [5.5.5.5]fenestrane $\quad \boldsymbol{D}_{\mathbf{2 d}}$

$1 \backslash 1 \backslash G I N C-R S C Q C 2 \backslash F O p t \backslash R B 3 L Y P \backslash 6-31 G(d) \backslash C 13 H 20 \backslash R A S M U S S E N \backslash 04-J u l-1999 \backslash 0 \backslash \backslash \#$ P B3LYP/6-31G(D) 5D OPT FREQ=NORAMAN NAME=RASMUSSEN MAXDISK=262144000 \} \all-trans-[5.5.5.5]fenestrane 5D D2<br>0,1\C,0.,0.,0.\C,1.1576196388,-1 $.1576196388,0.2169180385 \backslash C, 1.1576196388,1.1576196388,-0.2169180385 \backslash C$, $1.1576196388,1.1576196388,0.2169180385 \backslash C,-1.1576196388,-1.1576196388$, $0.2169180385 \backslash C, 2.5443882851,-0.5980848379,0.5018468849 \backslash C, 2.5443882851$, $0.5980848379,-0.5018468849 \backslash C, 0.5980848379,2.5443882851,-0.5018468849 \backslash C$ , - 0. $5980848379,2.5443882851,0.5018468849 \backslash C,-2.5443882851,0.5980848379$, $0.5018468849 \backslash C,-2.5443882851,-0.5980848379,-0.5018468849 \backslash C,-0.59808483$ $79,-2.5443882851,-0.5018468849 \backslash \mathrm{C}, 0.5980848379,-2.5443882851,0.50184688$ $49 \backslash \mathrm{H}, 1.255839825,-1.255839825,-0.8833881686 \backslash \mathrm{H}, 1.255839825,1.255839825$, $0.8833881686 \backslash \mathrm{H},-1.255839825,1.255839825,-0.8833881686 \backslash \mathrm{H},-1.255839825$, $1.255839825,0.8833881686 \backslash \mathrm{H}, 2.6846604515,-0.2346018541,1.5291527537 \backslash \mathrm{H}, 3$ $.3285285365,-1.3355090838,0.2919756652 \backslash H,-0.2346018541,2.6846604515,1$. $5291527537 \backslash \mathrm{H},-1.3355090838,3.3285285365,0.2919756652 \backslash \mathrm{H},-2.6846604515,0$ $.2346018541,1.5291527537 \backslash \mathrm{H},-3.3285285365,1.3355090838,0.2919756652 \backslash \mathrm{H}, 0$ $.2346018541,-2.6846604515,1.5291527537 \backslash \mathrm{H}, 1.3355090838,-3.3285285365,0$. $2919756652 \backslash \mathrm{H}, 3.3285285365,1.3355090838,-0.2919756652 \backslash \mathrm{H}, 2.6846604515,0$. $2346018541,-1.5291527537 \backslash \mathrm{H}, 1.3355090838,3.3285285365,-0.2919756652 \backslash \mathrm{H}, 0$ $.2346018541,2.6846604515,-1.5291527537 \backslash \mathrm{H},-3.3285285365,-1.3355090838$, $0.2919756652 \backslash \mathrm{H},-2.6846604515,-0.2346018541,-1.5291527537 \backslash \mathrm{H},-1.33550908$ $38,-3.3285285365,-0.2919756652 \backslash \mathrm{H},-0.2346018541,-2.6846604515,-1.529152$ $7537 \backslash \backslash$ Version=IBM-RS6000-G98RevA. $6 \backslash$ State=1-A1 \HF=-507.2138535\RMSD=5.6 05e-09 \RMSF=2.189e-05\Dipole=0.,0.,0. \PG=D02D [O (C1) , 2SGD (C2H2) , X (C8H1 6)] <br>@

Table C-26. Guassian archive files for the MP2(fc)/6-31G(d) optimized neutral species in Chapter 4 other than the alkaplanes.

## Small Molecules

## ${ }^{3} \mathrm{CH}_{2} \quad C_{2 v}$

$1 \backslash 1 \backslash G I N C-P C \backslash F O p t \backslash U M P 2-F C \backslash 6-31 G(d) \backslash C 1 H 2(3) \backslash R A S M U S S E N \backslash 28-M a r-2000 \backslash 0 \backslash \backslash \# P$ UMP2/6-31G(D) 5D OPT=(TIGHT) FREQ=NORAMAN NAME=RASMUSSEN MAXDISK=20971 $52000 \backslash \backslash$ methylene $C 2 v$ triplet $\backslash \backslash 0,3 \backslash H,-0.3775920627,0 .,-0.9661290965 \backslash \mathrm{C}$, $0.0846730266,0 ., 0.0710152962 \backslash \mathrm{H}, 0.8856302223,0 ., 0.5400373193 \backslash \backslash$ Version $=$ S GI-G98RevA. $6 \backslash$ State $=3-B 1 \backslash H F=-38.9212236 \backslash M P 2=-39.002256 \backslash P U H F=-38.9239086$ $\backslash P M P 2-0=-39.0040584 \backslash S 2=2.015396 \backslash \mathrm{~S} 2-1=2.005244 \backslash \mathrm{~S} 2 \mathrm{~A}=2.000071 \backslash \mathrm{RMSD}=8.760 \mathrm{e}$ $-09 \backslash \mathrm{RMSF}=4.495 \mathrm{e}-06 \backslash \mathrm{Dipole}=0.190502,0 .,-0.1597741 \backslash \mathrm{PG}=\mathrm{C} 02 \mathrm{~V} \quad[\mathrm{C} 2(\mathrm{C} 1)$, $\mathrm{SGV}(\mathrm{H}$ 2) ] <br>@

## $\mathrm{CH}_{4} \quad \boldsymbol{T}_{\mathrm{d}}$

$1 \backslash 1 \backslash G I N C-R S C Q C 8 \backslash F r e q \backslash R M P 2-F C \backslash 6-31 G(d) \backslash C 1 H 4 \backslash R A S M U S S E N \backslash 24-F e b-1999 \backslash 0 \backslash \backslash \# P$ RMP2/6-31G* 5D OPT= (CALCALL, VERYTIGHT) NAME=RASMUSSEN MAXDISK=1048576 $000 \backslash \backslash$ Methane Td singlet $\backslash$ \0, 1 \C, 0., 0., 0. $\backslash \mathrm{H}, 0 ., 0 ., 1.090277068 \backslash \mathrm{H}, 1.027923$ $0776,0 .,-0.3634256893 \backslash H,-0.5139615388,0.8902074983,-0.3634256894 \backslash H,-0$.

5139615388,-0.8902074983,-0.3634256894 <br>Version=IBM-RS6000-G94RevE.1 \H $\mathrm{F}=-40.1947226 \backslash \mathrm{MP} 2=-40.3312554 \backslash \mathrm{RMSD}=4.004 \mathrm{e}-09 \backslash \mathrm{RMSF}=3.700 e-07 \backslash \mathrm{Dipole}=0 .$, $0 ., 0 . \backslash$ DipoleDeriv=-0.0271221,0.,0., 0., -0.0271221,0., 0., 0., -0.0271221, 0 $.0743528,0 ., 0 ., 0 ., 0.0743528,0 ., 0 ., 0 .,-0.1283641,-0.10584,0 ., 0.0637078$, $0 ., 0.0743528,0 ., 0.0637078,0 ., 0.0518287,0.0293046,0.0780258,-0.0318539$, $0.0780258,-0.0607918,0.0551725,-0.0318539,0.0551725,0.0518287,0.029304$ 6,-0.0780258,-0.0318539,-0.0780258,-0.0607918,-0.0551725,-0.0318539,-0 $.0551725,0.0518287 \backslash$ Polar=12.1475929,0.,12.1475929,0., 0.,12.1475929\PG= $\mathrm{TD}[\mathrm{O}(\mathrm{C} 1), 4 \mathrm{C} 3(\mathrm{H} 1)] \backslash \mathrm{NImag}=0 \backslash \backslash 0.59213776,0.0 .59213776,0.0 ., 0.59213776$, $-0.05164684,0 ., 0 ., 0.04907422,0 .,-0.05164684,0 ., 0 ., 0.04907422,0 ., 0 .,-0$. $34080963,0 ., 0 ., 0.36583143,-0.30868043,0.0 .09087510,0.00304727,0 .,-0.0$ $0188482,0.33063619,0 \ldots,-0.05164684,0 \ldots, 0 \ldots-0.00133219,0 \ldots, 0 ., 0.04907422,0$ $.09087510,0 .,-0.08377604,0.03409458,0 .,-0.00834060,-0.09954719,0 ., 0.08$ $426946,-0.11590524,0.11129881,-0.04543755,-0.00023732,-0.00189636,0.00$ $094241,-0.01250151,0.02720599,-0.01271125,0.11946471,0.11129881,-0.244$ $42204,0.07870014,-0.00189636,0.00195241,-0.00163230,-0.00217107,0.0019$ $5241,-0.00124381,-0.12191991,0.26024570,-0.04543755,0.07870014,-0.0837$ $7604,-0.01704729,0.02952678,-0.00834060,0.00527846,-0.01163017,0.00392$ $359,0.04977359,-0.08621039,0.08426946,-0.11590524,-0.11129881,-0.04543$ $755,-0.00023732,0.00189636,0.00094241,-0.01250151,-0.02720599,-0.01271$ 125, 0.00917937,0.01468853,0.00743279,0.11946471, -0.11129881, -0. 2444220 $4,-0.07870014,0.00189636,0.00195241,0.00163230,0.00217107,0.00195241,0$ $.00124381,-0.01468853,-0.01972847,-0.01038636,0.12191991,0.26024570,-0$ $.04543755,-0.07870014,-0.08377604,-0.01704729,-0.02952678,-0.00834060$, $0.00527846,0.01163017,0.00392359,0.00743279,0.01038636,0.00392359,0.04$ $977359,0.08621039,0.08426946 \backslash \backslash 0 ., 0 ., 0 ., 0 ., 0 .,-0.00000072,-0.00000068,0$ ., 0.00000024, 0.00000034, $-0.00000058,0.00000024,0.00000034,0.00000058,0$ $.00000024 \backslash \backslash \backslash @$

## $\mathrm{NH}_{3} \quad \mathrm{C}_{3 \mathrm{v}}$

$1 \backslash 1 \backslash G I N C-R S C Q C 8 \backslash F r e q \backslash R M P 2-F C \backslash 6-31 G(d) \backslash H 3 N 1 \backslash R A S M U S S E N \backslash 24-F e b-1999 \backslash 0 \backslash \backslash \# P$ MP2/6-31G* 5D NAME=RASMUSSEN OPT= (CALCALL,VERYTIGHT) MAXDISK=10485760 $00 \backslash \backslash$ ammonia $\mathrm{C} 3 \mathrm{v} \backslash \backslash 0,1 \backslash \mathrm{H}, 0.0 .270532406,0.9406828486 \backslash \mathrm{H}, 0.8146552438,0.27$ $0532406,-0.4703414243 \backslash H,-0.8146552438,0.270532406,-0.4703414243 \backslash N, 0 .,-$ $0.1159424597,0 . \backslash \backslash V e r s i o n=I B M-R S 6000-G 94 R e v E .1 \backslash$ State=1-A1 $\backslash H F=-56.183190$ $8 \backslash \mathrm{MP} 2=-56.3519903 \backslash \mathrm{RMSD}=5.201 \mathrm{e}-09 \backslash \mathrm{RMSF}=1.249 \mathrm{e}-07 \backslash \mathrm{Dipole}=0 ., 0.7693324,0$. \DipoleDeriv=0.1836276,0.,0.,0.,0.2175475,-0.1814189, 0., -0.0909631,0.0 $770651,0.1037057,-0.0787764,0.0461429,-0.1571134,0.2175475,0.0907094,0$ $.0461429,0.0454816,0.1569869,0.1037057,0.0787764,-0.0461429,0.1571134$, $0.2175475,0.0907094,-0.0461429,0.0454816,0.1569869,-0.391039,0 ., 0 ., 0 .$, $-0.6526424,0 ., 0 ., 0 .,-0.391039 \backslash \operatorname{Pol} \operatorname{lor}=9.2290106,0 ., 5.4594397,0 ., 0 ., 9.229$ $0106 \backslash \mathrm{PG}=\mathrm{C} 03 \mathrm{~V}[\mathrm{C} 3(\mathrm{~N} 1), 3 \mathrm{SGV}(\mathrm{H} 1)] \backslash \mathrm{NImag}=0 \backslash \backslash 0.06457547,0 ., 0.07675906,0 ., 0$. $14309137,0.41232358,0.00120960,-0.00258731,-0.00466775,0.32538655,0.01$ $589128,0.00166553,-0.01216240,0.12392076,0.07675906,0.03658431,0.01984$ $345,-0.01721743,-0.15057935,-0.07154569,0.15151250,0.00120960,0.002587$ $31,0.00466775,-0.02643094,0.01847859,-0.02062603,0.32538655,-0.0158912$ $8,0.00166553,-0.01216240,-0.01847859,0.00166553,-0.00768105,-0.1239207$ $6,0.07675906,-0.03658431,0.01984345,-0.01721743,0.02062603,-0.00768105$ $, 0.01042312,0.15057935,-0.07154569,0.15151250,-0.06699468,0 ., 0 .,-0.300$ 16522,-0.15829063, 0.13462107,-0.30016522,0.15829063,-0.13462107,0.6673 2511, 0., - $0.08009013,-0.11876657,-0.10285486,-0.08009013,0.05938328,0.1$ $0285486,-0.08009013,0.05938328,0 ., 0.24027038,0 \ldots,-0.18277827,-0.3778887$

3, 0.13462107,0.09138914,-0.14471819,-0.13462107,0.09138914, -0.14471819 $, 0 ., 0 ., 0.66732511 \backslash \backslash 0 .,-0.00000012,-0.00000002,-0.00000002,-0.00000012$, $0.00000001,0.00000002,-0.00000012,0.00000001,0 ., 0.00000037,0 . \backslash \backslash \backslash @$

## $\mathrm{H}_{2} \mathrm{O} \quad C_{2 v}$

$1 \backslash 1 \backslash G I N C-R S C Q C 8 \backslash F r e q \backslash R M P 2-F C \backslash 6-31 G(d) \backslash H 2 O 1 \backslash R A S M U S S E N \backslash 24-F e b-1999 \backslash 0 \backslash \backslash \# P$ MP2/6-31G* 5D OPT= (CALCALL, VERYTIGHT) NAME=RASMUSSEN MAXDISK=10485760 $00 \backslash \backslash$ water $-\mathrm{C} 2 \mathrm{~V} \backslash \backslash 0,1 \backslash \mathrm{H},-0.1257249842,0 .,-0.8918185828 \backslash \mathrm{O},-0.09132278,0$. , $0.0765924466 \backslash \mathrm{H}, 0.8563072245,0 ., 0.2790790096 \backslash \backslash$ Version=IBM-RS6000-G94Re $\mathrm{vE} .1 \backslash$ State $=1-\mathrm{A} 1 \backslash \mathrm{HF}=-76.0083941 \backslash \mathrm{MP} 2=-76.1939531 \backslash \mathrm{RMSD}=6.280 \mathrm{e}-09 \backslash \mathrm{RMSF}=4.1$ $88 e-08 \backslash$ Dipole $=0.6619523,0 .,-0.5551796 \backslash \operatorname{DipoleDeriv=0.3105371,0.,0.05303}$ $77,0 ., 0.3835736,0 ., 0.0260772,0 ., 0.130366,-0.4328005,0 .,-0.0458262,0 .,-$ $0.7671473,0 .,-0.0458262,0 .,-0.4490056,0.1222634,0 .,-0.0072116,0 ., 0.383$ 5736, 0., 0.019749, 0., 0.3186396\Polar=5.9257373,0., 2.7181209, 0.910101, 0. $, 6.2475678 \backslash \mathrm{PG}=\mathrm{C} 02 \mathrm{~V} \quad[\mathrm{C} 2(\mathrm{O} 1), \mathrm{SGV}(\mathrm{H} 2)] \backslash \mathrm{NImag}=0 \backslash \backslash 0.05621492,0 ., 0.00000002$, $0.03449589,0 ., 0.52672941,-0.05077077,0 \ldots,-0.04926609,0.54596409,0 .,-0.0$ $0000004,0 ., 0 ., 0.00000009,0.02286274,0 .,-0.51375519,0.10498184,0 ., 0.583$ $08784,-0.00544414,0 ., 0.01477020,-0.49519332,0 .,-0.12784458,0.50063746$, $0 ., 0.00000003,0 ., 0 \ldots,-0.00000004,0 ., 0 ., 0.00000002,-0.05735863,0 .,-0.012$ $97422,-0.05571575,0 .,-0.06933265,0.11307438,0 ., 0.08230686 \backslash \backslash 0.00000005$, $0 .,-0.00000002,-0.00000008,0 ., 0.00000007,0.00000003,0 .,-0.00000004 \backslash \backslash \backslash @$

## Unstrained Hydrocarbons

## ethane $\quad D_{2 d}$

$1 \backslash 1 \backslash G I N C-R S C Q C 2 \backslash F O p t \backslash R M P 2-F C \backslash 6-31 G(d) \backslash C 2 H 6 \backslash R A S M U S S E N \backslash 15-J u l-1998 \backslash 0 \backslash \backslash \# P$ RMP2/6-31G(D) 5D OPT FREQ=NORAMAN MAXDISK=786432000 GEOM= (NODISTANCE, NOANGLE, NODIHEDRAL) NAME=RASMUSSEN <br>Ethane D3d<br>0, 1 \C, 0., 0., -0. 7634609 $439 \backslash \mathrm{C}, 0 ., 0 ., 0.7634609439 \backslash \mathrm{H}, 1.0202526205,0 .,-1.1576074281 \backslash \mathrm{H}, 0.510126310$ $2,0.8835646876,1.1576074281 \backslash H,-0.5101263102,0.8835646876,-1.1576074281$ $\backslash \mathrm{H},-1.0202526205,0 ., 1.1576074281 \backslash \mathrm{H},-0.5101263102,-0.8835646876,-1.1576$ $074281 \backslash H, 0.5101263102,-0.8835646876,1.1576074281 \backslash \backslash$ Version=IBM-RS6000-G $94 R e v E .1 \backslash S t a t e=1-A 1 G \backslash H F=-79.2279888 \backslash M P 2=-79.4921958 \backslash R M S D=1.112 e-09 \backslash R M S$ $\mathrm{F}=1.516 \mathrm{e}-04 \backslash \mathrm{Dipole}=0 ., 0 ., 0 . \backslash \mathrm{PG}=\mathrm{D} 03 \mathrm{D} \quad[\mathrm{C} 3(\mathrm{C} 1 . \mathrm{C} 1), 3 \mathrm{SGD}(\mathrm{H} 2)] \backslash \backslash @$

## propane $\quad C_{2 v}$

$1 \backslash 1 \backslash G I N C-R S C Q C 9 \backslash F O p t \backslash R M P 2-F C \backslash 6-31 G(d) \backslash C 3 H 8 \backslash R A S M U S S E N \backslash 17-J u l-1998 \backslash 0 \backslash \backslash \# P$ RMP2/6-31G* 5D OPT FREQ=NORAMAN MAXDISK=1048576000 GEOM= (NODISTANCE,N OANGLE, NODIHEDRAL) NAME=RASMUSSEN SCF=DIRECT<br>Propane C2V<br>0,1\C,-0.48 $99857067,0 .,-0.3255239756 \backslash C,-0.4853341948,0 ., 1.2012756464 \backslash C, 0.91928095$ $89,0 .,-0.9129813677 \backslash \mathrm{H},-1.0374179159,0.8773340417,-0.6892127663 \backslash \mathrm{H},-1.03$ $74179159,-0.8773340417,-0.6892127663 \backslash \mathrm{H}, 0.0311295648,0.8841173509,1.588$ $6001947 \backslash \mathrm{H}, 0.0311295648,-0.8841173509,1.5886001947 \backslash \mathrm{H},-1.502040705,0 ., 1$. $6054886271 \backslash \mathrm{H}, 1.4764990227,-0.8841173509,-0.587001077 \backslash \mathrm{H}, 1.4764990227,0$. $8841173509,-0.587001077 \backslash \mathrm{H}, 0.8978530176,0 .,-2.0068831481 \backslash \backslash V e r s i o n=I B M-R$ S6000-G94RevE. I \State=1-A1 \HF=-118.2625808 \MP2=-118.656485\RMSD=3.979e $-09 \backslash \mathrm{RMSF}=4.106 \mathrm{e}-05 \backslash \mathrm{Dipole}=-0.0170699,0 .,-0.0113404 \backslash \mathrm{PG}=\mathrm{CO} 2 \mathrm{~V} \quad[\mathrm{C} 2(\mathrm{C} 1)$, SGV ( C 2 H 2 ) , SGV' (H2) , X (H4) ] <br>@

## isobutane $\quad C_{3 v}$

$1 \backslash 1 \backslash G I N C-R S C Q C 6 \backslash F O p t \backslash R M P 2-F C \backslash 6-31 G(d) \backslash C 4 H 10 \backslash R A S M U S S E N \backslash 15-J u l-1998 \backslash 0 \backslash \backslash \#$ P RMP2/6-31G* 5D FOPT FREQ=NORAMAN MAXDISK=471859200 GEOM= (NODISTANCE,

NOANGLE, NODIHEDRAL) NAME=RASMUSSEN <br>isobutane C3v <br>0,1\C,0.,0.,0.37625 $646 \backslash \mathrm{H}, 0.0 ., 1.4749758138 \backslash \mathrm{C}, 1.4530961503,0 .,-0.0962729279 \backslash \mathrm{C},-0.72654807$ 51,-1.2584181803,-0.0962729279\C,-0.7265480751,1.2584181803,-0.0962729 $279 \backslash \mathrm{H}, 1.9869443455,-0.8861166274,0.2624145809 \backslash \mathrm{H}, 1.9869443455,0.8861166$ 274,0.2624145809\H,1.4975950643,0.,-1.1913631188\H,-1.7608716828,-1.27 76859654,0.2624145809\H,-0.2260726627,-2.1638025929,0.2624145809\H,-0. 7487975322,-1.2969553703,-1.1913631188\H,-0.2260726627,2.1638025929, 0. $2624145809 \backslash \mathrm{H},-1.7608716828,1.2776859654,0.2624145809 \backslash \mathrm{H},-0.7487975322,1$ .2969553703,-1.1913631188<br>Version=IBM-RS6000-G94RevD.1 \State=1-A1 \HF= $-157.2975405 \backslash \mathrm{MP} 2=-157.8235036 \backslash \mathrm{RMSD}=7.398 \mathrm{e}-09 \backslash \mathrm{RMSF}=4.952 \mathrm{e}-05 \backslash \mathrm{Dipole}=0 .$, $0 ., 0.0318221 \backslash \mathrm{PG}=\mathrm{C03V}$ [C3 (C1H1), 3SGV (C1H1), X(H6)] <br>@

## neopentane $T_{d}$

$1 \backslash 1 \backslash G I N C-R S C Q C 9 \backslash F O p t \backslash R M P 2-F C \backslash 6-31 G(d) \backslash C 5 H 12 \backslash R A S M U S S E N \backslash 16-J u l-1998 \backslash 0 \backslash \ \#$ N RMP2/6-31G* 5D OPT=READFC GUESS=CHECK MAXDISK=1048576000 GEOM=(CHECK ,NODISTANCE,NOANGLE,NODIHEDRAL) NAME=RASMUSSEN $\backslash \backslash$ Neopentane 5D Td<br>0,1\} $\mathrm{C}, 0 ., 0 ., 0 . \backslash \mathrm{C}, 0 ., 0 ., 1.5304947093 \backslash \mathrm{C}, 1.44296425,0 .,-0.5101649031 \backslash \mathrm{C},-0.721$ 482125,1.2496436972,-0.5101649031\C,-0.721482125,-1.2496436972,-0.5101 $649031 \backslash \mathrm{H}, 0.5115604962,-0.8860487706,1.9214710638 \backslash \mathrm{H},-1.0231209924,0 ., 1$. $9214710638 \backslash \mathrm{H}, 0.5115604962,0.8860487706,1.9214710638 \backslash \mathrm{H}, 1.9821004575,0.8$ 860487706,-0.1581864934\H,1.4705399613,0.,-1.6050980769\H,1.9821004575 , -0.8860487706,-0.1581864934 \H, -0.7352699806,1.2735249637,-1.605098076 $9 \backslash \mathrm{H},-0.2237094844,2.1595737343,-0.1581864934 \backslash \mathrm{H},-1.758390973,1.27352496$ 37,-0.1581864934 \H,-1.758390973,-1.2735249637,-0.1581864934 \H, -0. 22370 94844,-2.1595737343,-0.1581864934\H,-0.7352699806,-1.2735249637,-1.605 0980769 <br>Version=IBM-RS6000-G94RevE. 1 \HF=-196.3320553 \MP2=-196.9924722 $\backslash \mathrm{RMSD}=3.454 \mathrm{e}-09 \backslash \mathrm{RMSF}=1.666 \mathrm{e}-04 \backslash \mathrm{Dipole=0.,0.,0}. \mathrm{\backslash PG=TD} \mathrm{[O(C1)}, \mathrm{4C3(C1)}, \mathrm{6S}$ GD (H2) ] <br>@

## Simple Alicyclic Hydrocarbons

## 4-49 cyclopropane $\boldsymbol{D}_{3 \mathrm{~h}}$

$1 \backslash 1 \backslash G I N C-R S C Q C 9 \backslash F O p t \backslash R M P 2-F C \backslash 6-31 G(d) \backslash C 3 H 6 \backslash R A S M U S S E N \backslash 18-O c t-1999 \backslash 0 \backslash \ \# P$ MP2/6-31G(D) 5D OPT FREQ=NORAMAN NAME=RASMUSSEN MAXDISK=917504000<br>CY clopropane D3h 5D <br>0,1\C,0.4339224791,0.0000000001,0.7515757804\C,0.43 $39224792,0 .,-0.7515757804 \backslash \mathrm{C},-0.8678449583,0.0 . \backslash \mathrm{H},-1.4576863463,0.9111$ $606953,-0.0000000001 \backslash \mathrm{H},-1.4576863463,-0.9111606953,0 . \backslash \mathrm{H}, 0.7288431731,-$ $0.9111606952,1.2623934067 \backslash \mathrm{H}, 0.7288431731,0.9111606954,1.2623934066 \backslash \mathrm{H}, 0$ $.7288431732,0.9111606952,-1.2623934067 \backslash \mathrm{H}, 0.7288431732,-0.9111606954,-1$ $.2623934066 \backslash \backslash$ Version=IBM-RS6000-G98RevA. $6 \backslash$ State=1-A1'\HF=-117.0579053\} MP2 $=-117.4447365 \backslash R M S D=3.978 e-09 \backslash R M S F=4.052 e-04 \backslash$ Dipole=0.,0., 0. $\backslash P G=D 03 H$ [3C2 (C1),3SGV(H2)] <br>@

## 4-50 cyclobutane $\boldsymbol{C}_{2}$

$1 \backslash 1 \backslash G I N C-P A L O \backslash F O p t \backslash R M P 2-F C \backslash 6-31 G(d) \backslash C 4 H 8 \backslash R A S M U S S E N \backslash 14-O c t-1999 \backslash 0 \backslash \backslash \# P M$ P2/6-31G* 5D OPT FREQ=NORAMAN NAME=RASMUSSEN GEOM= (CHECK,NODISTANCE,NO ANGLE, NODIHEDRAL) SYMM=LOOSE <br>cyclobutane C9H14 C2v $\backslash \backslash 0,1 \backslash C, 1.072793747$ 3,0., 0.1469968377\H,1.3472269869,0.,1.2066807509\C,-1.0727937473,0.,0. $1469968377 \backslash \mathrm{H}, 0 .,-1.3472269869,-1.2066807509 \backslash \mathrm{H}, 0 ., 1.3472269869,-1.20668$ $07509 \backslash \mathrm{C}, 0 ., 1.0727937473,-0.1469968377 \backslash \mathrm{H}, 0 ., 1.9873544538,0.4534118738 \backslash \mathrm{H}$ ,1.9873544538,0.,-0.4534118738\H,-1.3472269869,0.,1.2066807509\C,0.,-1 $.0727937473,-0.1469968377 \backslash \mathrm{H}, 0 .,-1.9873544538,0.4534118738 \backslash \mathrm{H},-1.9873544$

538,0.,-0.4534118738<br>Version=Sun-SVR4-Unix-G98RevA.7\State=1-A1 \HF=-1 $56.0956627 \backslash \mathrm{MP} 2=-156.6127414 \backslash \mathrm{RMSD}=3.364 \mathrm{e}-09 \backslash \mathrm{RMSF}=2.033 \mathrm{e}-05 \backslash \mathrm{Dipole}=0 ., 0$. , 0. \PG=D02D [2SGD (C2H4)] <br>@

## 4-51 cyclopentane $\boldsymbol{C}_{\mathbf{1}}$

 P MP2/6-31G(D) 5D OPT=(CALCFC,VERYTIGHT) FREQ=NORAMAN SYMM=LOOSE MAXDI SK=917504000 GEOM=CHECK NAME=RASMUSSEN GUESS=CHECK <br>cyclopentane C2 <br>0 , $1 \backslash \mathrm{H}, 1.8343343818,-1.3334773099,-0.1459138317 \backslash \mathrm{C}, 1.021973146,-0.7207269$ $626,0.2586204643 \backslash C, 1.0237357024,0.7182102913,-0.2586364053 \backslash C,-0.365455$ 2801,1.2280140591,0.1447025609\C,-1.3003709581,0.0016111514, -0.0000349 $799 \backslash \mathrm{C},-0.3684890206,-1.2271197397,-0.144651167 \backslash \mathrm{H}, 1.1221153797,-0.71715$ $13276,1.3513330723 \backslash \mathrm{H}, 1.1238156445,0.7143946294,-1.3513542348 \backslash \mathrm{H}, 1.83762$ 24846,1.3289549333,0.1458647882 \Н, -0.338491513,1.5587714895,1.18917163 $45 \backslash \mathrm{H},-0.6959086841,2.0832071918,-0.4531818323 \backslash \mathrm{H},-1.954027632,0.1003923$ $63,-0.8722441731 \backslash \mathrm{H},-1.9544091387,-0.0955370002,0.872071286 \backslash \mathrm{H},-0.342363$ 5162,-1.5580617911,-1.1890823036\H,-0.7010489448,-2.0814259755,0.45333 $27563 \backslash \backslash$ Version=IBM-RS6000-G98RevA. $6 \backslash \mathrm{HF}=-195.1619966 \backslash \mathrm{MP} 2=-195.8094737 \backslash \mathrm{R}$ MSD=2.129e-09 $\operatorname{RMSF}=3.148 e-09 \backslash$ Dipole $=-0.0012896,0.0000012,-0.0000005 \backslash$ PG =C01 [X(C5H10)] <br>@

## C-4-52 cyclohexane (chair) $\boldsymbol{D}_{3 \mathrm{~d}}$

$1 \backslash 1 \backslash$ GINC-RSCQC9 \FOpt \RMP2-FC\6-31G(d) \C6H12 \RASMUSSEN $\backslash 15-J u l-1994 \backslash 0 \backslash \ \#$ P RMP2/6-31G* 5D OPT=READFC FREQ=NORAMAN NAME=RASMUSSEN GUESS=CHECK MA XDISK=1048576000 GEOM=(CHECK,NODISTANCE,NOANGLE,NODIHEDRAL) SCF=DIRECT $\backslash \backslash$ Cyclohexane D3d<br>0,1\C,1.262028478,-0.7286324815, 0.2327730824\C,-1.2 62028478,-0.7286324815,0.2327730824\C,0.,1.457264963,0.2327730824\C,1. $262028478,0.7286324815,-0.2327730824 \backslash C, 0 .,-1.457264963,-0.2327730824 \backslash C$ ,-1.262028478, 0.7286324815,-0.2327730824 \H,1.3091102009,-0.7558151269, $1.3303694404 \backslash \mathrm{H},-1.3091102009,-0.7558151269,1.3303694404 \backslash \mathrm{H}, 0 ., 1.5116302$ 538,1.3303694404 \H, 1.3091102009,0.7558151269,-1.3303694404 \H, 0., -1. 511 6302538,-1.3303694404\H,-1.3091102009,0.7558151269,-1.3303694404 \H, 2.1 574786936,-1.2456209045,-0.1333734436\H,-2.1574786936,-1.2456209045,-0 $.1333734436 \backslash \mathrm{H}, 0.2 .491241809,-0.1333734436 \backslash \mathrm{H}, 2.1574786936,1.2456209045$ , 0.1333734436\H, 0.,-2.491241809, 0.1333734436\H,-2.1574786936,1.2456209 045,0.1333734436<br>Version=IBM-RS6000-G94RevE.1\State=1-A1G\HF=-234.206 $0933 \backslash \mathrm{MP} 2=-234.9845819 \backslash \mathrm{RMSD}=4.486 \mathrm{e}-10 \backslash \mathrm{RMSF}=9.825 \mathrm{e}-06 \backslash \mathrm{Dipole}=0 ., 0 ., 0 . \backslash \mathrm{PG}$ =D03D [3SGD (C2H4)] <br>@

## BC-4-53 cyclooctane (boat-chair) <br> $C_{\text {s }}$

$1 \backslash 1 \backslash G I N C-P C \backslash F O p t \backslash R M P 2-F C \backslash 6-31 G(d) \backslash C 8 H 16 \backslash R A S M U S S E N \backslash 28-O c t-1999 \backslash 0 \backslash \backslash \# P M P$ 2/6-31G* 5D OPT FREQ=NORAMAN NAME=RASMUSSEN GUESS=CHECK MAXDISK=209715 2000 GEOM= (CHECK, NODISTANCE, NOANGLE,NODIHEDRAL) SYMM=LOOSE \ \cyclooctan e Cs chair <br>0,1\H,0.8421492907,1.5393443075,2.1260576805\C,-0.64042329 93, 0.0840212168,1.5951715034 \Н, 1.2195503819,-1.0283520645,-1.382311949 $1 \backslash H, 1.4994203526,2.3718205749,0 . \backslash H,-0.930294668,0.1128934931,2.6529254$ $063 \backslash \mathrm{H},-1.5825447341,0.0661349659,-1.0379780198 \backslash \mathrm{H},-0.930294668,0.112893$ 4931,-2.6529254063\H, 0.3200537155,-2.891852403,0. \H,-1.2690708336,-2.1 505871491,0. \C, 0.1314106124,1.3795526958,1.3039818182\C, -0.1940418076, $-1.9211882233,0 . \backslash \mathrm{H},-0.5659485927,2.2278120993,-1.3383199529 \backslash \mathrm{H},-0.56594$ 85927,2.2278120993,1.3383199529\C,0.1314106124,1.3795526958,-1.3039818 $182 \backslash C, 0.1393705887,-1.2151054085,-1.3208775205 \backslash C, 0.1393705887,-1.21510$

54085, 1. $3208775205 \backslash \mathrm{H},-1.5825447341,0.0661349659,1.0379780198 \backslash \mathrm{H}, 0.84214$ $92907,1.5393443075,-2.1260576805 \backslash \mathrm{H},-0.0797822595,-1.9319571215,-2.1219$ $940359 \backslash \mathrm{H},-0.0797822595,-1.9319571215,2.1219940359 \backslash \mathrm{C}, 0.9273307112,1.434$ $530863,0 . \backslash \mathrm{C},-0.6404232993,0.0840212168,-1.5951715034 \backslash \mathrm{H}, 1.2195503819,-1$ $.0283520645,1.3823119491 \backslash \mathrm{H}, 1.6793096861,0.6371897294,0 . \backslash \backslash V e r s i o n=S G I-G$ 98RevA. $6 \backslash$ State $=1-A^{\prime} \backslash H F=-312.2536114 \backslash M P 2=-313.29633 \backslash \mathrm{RMSD}=3.098 \mathrm{e}-09 \backslash \mathrm{RMSF}$ $=1.755 \mathrm{e}-05 \backslash \mathrm{Dipole}=0.0051185,-0.0169428,0 . \backslash \mathrm{PG}=\mathrm{CS} \quad[\mathrm{SG}(\mathrm{C} 2 \mathrm{H} 4), \mathrm{X}(\mathrm{C} 6 \mathrm{H} 12)] \backslash \backslash @$

## CC-4-54 bicyclo[3.3.1]nonane (chair-chair) $\boldsymbol{C}_{2 v}$

$1 \backslash 1 \backslash G I N C-P C \backslash F O p t \backslash R M P 2-F C \backslash 6-31 G(d) \backslash C 9 H 16 \backslash R A S M U S S E N \backslash 31-O c t-1999 \backslash 0 \backslash \backslash \# P M P$ 2/6-31G(D) 5D OPT FREQ=NORAMAN NAME=RASMUSSEN GUESS=CHECK MAXDISK=2097 152000 GEOM=CHECK <br>bicyclononane C2v (chair-chair) <br>0, 1 \H, 0., -0.883642 $8017,-2.1870618961 \backslash \mathrm{H}, 2.1415026433,0 .,-1.2818742537 \backslash \mathrm{H},-2.1415026433,0 .$, $-1.2818742537 \backslash \mathrm{C},-1.245592464,0 .,-0.6441313481 \backslash \mathrm{H}, 0 .,-2.6119328769,1.321$ $0516261 \backslash \mathrm{C}, 0 ., 0 .,-1.5335229741 \backslash \mathrm{H}, 0 .,-0.967694081,1.9003811462 \backslash \mathrm{H},-1.4260$ $775035,-2.1270815465,-0.5260710812 \backslash \mathrm{C}, 0 .,-1.5664539469,0.9868924176 \backslash \mathrm{H}, 0$ ., 0.8836428017, -2.1870618961 \C, 0., 1.5664539469, 0.9868924176\H,-2.14913 $38545,1.2993877615,0.8468196682 \backslash \mathrm{H}, 0.0 .967694081,1.9003811462 \backslash \mathrm{C},-1.277$ $1307606,-1.2970347414,0.1791673925 \backslash C, 1.2771307606,-1.2970347414,0.1791$ $673925 \backslash \mathrm{C}, 1.2771307606,1.2970347414,0.1791673925 \backslash \mathrm{C},-1.2771307606,1.2970$ $347414,0.1791673925 \backslash \mathrm{H},-2.1491338545,-1.2993877615,0.8468196682 \backslash \mathrm{H}, 2.149$ $1338545,-1.2993877615,0.8468196682 \backslash \mathrm{H}, 1.4260775035,2.1270815465,-0.5260$ $710812 \backslash \mathrm{H},-1.4260775035,2.1270815465,-0.5260710812 \backslash \mathrm{H}, 1.4260775035,-2.12$ $70815465,-0.5260710812 \backslash \mathrm{C}, 1.245592464,0 .,-0.6441313481 \backslash \mathrm{H}, 2.1491338545,1$ $.2993877615,0.8468196682 \backslash \mathrm{H}, 0 ., 2.6119328769,1.3210516261 \backslash \backslash V e r s i o n=S G I-G$ 98RevA. $6 \backslash$ State $=1-A 1 \backslash H F=-350.1387609 \backslash M P 2=-351.3088056 \backslash R M S D=8.617 e-09 \backslash R M$
 2) , X (C4H8) ] <br>@

## Strained Hydrocarbons

## 4-55 tetrahedrane $\boldsymbol{T}_{\mathbf{d}}$

$1 \backslash 1 \backslash G I N C-R S C Q C 6 \backslash F O p t \backslash R M P 2-F C \backslash 6-31 G(d) \backslash C 4 H 4 \backslash R A S M U S S E N \backslash 21-J u l-1998 \backslash 0 \backslash \backslash \# P$ RMP2/6-31G* 5D OPT=TIGHT NAME=RASMUSSEN MAXDISK=471859200 GEOM=CHECK GUESS = CHECK $\backslash$ Tetrahedrane Td 5D $\backslash \backslash 0,1 \backslash C, 0.7386392908,0 ., 0.5222968514 \backslash C$, $-0.5944109979,0.6030964555,0.3183272434 \backslash C,-0.3736623743,-0.8238450792$, $0.006141546 \backslash \mathrm{C}, 0.2294340813,0.2207486237,-0.8467656408 \backslash \mathrm{H},-1.2994377315$, $1.3184249498,0.6958929639 \backslash \mathrm{H},-0.816860707,-1.8010019744,0.0134259908 \backslash \mathrm{H}$, $0.5015642429,0.4825770246,-1.8511084542 \backslash \mathrm{H}, 1.6147341956,-0.0000000001,1$ $.1417894995 \backslash \backslash V e r s i o n=I B M-R S 6000-G 94 R e v D .1 \backslash$ State $=1-A 1 \backslash H F=-153.5963695 \backslash M$ $\mathrm{P} 2=-154.102365 \backslash \mathrm{RMSD}=8.804 \mathrm{e}-10 \backslash \mathrm{RMSF}=9.554 \mathrm{e}-07 \backslash \mathrm{Dipole=0.,0.,0}. \mathrm{\backslash PG=TD} \mathrm{\quad[4C}$ 3 (.C1H1)] <br>@

## 4-56 pyramidane $\boldsymbol{C}_{\mathbf{4}}$

$1 \backslash 203 \backslash G I N C-R S C Q C 2 \backslash F O P T \backslash R M P 2-F C \backslash 6-31 G(D) \backslash C 5 H 4 \backslash R A S M U S S E N \backslash 15-M a y-1994 \backslash 1 \backslash \backslash$
 ISK=37500000 OPTCYC=100 GEOM= (CHECK, NODISTANCE, NOANGLE,NODIHEDRAL) 5D GUESS = CHECK $\backslash$ Pyramidane ([3.3.3.3]fenestrane) C4v RMP2/6-31G* 5D $\backslash \backslash 0,1 \backslash$ $C \backslash X, 1,0.5 \backslash X, 1,0.5,2,90 . \backslash X, 1,0.5,2,90 ., 3,90 ., 0 \backslash X, 1,0.5,4,90 ., 2,180 ., 0 \backslash X$ $, 1,0.5,2,90 ., 3,180 ., 0 \backslash X, 1,0.5,2,90.4,180 ., 0 \backslash C, 1, c c, 2, c c x, 4,0 ., 0 \backslash C, 1, c$ $c, 2, c c x, 3,0 ., 0 \backslash C, 1, c c, 2, c c x, 7,0 ., 0 \backslash C, 1, c c, 2, c c x, 6,0 ., 0 \backslash H, 8, h c, 1, h c c, 2$, $0 ., 0 \backslash H, 9, h c, 1, h c c, 2,0 ., 0 \backslash H, 10, h c, 1, h c c, 2,0 ., 0 \backslash H, 11, h c, 1, h c c, 2,0 ., 0 \backslash \backslash c c$
$=1.64621025 \backslash \mathrm{ccx}=141.55735791 \backslash \mathrm{hc}=1.0809544 \backslash \mathrm{hcc}=119.23362354 \backslash \backslash$ Version=IB M-RS6000-G92RevB $\backslash$ State $=1-A 1 \backslash H F=-191.4552433 \backslash M P 2=-192.0917766 \backslash$ RMSD $=8.21$ $3 \mathrm{e}-09 \backslash \mathrm{RMSF}=3.304 \mathrm{e}-05 \backslash \mathrm{Dipole}=-0 .,-0 .,-0.626269 \backslash \mathrm{PG}=\mathrm{C} 04 \mathrm{~V} \quad[\mathrm{C} 4(\mathrm{C} 1), 2 \mathrm{SGV}(\mathrm{C} 2 \mathrm{H}$ 2)] <br>@

## 4-57 [1.1.1]propellane $\boldsymbol{D}_{3}$

$1 \backslash 1 \backslash G I N C-P C \backslash F O p t \backslash R M P 2-F C \backslash 6-31 G(d) \backslash C 5 H 6 \backslash R A S M U S S E N \backslash 02-N o v-1999 \backslash 0 \backslash \backslash \# P M P 2$ /6-31G(D) 5D OPT FREQ=NORAMAN NAME=RASMUSSEN SYMM=LOOSE MAXDISK=209715 2000 GEOM=CHECK GUESS=CHECK <br>propellane D3 <br>0,1\C,1.2450733828,0.33463 $1919,0 . \backslash \mathrm{C}, 0.0 .0 .0 .7975429423 \backslash \mathrm{H}, 1.5719927838,1.3725496517,0 . \backslash \mathrm{C},-0.33273$ 69487,-1.2455811386,0.\C,-0.9123364342,0.9109492196,0. \H, -0.678114845, $1.9736296805,0 . \backslash \mathrm{C}, 0 ., 0 .,-0.7975429423 \backslash \mathrm{H},-1.9746592582,0.6751108594,0 . \backslash$ H, $2.0482708635,-0.3995501578,0 . \backslash \mathrm{H}, 0.4026664745,-2.0476605112,0 . \backslash \mathrm{H},-1.3$ 701560184,-1.5740795227,0. <br>Version=SGI-G98RevA. $6 \backslash$ State=1-A1 $\backslash \mathrm{HF}=-192$. $6883707 \backslash M P 2=-193.3431179 \backslash \mathrm{RMSD}=7.885 \mathrm{e}-09 \backslash \mathrm{RMSF}=4.599 \mathrm{e}-05 \backslash \mathrm{Dipole=0.,0.,0}$. \PG=D03H [C3 (C1.C1), 3C2 (C1), SGH (H6) ] <br>@

## 4-58 spiropentane $\boldsymbol{D}_{\mathbf{2 d}}$

$1 \backslash 1 \backslash G I N C-P C \backslash F O p t \backslash R M P 2-F C \backslash 6-31 G(d) \backslash C 5 H 8 \backslash R A S M U S S E N \backslash 21-J u 1-1998 \backslash 0 \backslash \ \# P R M P$ 2/6-31G* 5D OPT=TIGHT NAME=RASMUSSEN MAXDISK=2359296000 GEOM=(CHECK,NO DISTANCE,NOANGLE,NODIHEDRAL) GUESS=CHECK <br>Spiropentane D2d 5D<br>0,1\C,0 ., 0., 0. \C, -0.5395631531,-1.2677687665,-0.5395631531 \C, 0.5395631531,-1. $2677687665,0.5395631531 \backslash C,-0.5395631531,1.2677687665,0.5395631531 \backslash C, 0$. 5395631531,1.2677687665,-0.5395631531 \H,-1.5420398508,-1.5701905487,-0 . $2486373311 \backslash \mathrm{H}, 1.5420398508,-1.5701905487,0.2486373311 \backslash \mathrm{H},-1.5420398508$, $1.5701905487,0.2486373311 \backslash \mathrm{H}, 1.5420398508,1.5701905487,-0.2486373311 \backslash \mathrm{H}$, $-0.2486373311,-1.5701905487,-1.5420398508 \backslash \mathrm{H}, 0.2486373311,-1.5701905487$ , 1. $5420398508 \backslash \mathrm{H},-0.2486373311,1.5701905487,1.5420398508 \backslash \mathrm{H}, 0.2486373311$ ,1.5701905487,-1.5420398508<br>Version=SGI-G94RevD. $3 \backslash$ State=1-A1 $\backslash H F=-193$. $9162852 \backslash \mathrm{MP} 2=-194.558386 \backslash \mathrm{RMSD}=7.683 \mathrm{e}-09 \backslash \mathrm{RMSF}=4.644 \mathrm{e}-06 \backslash$ Dipole=0.,0.,0. $\backslash$ PG=D02D [O(C1), 2SGD (C2), X(H8)]<br>@

## 4-59 prismane $\boldsymbol{D}_{\mathbf{3 h}}$

$1 \backslash 1 \backslash$ GINC-VPP11 \FOpt \RMP2-FC\6-31G(d) \C6H6\DRR501\25-Feb-1999\0<br>\#P MP2 /6-31G* 5D OPT=NEWESTMFC GUESS=CHECK GEOM=CHECK MAXDISK=2621440000<br>Pr ismane $\mathrm{D} 3 \mathrm{~h} \backslash \backslash 0,1 \backslash \mathrm{C},-0.4386937085,0.7598397997,0.7755181988 \backslash \mathrm{C},-0.4386937$ 15,-0.7598397959,-0.7755181988\C,-0.4386937085,0.7598397997,-0.7755181 $988 \backslash C,-0.438693715,-0.7598397959,0.7755181988 \backslash C, 0.8773874236,-0.000000$ $0038,0.7755181988 \backslash \mathrm{C}, 0.8773874236,-0.0000000038,-0.7755181988 \backslash \mathrm{H},-0.8375$ 179288,1.4506236194,1.5116636063\H, -0.8375179413,-1.4506236122,1.51166 $36063 \backslash \mathrm{H},-0.8375179288,1.4506236194,-1.5116636063 \backslash \mathrm{H},-0.8375179413,-1.45$ 06236122,-1.5116636063\H,1.6750358701,-0.0000000072,1.5116636063\H,1.6 750358701,-0.0000000072,-1.5116636063<br>Version=Fujitsu-VP-Unix-G98RevA $.6 \backslash$ State $=1-\mathrm{A} 1^{\prime} \backslash \mathrm{HF}=-230.501355 \backslash \mathrm{MP} 2=-231.2617837 \backslash \mathrm{RMSD}=4.078 \mathrm{e}-09 \backslash \mathrm{RMSF}=1.0$ 95e-04\Dipole=0., 0., 0. \PG=D03H [3SGV (C2H2)] <br>@

## 4-60 cubane <br> $O_{h}$

$1 \backslash 1 \backslash G I N C-R S C Q C 9 \backslash F O p t \backslash R M P 2-F C \backslash 6-31 G(d) \backslash C 8 H 8 \backslash R A S M U S S E N \backslash 21-J u l-1998 \backslash 0 \backslash \ \# P$ RMP2/6-31G* 5D OPT NAME=RASMUSSEN MAXDISK=1048576000 GEOM= (CHECK,NOAN GLE,NODIHEDRAL) GUESS=CHECK <br>Cubane Oh <br>0,1\C,0.782871039,0.782871039, $0.782871039 \backslash C, 0.782871039,0.782871039,-0.782871039 \backslash C,-0.782871039,0.78$ 2871039,-0.782871039\C,-0.782871039,0.782871039,0.782871039\C,0.782871

039, - 0. $782871039,0.782871039 \backslash C, 0.782871039,-0.782871039,-0.782871039 \backslash C$ , - 0.782871039, -0.782871039, -0.782871039 \C, -0.782871039, -0.782871039, 0. $782871039 \backslash \mathrm{H}, 1.4140650175,1.4140650175,1.4140650175 \backslash \mathrm{H}, 1.4140650175,1.41$ $40650175,-1.4140650175 \backslash \mathrm{H},-1.4140650175,1.4140650175,-1.4140650175 \backslash \mathrm{H},-1$ $.4140650175,1.4140650175,1.4140650175 \backslash \mathrm{H}, 1.4140650175,-1.4140650175,1.4$ $140650175 \backslash \mathrm{H}, 1.4140650175,-1.4140650175,-1.4140650175 \backslash \mathrm{H},-1.4140650175,-$ $1.4140650175,-1.4140650175 \backslash \mathrm{H},-1.4140650175,-1.4140650175,1.4140650175 \backslash$ $\backslash$ Version=IBM-RS6000-G94RevE. 1 \HF=-307.3916541 \MP2=-308.4034279\RMSD=5. $533 \mathrm{e}-10 \backslash \mathrm{RMSF}=1.061 \mathrm{e}-04 \backslash \mathrm{Dipole=0.,0.,0}. \mathrm{\backslash PG=OH} \mathrm{\quad[4C3(H1Cl.C1H1)]} \mathrm{\backslash} \mathrm{\backslash @}$

## 4-61 tetramethyltetrahedrane $\quad \boldsymbol{T}_{\mathbf{d}}$

$1 \backslash 1 \backslash$ GINC-PC $\backslash$ FOpt $\backslash$ RMP2-FC $\backslash 6-31 G(d) \backslash C 8 H 12 \backslash R A S M U S S E N \backslash 21-O c t-1999 \backslash 0 \backslash \backslash \# P ~ M P$ 2/6-31G(D) 5D OPT FREQ=NORAMAN NAME=RASMUSSEN SYMM=LOOSE MAXDISK=20971 52000 GEOM=CHECK GUESS=CHECK $\operatorname{IOP}(3 / 32=2) \backslash \backslash$ tetramethyltetrahedrane Td 5 $D \backslash \backslash 0,1 \backslash C,-0.5252314022,0.5252314022,0.5252314022 \backslash C, 0.5252314022,0.5252$ $314022,-0.5252314022 \backslash C,-0.5252314022,-0.5252314022,-0.5252314022 \backslash C, 0.5$ $252314022,-0.5252314022,0.5252314022 \backslash C, 1.3800330998,1.3800330998,-1.38$ $00330998 \backslash C,-1.3800330998,-1.3800330998,-1.3800330998 \backslash C, 1.3800330998,-1$ $.3800330998,1.3800330998 \backslash \mathrm{C},-1.3800330998,1.3800330998,1.3800330998 \backslash \mathrm{H},-$ $2.0244402704,0.7718629436,2.0244402704 \backslash H,-2.0244402704,2.0244402704,0$. $7718629436 \backslash \mathrm{H},-0.7718629436,2.0244402704,2.0244402704 \backslash \mathrm{H}, 2.0244402704,0$. $7718629436,-2.0244402704 \backslash \mathrm{H}, 2.0244402704,2.0244402704,-0.7718629436 \backslash \mathrm{H}, 0$ $.7718629436,2.0244402704,-2.0244402704 \backslash H,-0.7718629436,-2.0244402704$, $2.0244402704 \backslash \mathrm{H},-2.0244402704,-0.7718629436,-2.0244402704 \backslash \mathrm{H},-2.02444027$ $04,-2.0244402704,-0.7718629436 \backslash \mathrm{H}, 2.0244402704,-2.0244402704,0.77186294$ $36 \backslash \mathrm{H}, 0.7718629436,-2.0244402704,2.0244402704 \backslash \mathrm{H}, 2.0244402704,-0.7718629$ $436,2.0244402704 \backslash \backslash V e r s i o n=S G I-G 98 R e v A .6 \backslash H F=-309.7589918 \backslash M P 2=-310.79087$ $76 \backslash \mathrm{RMSD}=8.290 \mathrm{e}-09 \backslash \mathrm{RMSF}=7.114 \mathrm{e}-05 \backslash \mathrm{Dipole=0.,0.,0}. \mathrm{\backslash PG=TD} \mathrm{\quad[4C3(.ClC1),6SG}$ D (H2) ] <br>@

## 4-62 tetra-tert-butyltetrahedrane $\quad T$

$1 \backslash 1 \backslash G I N C-P C \backslash F O p t \backslash R M P 2-F C \backslash 6-31 G(d) \backslash C 20 H 36 \backslash R A S M U S S E N \backslash 23-A p r-1999 \backslash 0 \backslash \backslash \# P R$ MP2/6-31G* 5D OPT=NEWESTMFC NAME=RASMUSSEN GUESS=CHECK GEOM= (CHECK,NOD ISTANCE, NOANGLE, NODIHEDRAL) MAXDISK=1800000000<br>tetrakis(tert-butyl)te trahedrane $\mathrm{Td} \backslash \backslash 0,1 \backslash \mathrm{C},-1.9656074252,-0.0003653501,1.3897623166 \backslash \mathrm{C},-2.427$ 5498379,-1.4420443962,1.6344561164\C,1.6596886932,2.4499807249,1.37366 $8425 \backslash C, 0.9939344673,2.1924591356,0.0164071156 \backslash C,-0.6103258105,-0.58750$ 91869,-2.2533058693\C,2.0512893671,2.2908878604,-1.0899457766\C,1.5819 987684,-1.6045845986,0.8471364371\C,-0.7469623892,-0.0001388389, 0.5281 319999 \C,-1.6491333158,0.6624296414,2.7359611345\C,1.742248447,-1.4251 339443,2.3616732717\C,-0.0867212267,3.2536574785,-0.223896168\C,-3.090 6567236,0.7782825516,0.6971759743\C,1.084198664,-3.026015093,0.5582857 $391 \backslash C, 2.9421121206,-1.399766579,0.169017297 \backslash C, 0.6516558785,-0.89007202$ 69,-3.0703507056\C,-1.3659879763,0.5762904801,-2.9061836115\C,-1.51114 40902,-1.8284966974,-2.2398616963\C,0.6011849389,-0.6097679171,0.32192 $54511 \backslash C, 0.3777110602,0.8331696824,0.0062349674 \backslash C,-0.2319336098,-0.2232$ 629264,-0.8562924184 \Н, -1.6984552793, 0.297439927,-3.9133762581\Н, -0. 72 03512938,1.4561242461,-2.989150523\H,-2.2462001769,0.8484914055,-2.315 $52942 \backslash \mathrm{H}, 1.3382290877,-0.0379398051,-3.0552795085 \backslash \mathrm{H}, 0.3882532284,-1.103$ 1834392,-4.1133903673\H,1.173969194,-1.7614759775,-2.663310603\H,-1.74 82124985,-2.1383342481,-3.2648145869\H,-2.4503394995,-1.6167237621,-1. 7193793271 पН, -1.0162009937,-2.6627897928,-1.7331807334 \H, 1.5888845353,
$2.1776633562,-2.0754404102 \backslash \mathrm{H}, 2.8101623279,1.5110252767,-0.9730466069 \backslash \mathrm{H}$ , $2.5503627497,3.2667884253,-1.0542664807 \backslash \mathrm{H}, 0.3643564623,4.251967657,-0$ $.2752271706 \backslash \mathrm{H},-0.8184157994,3.2490477312,0.5900076914 \backslash \mathrm{H},-0.6146931489$, $3.0650846494,-1.1638031706 \backslash \mathrm{H}, 2.0660035165,3.4679149782,1.411711641 \backslash \mathrm{H}, 2$ $.4812541721,1.746065218,1.539109692 \backslash \mathrm{H}, 0.9381045967,2.336048448,2.18857$ $64344 \backslash \mathrm{H}, 1.0260079148,-3.2016714572,-0.5204155023 \backslash \mathrm{H}, 0.0902756179,-3.184$ 7662114,0.9879999426\H,1.769611139,-3.7649576684, 0.9906082753\H, 2.8489 028716,-1.471784875,-0.9190381413\H,3.6545576011,-2.1623795039, 0.50602 $1941 \backslash \mathrm{H}, 3.3509490463,-0.4150509978,0.4160502545 \backslash \mathrm{H}, 2.0483835851,-0.40221$ 72573,2.6018023295\H,2.5034134912,-2.1134253153,2.7484702859\H, 0.79865 75333,-1.6327830895,2.8758286081\H,-2.7708064746,1.7985262198,0.463642 $4403 \backslash \mathrm{H},-3.9723486191,0.8327987738,1.347081005 \backslash \mathrm{H},-3.3818637189,0.285709$ 5419,-0.2357806195\H,-2.612345736,-1.957299425,0.6867736974 \H,-3.35532 09616,-1.450803037,2.219172453\H,-1.6671907748,-2.0010045127,2.1887623 252\H,-1.3815613094,1.7140997035,2.5937184139\H,-0.8138115566,0.157621 3671,3.2310827365\H,-2.5222208297,0.6161734506,3.3980092626<br>Version=S GI-G98RevA. $6 \backslash \mathrm{HF}=-778.1615954 \backslash \mathrm{MP} 2=-780.8061327 \backslash \mathrm{RMSD}=7.309 \mathrm{e}-09 \backslash \mathrm{RMSF}=1.38$ 3e-06\Dipole=0.,0.,0.\PG=T [4C3(.C1C1), X(C12H36)]<br>@

## 4-63 pagodane $\boldsymbol{D}_{\mathbf{2 h}}$

$1 \backslash 1 \backslash$ GINC-PALO $\$ FOpt $\backslash$ RMP2-FC $\backslash 6$-31G(d) \C20H20 MP2/6-31G(D) 5D OPT NAME=RASMUSSEN SYMM=LOOSE <br>pagodane D2h <br>0,1\C,-0 $.7746330887,-0.7841897533,0 . \backslash C, 0.7746330887,-0.7841897533,0 . \backslash C,-0.7746$ 330887,0.7841897533,0.\C,0.7746330887,0.7841897533,0.\C,1.2723795069,$1.1438354155,1.3984551389 \backslash \mathrm{C}, 1.2723795069,1.1438354155,-1.3984551389 \backslash \mathrm{C}$, $1.2723795069,-1.1438354155,-1.3984551389 \backslash \mathrm{C},-1.2723795069,-1.1438354155$ ,1.3984551389\C,-1.2723795069,-1.1438354155,-1.3984551389\C,-1.2723795 069,1.1438354155,1.3984551389\C,-1.2723795069,1.1438354155,-1.39845513 $89 \backslash C, 1.2723795069,1.1438354155,1.3984551389 \backslash \mathrm{C},-2.2387682423,0.1 .75882$ $5521 \backslash C, 2.2387682423,0.1 .758825521 \backslash C,-2.2387682423,0 .,-1.758825521 \backslash C, 2$ . $2387682423,0 .,-1.758825521 \backslash C, 0 .,-0.7918263247,2.2172030659 \backslash C, 0 ., 0.791$ 8263247,2.2172030659\C,0.,0.7918263247,-2.2172030659\C,0.,-0.791826324 7,-2.2172030659\H,0.,-1.2087595152,-3.2324283161 \H, 0.,1.2087595152,-3. $2324283161 \backslash \mathrm{H}, 0 .,-1.2087595152,3.2324283161 \backslash \mathrm{H}, 0 ., 1.2087595152,3.2324283$ $161 \backslash \mathrm{H},-1.6416730396,-2.1667709346,-1.5385188076 \backslash \mathrm{H},-1.6416730396,2.1667$ 709346,-1.5385188076\H,1.6416730396,2.1667709346,-1.5385188076\H,1.641 6730396,-2.1667709346,-1.5385188076\Н, -1.6416730396,-2.1667709346,1.53 $85188076 \backslash \mathrm{H},-1.6416730396,2.1667709346,1.5385188076 \backslash \mathrm{H}, 1.6416730396,-2.1$ $667709346,1.5385188076 \backslash \mathrm{H}, 1.6416730396,2.1667709346,1.5385188076 \backslash \mathrm{H}, 2.52$ $22611338,0 .,-2.8197446032 \backslash \mathrm{H},-2.5222611338,0 .,-2.8197446032 \backslash \mathrm{H},-2.522261$ 1338, 0., 2. $8197446032 \backslash \mathrm{H}, 2.5222611338,0 ., 2.8197446032 \backslash \mathrm{H},-3.1546140256,0$. ,-1.1559557218\H,-3.1546140256,0.,1.1559557218\H,3.1546140256,0., -1. 15 59557218\H, 3.1546140256,0.,1.1559557218<br>Version=Sun-SVR4-Unix-G98RevA $.7 \backslash$ State $=1-\mathrm{AG} \backslash \mathrm{HF}=-768.9731577 \backslash \mathrm{MP} 2=-771.5719508 \backslash \mathrm{RMSD}=8.874 \mathrm{e}-09 \backslash \mathrm{RMSF}=3.8$ 02e-05\Dipole=0., 0., 0. \PG=D02H [SG(C4), SG' (C4H4), SG" (C4H8) , X(C8H8)] <br>@

## 4-64 dodecahedrane $\quad I_{h}$

$1 \backslash 1$ \GINC-PC\FOpt \RMP2-FC\6-31G(d) \C20H20\RASMUSSEN $\backslash 04$-Nov-1999\0<br>\#P M P2/6-31G(D) 5D OPT NAME=RASMUSSEN SYMM=LOOSE MAXDISK=2097152000<br>dodec ahedrane $\operatorname{Ih} \backslash \backslash 0,1 \backslash C, 0 ., 1.317454462,1.7245702801 \backslash C,-1.252973651,0.407115$ 8181,1.7245702801\C,-0.7743803033,-1.0658430491,1.7245702801\C,0.77438 03033,-1.0658430491,1.7245702801 \C,1.252973651,0.4071158181,1.72457028
$01 \backslash C, 2.0273539544,0.658727231,0.4071158181 \backslash C, 1.252973651,1.7245702801$, $-0.4071158181 \backslash C, 0 ., 2.1316860982,0.4071158181 \backslash C,-1.252973651,1.72457028$ $01,-0.4071158181 \backslash C,-2.0273539544,0.658727231,0.4071158181 \backslash C,-2.0273539$ $544,-0.658727231,-0.4071158181 \backslash C,-1.252973651,-1.7245702801,0.40711581$ $81 \backslash C, 0 .,-2.1316860982,-0.4071158181 \backslash C, 1.252973651,-1.7245702801,0.4071$ $158181 \backslash \mathrm{C}, 2.0273539544,-0.658727231,-0.4071158181 \backslash \mathrm{C}, 1.252973651,-0.4071$ 158181,-1.7245702801 \C, 0.7743803033,1.0658430491,-1.7245702801\C,-0.77 $43803033,1.0658430491,-1.7245702801 \backslash C,-1.252973651,-0.4071158181,-1.72$ $45702801 \backslash \mathrm{C}, 0 .,-1.317454462,-1.7245702801 \backslash \mathrm{H}, 0 ., 1.9830908035,2.595899563$ $1 \backslash H,-1.886031431,0.6128087597,2.5958995631 \backslash \mathrm{H},-1.1656315282,-1.60435416$ $14,2.5958995631 \backslash \mathrm{H}, 1.1656315282$, - $1.6043541614,2.5958995631 \backslash \mathrm{H}, 1.88603143$ $1,0.6128087597,2.5958995631 \backslash \mathrm{H}, 3.0516629593,0.9915454017,0.6128087597 \backslash \mathrm{H}$ , 1.886031431,2.5958995631,-0.6128087597\H,0.,3.2087083228, 0.6128087597 $\backslash \mathrm{H},-1.886031431,2.5958995631,-0.6128087597 \backslash \mathrm{H},-3.0516629593,0.991545401$ $7,0.6128087597 \backslash \mathrm{H},-3.0516629593,-0.9915454017,-0.6128087597 \backslash \mathrm{H},-1.886031$ $431,-2.5958995631,0.6128087597 \backslash \mathrm{H}, 0 .,-3.2087083228,-0.6128087597 \backslash \mathrm{H}, 1.88$ $6031431,-2.5958995631,0.6128087597 \backslash \mathrm{H}, 3.0516629593,-0.9915454017,-0.612$ $8087597 \backslash \mathrm{H}, 1.886031431,-0.6128087597,-2.5958995631 \backslash \mathrm{H}, 1.1656315282,1.604$ $3541614,-2.5958995631 \backslash H,-1.1656315282,1.6043541614,-2.5958995631 \backslash H,-1$. $886031431,-0.6128087597,-2.5958995631 \backslash \mathrm{H}, 0 .,-1.9830908035,-2.5958995631$ $\backslash \backslash V e r s i o n=S G I-G 98 R e v A .6 \backslash S t a t e=1-A G \backslash H F=-769.0426886 \backslash \mathrm{MP} 2=-771.6183563 \backslash \mathrm{RM}$ $S D=5.808 \mathrm{e}-09 \backslash \mathrm{RMSF}=7.410 \mathrm{e}-05 \backslash \mathrm{Dipole}=0 ., 0.0 . \backslash \mathrm{PG}=\mathrm{IH} \quad[10 \mathrm{C} 3(\mathrm{H} 1 \mathrm{Cl} . \mathrm{C} 1 \mathrm{H} 1)] \backslash \backslash @$

## Capping Hydrocarbons

## 4-65 bicyclo[2.2.0]hexane $\boldsymbol{C}_{\mathbf{2}}$

$1 \backslash 1 \backslash G I N C-P A L O \backslash F O p t \backslash R M P 2-F C \backslash 6-31 G(d) \backslash C 6 H 10 \backslash R A S M U S S E N \backslash 14-O c t-1999 \backslash 0 \backslash \ \# P$ MP2/6-31G* 5D OPT FREQ=NORAMAN NAME=RASMUSSEN GEOM= (CHECK,NODISTANCE,N OANGLE, NODIHEDRAL) GUESS=CHECK <br>bicyclohexane C2 <br>0,1\H,-2.4392280943, $-0.3740737391,-0.1326749111 \backslash \mathrm{H},-1.0349573792,0.9291711906,1.4810359265 \backslash$ H, 2.4392280943,0.3740737391,-0.1326749111 \C, -1.3833874941,-0.269615732 $1,-0.3980785304 \backslash \mathrm{H}, 1.0349573792,-0.9291711906,1.4810359265 \backslash \mathrm{C},-0.5231717$ 514,0.5810612547,0.578483969\Н, 0.1407223773,2.0987563373,-0.9607334387 \H, 0.9711704656,2.1803191138,0.6097706412 \H, 1.3288331176,-0.0898063194 ,-1.4315764871 \H, -0.9711704656,-2.1803191138, 0.6097706412 \H, -0.1407223 $773,-2.0987563373,-0.9607334387 \backslash \mathrm{C}, 0.5231717514,-0.5810612547,0.5784839$ $69 \backslash \mathrm{H},-1.3288331176,0.0898063194,-1.4315764871 \backslash \mathrm{C}, 0.4921996743,1.5062504$ 331,-0.1080423938\C,1.3833874941,0.2696157321,-0.3980785304\C,-0.49219 96743,-1.5062504331,-0.1080423938<br>Version=Sun-SVR4-Unix-G98RevA.7\Sta $\mathrm{te}=1-\mathrm{A} \backslash \mathrm{HF}=-232.9630472 \backslash \mathrm{MP} 2=-233.7356193 \backslash \mathrm{RMSD}=5.448 \mathrm{e}-09 \backslash \mathrm{RMSF}=9.277 \mathrm{e}-06 \backslash$ Dipole=0.,0.,0.040946\PG=C02 [X(C6H10)] <br>@

## TB-4-52 cyclohexane (twistboat) $\boldsymbol{C}_{2}$

$1 \backslash 1 \backslash G I N C-P A L O \backslash F O p t \backslash R M P 2-F C \backslash 6-31 G(d) \backslash C 6 H 12 \backslash R A S M U S S E N \backslash 14-O c t-1999 \backslash 0 \backslash \ \# P$ MP2/6-31G* 5D OPT FREQ=NORAMAN NAME=RASMUSSEN GEOM= (CHECK,NODISTANCE,N OANGLE,NODIHEDRAL) GUESS=CHECK <br>cyclohexane C1 twist <br>0,1\H,0.41836158 95,-1.1785587595,-1.4650738223\C,0.6510844852,-1.2152970219,-0.3935284 $956 \backslash \mathrm{H},-1.2167945711,-2.1402585613,0.2312197127 \backslash \mathrm{H}, 1.2167879202,2.140270$ 709, 0.2311420814\C,-0.6510731397,1.2152763129,-0.3936111448\H,-0.41831 92628,1.1784817455,-1.4651478164 \H, 2.1743940834,-0.2742464092,0.836288 $798 \backslash \mathrm{H},-2.176115863,-0.2615951889,-0.8360876885 \backslash \mathrm{H}, 0.4251206649,1.176217$ $7732,1.4650436518 \backslash \mathrm{H},-1.2043640514,2.1472687958,-0.2313610944 \backslash \mathrm{H},-2.1744$
$184157,0.2742902723,0.8362114426 \backslash \mathrm{H}, 1.2043707147,-2.1472809576,-0.23121$ $3438 \backslash \mathrm{H},-0.4251628263,-1.1761405351,1.4650932016 \backslash \mathrm{C}, 1.5185107858,-0.0044$ $162356,0.0000578879 \backslash \mathrm{C}, 0.6581014319,1.2115230984,0.3935052601 \backslash \mathrm{C},-1.5185$ $107942,0.0044162005,0.0000137657 \backslash \mathrm{C},-0.6581127855,-1.2115023628,0.39354$ $99665 \backslash \mathrm{H}, 2.1761401167,0.2615511672$, - $0.8360384679 \backslash \backslash V e r s i o n=$ Sun-SVR4-Unix $-G 98 R e v A .7 \backslash H F=-234.1952006 \backslash M P 2=-234.9740811 \backslash R M S D=3.080 e-09 \backslash R M S F=6.353 e$ -05\Dipole=0., 0., -0.0000015\PG=C01 [X(C6H12)]<br>@

## 4-66 cycloheptane <br> $C_{1}$

$1 \backslash 1 \backslash G I N C-V P P 04 \backslash F O p t \backslash R M P 2-F C \backslash 6-31 G(d) \backslash C 7 H 14 \backslash D R R 501 \backslash 04-A p r-2000 \backslash 0 \backslash \backslash \# P$ MP 2/6-31G(D) 5D OPT MAXDISK=1980000000<br>cycloheptane C1<br>0,1\C,0.5474272 152,-0.3031157924,-0.8056461915 \H, -1.4288159641, 1.7227747585, 1.3246540 $826 \backslash \mathrm{C},-0.3154867518,1.7771474038,-0.5213746768 \backslash \mathrm{H}, 1.3046997359,1.449655$ $8811,-2.0084317603 \backslash \mathrm{C}, 0.3896048975,0.9445304794,-1.6818484782 \backslash \mathrm{H}, 0.95404$ $96784,0.2179197046,0.052044469 \backslash \mathrm{H},-0.518033377,-0.4592770769,-0.6928762$ $762 \backslash \mathrm{C}, 0.9591049709,-1.6914263853,-0.3033435698 \backslash \mathrm{C}, 0.0091858845,-1.60736$ $31178,0.9725457864 \backslash \mathrm{H}, 2.0170425515,-1.7744727755,-0.0319909178 \backslash \mathrm{H}, 0.6859$ $70331,-2.5523036277,-0.9226472938 \backslash \mathrm{H}, 0.4233673269,-2.166543003,1.821630$ $2784 \backslash \mathrm{H},-0.9324188063,-2.1021095973,0.6999169001 \backslash \mathrm{C},-0.3724653262,-0.156$ $22288,1.5137972299 \backslash \mathrm{C},-1.075407611,0.9579296438,0.6169650701 \backslash \mathrm{H}, 0.519034$ $107,0.2930870574,1.9749464476 \backslash \mathrm{H},-1.0664081905,-0.3412585366,2.34740673$ $5 \backslash \mathrm{H}, 0.4728360301,2.3565185224,-0.0227768484 \backslash \mathrm{H},-1.9875642432,0.52016549$ $73,0.1861017487 \backslash \mathrm{H},-0.2632444291,0.8027017284,-2.549871191 \backslash \mathrm{H},-1.0322944$ 244,2.5042653586,-0.9246773942<br>Version=Fujitsu-VP-Unix-G98RevA. 7 \HF=$273.0757024 \backslash M P 2=-274.0019328 \backslash R M S D=5.987 e-09 \backslash R M S F=5.966 e-05 \backslash D i p o l e=-0.1$ 092023,0.0604583,0.160691\PG=C01 [X(C7H14)] <br>@

## 4-67 norbornane $\boldsymbol{C}_{\mathbf{2 v}}$

$1 \backslash 1 \backslash G I N C-$ PALO $\backslash$ FOpt $\backslash$ RMP2-FC $\backslash 6-31 G(d) \backslash C 7 H 12 \backslash R A S M U S S E N \backslash 14-O c t-1999 \backslash 0 \backslash \ \# P$ GEOM=ALLCHECK GUESS=TCHECK RMP2(FC)/6-31G(D) FOPT<br>bicycloheptane C2v $\backslash 0,1 \backslash \mathrm{H}, 0.8928185487,0.2 .0181348967 \backslash \mathrm{H},-0.8928185487,0 ., 2.0181348967 \backslash \mathrm{H}$, $0 .,-2.150407647,0.7293974312 \backslash H,-2.1527765812,-1.1717240568,-0.01467211$ $91 \backslash \mathrm{H}, 0 ., 2.150407647,0.7293974312 \backslash \mathrm{C}, 0.0 ., 1.3815116313 \backslash \mathrm{H}, 1.1998332789,1$ . $2036410029,-1.4995748094 \backslash \mathrm{H},-2.1527765812,1.1717240568,-0.0146721191 \backslash \mathrm{H}$ ,1.1998332789,-1.2036410029,-1.4995748094\C,0.,-1.1276035,0.3383864661 \H,-1.1998332789,-1.2036410029,-1.4995748094\C,0.,1.1276035,0.33838646 $61 \backslash \mathrm{H},-1.1998332789,1.2036410029,-1.4995748094 \backslash \mathrm{C}, 1.2478018377,0.7785122$ $79,-0.4911576801 \backslash C, 1.2478018377,-0.778512279,-0.4911576801 \backslash C,-1.247801$ 8377,-0.778512279,-0.4911576801 \C,-1.2478018377,0.778512279,-0.4911576 $801 \backslash \mathrm{H}, 2.1527765812,1.1717240568,-0.0146721191 \backslash \mathrm{H}, 2.1527765812,-1.171724$ 0568,-0.0146721191 <br>Version=Sun-SVR4-Unix-G98RevA. $7 \backslash$ State=1-A1 \HF=-272 $.059161 \backslash \mathrm{MP} 2=-272.966536 \backslash \mathrm{RMSD}=1.850 \mathrm{e}-09 \backslash \mathrm{RMSF}=5.099 \mathrm{e}-05 \backslash$ Dipole=0.,0.,0.0 $235243 \backslash \mathrm{PG}=\mathrm{CO} 2 \mathrm{~V}$ [C2(C1),SGV(C2H2),SGV'(H2),X(C4H8)]<br>@

## 4-68 cis-bicyclo[3.3.0]octane $\quad C_{2 v}$

$1 \backslash 1 \backslash G I N C-P A L O \backslash F O p t \backslash R M P 2-F C \backslash 6-31 G(d) \backslash C 8 H 14 \backslash R A S M U S S E N \backslash 14-O c t-1999 \backslash 0 \backslash \ \# P$ MP2/6-31G* 5D OPT FREQ=NORAMAN NAME=RASMUSSEN GEOM= (CHECK,NODISTANCE,N OANGLE,NODIHEDRAL) SYMM=LOOSE<br>bicyclooctane C2v $\backslash \backslash 0,1 \backslash \mathrm{H}, 0 ., 2.605704831$ 3,-1.0492991401 \C, 0.7833932827,0.,-0.4706269325\H,0.,-3.1208686173,0.6 $428275147 \backslash \mathrm{C},-0.7833932827,0 .,-0.4706269325 \backslash \mathrm{H},-1.1481562816,0 .,-1.50568$ $52336 \backslash \mathrm{H}, 0 ., 3.1208686173,0.6428275147 \backslash \mathrm{H}, 1.3268542036,1.1464261522,1.291$ $5113202 \backslash \mathrm{C}, 0 .,-2.243173019,-0.0134043819 \backslash \mathrm{H},-1.3268542036,1.1464261522,1$
$.2915113202 \backslash \mathrm{H}, 0 .,-2.6057048313,-1.0492991401 \backslash \mathrm{H},-1.3268542036,-1.146426$ 1522, 1.2915113202 \H, 1.1481562816, 0., -1. $5056852336 \backslash \mathrm{H}, 1.3268542036,-1.14$ $64261522,1.2915113202 \backslash \mathrm{C}, 1.1971077748,1.3137914513,0.2140412851 \backslash \mathrm{C},-1.19$ $71077748,1.3137914513,0.2140412851 \backslash \mathrm{C},-1.1971077748,-1.3137914513,0.214$ $0412851 \backslash \mathrm{C}, 1.1971077748,-1.3137914513,0.2140412851 \backslash \mathrm{H}, 2.1412794302,1.717$ $6253043,-0.167586658 \backslash \mathrm{H},-2.1412794302,1.7176253043,-0.167586658 \backslash \mathrm{H},-2.14$ $12794302,-1.7176253043,-0.167586658 \backslash \mathrm{H}, 2.1412794302,-1.7176253043,-0.16$ $7586658 \backslash C, 0 ., 2.243173019,-0.0134043819 \backslash \backslash V e r s i o n=S u n-S V R 4-U n i x-G 98 R e v A$. $7 \backslash$ State $=1-\mathrm{A} \backslash \mathrm{HF}=-311.1001761 \backslash \mathrm{MP} 2=-312.1362913 \backslash \mathrm{RMSD}=4.289 \mathrm{e}-09 \backslash \mathrm{RMSF}=1.99$ $8 \mathrm{e}-05 \backslash$ Dipole=0., 0., -0.0455532\PG=C02V [SGV (C2H4), SGV' (C2H2) , X (C4H8)] <br> @

## Cr-4-53 cyclooctane (crown) $\boldsymbol{C}_{\mathbf{4 v}}$

$1 \backslash 1 \backslash G I N C-P A L O \backslash F O p t \backslash R M P 2-F C \backslash 6-31 G(d) \backslash C 8 H 16 \backslash R A S M U S S E N \backslash 14-O c t-1999 \backslash 0 \backslash \ \# P$ MP2/6-31G* 5D OPT FREQ=NORAMAN NAME=RASMUSSEN GEOM= (CHECK,NODISTANCE,N OANGLE,NODIHEDRAL) SYMM=LOOSE<br>cyclooctane C2v crown<br>0,1\H,2.07957831 $2,2.0795209238,-0.1031861573 \backslash C,-1.3141577043,-1.3141564396,-0.28521460$ $16 \backslash \mathrm{H}, 1.2316373,1.2314901386,-1.3783355372 \backslash \mathrm{H},-1.2316373,-1.2314901386,-$ $1.3783355372 \backslash \mathrm{H},-1.2316373,1.2314901386,-1.3783355372 \backslash \mathrm{H}, 2.079578312,-2$. $0795209238,-0.1031861573 \backslash H, 1.2316373,-1.2314901386,-1.3783355372 \backslash \mathrm{H},-2$. $079578312,-2.0795209238,-0.1031861573 \backslash \mathrm{H}, 1.7413235719,0 ., 1.3784459928 \backslash \mathrm{H}$ ,-2.079578312,2.0795209238,-0.1031861573 \Н, 0.,1.7420719169,1.378227163 \H,0.,-1.7420719169,1.378227163\H,-1.7413235719,0.,1.3784459928\C,0.,$1.8586262932,0.2850789712 \backslash C, 1.8583715899,0 ., 0.2853511364 \backslash C, 0 ., 1.858626$ 2932,0.2850789712\C,-1.8583715899,0.,0.2853511364 \H, 0.,-2.9410130209, 0 $.1027996538 \backslash \mathrm{H}, 2.9408390112,0.0 .103565153 \backslash \mathrm{H}, 0 ., 2.9410130209,0.10279965$ $38 \backslash \mathrm{H},-2.9408390112,0.0 .103565153 \backslash \mathrm{C}, 1.3141577043,-1.3141564396,-0.2852$ $146016 \backslash \mathrm{C}, 1.3141577043,1.3141564396,-0.2852146016 \backslash \mathrm{C},-1.3141577043,1.314$ 1564396,-0.2852146016<br>Version=Sun-SVR4-Unix-G98RevA.7\State=1-A1 \HF=$312.253007 \backslash \mathrm{MP} 2=-313.2929085 \backslash \mathrm{RMSD}=2.801 e-09 \backslash \mathrm{RMSF}=1.218 \mathrm{e}-05 \backslash \mathrm{Dipole=0} ., 0$. , -0.0000015 ${ }^{2} \mathrm{PG}=\mathrm{CO} 2 \mathrm{~V}$ [SGV (C2H4), SGV'(C2H4), X(C4H8)]<br>@

## TBTB-4-54 bicyclo[3.3.1]nonane (twistboat-twistboat) $\quad \boldsymbol{C}_{\mathbf{2}}$

$1 \backslash 1 \backslash G I N C-P A L O \backslash F O p t \backslash R M P 2-F C \backslash 6-31 G(d) \backslash C 9 H 16 \backslash R A S M U S S E N \backslash 14-O c t-1999 \backslash 0 \backslash \ \# P$ MP2/6-31G* 5D OPT FREQ=NORAMAN NAME=RASMUSSEN GEOM= (CHECK,NODISTANCE,N OANGLE, NODIHEDRAL) GUESS=CHECK <br>bicyclononane C1 <br>0,1\H,0.8773425467,$0.0470929282,2.0367307775 \backslash \mathrm{H}, 0.0724393412,-2.1392229353,1.0622687007 \backslash \mathrm{H}$, $-0.0713323889,2.1389881426,1.0628204295 \backslash \mathrm{H}, 2.8387029721,-0.1365967746,-$ $1.1306662096 \backslash \mathrm{H},-2.8398750755,0.1368515362,-1.1276716558 \backslash \mathrm{C}, 0.0007073541$ ,-0.000153112,1.3790762965\H,1.4972224082,1.8204334911,-1.0778900843\H , 2.6175531487,-0.4592800727,0.5754456055\Н, 0.5319438928,-0.918483251,$1.6043704049 \backslash \mathrm{H},-0.8752593117,0.0466392608,2.0376326859 \backslash \mathrm{H},-1.4983281382$ ,-1.8201924878,-1.0767450486\H,-2.6169438798, 0.4591421447,0.578282992\} H, -0.5336135035,0.9188586503,-1.6036078943\C,1.5157475082,1.2742360306 , -0.1263048957\C,0.9933218482,-1.1663520453,-0.6416285897\C,-1.5158724 281,-1.2742132063,-0.1250162259\C,-0.9939890492,1.1665003347,-0.640327 $7903 \backslash \mathrm{H}, 2.1819137884,1.836754068,0.5400095913 \backslash \mathrm{H}, 1.4408587624,-2.1587179$ $408,-0.7764707165 \backslash \mathrm{H},-2.1813445273,-1.8368875065,0.5418597873 \backslash \mathrm{H},-1.4416$ $727657,2.1588949926,-0.7744695192 \backslash C, 2.0881963718,-0.1427580596,-0.3313$ $826351 \backslash C,-0.0925522782,-1.2308647746,0.4686909118 \backslash C,-2.0885345068,0.14$ $28289952,-0.3291708637 \backslash \mathrm{C}, 0.0930406349,1.2307611057,0.4688706195 \backslash \backslash \mathrm{Versi}$ on=Sun-SVR4-Unix-G98RevA. $7 \backslash \mathrm{HF}=-350.123117 \backslash \mathrm{MP} 2=-351.2948227 \backslash \mathrm{RMSD}=3.543 \mathrm{e}$
$-09 \backslash \mathrm{RMSF}=1.352 \mathrm{e}-05 \backslash \mathrm{Dipole}=0.0000113,-0.000002,0.0213998 \backslash \mathrm{PG}=\mathrm{C01}$ [X(C9H1 6)] <br>@

## Bridged Spiropentanes

## 4-26 [3.3.3]fenestrane $\quad \boldsymbol{C}_{\mathbf{1}}$

$1 \backslash 1 \backslash G I N C-P C \backslash F O p t \backslash R M P 2-F C \backslash 6-31 G(d) \backslash C 5 H 6 \backslash R A S M U S S E N \backslash 04-N O v-1999 \backslash 0 \backslash \backslash \# P ~ M P 2$ /6-31G(D) 5D OPT= (READFC,TIGHT) FREQ=NORAMAN NAME=RASMUSSEN MAXDISK=20 97152000 GEOM=CHECK GUESS=CHECK NOSYMM $\backslash \backslash[3.3 .3]$ fenestrane $C 1 \backslash \backslash 0,1 \backslash H, 1$. $6566522739,-0.91131785,-1.3572958237 \backslash \mathrm{C}, 1.4192235947,-0.2833672819,-0.4$ $968373026 \backslash C, 0.1171830693,0.4372075207,-0.464597015 \backslash C, 0.386999874,-0.81$ $08699224,0.4658542258 \backslash H, 2.2772228777,0.2704917096,-0.1130098357 \backslash \mathrm{C},-1.3$ $582000672,0.4974173326,-0.2359432462 \backslash \mathrm{C},-0.3382647149,0.4232483833,0.91$ $01762225 \backslash \mathrm{H},-0.1763322414,-1.6969100637,0.1758023446 \backslash \mathrm{H},-0.1417442939,1$. $1054353411,1.7320736066 \backslash \mathrm{H},-1.8452176421,1.4479944289,-0.4597494011 \backslash \mathrm{H}$, -$1.9915877595,-0.3773326698,-0.3985105815 \backslash \backslash V e r s i o n=S G I-G 98 R e v A .6 \backslash H F=-19$ $2.6284468 \backslash M P 2=-193.2801211 \backslash R M S D=9.950 e-09 \backslash R M S F=8.340 e-07 \backslash D i p o l e=-0.013$ 197,0.0203119,-0.2202737\PG=C01 [X(C5H6)] <br>@

## 4-25 [3.4.3]fenestrane $\boldsymbol{C}_{\mathbf{2}}$

$1 \backslash 1 \backslash A N U-A R G E N T \backslash F O P T \backslash R M P 2-F C \backslash 6-31 G(D) \backslash C 6 H 8 \backslash R A S M U S S E N \backslash 28-N o v-1994 \backslash 1 \backslash \ \# P$ RMP2/6-31G* 5D FOPT=READFC NAME=RASMUSSEN TEST SCF=DIRECT MAXDISK=2437 50000 GEOM = (CHECK, NODISTANCE, NOANGLE, NODIHEDRAL) GUESS=CHECK $\backslash \backslash[3.4 .3]$ f enestrane $C 2 \backslash \backslash 0,1 \backslash C \backslash C, 1, c l \backslash C, 1, r 1 a, 2, a 1 a \backslash C, 1, r 1 a, 2, a 1 a, 3,180 ., 0 \backslash C, 1, r 2$ $a, 4, a 2 a, 3, d 2 a, 0 \backslash C, 1, r 2 a, 3, a 2 a, 4, d 2 a, 0 \backslash H, 5, h 3 a, 1, h a 3 a, 3, h d 3 a, 0 \backslash H, 6, h 3 a$, 1, ha3a, 4, hd3a, $0 \backslash H, 3, h 1 a, 1, h a 1 a, 6, h d 1 a, 0 \backslash H, 4, h 2 a, 1, h a 2 a, 5, h d 2 a, 0 \backslash H, 3, h 2$ $a, 1, h a 2 a, 6, h d 2 a, 0 \backslash H, 4, h 1 a, 1, h a 1 a, 5, h d 1 a, 0 \backslash H, 2, h 6 a, 1, h a 6 a, 3, h d 6 a, 0 \backslash H, 2$, $h 6 a, 1$, ha6a, 4, hd6a, $0 \backslash \backslash c l=2.1559663 \backslash r 1 a=1.4665557 \backslash r 2 a=1.51612963 \backslash a 1 a=91$. $20037275 \backslash a 2 a=61.90646495 \backslash d 2 a=143.94667725 \backslash h 3 a=1.08896925 \backslash h a 3 a=123.5396$ $714 \backslash h d 3 a=75.13498892 \backslash h a 1 a=118.38146571 \backslash h a 2 a=119.28200678 \backslash h a 6 a=125.8311$ $8906 \backslash h d 1 a=101.16031288 \backslash h d 2 a=-112.2781889 \backslash h d 6 a=45.07435081 \backslash h 1 a=1.089056$ $52 \backslash h 2 a=1.09004287 \backslash h 6 a=1.0967593 \backslash \backslash V e r s i o n=I B M-R S 6000-G 92 R e v B \backslash S t a t e=1-A \backslash$ $\mathrm{HF}=-231.704008 \backslash \mathrm{MP} 2=-232.4780644 \backslash \mathrm{RMSD}=9.758 \mathrm{e}-09 \backslash \mathrm{RMSF}=1.413 \mathrm{e}-05 \backslash \mathrm{Dipole}=0$ ., -0.,-0.018111 \PG=C02 [C2 (C1C1), X(C4H8)] <br>@

## 4-45 [3.5.3]fenestrane $\boldsymbol{C}_{\mathbf{2}}$

$1 \backslash 1 \backslash A N U-A R G E N T \backslash F O P T \backslash R M P 2-F C \backslash 6-31 G(D) \backslash C 7 H 10 \backslash R A S M U S S E N \backslash 30-N O V-1994 \backslash 1 \backslash \backslash \#$ RMP2/6-31G* 5D FOPT=READFC NAME=RASMUSSEN SCF=DIRECT TEST MAXDISK=243 $750000 \mathrm{GEOM}=(\mathrm{CHECK}, N O D I S T A N C E, N O A N G L E, N O D I H E D R A L) ~ G U E S S=C H E C K \backslash \backslash[3.5 .3]$ fenestrane $7 \mathrm{a} C 2 \backslash \backslash 0,1 \backslash C \backslash X, 1,1 . \backslash C, 1, r 1 a, 2, a 1 a \backslash C, 1, r 1 a, 2, a 1 a, 3,180 ., 0 \backslash C$, $1, r 2 a, 4, a 2 a, 3, d 2 a, 0 \backslash C, 1, r 2 a, 3, a 2 a, 4, d 2 a, 0 \backslash C, 5, r 3 a, 1, a 3 a, 3, d 3 a, 0 \backslash C, 6, r 3$ $a, 1, a 3 a, 4, d 3 a, 0 \backslash H, 5, h 3 a, 1, h a 3 a, 3, h d 3 a, 0 \backslash H, 6, h 3 a, 1, h a 3 a, 4, h d 3 a, 0 \backslash H, 3, h 1$ $a, 1, h a 1 a, 6, h d 1 a, 0 \backslash H, 4, h 2 a, 1, h a 2 a, 5, h d 2 a, 0 \backslash H, 3, h 2 a, 1, h a 2 a, 6, h d 2 a, 0 \backslash H, 4$, h1a, 1 , hala, 5 , hd1a, $0 \backslash H, 7, h 5 a, 5, h a 5 a, 1, h d 5 a, 0 \backslash H, 8, h 5 a, 6, h a 5 a, 1, h d 5 a, 0 \backslash H$, $7, h 6 a, 5, h a 6 a, 1, h d 6 a, 0 \backslash H, 8, h 6 a, 6, h a 6 a, 1, h d 6 a, 0 \backslash \backslash r 1 a=1.47655571 \backslash r 2 a=1.48$ $170952 \backslash \mathrm{ala}=79.02745075 \backslash \mathrm{a} 2 \mathrm{a}=62.58242051 \backslash \mathrm{~d} 2 \mathrm{a}=139.2418273 \backslash \mathrm{r} 3 \mathrm{a}=1.53193336 \backslash$ $a 3 a=105.54147758 \backslash d 3 a=-81.91928133 \backslash h 3 a=1.08900735 \backslash h a 3 a=120.72670433 \backslash h d 3$ $a=56.5921153 \backslash h a 1 a=119.19224468 \backslash h a 2 a=118.37541432 \backslash h a 5 a=110.61817981 \backslash h a 6$ $a=112.59519358 \backslash h d 1 a=105.00571988 \backslash h d 2 a=-108.09854561 \backslash h d 5 a=-89.28001905 \backslash$ $h d 6 a=150.901805 \backslash h 1 a=1.08888979 \backslash h 2 a=1.08891854 \backslash h 5 a=1.09789558 \backslash h 6 a=1.096$ $22908 \backslash \backslash$ Version=IBM-RS6000-G92RevB $\backslash$ State $=1-A \backslash H F=-270.7984122 \backslash M P 2=-271.7$ $006233 \backslash \mathrm{RMSD}=3.904 \mathrm{e}-09 \backslash \mathrm{RMSF}=3.199 \mathrm{e}-06 \backslash \mathrm{Dipole=-0.,-0.,-0.0578713} \mathrm{\backslash PG=C02}$

$[\mathrm{C} 2(\mathrm{C} 1), \mathrm{X}(\mathrm{C} 6 \mathrm{H} 10)] \backslash \backslash @$

## 4-46 tetracyclo-[3.3.1.0 $\mathbf{0}^{2,4} .0^{2,8}$ ]nonane $\boldsymbol{C}_{\mathbf{1}}$

$1 \backslash 1 \backslash \mathrm{GINC}-\mathrm{RSCQC} 2 \backslash$ FOpt $\backslash \mathrm{RMP} 2-\mathrm{FC} \backslash 6-31 \mathrm{G}(\mathrm{d}) \backslash \mathrm{C} 9 \mathrm{H} 12 \backslash$ DANNE $\backslash 03$-Dec-1995\0<br>\#P RM P2/6-31G* 5D FOPT SCF=TIGHT MAXDISK=500000000 GEOM= (NODISTANCE, NOANGLE , NODIHEDRAL $\backslash \backslash$ Baird $C 1 \backslash \backslash 0,1 \backslash C, 0.1059936544,-1.3141277831,0.4409114962 \backslash$ C, 1. $2904125998,-0.3786233175,0.6758759938 \backslash C, 1.7286778177,0.4800236689$, $-0.5101625834 \backslash C,-1.3637869152,0.4577062327,1.7125847986 \backslash C,-0.803398263$ $5,0.2874048662,-1.0465308867 \backslash C,-0.7221750908,-1.227431561,-0.827412661$ $8 \backslash C,-0.8605232509,0.9106531054,0.342981284 \backslash C,-0.0648497355,-0.03784865$ $46,1.1851211759 \backslash \mathrm{C}, 0.5939965325,0.734542203,-1.5518505182 \backslash \mathrm{H}, 0.108341666$ $9,-2.2421093718,1.012218595 \backslash \mathrm{H}, 2.0865380934,-0.7457571392,1.3257614207 \backslash$ H, - $0.306188867,-1.7455491981,-1.70124994 \backslash \mathrm{H},-1.4110559146,1.252425733,2$ $.4558397805 \backslash \mathrm{H}, 2.1063614559,1.4360780314,-0.1274519919 \backslash \mathrm{H}, 2.5776182857$, -$0.0100345072,-1.0019678827 \backslash \mathrm{H},-2.147530886,-0.2911700938,1.8174153304 \backslash \mathrm{H}$ , $-0.5206461582,1.9485706638,0.3699493933 \backslash H, 0.5640750926,1.8009010085,-$ $1.805169044 \backslash \mathrm{H}, 0.8117864545,0.1978034662,-2.4833801919 \backslash \mathrm{H},-1.7131772809$, $-1.6575972155,-0.6297549071 \backslash \mathrm{H},-1.5822060325,0.5826460631,-1.7613191528$ $\backslash$ Version=IBM-RS6000-G94RevC. $2 \backslash \mathrm{HF}=-347.6766297 \backslash \mathrm{MP} 2=-348.8427814 \backslash \mathrm{RMSD}=7$ $.392 \mathrm{e}-09 \backslash \mathrm{RMSF}=5.271 \mathrm{e}-05 \backslash \mathrm{Dipole}=0.0444677,0.002156,-0.1037839 \backslash \mathrm{PG}=\mathrm{C01}$ [X (C9H12)] <br>@

## Fenestranes

## $\boldsymbol{C}_{\mathrm{s}}$-4-18 trans,cis,cis,cis-[4.4.4.4]fenestrane $\quad \boldsymbol{C}_{\mathrm{s}}$

$1 \backslash 1 \backslash G I N C-V P P 09 \backslash F O p t \backslash R M P 2-F C \backslash 6-31 G(d) \backslash C 9 H 12 \backslash R A S M U S S E N \backslash 29-A u g-1996 \backslash 0 \backslash \backslash \# P$

 $0000 \mathrm{GEOM}=($ NODISTANCE, NOANGLE, NODIHEDRAL) <br>[4.4.4.4]fenestrane 5D Cs $\backslash \backslash$ $0,1 \backslash C,-0.0666978099,-0.0671534573,0.5696359847 \backslash \mathrm{C},-0.0666978099,1.38832$ $17126,0.5696359847 \backslash C, 0.1021884122,-0.6836492613,-0.8727452513 \backslash C,-1.498$ $6607128,1.25020228,-0.1146519102 \backslash \mathrm{C}, 1.4846097704,1.25020228,0.234654687$ $\backslash C, 1.4745312107,-0.2837587995,0.7154633397 \backslash \mathrm{C},-1.5999263108,-0.28375879$ $95,0.3554797911 \backslash C, 1.4542275051,-1.3026816755,-0.441118178 \backslash C,-1.3129900$ $398,-1.3026816755,-0.7651274657 \backslash \mathrm{H},-0.1829084406,1.8403535246,1.5621386$ $952 \backslash \mathrm{H}, 0.2000646802,0.0153322195,-1.7086624183 \backslash \mathrm{H},-2.2561383448,1.903966$ $6952,0.3291916494 \backslash \mathrm{H}, 2.1190664518,1.9039666952,0.8414777154 \backslash \mathrm{H},-1.534615$ 0977,1.3617408107, -1.2020442144 \H, 1.7707900002, 1.3617408107, -0. 8150193 $658 \backslash \mathrm{H}, 2.0360815395,-0.4833911809,1.6364951841 \backslash \mathrm{H},-2.3590549439,-0.48339$ 11809, 1. 1218753472 \H, 1. $3453036197,-2.3266419244,-0.0646321062 \backslash \mathrm{H},-1.293$ $9843929,-2.3266419244,-0.3736623199 \backslash H, 2.2731442532,-1.2786450843,-1.17$ $05312568 \backslash \mathrm{H},-1.9412546167,-1.2786450843,-1.6639888018 \backslash \backslash$ Version=Fujitsu-VP-Unix-G94RevD. $2 \backslash$ State=1-A' $\backslash \mathrm{HF}=-347.5740447 \backslash \mathrm{MP} 2=-348.7458982 \backslash \mathrm{RMSD}=6.5$ $40 e-09 \backslash \mathrm{RMSF}=1.457 \mathrm{e}-05 \backslash \mathrm{Dipole}=0.0595783,0.0 .0137398 \backslash \mathrm{PG}=\mathrm{CS} \quad[\mathrm{SG}(\mathrm{C} 3 \mathrm{H} 2), \mathrm{X}($ C6H10) ] <br>@

## $D_{2 \mathrm{~d}}-4-18 \quad$ all-cis-[4.4.4.4]fenestrane $\quad D_{2 \mathrm{~d}}$

$1 \backslash 230 \backslash G I N C-A R G E N T \backslash F O P T \backslash R M P 2-F C \backslash 6-31 G(D) \backslash C 9 H 12 \backslash R A S M U S S E N \backslash 25-M a y-1994 \backslash 1 \backslash$ <br>\#P RMP2=(DIRECT) 6-31G* 5D SCF=DIRECT NAME=RASMUSSEN OPT=READFC MAXDI SK=218750000 GEOM = (CHECK, NODISTANCE, NOANGLE, NODIHEDRAL) GUESS=CHECK <br>[ 4.4.4.4]fenestrane D2d RMP2/6-31G* $5 \mathrm{D} \backslash \backslash 0,1 \backslash \mathrm{C} \backslash \mathrm{X}, 1,0.5 \backslash \mathrm{X}, 1,0.5,2,90 . \backslash \mathrm{X}, 1$ $, 0.5,2,90 ., 3,90 ., 0 \backslash \mathrm{X}, 1,0.5,4,90 ., 2,180 ., 0 \backslash \mathrm{X}, 1,0.5,2,90 ., 3,180 ., 0 \backslash \mathrm{X}, 1,0$ $.5,2,90 ., 4,180 ., 0 \backslash C, 1, c c 1,2, \operatorname{ccx} 1,4,0 ., 0 \backslash C, 1, c c 1,2, c c x 1,7,0 ., 0 \backslash C, 1, c c 1$,

5, ccx1,3,0.,0\C,1, cc1,5, ccx1,6,0.,0\C,1,cc2,2,90.4,45.,0\C,1,cc2,2,90 $., 4,-45 ., 0 \backslash \mathrm{C}, 1, \mathrm{cc} 2,2,90 ., 7,45 ., 0 \backslash \mathrm{C}, 1, \mathrm{Cc} 2,2,90.7,-45 ., 0 \backslash \mathrm{H}, 8, \mathrm{hc} 3,1, \mathrm{hcc} 3$ $, 2,0 ., 0 \backslash \mathrm{H}, 9, \mathrm{hc} 3,1, \mathrm{hcc} 3,2,0 ., 0 \backslash \mathrm{H}, 10, \mathrm{hc} 3,1, \mathrm{hcc} 3,5,0.0 \backslash \mathrm{H}, 11, \mathrm{hc} 3,1, \mathrm{hcc} 3,5$ $, 0 ., 0 \backslash \mathrm{H}, 12, \mathrm{hc} 4,1, \mathrm{hcc} 4,2, \mathrm{hccx} 4,0 \backslash \mathrm{H}, 12, \mathrm{hc} 4,1, \mathrm{hcc} 4,5, \mathrm{hccx} 4,0 \backslash \mathrm{H}, 13, \mathrm{hc} 4,1, \mathrm{~h}$ $\mathrm{cc} 4,2,-\mathrm{hccx} 4,0 \backslash \mathrm{H}, 13, \mathrm{hc} 4,1, \mathrm{hcc} 4,5,-\mathrm{hccx} 4,0 \backslash \mathrm{H}, 14, \mathrm{hc} 4,1, \mathrm{hcc} 4,2, \mathrm{hccx} 4,0 \backslash \mathrm{H}$, 14, hc4, 1, hcc 4,5, hccx $4,0 \backslash H, 15, h c 4,1$, hcc $4,2,-\mathrm{hccx} 4,0 \backslash \mathrm{H}, 15, \mathrm{hc} 4,1, \mathrm{hcc} 4,5,-$ hccx $4,0 \backslash \backslash \mathrm{cc} 1=1.48985141 \backslash \mathrm{ccx} 1=65.00898842 \backslash \mathrm{cc} 2=2.07078997 \backslash \mathrm{hc} 3=1.09392002$ $\backslash \mathrm{hcc} 3=120.07850406 \backslash \mathrm{hc} 4=1.09604716 \backslash \mathrm{hcc} 4=125.93415277 \backslash \mathrm{hccx} 4=28.16088107 \backslash$ \Version=IBM-RS6000-G92RevB\State=1-A1 \HF=-347.5610013 \MP2=-348.726771 $5 \backslash R M S D=1.281 e-09 \backslash R M S F=5.004 e-06 \backslash D i p o l e=0 .,-0 .,-0 . \backslash \mathrm{PG}=\mathrm{D} 02 \mathrm{D} \quad[\mathrm{O}(\mathrm{C} 1), 2 \mathrm{SGD}($ C2H2), X(C4H8)] <br>@

## $\boldsymbol{C}_{2 \mathrm{v}}$-4-18 all-trans-[4.4.4.4]fenestrane $\quad \boldsymbol{C}_{2 \mathrm{v}}$

$1 \backslash 1 \backslash G I N C-I X \backslash F O P T \backslash R M P 2-F C \backslash 6-31 G(D) \backslash C 9 H 12 \backslash R A S M U S S E N \backslash 3-J u n-1994 \backslash 1 \backslash \ \# P R M P$ 2=(DIRECT) 6-31G* 5D SCF=DIRECT NAME=RASMUSSEN FOPT=READFC GEOM=(CHECK ,NODISTANCE,NOANGLE,NODIHEDRAL) GUESS=CHECK MAXDISK=200000000<br>[4.4.4. 4]fenestrane C2v RMP2/6-31G* $\backslash \backslash 0,1 \backslash C \backslash X, 1,0.5 \backslash X, 1,0.5,2,90 . \backslash X, 1,0.5,2,90$ ., 3, $90 ., 0 \backslash \mathrm{X}, 1,0.5,4,90 ., 2,180 ., 0 \backslash \mathrm{X}, 1,0.5,2,90 ., 3,180 ., 0 \backslash \mathrm{X}, 1,0.5,2,90 .$, $4,180 ., 0 \backslash c, 1, c c 1 a, 2, c c x 1 a, 4,0.0 \backslash c, 1, c c 1 a, 2, c c x 1 a, 7,0.0 \backslash c, 1, c c 1 b, 2, c c$ x1b, 3, 0., $0 \backslash \mathrm{C}, 1, \mathrm{cc} 1 \mathrm{~b}, 2, \mathrm{ccx} 1 \mathrm{~b}, 6,0 ., 0 \backslash \mathrm{C}, 1, \mathrm{cc} 2,2, \mathrm{ccx} 2,4, \mathrm{ccxx} 2,0 \backslash \mathrm{C}, 1, \mathrm{cc} 2,2$, ccx $2,4,-\operatorname{ccxx} 2,0 \backslash \mathrm{C}, 1, \mathrm{cc} 2,2, \mathrm{ccx} 2,7, \mathrm{ccxx} 2,0 \backslash \mathrm{C}, 1, \mathrm{cc} 2,2, \mathrm{ccx} 2,7,-\mathrm{ccxx} 2,0 \backslash \mathrm{H}, 8$
 H, 11, hc3b, 1, hcc3b, $2,0 ., 0 \backslash H, 12, h c 4,1, h c c 4,2, h c c x 4,0 \backslash H, 12, h c 5,1, h c c 5,2, h$ ccx5, 0 $\backslash \mathrm{H}, 13, \mathrm{hc} 4,1, \mathrm{hcc} 4,2,-\mathrm{hccx} 4,0 \backslash \mathrm{H}, 13, \mathrm{hc} 5,1, \mathrm{hcc} 5,2,-\mathrm{hccx} 5,0 \backslash \mathrm{H}, 14, \mathrm{hc} 4$, 1, hcc 4,2, hccx $4,0 \backslash H, 14, h c 5,1, h c c 5,2, h c c x 5,0 \backslash H, 15, h c 4,1, h c c 4,2,-h c c x 4,0 \backslash$ H, 15, hc5,1,hcc5,2,-hccx5, 0<br>cc1a=1.77578849 \ccx1a=100.18025781 \cc1b=1. $47463555 \backslash c c x 1 b=116.48801127 \backslash c c 2=2.25966222 \backslash c c x 2=120.91849634 \backslash c c x x 2=40$. $71056557 \backslash \mathrm{hc} 3 \mathrm{a}=1.09415886 \backslash \mathrm{hcc} 3 \mathrm{a}=130.885446 \backslash \mathrm{hc} 3 \mathrm{~b}=1.09740724 \backslash \mathrm{hcc} 3 \mathrm{~b}=104.68$ $213236 \backslash \mathrm{hc} 4=1.09450884 \backslash \mathrm{hcc} 4=118.57671404 \backslash \mathrm{hccx} 4=193.32254798 \backslash \mathrm{hc5}=1.09458$ $039 \backslash$ hcc5 $=132.83850149$ \hccx5 $=20.87869969 \backslash$ VVersion=HP-PARisc-HPUX-G92/DF T-RevG.1 \State=1-A1 \HF=-347.5314018 \MP2=-348.7127039 ${ }^{\text {RMSD }=7.898 e-09 \backslash R M ~}$ $\mathrm{SF}=2.575 \mathrm{e}-05 \backslash \mathrm{Dipole}=0 ., 0 .,-0.2154305 \backslash \mathrm{PG}=\mathrm{CO} 2 \mathrm{~V}$ [C2 (C1), SGV (C2H2), SGV' (C2 H2) , X (C4H8) ] <br>@

## $\boldsymbol{C}_{\mathbf{2}}$-4-18 trans,cis,trans,cis-[4.4.4.4]fenestrane $\boldsymbol{C}_{\mathbf{2}}$

$1 \backslash 224 \backslash$ GINC-ARGENT $\backslash$ FOPT $\backslash$ RMP2-FC $\backslash 6$-31G (D) \C9H12 \RASMUSSEN $\backslash 22-M a y-1994 \backslash 1 \backslash$ <br>\#P RMP2=(DIRECT) 6-31G* 5D SCF=DIRECT NAME=RASMUSSEN FOPT=READFC MAXD ISK=500000000 GEOM=(CHECK,NODISTANCE,NOANGLE,NODIHEDRAL) GUESS=CHECK <br> [4.4.4.4]fenestrane C2 RMP2/6-31G* <br>0,1\C\X,1,0.5\X,1,0.5,2,90.\X,1,0. $5,2,90 ., 3,90.0 \backslash X, 1,0.5,4,90 ., 2,180 ., 0 \backslash X, 1,0.5,2,90 ., 3,180 ., 0 \backslash X, 1,0.5$, $2,90.4,180 ., 0 \backslash C, 1, c c 1 b, 2, c c x 1 b, 4, c c x x 1 b, 0 \backslash c, 1, c c 1 a, 2, c c x 1 a, 4,-c c x x 1 a$, $0 \backslash C, 1, c c 1 b, 5, c c x 1 b, 7, c c x x 1 b, 0 \backslash c, 1, c c 1 a, 5, c c x 1 a, 7,-c c x x 1 a, 0 \backslash c, 1, c c 2,2, c$ $\mathrm{cx} 2,4,0 ., 0 \backslash \mathrm{C}, 1, \mathrm{cc} 2,5, \mathrm{ccx} 2,7,0 ., 0 \backslash \mathrm{C}, 1, \mathrm{cc} 3,2,90 ., 3,0 ., 0 \backslash \mathrm{C}, 1, \mathrm{cc} 4,5,90 ., 6$, $0 ., 0 \backslash H, 8, h c 3 b, 1, h c c 3 b, 2, h c c x 3 b, 0 \backslash H, 9, h c 3 a, 1, h c c 3 a, 2, h c c x 3 a, 0 \backslash H, 10, h c 3 b$ ,1,hcc3b,5, hccx3b, $0 \backslash \mathrm{H}, 11$, hc3a, 1, hcc $3 \mathrm{a}, 5, \mathrm{hccx} 3 \mathrm{a}, 0 \backslash \mathrm{H}, 12, \mathrm{hc} 4,1, \mathrm{hcc} 4,2$, hcc x4, 0\H, 12, hc5, 1, hcc5, 2, hccx $5,0 \backslash H, 13, h c 4,1, h c c 4,5, h c c x 4,0 \backslash H, 13, h c 5,1, h c$ C5, 5, hccx $5,0 \backslash \mathrm{H}, 14, \mathrm{hc} 6,1, \mathrm{hcc} 6,2$, hccx $6,0 \backslash \mathrm{H}, 14, \mathrm{hc} 6,1, \mathrm{hcc} 6,5, \mathrm{hccx} 6,0 \backslash \mathrm{H}, 15$, hc7,1,hcc7,2,-hccx7,0\H,15,hc7,1,hcc7,5,-hccx7,0<br>cc1a=1.5180778\ccx1a $=81.16994972 \backslash c \mathrm{cxx} 1 \mathrm{a}=42.86958805 \backslash \mathrm{cc} 1 \mathrm{~b}=1.5064807 \backslash \mathrm{ccx} 1 \mathrm{~b}=100.89803796 \backslash \mathrm{ccxx}$ $1 \mathrm{~b}=46.65285943 \backslash \mathrm{cc} 2=2.12128588 \backslash \mathrm{ccx} 2=115.55278552 \backslash \mathrm{cc} 3=2.13596485 \backslash \mathrm{cc} 4=2.2$ $965316 \backslash \mathrm{hc} 3 \mathrm{a}=1.09975123 \backslash \mathrm{hcc} 3 \mathrm{a}=125.18014239 \backslash \mathrm{hccx} 3 \mathrm{a}=23.3145075 \backslash \mathrm{hc} 3 \mathrm{~b}=1.099$ $52227 \backslash \mathrm{hcc} 3 \mathrm{~b}=95.97190955 \backslash \mathrm{hccx} 3 \mathrm{~b}=-15.94811318 \backslash \mathrm{hc} 4=1.09412344 \backslash \mathrm{hcc} 4=98.858$
$47839 \backslash h c c x 4=196.59682935 \backslash h c 5=1.09995618 \backslash h c c 5=150.17071593 \backslash h c c x 5=5.5337$ $6631 \backslash$ hc6 $=1.09652718 \backslash$ hcc6=125.93953907 \hccx6=-7.37792653 \hc7=1. 09192345 $\backslash$ hcc $7=125.19382996 \backslash$ hccx7 $=25.3623112 \backslash \backslash V e r s i o n=I B M-R S 6000-G 92 R e v B \backslash$ State $=$ $1-A \backslash H F=-347.3807152 \backslash M P 2=-348.570765 \backslash R M S D=4.888 e-09 \backslash R M S F=9.415 e-03 \backslash D i p o$ le=0.0854325,0.,-0. \PG=C02 [C2 (C1C1C1), X(C6H12)] <br>@

## all-cis-4-19 [5.5.5.5]fenestrane $\quad \boldsymbol{D}_{\mathbf{2}}$

$1 \backslash 1 \backslash$ GINC-RSCQC6 \FOpt \RMP2-FC\6-31G(d) \C13H20\RASMUSSEN $\backslash 25-A u g-1996 \backslash 0 \backslash \backslash$ \#P RMP2/6-31G* 5D SCF=(DIRECT) NAME=RASMUSSEN GUESS=CHECK MAXDISK=4500 $00000 \mathrm{GEOM}=(\mathrm{CHECK}$, NODISTANCE, NOANGLE, NODIHEDRAL) OPT $\backslash$ \all-cis-[5.5.5.5 ]fenestrane D2 5D $\backslash \backslash 0,1 \backslash C, 0.0 .0 . \backslash C, 0.9302059218,-0.934340018,-0.82269$ $93958 \backslash C, 0.9302059218,0.934340018,0.8226993958 \backslash \mathrm{C},-0.9302059218,0.934340$ $018,-0.8226993958 \backslash C,-0.9302059218,-0.934340018,0.8226993958 \backslash C, 2.317511$ $2035,-0.7394618541,-0.1943674778 \backslash C, 2.3175112035,0.7394618541,0.1943674$ $778 \backslash C, 0.3285774885,2.3392233276,0.6933675699 \backslash \mathrm{C},-0.3285774885,2.3392233$ $276,-0.6933675699 \backslash C,-2.3175112035,0.7394618541,-0.1943674778 \backslash C,-2.3175$ $112035,-0.7394618541,0.1943674778 \backslash C,-0.3285774885,-2.3392233276,0.6933$ $675699 \backslash \mathrm{C}, 0.3285774885,-2.3392233276,-0.6933675699 \backslash \mathrm{H}, 0.9746213671,-0.61$ $16696942,-1.8726679448 \backslash \mathrm{H}, 0.9746213671,0.6116696942,1.8726679448 \backslash \mathrm{H},-0.9$ $746213671,0.6116696942,-1.8726679448 \backslash H,-0.9746213671,-0.6116696942,1.8$ $726679448 \backslash \mathrm{H}, 2.4147248861,-1.357694902,0.7084547456 \backslash \mathrm{H}, 3.1326144556,-1.0$ $197214735,-0.8722698397 \backslash \mathrm{H},-1.0736321512,3.1346895354,-0.8167238408 \backslash \mathrm{H}, 0$ $.4344909169,2.4909633656,-1.4669168957 \backslash \mathrm{H},-2.4147248861,1.357694902,0.7$ $084547456 \backslash \mathrm{H},-3.1326144556,1.0197214735,-0.8722698397 \backslash \mathrm{H}, 1.0736321512,-3$ $.1346895354,-0.8167238408 \backslash \mathrm{H},-0.4344909169,-2.4909633656,-1.4669168957 \backslash$ H, 3.1326144556, 1.0197214735, 0.8722698397\H, 2.4147248861,1.357694902,-0 $.7084547456 \backslash \mathrm{H},-0.4344909169,2.4909633656,1.4669168957 \backslash \mathrm{H}, 1.0736321512,3$ $.1346895354,0.8167238408 \backslash \mathrm{H},-3.1326144556,-1.0197214735,0.8722698397 \backslash \mathrm{H}$, $-2.4147248861,-1.357694902,-0.7084547456 \backslash \mathrm{H}, 0.4344909169,-2.4909633656$, $1.4669168957 \backslash \mathrm{H},-1.0736321512,-3.1346895354,0.8167238408 \backslash \backslash \mathrm{Version=IBM-R}$ S6000-G94RevD.1 \State=1-A \HF=-503.9468916\MP2=-505.6371177\RMSD=9.024e $-09 \backslash \mathrm{RMSF}=1.368 \mathrm{e}-05 \backslash \mathrm{Dipole=0.,0.,0}. \mathrm{\backslash PG=D02} \mathrm{\quad[O(C1),X(C12H20)]} \mathrm{\backslash} \mathrm{\backslash @}$

## all-trans-4-19 [5.5.5.5]fenestrane $\quad D_{2 d}$

$1 \backslash 136 \backslash G I N C-E I G E N \backslash F O P T \backslash R M P 2-F C \backslash 6-31 G(D) \backslash C 13 H 20 \backslash R A S M U S S E N \backslash 28-M a y-1994 \backslash 1 \backslash$ <br>\#P RMP2=(DIRECT) 6-31G* 5D FOPT=READFC NAME=RASMUSSEN SCF=(DIRECT) MA XDISK=218750000 GEOM = (CHECK, NODISTANCE, NOANGLE, NODIHEDRAL) GUESS=CHECK $\backslash$ C13H20 all-trans-[5.5.5.5]fenestrane RMP2/6-31G* D2 <br>0,1\C\X,1,1. \X, $1, r 1,2,90 . \backslash X, 1, r 1,2,90 ., 3,-90 ., 0 \backslash X, 1, r 1,2,90 ., 3,180 ., 0 \backslash X, 1, r 1,2,90 ., 4$, $180 ., 0 \backslash X, 1,1 ., 3,90 ., 2,180 ., 0 \backslash C, 1, r 2,7, a 1,6,45 ., 0 \backslash C, 1, r 2,2, a 1,4,45 ., 0 \backslash C$ $, 1, r 2,7, a 1,4,45 ., 0 \backslash C, 1, r 2,2, a 1,6,45 ., 0 \backslash C, 3, r 3,1,90 ., 2, d 1,0 \backslash C, 3, r 3,1,90$ $., 7, d 1,0 \backslash C, 4, r 3,1,90 ., 7,-d 1,0 \backslash C, 4, r 3,1,90 ., 2,-d 1,0 \backslash C, 5, r 3,1,90 ., 2, d 1,0$ $\backslash C, 5, r 3,1,90 ., 7, d 1,0 \backslash C, 6, r 3,1,90 ., 7,-d 1,0 \backslash C, 6, r 3,1,90 ., 2,-d 1,0 \backslash H, 8, r 4$, $1, a 2,10,180 ., 0 \backslash H, 9, r 4,1, a 2,11,180 ., 0 \backslash H, 10, r 4,1, a 2,8,180 ., 0 \backslash H, 11, r 4,1, a$ $2,9,180 ., 0 \backslash H, 12, r 5,8, a 3,13, a 4,-1 \backslash H, 12, r 6,8, a 5,13, a 6,1 \backslash H, 15, r 5,10, a 3,14$ , $\mathrm{a} 4,1 \backslash \mathrm{H}, 15, r 6,10, \mathrm{a} 5,14, \mathrm{a} 6,-1 \backslash \mathrm{H}, 16, r 5,10, a 3,17, a 4,-1 \backslash \mathrm{H}, 16, r 6,10, a 5,17, a$ $6,1 \backslash H, 19, r 5,8, a 3,18, a 4,1 \backslash H, 19, r 6,8, a 5,18, a 6,-1 \backslash H, 13, r 6,9, a 5,12, a 6,1 \backslash H$, $13, r 5,9, a 3,12, a 4,-1 \backslash H, 14, r 6,9, a 5,15, a 6,-1 \backslash H, 14, r 5,9, a 3,15, a 4,1 \backslash H, 17, r 6$ $, 11, a 5,16, a 6,1 \backslash H, 17, r 5,11, a 3,16, a 4,-1 \backslash H, 18, r 6,11, a 5,19, a 6,-1 \backslash H, 18, r 5,1$ $1, a 3,19, a 4,1 \backslash \backslash r 1=2.5254519 \backslash r 2=1.63460817 \backslash r 3=0.77696071 \backslash r 4=1.10915933 \backslash a$ $1=97.94038231 \backslash a 2=89.58543639 \backslash d 1=48.77510316 \backslash r 5=1.09790152 \backslash r 6=1.0967435$ $3 \backslash a 3=114.56061891 \backslash a 4=110.36684386 \backslash a 5=111.44503929 \backslash a 6=113.21983234 \backslash \backslash$ Ver
sion $=I B M-R S 6000-G 92 R e v B \backslash S t a t e=1-A 1 \backslash H F=-503.6875517 \backslash M P 2=-505.4040565 \backslash R M$ $S D=5.508 e-09 \backslash R M S F=1.364 e-05 \backslash D i p o l e=0 ., 0 .,-0 . \backslash P G=D 02 D \quad[O(C 1), 2 S G D(C 2 H 2)$ , X(C8H16)] <br>@

## C.2.3.3 Ionized Species

Table C-27. Guassian archive files for the B3-LYP/6-31G(d) optimized ions in Chapter 4.
${ }^{3} \mathbf{C H}_{2}{ }^{+} \quad \boldsymbol{C}_{2 \mathrm{v}}$
$1 \backslash 1 \backslash$ GINC-PC $\backslash$ FOpt $\backslash \mathrm{UB} 3 L Y P \backslash 6-31 \mathrm{G}(\mathrm{d}) \backslash \mathrm{C} 1 \mathrm{H} 2(1+, 2) \backslash R A S M U S S E N \backslash 28-M a r-2000 \backslash 0 \backslash \backslash \#$ P UB3LYP/6-31G(D) 5D OPT=(VERYTIGHT) FREQ=NORAMAN NAME=RASMUSSEN MAXDI $\mathrm{SK}=2097152000 \mathrm{GEOM}=\mathrm{CHECK} \backslash$ \methylene radical cation C 2 v doublet $\backslash \backslash 1,2 \backslash \mathrm{H}$, $-0.4505587643,0 .,-0.9713775773 \backslash C,-0.0712559267,0.0 .0597623699 \backslash \mathrm{H}, 0.878$ 0943245,0.,0.6128033576<br>Version=SGI-G98RevA. $6 \backslash$ State $=2-A 1 \backslash H F=-38.77174$ $9 \backslash \mathrm{~S} 2=0.751709 \backslash \mathrm{~S} 2-1=0 . \backslash \mathrm{S} 2 \mathrm{~A}=0.750001 \backslash \mathrm{RMSD}=5.843 \mathrm{e}-09 \backslash \mathrm{RMSF}=2.920 \mathrm{e}-07 \backslash \mathrm{Dipol}$ $\mathrm{e}=0.1758347,0 .,-0.1474727 \backslash \mathrm{PG}=\mathrm{CO} 2 \mathrm{~V}$ [C2 (C1),SGV (H2)] <br>@
$\mathbf{C H}_{4}{ }^{+\boldsymbol{+}} \quad \boldsymbol{C}_{2 \mathrm{v}}$
$1 \backslash 1 \backslash$ GINC-PC $\backslash$ FOpt $\backslash \mathrm{UB} 3 L Y P \backslash 6-31 \mathrm{G}(\mathrm{d}) \backslash \mathrm{C} 1 \mathrm{H} 4(1+, 2) \backslash R A S M U S S E N \backslash 28-\mathrm{Mar}-2000 \backslash 0 \backslash \backslash \#$ P B3LYP/6-31G(D) 5D OPT=(VERYTIGHT) FREQ=NORAMAN NAME=RASMUSSEN MAXDIS K=2097152000 OPTCYC=100<br>Methane radical cation D2d doublet <br>1,2\C,0., $0 ., 0 . \backslash \mathrm{H}, 0.3843141972,1.0566490428,0 . \backslash \mathrm{H}, 0.3843141972,-1.0566490428,0 . \backslash \mathrm{H}$ ,-0.3843141972,0.,1.0566490428\H,-0.3843141972,0.,-1.0566490428<br>Versi on=SGI-G98RevA. $6 \backslash$ State $=2-B 2 \backslash H F=-40.0511566 \backslash S 2=0.751127 \backslash S 2-1=0 . \backslash S 2 A=0.7$ $50001 \backslash \mathrm{RMSD}=1.292 \mathrm{e}-09 \backslash \mathrm{RMSF}=9.686 \mathrm{e}-08 \backslash \mathrm{Dipole}=0 ., 0 ., 0 . \backslash \mathrm{PG}=\mathrm{D} 02 \mathrm{D} \quad[\mathrm{O}(\mathrm{Cl}), 2 \mathrm{SG}$ D (H2) ] <br>@

## $\mathrm{NH}_{3}{ }^{+} \quad \boldsymbol{C}_{3 \mathrm{v}}$

$1 \backslash 1 \backslash G I N C-R S C Q C 9 \backslash F O p t \backslash U B 3 L Y P \backslash 6-31 G(d) \backslash H 3 N 1(1+, 2) \backslash R A S M U S S E N \backslash 27-M a r-2000 \backslash$ $0 \backslash$ <br>\#P B3LYP/6-31G(D) 5D OPT=(TIGHT) FREQ=NORAMAN NAME=RASMUSSEN MAXDIS K=917504000 <br>ammonia radical cation C3v doublet $\backslash \backslash 1,2 \backslash \mathrm{H}, 0 ., 0 ., 1.0292390$ $207 \backslash \mathrm{H}, 0.8913471385,0 .,-0.5146195103 \backslash \mathrm{H},-0.8913471385,0 .,-0.5146195103 \backslash \mathrm{~N}$ , 0., 0., 0. <br>Version=IBM-RS6000-G98RevA. $6 \backslash$ State $=2-A 2 " \backslash H F=-56.1831845 \backslash$ S2 $=$ $0.753628 \backslash \mathrm{~S} 2-1=0 . \backslash \mathrm{S} 2 \mathrm{~A}=0.750008 \backslash \mathrm{RMSD}=1.605 \mathrm{e}-09 \backslash \mathrm{RMSF}=2.894 \mathrm{e}-06 \backslash$ Dipole=0., $0.0 . \backslash \mathrm{PG}=\mathrm{D} 03 \mathrm{H}[\mathrm{O}(\mathrm{N} 1), 3 \mathrm{C} 2(\mathrm{H} 1)] \backslash \backslash$
$\mathrm{H}_{2} \mathrm{O}^{+} \quad \boldsymbol{C}_{2 \mathrm{v}}$
$1 \backslash 1 \backslash$ GINC-RSCQC2 \FOpt \UB3LYP\6-31G(d) \H2O1 (1+, 2) \RASMUSSEN $\backslash 27-M a r-2000 \backslash$ $0 \backslash \backslash \# P$ B3LYP/6-31G(D) 5D OPT=(TIGHT) FREQ=NORAMAN NAME=RASMUSSEN MAXDIS $\mathrm{K}=524288000 \backslash$ \water radical cation C 2 v doublet $\backslash \backslash 1,2 \backslash \mathrm{H},-0.1744593668,0$. , $-0.9348797849 \backslash O,-0.0894707778,0 ., 0.0750391718 \backslash \mathrm{H}, 0.8902255892,0 ., 0.3345$ $664108 \backslash$ VVersion=IBM-RS6000-G98RevA.6\State $=2-\mathrm{B} 1 \backslash \mathrm{HF}=-75.9572789$ S $2=0.75$ $2686 \backslash$ S2-1 $=0 . \backslash S 2 A=0.750005 \backslash$ RMSD $=1.318 \mathrm{e}-09 \backslash \mathrm{RMSF}=1.087 \mathrm{e}-06 \backslash \mathrm{Dipole}=0.69581$ $22,0 .,-0.583578 \backslash \mathrm{PG}=\mathrm{CO} 2 \mathrm{~V}$ [C2(O1),SGV(H2)]<br>@

## spiropentane ${ }^{-+}$ <br> $D_{2}$

$1 \backslash 1 \backslash G I N C-P A L O \backslash F O p t \backslash U B 3 L Y P \backslash 6-31 G(d) \backslash C 5 H 8(1+, 2) \backslash R A S M U S S E N \backslash 28-M a r-2000 \backslash 0 \backslash$ <br>\#P UB3LYP/6-31G(D) 5D OPT FREQ=NORAMAN NAME=RASMUSSEN $\backslash$ \Spiropentane 5 D $\mathrm{C} 1 \backslash \backslash 1,2 \backslash \mathrm{C},-0.0000035521,0.0888898373,0.0000195455 \backslash \mathrm{C},-0.5054866952,-1$ $.3910511333,-0.5062317657 \backslash C, 0.505464076,-1.3910051699,0.5062541961 \backslash C,-$ $0.5452246229,1.320746781,0.5460446572 \backslash C, 0.545251583,1.3206978856,-0.54$
$60756803 \backslash \mathrm{H},-1.5502313132,-1.527559538,-0.2324623573 \backslash \mathrm{H}, 1.550209734,-1.5$ $275192507,0.2324897156 \backslash \mathrm{H},-1.5625686125,1.6051708888,0.2722397573 \backslash \mathrm{H}, 1.5$ $626248976,1.6050692829,-0.2723242146 \backslash \mathrm{H},-0.2302918025,-1.5277979424,-1$. $5505454471 \backslash \mathrm{H}, 0.230256027,-1.5277824691,1.5505611821 \backslash \mathrm{H},-0.2701282055,1$. $6054015652,1.5629477508 \backslash \mathrm{H}, 0.2701245427,1.605348259,-1.5629721038 \backslash$ Vers ion=Sun-SVR4-Unix-G98RevA. $7 \backslash \mathrm{HF}=-194.9308169 \backslash \mathrm{~S} 2=0.752326 \backslash \mathrm{~S} 2-1=0 . \backslash \mathrm{S} 2 \mathrm{~A}=0$. $750005 \backslash \mathrm{RMSD}=3.222 e-09 \backslash \mathrm{RMSF}=6.123 e-05 \backslash \mathrm{Dipole}=-0.0000443,-0.5537083,-0.0$ $000366 \backslash \mathrm{PG}=\mathrm{C01}[\mathrm{X}(\mathrm{C} 5 \mathrm{H} 8)] \backslash \backslash @$

## neopentane ${ }^{+} \quad \boldsymbol{C}_{3 \mathrm{v}}$

$1 \backslash 1 \backslash G I N C-P C \backslash F O p t \backslash U B 3 L Y P \backslash 6-31 G(d) \backslash C 5 H 12(1+, 2) \backslash R A S M U S S E N \backslash 29-M a r-2000 \backslash 0 \backslash \backslash$ \#P UB3LYP/6-31G(D) 5D OPT=READFC FREQ=NORAMAN NAME=RASMUSSEN MAXDISK=2 $097152000 \backslash$ \Neopentane 5D C1 <br>1,2\C,0.1210292538,-0.2111685958, 0.085476 $1491 \backslash C,-0.0104750494,0.0073415686,1.5638131354 \backslash C, 1.4758065574,0.007906$ $665,-0.5209312692 \backslash \mathrm{C},-0.8271057067,1.4405654925,-0.5865031525 \backslash \mathrm{C},-0.7455$ 105147,-1.2689976016,-0.5322079173\H, 0.4884860027,-0.8537160137,2.0457 $216752 \backslash \mathrm{H},-1.0470640174,0.0014529588,1.9106759707 \backslash \mathrm{H}, 0.5078903874,0.9031$ 56047,1.9158132661 \H,1.9794088187,0.9002596781,-0.1402150571 \H, 1.46493 83418,0.0103401903,-1.6140161784 \H, 2.0922716342,-0.8573157561,-0.21467 $23221 \backslash \mathrm{H},-0.7403804119,1.2859528677,-1.6580867627 \backslash \mathrm{H},-0.2026328175,2.213$ 5875663,-0.1475864933\H,-1.8083172886,1.2908565837,-0.1446391282\H,-1. $7741163826,-1.2548123698,-0.1626587984 \backslash \mathrm{H},-0.312720071,-2.2383118692,-0$ $.2231552541 \backslash \mathrm{H},-0.7302314383,-1.2553350555,-1.6250625903 \backslash \backslash$ Version=SGI-G 98RevA.6\HF=-197.4092518\S2=0.752286\S2-1=0. \S2A=0.750004 \RMSD=6.001e$09 \backslash \mathrm{RMSF}=8.238 \mathrm{e}-05 \backslash \mathrm{Dipole}=-0.1604816,0.2796694,-0.1135103 \backslash \mathrm{PG}=\mathrm{C01} \quad[\mathrm{X}(\mathrm{C} 5 \mathrm{H}$ 12)] <br>@

## 4-27 ${ }^{+} \quad$ octaplane $^{+} \quad \boldsymbol{C}_{4 \mathrm{~h}}$

$1 \backslash 1 \backslash G I N C-P C \backslash F O p t \backslash U B 3 L Y P \backslash 6-31 G(d) \backslash C 21 H 28(1+, 2) \backslash R A S M U S S E N \backslash 03-J u l-1999 \backslash 0 \backslash$ <br>\#P UB3LYP/6-31G(D) 5D OPT=NEWESTMFC NAME=RASMUSSEN MAXDISK=2621440000 GEOM $=($ NODISTANCE, NOANGLE, NODIHEDRAL) <br>octaplanium cation $C 4 h \backslash \backslash 1,2 \backslash C, 0$ ., 0., 0. \C, 0.0086050118,1.6259442136,0.\C,-0.0086050118,-1.6259442136,0 $. \backslash C, 1.6259442136,-0.0086050118,0 . \backslash C,-1.6259442136,0.0086050118,0 . \backslash \mathrm{C}, 0$. $3588023048,1.8542594512,1.5028176415 \backslash C,-0.3588023048,-1.8542594512,1.5$ $028176415 \backslash C, 1.8542594512,-0.3588023048,-1.5028176415 \backslash C,-1.8542594512,0$ $.3588023048,-1.5028176415 \backslash C, 0.3588023048,1.8542594512,-1.5028176415 \backslash C$, $-0.3588023048,-1.8542594512,-1.5028176415 \backslash C, 1.8542594512,-0.3588023048$ ,1.5028176415\C,-1.8542594512,0.3588023048,1.5028176415\C,1.0548915334 ,-1.5439386932,2.1302194233\C,1.5439386932,1.0548915334,-2.1302194233\} C, -1.0548915334,1.5439386932,2.1302194233\C,-1.5439386932,-1.054891533 $4,-2.1302194233 \backslash C, 1.5439386932,1.0548915334,2.1302194233 \backslash C,-1.05489153$ $34,1.5439386932,-2.1302194233 \backslash C,-1.5439386932,-1.0548915334,2.13021942$ $33 \backslash C, 1.0548915334,-1.5439386932,-2.1302194233 \backslash \mathrm{H},-1.0129647963,2.006884$ 1396,0.\H,1.0129647963,-2.0068841396,0. \H,2.0068841396,1.0129647963,0. \H,-2.0068841396,-1.0129647963,0. \H,-2.9197820725, 0.552262399,1.681691 $1887 \backslash \mathrm{H},-0.552262399,-2.9197820725,-1.6816911887 \backslash \mathrm{H}, 2.9197820725,-0.5522$ 62399,1.6816911887\H, 0.552262399,2.9197820725,-1.6816911887\H, 0.552262 399,2.9197820725,1.6816911887\H,-0.552262399,-2.9197820725,1.681691188 $7 \backslash H,-2.9197820725,0.552262399,-1.6816911887 \backslash \mathrm{H}, 2.9197820725,-0.55226239$ 9,-1.6816911887\H,1.6559872061,-2.454097957,-2.0200268674 \H, 2.45409795 7,1.6559872061,2.0200268674 \H,-1.6559872061,2.454097957,-2.0200268674 \} H, -2.454097957,-1.6559872061,2.0200268674 \H,1.6559872061,-2.454097957,
$2.0200268674 \backslash \mathrm{H}, 2.454097957,1.6559872061,-2.0200268674 \backslash \mathrm{H},-1.6559872061$, $2.454097957,2.0200268674 \backslash \mathrm{H},-2.454097957,-1.6559872061,-2.0200268674 \backslash \mathrm{H}$, $0.9637466179,-1.3714138993,3.2081936929 \backslash \mathrm{H}, 1.3714138993,0.9637466179,-3$ . 2081936929 \H, $-0.9637466179,1.3714138993,3.2081936929 \backslash \mathrm{H},-1.3714138993$, $-0.9637466179,-3.2081936929 \backslash \mathrm{H}, 1.3714138993,0.9637466179,3.2081936929 \backslash \mathrm{H}$ , 0.9637466179,-1.3714138993,-3.2081936929\H,-0.9637466179,1.3714138993 ,-3.2081936929\H,-1.3714138993,-0.9637466179,3.2081936929<br>Version=SGI $-G 98 R e v A .6 \backslash H F=-816.497086 \backslash S 2=0.755339 \backslash S 2-1=0 . \backslash S 2 A=0.750017 \backslash R M S D=3.120 e$ $-09 \backslash$ RMSF=4.647e-05\Dipole=0.,0.,0. $\backslash \mathrm{PG}=\mathrm{CO} 4 \mathrm{H} \quad$ [O(C1), SGH (C4H4), X(C16H24)] <br>@

## 4-28 ${ }^{+\boldsymbol{t}} \quad$ spirooctaplane $^{+} \quad \boldsymbol{D}_{\mathbf{2 h}}$

$1 \backslash 1 \backslash G I N C-P C \backslash F O p t \backslash U B 3 L Y P \backslash 6-31 G(d) \backslash C 21 H 24(1+, 2) \backslash R A S M U S S E N \backslash 02-J u l-1999 \backslash 0 \backslash$ <br>\#P UB3LYP/6-31G(D) 5D OPT=NEWESTMFC NAME=RASMUSSEN MAXDISK=2621440000 GEOM $=($ NODISTANCE, NOANGLE, NODIHEDRAL) <br>spiro[2.2]octaplanium cation 5D $\mathrm{D} 2 \mathrm{~h} \backslash \backslash 1,2 \backslash \mathrm{C}, 0.0 .0 .0 . \backslash \mathrm{C},-0.7410682227,-1.2973198702,0 . \backslash \mathrm{C}, 0.7410682227$, $1.2973198702,0 . \backslash C, 0.7410682227,1.2973198702,0 . \backslash C,-0.7410682227,1.29731$ $98702,0 . \backslash C,-1.2925857652,-1.3368405988,1.4368455485 \backslash \mathrm{C}, 1.2925857652,-1$. $3368405988,-1.4368455485 \backslash C, 1.2925857652,1.3368405988,1.4368455485 \backslash C,-1$ . $2925857652,1.3368405988,-1.4368455485 \backslash C,-1.2925857652,-1.3368405988,-$ $1.4368455485 \backslash C, 1.2925857652,-1.3368405988,1.4368455485 \backslash C, 1.2925857652$, $1.3368405988,-1.4368455485 \backslash C,-1.2925857652,1.3368405988,1.4368455485 \backslash \mathrm{C}$ ,-2.0185444295,0.,1.8055991041\C,-2.0185444295,0.,-1.8055991041\C,2.01 85444295,0.,1.8055991041\C,2.0185444295,0.,-1.8055991041\C,0.,-1.67476 31071,2.2666137777\C,0.,-1.6747631071,-2.2666137777\C,0.,1.6747631071, $2.2666137777 \backslash \mathrm{C}, 0 ., 1.6747631071,-2.2666137777 \backslash \mathrm{H},-2.0249725103,-2.143208$ 7576,1.5541699528\H, 2.0249725103,-2.1432087576,-1.5541699528\H, 2. 02497 25103,2.1432087576,1.5541699528\H,-2.0249725103,2.1432087576,-1.554169 9528\H, 2.0249725103,-2.1432087576,1.5541699528\H,2.0249725103,2.143208 7576,-1.5541699528\H,-2.0249725103,2.1432087576,1.5541699528\H,-2.0249 725103,-2.1432087576,-1.5541699528\H,-2.228833361,0.,2.8810851675\H,-2 . $9967683661,0 ., 1.3082813706 \backslash H,-2.228833361,0 .,-2.8810851675 \backslash H,-2.99676$ 83661,0.,-1.3082813706\H,2.228833361,0., 2.8810851675\H,2.9967683661, 0. ,1.3082813706\H, 2.228833361,0.,-2.8810851675\H,2.9967683661,0.,-1.3082 813706\H,0.,-1.1766719112,3.2402920111\H,0.,-2.7505009296,2.4662072771 $\backslash \mathrm{H}, 0 .,-1.1766719112,-3.2402920111 \backslash \mathrm{H}, 0 .,-2.7505009296,-2.4662072771 \backslash \mathrm{H}, 0$ ., 1.1766719112,3.2402920111 \H, 0., 2.7505009296,2.4662072771\H,0.,1.1766 719112,-3.2402920111 \H, 0., 2.7505009296,-2.4662072771<br>Version=SGI-G98R evA. $6 \backslash$ State $=2-B 3 U \backslash H F=-814.2567566 \backslash S 2=0.754542 \backslash S 2-1=0 . \backslash S 2 A=0.750014 \backslash$ RMS $\mathrm{D}=8.441 \mathrm{e}-09 \backslash \mathrm{RMSF}=2.728 \mathrm{e}-05 \backslash \mathrm{Dipole}=0 ., 0 ., 0 . \backslash \mathrm{PG}=\mathrm{D} 02 \mathrm{H} \quad\left[\mathrm{O}(\mathrm{C} 1), \mathrm{SG}(\mathrm{C} 4), \mathrm{SG}{ }^{\prime}(\mathrm{C}\right.$ 4H8) , SG" (C4H8) , X (C8H8) ] <br>@

## 4-29 ${ }^{\boldsymbol{+}} \quad$ dimethanospirooctaplane ${ }^{\boldsymbol{+}} \quad \boldsymbol{D}_{\mathbf{2 h}}$

$1 \backslash 1 \backslash G I N C-P C \backslash F O p t \backslash U B 3 L Y P \backslash 6-31 G(d) \backslash C 23 H 24(1+, 2) \backslash R A S M U S S E N \backslash 03-J u l-1999 \backslash 0 \backslash$ <br>\#P UB3LYP/6-31G(D) 5D OPT=NEWESTMFC NAME=RASMUSSEN MAXDISK=2621440000
 cation $D 2 h \backslash \backslash 1,2 \backslash C, 0 ., 0 ., 0 . \backslash C,-0.7212914585,-1.3445757558,0 . \backslash C, 0.721291$ 4585,-1.3445757558,0.\C,0.7212914585,1.3445757558,0.\C,-0.7212914585,1 $.3445757558,0 . \backslash C,-1.3118089873,-1.3191997436,1.3895639008 \backslash C, 1.31180898$ $73,-1.3191997436,-1.3895639008 \backslash C, 1.3118089873,1.3191997436,1.389563900$ $8 \backslash C,-1.3118089873,1.3191997436,-1.3895639008 \backslash C,-1.3118089873,-1.319199$ $7436,-1.3895639008 \backslash C, 1.3118089873,-1.3191997436,1.3895639008 \backslash C, 1.31180$

89873,1.3191997436,-1.3895639008\C,-1.3118089873,1.3191997436,1.389563 $9008 \backslash C,-2.1699312345,0 ., 1.3745169014 \backslash C,-2.1699312345,0 .,-1.3745169014 \backslash$ C, 2. 1699312345, 0., 1.3745169014 \C, 2.1699312345, 0., -1.3745169014\C, 0., -1 $.5247790478,2.2780713554 \backslash C, 0 .,-1.5247790478,-2.2780713554 \backslash C, 0 ., 1.52477$ $90478,2.2780713554 \backslash \mathrm{C}, 0 ., 1.5247790478,-2.2780713554 \backslash \mathrm{C},-2.9938250358,0 .$, $0 . \ \mathrm{C}, 2.9938250358,0.0 . \backslash \mathrm{H},-1.9952783383,-2.158633338,1.5626738693 \backslash \mathrm{H}, 1$. $9952783383,-2.158633338,-1.5626738693 \backslash \mathrm{H}, 1.9952783383,2.158633338,1.562$ $6738693 \backslash \mathrm{H},-1.9952783383,2.158633338,-1.5626738693 \backslash \mathrm{H}, 1.9952783383,-2.15$ $8633338,1.5626738693 \backslash \mathrm{H}, 1.9952783383,2.158633338,-1.5626738693 \backslash \mathrm{H},-1.995$ $2783383,2.158633338,1.5626738693 \backslash \mathrm{H},-1.9952783383,-2.158633338,-1.56267$ $38693 \backslash \mathrm{H},-2.8875309889,0 ., 2.2005894574 \backslash \mathrm{H},-2.8875309889,0 .,-2.2005894574$ \H, 2. $8875309889,0 ., 2.2005894574 \backslash H, 2.8875309889,0 .,-2.2005894574 \backslash H, 0 .,-$ $0.9529445746,3.2043218439 \backslash H, 0 .,-2.5770833125,2.5773337358 \backslash H, 0 .,-0.9529$ $445746,-3.2043218439 \backslash H, 0 .,-2.5770833125,-2.5773337358 \backslash \mathrm{H}, 0 ., 0.952944574$ $6,3.2043218439 \backslash \mathrm{H}, 0 ., 2.5770833125,2.5773337358 \backslash \mathrm{H}, 0 ., 0.9529445746,-3.204$ $3218439 \backslash \mathrm{H}, 0 ., 2.5770833125,-2.5773337358 \backslash \mathrm{H},-3.6536920328,0.8761209824,0$ $. \backslash H,-3.6536920328,-0.8761209824,0 . \backslash H, 3.6536920328,-0.8761209824,0 . \backslash H, 3$ $.6536920328,0.8761209824,0 . \backslash \backslash V e r s i o n=S G I-G 98 R e v A .6 \backslash$ State=2-B2U\HF=-890 $.3968935 \backslash S 2=0.755141 \backslash S 2-1=0 . \backslash S 2 A=0.750016 \backslash R M S D=4.013 e-09 \backslash R M S F=8.259 e-0$ $5 \backslash$ Dipole=0., 0., 0. \PG=D02H [O (C1) , C2 (C1.C1) , SG (C4H8) , SG' (C4H4) , SG" (C4H4 ) , X (C8H8) ] <br>@

Table C-28. Guassian archive files for the MP2(fc)/6-31G(d) optimized ions in Chapter 4.

## ${ }^{3} \mathrm{CH}_{2}{ }^{-+} \quad \boldsymbol{C}_{2 \mathrm{v}}$

$1 \backslash 1 \backslash G I N C-R S C Q C 9 \backslash F O p t \backslash U M P 2-F C \backslash 6-31 G(d) \backslash C 1 H 2(1+, 2) \backslash R A S M U S S E N \backslash 28-M a r-2000$ \0<br>\#P UMP2/6-31G* 5D OPT=(TIGHT) FREQ=NORAMAN NAME=RASMUSSEN MAXDISK= $917504000 \backslash$ \methylene radical cation C 2 v doublet <br>1,2\H,-0.4417167277,0 ., - $0.9657533247 \backslash \mathrm{C},-0.0720631221,0 ., 0.060439365 \backslash \mathrm{H}, 0.8740954601,0 ., 0.603$ $1171348 \backslash \backslash$ Version=IBM-RS6000-G98RevA. $6 \backslash$ State=2-A1 $\backslash \mathrm{HF}=-38.5658546 \backslash \mathrm{MP} 2=-3$ $8.6340268 \backslash P U H F=-38.5674656 \backslash P M P 2-0=-38.6349722 \backslash S 2=0.754413 \backslash S 2-1=0.75076$ $2 \backslash S 2 A=0.750008 \backslash R M S D=3.099 e-09 \backslash R M S F=1.887 e-06 \backslash D i p o l e=0.175703,0 .,-0.147$ $3622 \backslash \mathrm{PG}=\mathrm{CO} 2 \mathrm{~V}$ [C2 (C1), SGV (H2) ] <br>@

## $\mathrm{CH}_{4}{ }^{++} \quad \boldsymbol{C}_{2 \mathrm{v}}$

$1 \backslash 1 \backslash G I N C-P C \backslash F r e q \backslash U M P 2-F C \backslash 6-31 G(d) \backslash C 1 H 4(1+, 2) \backslash R A S M U S S E N \backslash 27-M a r-2000 \backslash 0 \backslash \backslash$ \#P UMP2/6-31G* 5D OPT=(CALCALL,VERYTIGHT) NAME=RASMUSSEN MAXDISK=20971 52000 GEOM=CHECK GUESS=CHECK SYM=LOOSE OPTCYC=100<br>Methane radical cat ion C2v doublet <br>1,2\C,-0.0842874545,0.,-0.0581591168\H,0.4335875004,$0.0000000303,0.9958216688 \backslash \mathrm{H}, 1.084878695,0.0000000303,0.0519339344 \backslash \mathrm{H},-0$ $.5063707628,0.955491451,-0.3494004096 \backslash \mathrm{H},-0.5063707054,-0.955491451,-0$. $3494004929 \backslash$ VVersion=SGI-G98RevA. $6 \backslash$ State $=2-\mathrm{B} 2 \backslash \mathrm{HF}=-39.7538524$ \MP2 $=-39.86$ $78292 \backslash$ PUHF $=-39.7554742 \backslash$ PMP2-0 $=-39.8687489 \backslash S 2=0.75455 \backslash S 2-1=0.750604 \backslash$ S2A $=0.750012 \backslash$ RMSD $=7.814 \mathrm{e}-09 \backslash \mathrm{RMSF}=2.529 \mathrm{e}-08 \backslash \mathrm{Dipole}=0.5127257,0 ., 0.3537854 \backslash$ DipoleDeriv=0.0368844,0.,0.1445041,0.,0.0325089,0.,0.144504,0.,-0.0728 299,0.2270789,0., 0.0358914,0.,0.2565411,0.,-0.1204394,0., 0.4118483,0.3 60521,0.,-0.1710972,0.,0.2565411,0.,-0.0147664,0.,0.2784062,0.1877578, $-0.0599761,-0.0046491,-0.0608668,0.2272045,-0.0419986,-0.0046491,-0.04$ 1384,0.1912877,0.1877578,0.0599761,-0.0046491,0.0608668,0.2272045,0.04 19986,-0.0046491,0.041384,0.1912877 \Polar=11.1497316,0.,9.3291889, 2.16

$73,-0.00000002,0.71599552,0.20800466,0.00000002,0.28711883,-0.05494885$ , 0., - $0.06478495,0.06559344,0 .,-0.04275138,0 ., 0 ., 0.01888684,-0.10795980$ , 0., - $0.16053778,0.07625953,0 ., 0.18648322,-0.20455535,0 .,-0.05116566,-0$ $.00160180,0 ., 0.02336044,0.22186248,0 .,-0.04275138,0 ., 0 ., 0.01360141,0 .$, $0 ., 0.01888684,-0.00799081,0 .,-0.01093128,0.01712831,0 .,-0.01697228,0.0$ $1693613,0 ., 0.03021418,-0.09277077,0.10151694,-0.04602702,-0.00452139,0$ $.01117301,0.00416991,-0.00785266,0.01297438,-0.01303681,0.09129398,0.1$ $1354329,-0.31524638,0.07834589,-0.00445386,0.00513156,-0.00152194,-0.0$ $0300359,0.00513156,-0.00362376,-0.11587509,0.31209458,-0.04602702,0.07$ $004760,-0.05782488,-0.01430144,0.00963628,-0.00448658,0.00543454,0.007$ $02564,-0.00115531,0.05350851,-0.07995486,0.05066780,-0.09277076,-0.101$ 51692,-0.04602703,-0.00452139,-0.01117301,0.00416991,-0.00785266,-0.01 $297438,-0.01303681,0.01385084,0.00978924,0.00138541,0.09129397,-0.1135$ $4327,-0.31524638,-0.07834592,0.00445386,0.00513156,0.00152195,0.003003$ $59,0.00513156,0.00362376,-0.00978924,-0.00711132,-0.00675467,0.1158750$ $7,0.31209458,-0.04602703,-0.07004763,-0.05782489,-0.01430144,-0.009636$ $28,-0.00448658,0.00543454,-0.00702564,-0.00115531,0.00138541,0.0067546$ $7,0.01279897,0.05350851,0.07995488,0.05066781 \backslash \backslash-0.00000001,0 ., 0 ., 0 ., 0$. , $-0.00000006,-0.00000005,0 ., 0.00000002,0.00000003,0.00000001,0.0000000$ $2,0.00000003,-0.00000001,0.00000002 \backslash \backslash \backslash @$
$\mathrm{NH}_{3}{ }^{-+} \quad \boldsymbol{C}_{3 \mathrm{v}}$
$1 \backslash 1 \backslash G I N C-P C \backslash F r e q \backslash U M P 2-F C \backslash 6-31 G(d) \backslash H 3 N 1(1+, 2) \backslash R A S M U S S E N \backslash 27-M a r-2000 \backslash 0 \backslash \backslash$ \#P MP2/6-31G* 5D NAME=RASMUSSEN OPT= (CALCALL, VERYTIGHT) MAXDISK=209715 $2000 \backslash \backslash a m m o n i a ~ r a d i c a l ~ c a t i o n ~ C 3 v ~ d o u b l e t \backslash \backslash 1,2 \backslash H, 0 ., 0.0000000126,1.0264$ $093705 \backslash \mathrm{H}, 0.8888965895,0.0000000126,-0.5132046853 \backslash \mathrm{H},-0.8888965895,0.000$ $0000126,-0.5132046853 \backslash N, 0 ., 0.0 . \backslash \backslash V e r s i o n=S G I-G 98 R e v A .6 \backslash$ State $=2-A 1 \backslash H F=$ $-55.8717668 \backslash \mathrm{MP} 2=-56.0015737 \backslash \mathrm{PUHF}=-55.8754024 \backslash \mathrm{PMP} 2-0=-56.0039007 \backslash \mathrm{~S} 2=0.7$ $60909 \backslash S 2-1=0.753025 \backslash S 2 A=0.750073 \backslash \mathrm{RMSD}=5.855 e-09 \backslash \mathrm{RMSF}=2.101 e-08 \backslash \mathrm{Dipole=}$ $0 ., 0 ., 0 . \backslash$ DipoleDeriv=0.2915241, 0., 0., 0., 0.3535442, 0., 0., 0., 0.4863638, 0 $.4376539,0 .,-0.0843681,0.0 .3535442,0 \ldots, 0.0843681,0 ., 0.340234,0.437653$ $9,0 ., 0.0843681,0 ., 0.3535442,0.0 .0843681,0 ., 0.340234,-0.1668319,0 ., 0 .$, $0 .,-0.0606325,0 ., 0 ., 0 \ldots,-0.1668319 \backslash \operatorname{Polar}=6.6491993,0 ., 3.0745863,0 ., 0 ., 6$ $.6491994 \backslash \mathrm{PG}=\mathrm{C0} 3 \mathrm{~V} \quad[\mathrm{C} 3(\mathrm{~N} 1), 3 \mathrm{SGV}(\mathrm{H} 1)] \backslash \mathrm{NImag}=0 \backslash \backslash 0.05858385,0 ., 0.00794986,0$ ., 0., 0.44809737,0.01153094, 0., -0.00326144, 0.35071899, 0., 0.00794984, 0., $0 ., 0.00794986,0.02716600,0 .,-0.00227036,-0.16866430,0 ., 0.15596223,0.01$ $153094,0 ., 0.00326144,-0.00917101,0 .,-0.01521372,0.35071899,0 ., 0.007949$ $84,0 ., 0 ., 0.00794984,0 ., 0 ., 0.00794986,-0.02716600,0 .,-0.00227036,0.0152$ $1372,0 ., 0.01843159,0.16866430,0 ., 0.15596223,-0.08164573,0 ., 0 .,-0.35307$ $891,0 ., 0.15671202,-0.35307891,0 .,-0.15671202,0.78780356,0 .,-0.02384953$ $, 0 ., 0 .,-0.02384953,0 ., 0 .,-0.02384953,0 ., 0 ., 0.07154859,0 ., 0 .,-0.4435566$ 5, 0.15671202,0.,-0.17212346,-0.15671202,0.,-0.17212346,0.,0., 0.7878035 $7 \backslash \backslash 0 ., 0 ., 0.00000004,0.00000004,0 .,-0.00000002,-0.00000004,0 .,-0.000000$ 02,0.,0., 0.<br>\@

## $\mathrm{H}_{2} \mathrm{O}^{+} \quad \boldsymbol{C}_{2 \mathrm{v}}$

$1 \backslash 1 \backslash G I N C-V P P 09 \backslash$ Freq $\backslash$ UMP2-FC $\backslash 6$-31G (d) \H2O1 (1+, 2) \RASMUSSEN $\backslash 27$-Mar-2000\} $0 \backslash \ \# \mathrm{P}$ UP2/6-31G* 5D OPT= (CALCALL, VERYTIGHT) NAME=RASMUSSEN MAXDISK=20 $97152000 \backslash$ \water radical cation C 2 v doublet $\backslash 1,2 \backslash \mathrm{H},-0.1756771068,0 .,-0$. $9331765847 \backslash \mathrm{O},-0.0890824095,0.0 .0747134471 \backslash \mathrm{H}, 0.8883363828,0 ., 0.3354690$ $076 \backslash$ Version=Fujitsu-VP-Unix-G98RevA. $7 \backslash$ State $=2-\mathrm{B} 1 \backslash \mathrm{HF}=-75.6127933 \backslash \mathrm{MP} 2=-$ $75.7516632 \backslash \mathrm{PUHF}=-75.6160524 \backslash \mathrm{PMP} 2-0=-75.7536892 \backslash \mathrm{~S} 2=0.757819 \backslash \mathrm{~S} 2-1=0.7518$
$85 \backslash S 2 A=0.750038 \backslash R M S D=6.638 e-09 \backslash R M S F=2.947 e-07 \backslash$ Dipole=0.7148644,0., -0.5 99557\DipoleDeriv=0.4602155, 0., 0.06488, 0., 0.5246517, 0., 0.0613011,0., 0. 5993755,-0.0337387,0.,-0.146215,0., -0.0493035, 0., -0.146215, 0., -0.08544 $34,0.5735232,0.0 .081335,0.0 .5246517,0.0 .0849139,0 ., 0.4860679 \backslash \operatorname{Pol}$ ar= $4.3518352,0 ., 2.6397989,0.9139861,0 ., 4.6750394 \backslash \mathrm{PG}=\mathrm{C} 02 \mathrm{~V} \quad[\mathrm{C} 2(\mathrm{O} 1), \mathrm{SGV}(\mathrm{H} 2)]$ $\backslash N I m a g=0 \backslash \backslash 0.04493870,0 .,-0.00000023,0.03967928,0 ., 0.40386061,-0.047426$ $58,0 .,-0.04156180,0.42928857,0 ., 0.00000006,0 ., 0 .,-0.00000013,0.0024815$ $5,0 .,-0.39922687,0.09821188,0.0 .46401832,0.00248788,0 \ldots, 0.00188252,-0$. $38186200,0 .,-0.10069343,0.37937412,0 ., 0.00000016,0 ., 0 ., 0.00000006,0 ., 0$ ., - 0.00000023,-0.04216084, 0., -0.00463374,-0.05665008, 0., -0.06479145, 0. $09881091,0 ., 0.06942519 \backslash \backslash 0.00000034,0 ., 0.00000051,0.00000011,0 .,-0.0000$ 0009,-0.00000045, 0.,-0.00000043<br>\@

## spiropentane ${ }^{++} \quad D_{2}$

$1 \backslash 1 \backslash G I N C-P C \backslash F O p t \backslash U M P 2-F C \backslash 6-31 G(d) \backslash C 5 H 8(1+, 2) \backslash R A S M U S S E N \backslash 29-M a r-2000 \backslash 0 \backslash \backslash$ \#P UMP2/6-31G(D) 5D OPT FREQ=NORAMAN NAME=RASMUSSEN MAXDISK=2097152000 $\backslash \backslash$ Spiropentane 5D C1 <br>1,2\C, 0.0006385685,-0.0002016214,-0.0000343265\C , - 0. $6416280542,-1.3385313529,-0.3591623691 \backslash \mathrm{C}, 0.6406401511,-1.339055895$ $5,0.3599618139 \backslash C,-0.6387708645,1.3391294844,0.362619507 \backslash C, 0.6394027191$ , 1. 33875862 , $-0.3633192861 \backslash \mathrm{H},-1.5637054182,-1.5667351448,0.1664587787 \backslash \mathrm{H}$ , 1. 5623839832 , - $1.5690373531,-0.1654843938 \backslash \mathrm{H},-1.5636322653,1.567872218$, $-0.1578205497 \backslash \mathrm{H}, 1.5644933459,1.5683504815,0.1563607934 \backslash \mathrm{H},-0.6416075641$ ,-1.5194886766,-1.4364456742\H, 0.6402982236,-1.5192958473,1.4373723517 $\backslash \mathrm{H},-0.6327187179,1.5193218549,1.4400188143 \backslash \mathrm{H}, 0.6327932927,1.5184170593$ ,-1.4408521554 <br>Version=SGI-G98RevA. $6 \backslash \mathrm{HF}=-193.609571 \backslash \mathrm{MP} 2=-194.2241581 \backslash$ $\mathrm{PUHF}=-193.612117 \backslash \mathrm{PMP} 2-0=-194.2255732 \backslash \mathrm{~S} 2=0.75874 \backslash \mathrm{~S} 2-1=0.750942 \backslash \mathrm{~S} 2 \mathrm{~A}=0.75$ $0064 \backslash \mathrm{RMSD}=5.182 \mathrm{e}-09 \backslash \mathrm{RMSF}=4.096 \mathrm{e}-05 \backslash \mathrm{Dipole}=-0.0004768,0.0011556,-0.0000$ $441 \backslash \mathrm{PG}=\mathrm{CO1}[\mathrm{X}(\mathrm{C} 5 \mathrm{H} 8)] \backslash \backslash$

## neopentane ${ }^{+} \quad C_{3 v}$

$1 \backslash 1 \backslash G I N C-P C \backslash F O p t \backslash U M P 2-F C \backslash 6-31 G(d) \backslash C 5 H 12(1+, 2) \backslash R A S M U S S E N \backslash 29-M a r-2000 \backslash 0 \backslash$ <br>\#P UMP2/6-31G(D) 5D OPT FREQ=NORAMAN NAME=RASMUSSEN MAXDISK=209715200 $0 \backslash \backslash$ Neopentane 5D C1 <br>1,2\C,0.1094122742,0.1871076755,0.0757758625\C, -0 $.0078975916,-0.0076873016,1.5543129513 \backslash C, 1.4625580041,-0.0250358683,-0$ $.5258195073 \backslash C,-0.7362116683,1.2617829573,-0.5307719751 \backslash C,-0.8185483712$ ,-1.4002716359,-0.5670462234 \H, 0.5077856331,-0.9022690795,1.9093440287 \H,-1.0415548722,0.0051610822,1.9059116115\H, 0.4996792784,0.8604155431 , 2.0075954842 \H, 2.0657614737,0.8424959851,-0.2092305914 \H, 1.4490222497 ,-0.0250333393,-1.6176439627\H,1.9624555806,-0.9189607084,-0.14738745\} H, -0.7256816082,1.2482812766,-1.6225438119\H,-0.2766518221,2.213166283 5,-0.2139558334 \H,-1.7618295785,1.2602395109,-0.1561567362\H,-1.799260 211,-1.2445110824,-0.1289927052 \H,-0.2029753025,-2.1779149436,-0.12627 20878\H,-0.7326267045,-1.2564454902,-1.6393745937<br>Version=SGI-G98RevA $.6 \backslash \mathrm{HF}=-195.9998054 \backslash \mathrm{MP} 2=-196.6251415 \backslash \mathrm{PUHF}=-196.0019972 \backslash \mathrm{PMP} 2-0=-196.6264$ $407 \backslash \mathrm{~S} 2=0.758225 \backslash \mathrm{~S} 2-1=0.751499 \backslash \mathrm{~S} 2 \mathrm{~A}=0.750054 \backslash \mathrm{RMSD}=3.180 \mathrm{e}-09 \backslash \mathrm{RMSF}=1.102 \mathrm{e}-$ $05 \backslash$ Dipole $=-0.2072548,-0.3544027,-0.1436705 \backslash \mathrm{PG}=\mathrm{C01} \quad[\mathrm{X}(\mathrm{C} 5 \mathrm{H} 12)] \backslash \backslash @$

Table C-29. Guassian archive files for the MP2(fc)/6-311+G(2d,p)(red) optimized ions in Chapter 4.

## 4-27 ${ }^{+\boldsymbol{+}} \quad$ octaplane $^{+\boldsymbol{}} \quad \boldsymbol{C}_{\mathbf{4 h}}$

$1 \backslash 1 \backslash G I N C-V P P 05 \backslash S P \backslash R M P 2-F C \backslash 6-311+G(2 d, p) \backslash C 21 H 28 \backslash R A S M U S S E N \backslash 04-J u l-1999 \backslash 0$ <br>\#P MP2/6-311+G(2D,P) NAME=RASMUSSEN GEOM=(CHECK,NOANGLE,NODIHEDRAL) GUESS=CHECK MAXDISK=1800000000<br>Octaplane $S 4 \backslash \backslash 0,1 \backslash C, 0,0 ., 0 ., 0 . \backslash C, 0,1.5$ 829410884,0.0032190317,0.1399557932\C,0,-0.0032190317,1.5829410884, -0. $1399557932 \backslash C, 0,-1.5829410884,-0.0032190317,0.1399557932 \backslash C, 0,0.00321903$ 17,-1.5829410884,-0.1399557932\C, 0,1.8476752014, 0.40855226,1.572194728 $1 \backslash C, 0,-0.40855226,1.8476752014,-1.5721947281 \backslash C, 0,-1.8476752014,-0.4085$ $5226,1.5721947281 \backslash C, 0,0.40855226,-1.8476752014,-1.5721947281 \backslash C, 0,1.832$ $1431227,0.3325361416,-1.4100718371 \backslash C, 0,-0.3325361416,1.8321431227,1.41$ $00718371 \backslash C, 0,-1.8321431227,-0.3325361416,-1.4100718371 \backslash C, 0,0.332536141$ $6,-1.8321431227,1.4100718371 \backslash C, 0,1.4103765803,-0.9767665185,2.19044041$ $94 \backslash C, 0,0.9767665185,1.4103765803,-2.1904404194 \backslash C, 0,-1.4103765803,0.976$ $7665185,2.1904404194 \backslash C, 0,-0.9767665185,-1.4103765803,-2.1904404194 \backslash C, 0$ ,-1.6528673292,1.076307557,-2.0428813679\C,0,-1.076307557,-1.652867329 $2,2.0428813679 \backslash C, 0,1.6528673292,-1.076307557,-2.0428813679 \backslash C, 0,1.07630$ 7557,1.6528673292,2.0428813679\H, 0,1.9983469492,-1.0187491442,0.136638 0451 \H, 0, 1.0187491442,1.9983469492, -0.1366380451 \H, 0, -1.9983469492, 1.0 $187491442,0.1366380451 \backslash \mathrm{H}, 0,-1.0187491442,-1.9983469492,-0.1366380451 \backslash \mathrm{H}$ $, 0,2.9149010986,0.5554213943,1.8203247561 \backslash \mathrm{H}, 0,-0.5554213943,2.91490109$ $86,-1.8203247561 \backslash H, 0,-2.9149010986,-0.5554213943,1.8203247561 \backslash \mathrm{H}, 0,0.55$ 54213943,-2.9149010986,-1.8203247561 \H, 0, -0.6084299052,2.8916407652,1. 5487005999\H, 0,-2.8916407652,-0.6084299052,-1.5487005999\H, 0, 0.6084299 052,-2.8916407652,1.5487005999\H, 0, 2.8916407652,0.6084299052,-1.548700 5999 \H, 0, 1. $0477349934,-0.8387048625,3.2185533445 \backslash \mathrm{H}, 0,2.3269692657,-1.5$ $774543511,2.2709311203 \backslash \mathrm{H}, 0,0.8387048625,1.0477349934,-3.2185533445 \backslash \mathrm{H}, 0$ , 1.5774543511,2.3269692657,-2.2709311203\H, 0,-1.0477349934,0.838704862 5, 3.2185533445\H, 0, -2.3269692657,1.5774543511,2.2709311203\H, 0, -0.8387 048625,-1.0477349934,-3.2185533445 \H, 0,-1.5774543511,-2.3269692657,-2. $2709311203 \backslash \mathrm{H}, 0,-1.6453482676,1.002971558,-3.1395966745 \backslash \mathrm{H}, 0,-2.53769607$ 64,1.6770132088,-1.7863004899\H,0,-1.002971558,-1.6453482676,3.1395966 $745 \backslash \mathrm{H}, 0,-1.6770132088,-2.5376960764,1.7863004899 \backslash \mathrm{H}, 0,1.6453482676,-1.0$ 02971558,-3.1395966745\H, 0,2.5376960764,-1.6770132088,-1.7863004899\H, $0,1.002971558,1.6453482676,3.1395966745 \backslash \mathrm{H}, 0,1.6770132088,2.5376960764$, $1.7863004899 \backslash \backslash V e r s i o n=F u j i t s u-V P-U n i x-G 94 R e v E .2 \backslash H F=-811.2429879 \backslash M P 2=-8$ $14.5653974 \backslash \mathrm{RMSD}=7.722 \mathrm{e}-09 \backslash \mathrm{PG}=\mathrm{SO4}[\mathrm{O}(\mathrm{C} 1), \mathrm{X}(\mathrm{C} 20 \mathrm{H} 28)] \backslash \backslash$

## 4-28 ${ }^{+} \quad$ spirooctaplane $^{+} \quad \boldsymbol{D}_{\mathbf{2 h}}$

$1 \backslash 1 \backslash G I N C-V P P 02 \backslash S P \backslash U M P 2-F C \backslash 6-311+G(2 d, p) \backslash C 21 H 24(1+, 2) \backslash R A S M U S S E N \backslash 11-A p r-$ 1999\0<br>\#P UMP2/6-311+G(2D, P) 5D NAME=RASMUSSEN GEOM=(CHECK,NODISTANCE ,NOANGLE,NODIHEDRAL) GUESS=CHECK MAXDISK=1800000000<br>spiro[2.2]octapla nium cation 5D D2h <br>1,2\C,0.,0.,0.\C,-0.7460818781,-1.291492274,0. \C, 0 $.7460818781,-1.291492274,0 . \backslash C, 0.7460818781,1.291492274,0 . \backslash \mathrm{C},-0.7460818$ 781,1.291492274,0.\C,-1.2887794024,-1.3233479943,1.4286696437\C,1.2887 794024,-1.3233479943,-1.4286696437\C,1.2887794024,1.3233479943,1.42866 $96437 \backslash \mathrm{C},-1.2887794024,1.3233479943,-1.4286696437 \backslash \mathrm{C},-1.2887794024,-1.32$ 33479943,-1.4286696437\C,1.2887794024,-1.3233479943,1.4286696437\C,1.2 887794024,1.3233479943,-1.4286696437\C,-1.2887794024,1.3233479943,1.42 $86696437 \backslash \mathrm{C},-2.0224822627,0 ., 1.7788328491 \backslash \mathrm{C},-2.0224822627,0 .,-1.7788328$
$491 \backslash \mathrm{C}, 2.0224822627,0 ., 1.7788328491 \backslash \mathrm{C}, 2.0224822627,0 .,-1.7788328491 \backslash \mathrm{C}, 0$ ., -1. $6401718048,2.2562731507 \backslash C, 0 .,-1.6401718048,-2.2562731507 \backslash C, 0 ., 1.6$ $401718048,2.2562731507 \backslash \mathrm{C}, 0 ., 1.6401718048,-2.2562731507 \backslash \mathrm{H},-2.0133094061$ , - 2. $1415638931,1.5439866251 \backslash \mathrm{H}, 2.0133094061,-2.1415638931,-1.5439866251$ $\backslash H, 2.0133094061,2.1415638931,1.5439866251 \backslash H,-2.0133094061,2.1415638931$ , - 1. $5439866251 \backslash \mathrm{H}, 2.0133094061,-2.1415638931,1.5439866251 \backslash \mathrm{H}, 2.013309406$ $1,2.1415638931,-1.5439866251 \backslash \mathrm{H},-2.0133094061,2.1415638931,1.5439866251$ $\backslash H,-2.0133094061,-2.1415638931,-1.5439866251 \backslash \mathrm{H},-2.2576657022,0 ., 2.8509$ $959275 \backslash \mathrm{H},-2.9895318125,0 ., 1.2569772022 \backslash \mathrm{H},-2.2576657022,0 .,-2.850995927$ $5 \backslash \mathrm{H},-2.9895318125,0 .,-1.2569772022 \backslash \mathrm{H}, 2.2576657022,0 ., 2.8509959275 \backslash \mathrm{H}, 2$. $9895318125,0 ., 1.2569772022 \backslash \mathrm{H}, 2.2576657022,0 .,-2.8509959275 \backslash \mathrm{H}, 2.9895318$ 125, 0.,-1.2569772022 \H, 0.,-1.1244278378, 3.2222236709\H,0.,-2.713416255 $3,2.475818703 \backslash \mathrm{H}, 0 .,-1.1244278378,-3.2222236709 \backslash \mathrm{H}, 0 .,-2.7134162553,-2.4$ $75818703 \backslash \mathrm{H}, 0 ., 1.1244278378,3.2222236709 \backslash \mathrm{H}, 0 ., 2.7134162553,2.475818703 \backslash$ H, 0., 1. $1244278378,-3.2222236709 \backslash \mathrm{H}, 0 ., 2.7134162553,-2.475818703 \backslash \backslash V e r s i o$ n=Fujitsu-VP-Unix-G98RevA. $6 \backslash$ State $=2-B 3 U \backslash H F=-808.9940536 \backslash M P 2=-812.15307$ $13 \backslash \mathrm{PUHF}=-808.9980944 \backslash \mathrm{PMP} 2-0=-812.1556523 \backslash \mathrm{~S} 2=0.766488 \backslash \mathrm{~S} 2-1=0.754498 \backslash \mathrm{~S} 2 \mathrm{~A}$ $=0.750178 \backslash R M S D=1.281 e-09 \backslash P G=D 02 H \quad[O(C 1), S G(C 4), S G '(C 4 H 8), S G "(C 4 H 8), X(C$ 8H8) ] <br>@

## 4-29.+ dimethanospirooctaplane ${ }^{*+} \quad \boldsymbol{D}_{\mathbf{2 h}}$

$1 \backslash 1 \backslash G I N C-V P P 02 \backslash S P \backslash U M P 2-F C \backslash 6-311+G(2 d, p) \backslash C 23 H 24(1+, 2) \backslash R A S M U S S E N \backslash 12-A p r-$ $1999 \backslash 0 \backslash$ <br>\#P UMP2/6-311+G(2D, P) 5D NAME=RASMUSSEN GEOM = (CHECK, NODISTANCE , NOANGLE, NODIHEDRAL) GUESS=CHECK MAXDISK=1800000000<br>dimethanospiro[2. 2] octaplanium cation $\mathrm{D} 2 \mathrm{~h} \backslash \backslash 1,2 \backslash \mathrm{C}, 0 ., 0 ., 0 . \backslash \mathrm{C},-0.7251943656,-1.3371099203$ , 0. \C, 0.7251943656, -1.3371099203, 0. \C, 0.7251943656,1.3371099203,0. \C, $0.7251943656,1.3371099203,0 . \backslash C,-1.3058336218,-1.3075289439,1.385019851$ $3 \backslash C, 1.3058336218,-1.3075289439,-1.3850198513 \backslash C, 1.3058336218,1.30752894$ $39,1.3850198513 \backslash C,-1.3058336218,1.3075289439,-1.3850198513 \backslash C,-1.305833$ $6218,-1.3075289439,-1.3850198513 \backslash C, 1.3058336218,-1.3075289439,1.385019$ $8513 \backslash C, 1.3058336218,1.3075289439,-1.3850198513 \backslash C,-1.3058336218,1.30752$ $89439,1.3850198513 \backslash C,-2.1566883129,0 ., 1.3656714434 \backslash C,-2.1566883129,0 .$, $-1.3656714434 \backslash C, 2.1566883129,0$. , 1. $3656714434 \backslash C, 2.1566883129$, $0 .,-1.3656$ $714434 \backslash C, 0 .,-1.5090165936,2.2630696799 \backslash C, 0 .,-1.5090165936,-2.263069679$ $9 \backslash C, 0 ., 1.5090165936,2.2630696799 \backslash \mathrm{C}, 0 ., 1.5090165936,-2.2630696799 \backslash \mathrm{C},-2$. $9720380781,0 ., 0 . \backslash \mathrm{C}, 2.9720380781,0 ., 0 . \backslash \mathrm{H},-1.9897891837,-2.1527206592,1$. $5519036889 \backslash \mathrm{H}, 1.9897891837,-2.1527206592,-1.5519036889 \backslash \mathrm{H}, 1.9897891837,2$ $.1527206592,1.5519036889 \backslash \mathrm{H},-1.9897891837,2.1527206592,-1.5519036889 \backslash \mathrm{H}$, $1.9897891837,-2.1527206592,1.5519036889 \backslash \mathrm{H}, 1.9897891837,2.1527206592,-1$ $.5519036889 \backslash \mathrm{H},-1.9897891837,2.1527206592,1.5519036889 \backslash \mathrm{H},-1.9897891837$, $-2.1527206592,-1.5519036889 \backslash H,-2.8788757416,0 ., 2.1926176249 \backslash H,-2.87887$ $57416,0 .,-2.1926176249 \backslash \mathrm{H}, 2.8788757416,0 ., 2.1926176249 \backslash \mathrm{H}, 2.8788757416,0$ ., - $2.1926176249 \backslash \mathrm{H}, 0 .,-0.9439684021,3.1949625695 \backslash \mathrm{H}, 0 .,-2.5651137519,2.5$ $560893056 \backslash \mathrm{H}, 0 .,-0.9439684021,-3.1949625695 \backslash \mathrm{H}, 0 .,-2.5651137519,-2.55608$ $93056 \backslash \mathrm{H}, 0 ., 0.9439684021,3.1949625695 \backslash \mathrm{H}, 0 ., 2.5651137519,2.5560893056 \backslash \mathrm{H}$, $0 ., 0.9439684021,-3.1949625695 \backslash \mathrm{H}, 0 ., 2.5651137519,-2.5560893056 \backslash \mathrm{H},-3.633$ $9282144,0.8779961839,0 . \backslash \mathrm{H},-3.6339282144,-0.8779961839,0 . \backslash \mathrm{H}, 3.633928214$ $4,-0.8779961839,0 . \backslash H, 3.6339282144,0.8779961839,0 . \backslash \backslash V e r s i o n=F u j i t s u-V p-$ Unix-G98RevA. $6 \backslash$ State $=2-B 2 U \backslash H F=-884.6743513 \backslash M P 2=-888.1327725 \backslash P U H F=-884$. $6785538 \backslash P M P 2-0=-888.1355316 \backslash S 2=0.768339 \backslash S 2-1=0.755657 \backslash S 2 A=0.750206 \backslash R M S$ $\mathrm{D}=2.719 \mathrm{e}-09 \backslash \mathrm{PG}=\mathrm{D} 02 \mathrm{H} \quad\left[\mathrm{O}(\mathrm{C} 1), \mathrm{C} 2(\mathrm{C} 1 . \mathrm{C} 1), \mathrm{SG}(\mathrm{C} 4 \mathrm{H} 8), \mathrm{SG}{ }^{\prime}(\mathrm{C} 4 \mathrm{H} 4), \mathrm{SG} \mathrm{V}^{(\mathrm{C} 4 \mathrm{H} 4)}\right.$, X(C8 H8) ] <br>@

## C.2.3.4 Triplets

Table C-30. Gaussian archive files for the UB3-LYP/6-31G(d) and UMP2(fc)/6-31G(d) optimized triplets of octaplane (4-27) and spirooctaplane (4-28).

## UB3-LYP/6-31G(d)

## triplet-4-27 octaplane triplet <br> $\boldsymbol{C}_{\text {s }}$

$1 \backslash 1 \backslash$ MHPCC-FR27N05\FOpt\UB3LYP\6-31G(d) \C21H28 (3) \RASMUSSEN $\backslash 04$-Oct-199 8\0<br>\#P UB3LYP/6-31G* 5D OPT=(TIGHT,NEWESTMFC) GUESS=CHECK SCF=(NOVARA CC) NAME=RASMUSSEN SYMM=LOOSE GEOM=CHECK <br>Octaplane Cs 5D<br>0,3\C,-0.43 55600593,-0.0172836668,-0.0000014343\C,2.474679108,-0.3017806507,0.000 $0089161 \backslash C,-1.9070074553,-0.0219903984,-0.0000063828 \backslash C,-0.0090230927,-1$ $.4254887273,0.0000027027 \backslash \mathrm{C},-0.0893200942,1.437408218,-0.0000030569 \backslash \mathrm{C}, 1$ $.9634492159,-0.2951527292,1.4812513661 \backslash C,-1.9968920223,0.337931323,1.5$ $671180072 \backslash \mathrm{C},-0.3517710405,-1.7975028095,-1.4850670285 \backslash \mathrm{C}, 0.307240139,1$. 8018021293,-1.4288906268\C,1.9634591969,-0.2951584093,-1.4812370041\C, $-1.9968814626,0.3379253136,-1.5671327585 \backslash C,-0.3517810472,-1.7974971148$ ,1.485071551\C,0.3072305108,1.8018076086,1.4288857877\C,-1.5884057597, $-1.0784800823,2.1341100739 \backslash C, 1.0476819071,-1.433478969,-2.1085028693 \backslash C$ ,1.5851948342,1.139521069,1.9638605047\C,-1.0736793292,1.4816190802,-2 $.1509397874 \backslash C, 1.0476676994,-1.4334708836,2.1085154257 \backslash C, 1.5852080672,1$ $.1395135383,-1.963854193 \backslash C,-1.0736938227,1.4816273283,2.1509268712 \backslash C,-$ $1.5883913796,-1.0784882659,-2.1341166413 \backslash \mathrm{H}, 3.5089938394,0.0552359349,0$ $.0000117163 \backslash \mathrm{H},-2.367374416,-1.015855982,-0.0000060282 \backslash \mathrm{H}, 1.0365903621,-$ $1.6834760132,0.0000067202 \backslash \mathrm{H},-1.0712139676,1.9308941495,-0.0000073112 \backslash \mathrm{H}$ , 0.4507034074,2.8880658069,1.5309193668 $\mathrm{H},-3.0172782782,0.548805407,-1$ $.9213070942 \backslash \mathrm{H},-0.4946750639,-2.8770209071,1.6377508189 \backslash \mathrm{H}, 2.9054692386$, $-0.476045422,-2.020899218 \backslash \mathrm{H}, 2.9054556212,-0.4760376725,2.0209206212 \backslash \mathrm{H}$, $-3.0172912244,0.5488127745,1.9212846585 \backslash \mathrm{H}, 0.4507137231,2.8880599363,-1$ $.5309274046 \backslash \mathrm{H},-0.4946640284,-2.8770271873,-1.6377431197 \backslash \mathrm{H},-2.459103734$ 8,-1.7380284007,-2.0231003888\H,1.6477574702,-2.3519426786,2.061191499 $8 \backslash \mathrm{H}, 2.4278457399,1.7918783006,-1.6955829973 \backslash \mathrm{H},-1.6508186567,2.41513712$ $33,2.1163179443 \backslash \mathrm{H},-2.4591173669,-1.7380206428,2.0230904835 \backslash \mathrm{H}, 1.6477713$ 589,-2.3519505825,-2.0611713778\H,2.4278343146,1.7918848027,1.69559248 $54 \backslash \mathrm{H},-1.6508043964,2.4151290078,-2.1163383291 \backslash \mathrm{H},-1.4131018355,-0.99647$ $22246,3.2155997811 \backslash \mathrm{H}, 0.9486792588,-1.1935189077,-3.1763170043 \backslash \mathrm{H}, 1.5575$ 489321,1.1288949823,3.064016907\H,-0.9147352856,1.2666983517,-3.216188 $3683 \backslash \mathrm{H}, 0.948657856,-1.1935067276,3.1763279733 \backslash \mathrm{H},-1.413080168,-0.996484$ 5554,-3.2156054816\H,1.5575695782,1.1288832328,-3.0640107407\H,-0.9147 56957,1.2667106847,3.2161773471\VVersion=IBM-RS6000-G94RevE.2\State=3A" $\backslash \mathrm{HF}=-816.7342345 \backslash \mathrm{~S} 2=2.009 \backslash \mathrm{~S} 2-1=0 . \backslash \mathrm{S} 2 \mathrm{~A}=2 . \backslash \mathrm{RMSD}=4.840 \mathrm{e}-09 \backslash \mathrm{RMSF}=5.849 \mathrm{e}-$ $06 \backslash$ Dipole=0.0951063,0.0522677,0.0000002\PG=CS [SG(C5H4), X(C16H24)] <br>@

## triplet-4-28 spirooctaplane triplet

## $C_{s}$

$1 \backslash 1 \backslash$ MHPCC-FR26N04 \FOpt \UB3LYP\6-31G(d) \C21H24(3) \RASMUSSEN \04-Oct-199 $8 \backslash 0 \backslash \ \# P$ UB3LYP/6-31G* 5D OPT= (READFC) $S C F=(N O V A R A C C, R E S T A R T) ~ N A M E=R A S M$ USSEN SYMM=LOOSE GEOM=(CHECK,NODISTANCE,NOANGLE,NODIHEDRAL) <br>Spiro[2.2 ]octaplane Cs 5D<br>0,3\C,0.,0.2537642874,0.\C,-0.4643807337,1.590053005 , 0. \C,-1.4050481933,0.325831203,0.\C,0.7032375705,-1.7532009693,0.\C,1 $.2853448974,-0.3638995033,0 . \backslash C,-0.1287193527,1.9374973834,1.4789209412$
$\backslash C,-1.8355475985,-0.0462755605,-1.415085937 \backslash C, 0.1496295524,-1.93019806$ $21,1.4224738257 \backslash C, 1.8014290961,0.0338586634,-1.4156469999 \backslash \mathrm{C},-0.1287193$ $527,1.9374973834,-1.4789209412 \backslash C,-1.8355475985,-0.0462755605,1.4150859$ $37 \backslash C, 0.1496295524,-1.9301980621,-1.4224738257 \backslash \mathrm{C}, 1.8014290961,0.0338586$ 634,1.4156469999\C,1.3412814276,1.482649099,1.8243979991\C,1.341281427 $6,1.482649099,-1.8243979991 \backslash C,-1.336685165,-1.4900528403,1.7435476542 \backslash$ C, $-1.336685165,-1.4900528403,-1.7435476542 \backslash C,-1.2457337871,1.147166518$ , 2.2607871717\C,-1.2457337871,1.147166518,-2.2607871717\C,1.2174410934 ,-1.1478600522,2.2686193679\C,1.2174410934,-1.1478600522,-2.2686193679 \H, -0.2064304799,3.0042995964,1.7318785472\H,-2.9278334744,-0.05328840 32,-1.5481916019\H, 0.1773324729,-2.9888033914,1.7172172777\H,2.8979937 528,0.0182133512,-1.4817541952\H,-2.9278334744,-0.0532884032,1.5481916 $019 \backslash \mathrm{H}, 0.1773324729,-2.9888033914,-1.7172172777 \backslash \mathrm{H}, 2.8979937528,0.018213$ 3512,1.4817541952\H,-0.2064304799,3.0042995964,-1.7318785472\H,1.50217 99783,1.6058664152,2.9043475216\H,2.0236159897,2.1950560135,1.33832258 13\H,1.5021799783,1.6058664152,-2.9043475216\H,2.0236159897,2.19505601 35,-1.3383225813\H,-1.4951419201,-1.6863781497,2.8142583709\H,-2.00337 86234,-2.1858164375,1.2155210164 \H,-1.4951419201,-1.6863781497,-2.8142 $583709 \backslash \mathrm{H},-2.0033786234,-2.1858164375,-1.2155210164 \backslash \mathrm{H},-0.8846696701,0.8$ 154233065,3.2416622278\H,-2.0689261964,1.8453059077,2.4514936954\H,-0. $8846696701,0.8154233065,-3.2416622278 \backslash \mathrm{H},-2.0689261964,1.8453059077,-2$. $4514936954 \backslash \mathrm{H}, 0.810554438,-0.8124461968,3.2294686129 \backslash \mathrm{H}, 2.0386715132,-1$. 8357869737,2.5002583048\H, 0.810554438,-0.8124461968,-3.2294686129\H,2. 0386715132,-1.8357869737,-2.5002583048<br>Version=IBM-RS6000-G94RevE.2\S tate $=3-\mathrm{A} " \backslash \mathrm{HF}=-814.4062991 \backslash \mathrm{~S} 2=2.008 \backslash \mathrm{~S} 2-1=0 . \backslash \mathrm{S} 2 \mathrm{~A}=2 . \backslash \mathrm{RMSD}=6.613 \mathrm{e}-09 \backslash \mathrm{RMSF}=$ $5.886 \mathrm{e}-06 \backslash \mathrm{Dipole}=-0.0586935,0.0782697,0 . \backslash \mathrm{PG}=\mathrm{CS} \quad[\mathrm{SG}(\mathrm{C} 5), \mathrm{X}(\mathrm{C} 16 \mathrm{H} 24)] \backslash \backslash @$
triplet-4-29 dimethanospirooctaplane triplet $\boldsymbol{C}_{\text {s }}$
$1 \backslash 1 \backslash G I N C-$ PALO $\backslash$ FOpt \UB3LYP\6-31G(d) \C23H24 (3) \RASMUSSEN $\backslash 08-F e b-2000 \backslash 0 \backslash \backslash$ \#P UB3LYP/6-31G* 5D OPT=NEWESTMFC SCF=(NOVARACC) NAME=RASMUSSEN GEOM=( NODISTANCE, NOANGLE, NODIHEDRAL) <br>dimethanospiro[2.2]octaplane C1 5D Sur face: triplet diradical<br>0,3\C,-0.1313924696,0.2018633742,0.0000096098 \C, -0.5492054848,-1.1939576715,0.0000003092\C,0.7997493577,-1.79584613 89, 0.0000111058\C, 0.7071426088,1.3501792619,-0.000004\C,-0.8029835981, $1.4733552373,0.0000017475 \backslash C,-1.248490717,-1.2742588848,1.3512427656 \backslash \mathrm{C}$, $1.3315374292,-1.4214799306,-1.3808434695 \backslash \mathrm{C}, 1.2954545403,1.3052064265,1$ $.3880890387 \backslash \mathrm{C},-1.3590826804,1.3866823194,-1.4170402864 \backslash \mathrm{C},-1.2484905283$ ,-1.2742898393,-1.3512403925\C,1.3315372237,-1.4214548921,1.3808528331 $\backslash C, 1.2954435415,1.3052210654,-1.3880973773 \backslash C,-1.3590803149,1.386672850$ $9,1.4170484471 \backslash C,-2.1491119615,0.0169470206,1.3754351334 \backslash C,-2.14910151$ $28,0.0169375247,-1.3754390697 \backslash C, 2.118739373,-0.0404248531,1.343750846 \backslash$ $C, 2.1187304601,-0.0404305918,-1.3437702286 \backslash C, 0.0198854972,-1.530702737$ $3,2.2708530808 \backslash C, 0.0198883453,-1.530789003,-2.2708488575 \backslash C,-0.01732444$ $17,1.5489803122,2.2729713846 \backslash C,-0.0173371486,1.5490459315,-2.272972086$ $1 \backslash C,-2.9736465292,0.0000613086,-0.0000059481 \backslash C, 2.9516192813,-0.0139635$ $516,-0.000013304 \backslash \mathrm{H},-1.9202268248,-2.1419813787,1.424415991 \backslash \mathrm{H}, 2.0630263$ $824,-2.1533769282,-1.749393594 \backslash H, 2.0109097736,2.1129426799,1.610588980$ $6 \backslash \mathrm{H},-2.057344788,2.1863957661,-1.7081953236 \backslash \mathrm{H}, 2.0630327433,-2.15334476$ 87,1.7494092948\H,2.0108837987,2.1129755796,-1.6105594279\H,-2.0573505 $264,2.1863720554,1.7082420202 \backslash \mathrm{H},-1.9202176605,-2.1420188444,-1.4243716$ $166 \backslash \mathrm{H},-2.8737596119,-0.0373708214,2.1985094983 \backslash \mathrm{H},-2.8737495433,-0.0373$ 816809,-2.1985107668\H,2.8370333911,-0.0503002357,2.1753819207\H, 2. 837
$0258655,-0.0503113173,-2.1754001791 \backslash \mathrm{H}, 0.0666220119,-0.9267400121,3.178$ $125785 \backslash \mathrm{H},-0.0439021058,-2.5718189689,2.6075355563 \backslash \mathrm{H}, 0.0666202927,-0.92$ $68818856,-3.1781558882 \backslash \mathrm{H},-0.043895163,-2.5719100853,-2.6075076261 \backslash \mathrm{H},-0$ $.0349351041,0.9828237336,3.2059639109 \backslash \mathrm{H}, 0.020371449,2.6052818458,2.564$ $5181389 \backslash \mathrm{H},-0.0349565406,0.9829434244,-3.2059988228 \backslash \mathrm{H}, 0.0203508255,2.60$ $53480311,-2.564497707 \backslash \mathrm{H},-3.6556617758,0.8615376888,-0.0000037837 \backslash \mathrm{H},-3$. $608298603,-0.896416369,-0.0000112336 \backslash \mathrm{H}, 3.6298867706,-0.8780243894,-0.0$ $000125209 \backslash \mathrm{H}, 3.5916533139,0.8799296452,-0.0000202968 \backslash \backslash$ Version=Sun-SVR4-Unix-G98RevA. $7 \backslash \mathrm{HF}=-890.5590931 \backslash \mathrm{~S} 2=2.008026 \backslash \mathrm{~S} 2-1=0 . \backslash \mathrm{S} 2 \mathrm{~A}=2.000037 \backslash \mathrm{RMSD}=5$ $.430 e-09 \backslash \mathrm{RMSF}=3.251 e-05 \backslash \mathrm{Dipole}=0.000941,0.0844086,-0.0000239 \backslash \mathrm{PG}=\mathrm{C01}$ [X (C23H24)] <br>@

## UMP2(fc)/6-31G(d)

## triplet-4-27 octaplane triplet

## $C_{\text {s }}$

$1 \backslash 1 \backslash G I N C-V P P 07 \backslash F O p t \backslash U M P 2-F C \backslash 6-31 G(d) \backslash C 21 H 28(3) \backslash R A S M U S S E N \backslash 27-S e p-1998 \backslash 0$ <br>\#P UMP2/6-31G* 5D OPT=NEWESTMFC NAME=RASMUSSEN GEOM= (NODISTANCE,NOAN GLE, NODIHEDRAL) MAXDISK=1800000000<br>Octaplane Cs triplet optimized<br>0, $3 \backslash C, 0.4001577578,0 \ldots,-0.0034830418 \backslash C,-2.4051735388,0 ., 0.4608715341 \backslash C, 0$. $104575746,0 ., 1.4350160504 \backslash C, 1.8672040808,0 .,-0.109790049 \backslash C,-0.03650035$ $84,0 .,-1.4264046712 \backslash C,-1.9019866475,1.4729441714,0.438015699 \backslash C, 0.49453$ $68843,-1.472996232,1.7596937504 \backslash C, 1.9416282879,1.5432262802,-0.4872832$ $512 \backslash \mathrm{C},-0.4491361096,-1.4212992129,-1.7670919229 \backslash \mathrm{C},-1.9019866475,-1.472$ $9441714,0.438015699 \backslash \mathrm{C}, 0.4945368843,1.472996232,1.7596937504 \backslash \mathrm{C}, 1.941628$ $2879,-1.5432262802,-0.4872832512 \backslash \mathrm{C},-0.4491361096,1.4212992129,-1.76709$ $19229 \backslash C,-1.6571940468,1.9612296868,-1.0101767037 \backslash C,-0.914159209,-2.097$ $0344789,1.4965603892 \backslash C, 1.6602994362,2.1145726846,0.9457204041 \backslash C, 0.9433$ $490807,-2.1309519966,-1.5484279498 \backslash C, 1.6602994362,-2.1145726846,0.9457$ $204041 \backslash \mathrm{C}, 0.9433490807,2.1309519966,-1.5484279498 \backslash \mathrm{C},-1.6571940468,-1.96$ $12296868,-1.0101767037 \backslash \mathrm{C},-0.914159209,2.0970344789,1.4965603892 \backslash \mathrm{H},-3.4$ $412188235,0 ., 0.1074988577 \backslash \mathrm{H},-0.9134969049,0 ., 1.7989674059 \backslash \mathrm{H}, 2.39789573$ $23,0.0 .8512594166 \backslash \mathrm{H}, 0.9174493308,0 .,-1.979575665 \backslash \mathrm{H},-2.8329784504,2.00$ $14363022,0.7021981788 \backslash \mathrm{H}, 0.7206550545,-1.630161069,2.8260953054 \backslash \mathrm{H}, 2.947$ $8170749,1.8839134384,-0.7813695043 \backslash \mathrm{H},-0.6711222464,-1.5158815581,-2.84$ $21280961 \backslash \mathrm{H}, 0.7206550545,1.630161069,2.8260953054 \backslash \mathrm{H}, 2.9478170749,-1.883$ $9134384,-0.7813695043 \backslash \mathrm{H},-0.6711222464,1.5158815581,-2.8421280961 \backslash \mathrm{H},-2$. $8329784504,-2.0014363022,0.7021981788 \backslash \mathrm{H},-1.6244947361,3.0615606279,-1$. $0004661981 \backslash \mathrm{H},-2.5547445517,1.6936073487,-1.5856019988 \backslash \mathrm{H},-0.828555122$, $3.1631518254,1.2399650443 \backslash \mathrm{H},-1.4477792632,-2.0582741133,2.4562412597 \backslash \mathrm{H}$ , 1.4781001683, 3.1966755238, 0.8783664025 \H, 2.5847405473,2.0014390277,1. $5278819488 \backslash \mathrm{H}, 0.8048579325,-3.1967594183,-1.3174614327 \backslash \mathrm{H}, 1.4483718055$, -$2.0964792682,-2.5234878749 \backslash H, 1.4781001683,-3.1966755238,0.8783664025 \backslash \mathrm{H}$ , 2. 5847405473,-2.0014390277,1.5278819488\H,0.8048579325,3.1967594183,$1.3174614327 \backslash \mathrm{H}, 1.4483718055,2.0964792682,-2.5234878749 \backslash \mathrm{H},-1.6244947361$ ,-3.0615606279,-1.0004661981 \H, -2.5547445517,-1.6936073487,-1.58560199 $88 \backslash \mathrm{H},-0.828555122,3.1631518254,1.2399650443 \backslash \mathrm{H},-1.4477792632,2.05827411$ 33,2.4562412597<br>Version=Fujitsu-VP-Unix-G94RevE. $2 \backslash$ State=3-A" $\backslash \mathrm{HF}=-811$. $1799208 \backslash \mathrm{MP} 2=-813.9052408 \backslash \mathrm{PUHF}=-811.18574 \backslash \mathrm{PMP} 2-0=-813.9091148 \backslash \mathrm{~S} 2=2.033 \backslash$ $S 2-1=2.011 \backslash S 2 A=2.001 \backslash R M S D=2.256 e-09 \backslash R M S F=8.471 e-06 \backslash D i p o l e=-0.095363,0$. , - 0.0447324 \PG=CS [SG(C5H4),X(C16H24)]<br>@

## triplet-4-28 spirooctaplane triplet <br> $\boldsymbol{C}_{\mathrm{s}}$

1 \1 \GINC-VPP08\FOpt \UMP2-FC\6-31G(d) \C21H24 (3) \RASMUSSEN $\backslash 17-$ Sep-1998\0 <br>\#P UMP2/6-31G* 5D OPT=NEWESTMFC NAME=RASMUSSEN GEOM=(NODISTANCE,NOAN GLE,NODIHEDRAL) SCF=RESTART MAXDISK=150000000<br>Spiro[2.2]octaplane Cs optimized triplet $\backslash \backslash 0,3 \backslash \mathrm{C},-0.0138007285,-0.238179774,0 . \backslash \mathrm{C}, 0.3832108753$, $-1.599891508,0 . \backslash C, 1.3844526913,-0.3850417158,0 . \backslash C,-0.6186918585,1.7824$ $917274,0 . \backslash C,-1.2696911442,0.4306058424,0 . \backslash C, 0.0267782875,-1.9237588013$ ,1.4650457355\C,1.8286734043,-0.0413937184,-1.4062058081\C,-0.04576088 76,1.9139634417,1.4140982946\C,-1.7934575489,0.0521336773,-1.402934928 $4 \backslash C, 0.0267782875,-1.9237588013,-1.4650457355 \backslash C, 1.8286734043,-0.0413937$ 184,1.4062058081\C,-0.0457608876,1.9139634417,-1.4140982946\C,-1.79345 $75489,0.0521336773,1.4029349284 \backslash C,-1.4152360188,-1.4126475031,1.792196$ $6279 \backslash \mathrm{C},-1.4152360188,-1.4126475031,-1.7921966279 \backslash \mathrm{C}, 1.4101628464,1.4178$ $120982,1.7213656301 \backslash \mathrm{C}, 1.4101628464,1.4178120982,-1.7213656301 \backslash \mathrm{C}, 1.1683$ 811076,-1.1880741759,2.2476772713\C,1.1683811076,-1.1880741759,-2.2476 $772713 \backslash C,-1.1365999107,1.1810597471,2.2578526916 \backslash \mathrm{C},-1.1365999107,1.181$ 0597471,-2.2578526916\H, 0.0610128022,-2.9953550565,1.7160192231\H, 2.92 $11750426,-0.1004672103,-1.536924834 \backslash \mathrm{H},-0.0315914408,2.9729704711,1.714$ $07439 \backslash \mathrm{H},-2.8888456338,0.1335593091,-1.4726320196 \backslash \mathrm{H}, 2.9211750426,-0.100$ 4672103,1.536924834 \H, -0.0315914408,2.9729704711,-1.71407439\H,-2.8888 456338,0.1335593091,1.4726320196\H, 0.0610128022,-2.9953550565,-1.71601 $92231 \backslash \mathrm{H},-1.6026379018,-1.5454729597,2.867747928 \backslash \mathrm{H},-2.1192888213,-2.084$ 1788466,1.2787515591\H,-1.6026379018,-1.5454729597,-2.867747928\H,-2.1 192888213,-2.0841788466,-1.2787515591\H,1.5868166032,1.6177951263,2.78 $95332562 \backslash \mathrm{H}, 2.1037891584,2.0755728723,1.1788714058 \backslash \mathrm{H}, 1.5868166032,1.617$ $7951263,-2.7895332562 \backslash \mathrm{H}, 2.1037891584,2.0755728723,-1.1788714058 \backslash \mathrm{H}, 0.81$ 81159773,-0.8318834912,3.2248058037 \H, 1.9520942289,-1.9283826824, 2.447 $6754243 \backslash \mathrm{H}, 0.8181159773,-0.8318834912,-3.2248058037 \backslash \mathrm{H}, 1.9520942289,-1.9$ 283826824,-2.4476754243\H,-0.7380656377,0.8111709237,3.2102745709\H,-1 . 9166615633,1.9101492344,2.5068956403\H,-0.7380656377,0.8111709237,-3. 2102745709\H,-1.9166615633,1.9101492344,-2.5068956403<br>Version=Fujitsu -VP-Unix-G94RevE. $2 \backslash$ State=3-A" $\backslash \mathrm{HF}=-808.9538062 \backslash \mathrm{MP} 2=-811.6541216 \backslash \mathrm{PUHF}=-8$ $08.958985 \backslash$ PMP2-0 $=-811.6575078 \backslash S 2=2.029 \backslash S 2-1=2.009 \backslash S 2 A=2 . \backslash R M S D=6.047 e-0$ $9 \backslash \mathrm{RMSF}=6.582 \mathrm{e}-05 \backslash \mathrm{Dipole}=0.0617073,-0.08017,0 . \backslash \mathrm{PG}=\mathrm{CS}$ [SG(C5),X(C16H24)] <br>@

## C.2.3.5 Bond Dissociation Geometries

Table C-31. Gaussian archive files for the UB3-LYP/6-31G(d) optimized geometries in the $\mathrm{C}^{0}-\mathrm{C}^{\alpha}$ bond dissociation of dimethanospirooctaplane (4-29).

## equilibrium <br> $D_{2}$

$1 \backslash 1 \backslash$ MHPCC-FR27N13\FOpt \RB3LYP\6-31G(d) \C23H24\RASMUSSEN\30-Sep-1998\0 <br>\#P RB3LYP/6-31G* 5D FOPT=(READFC,TIGHT) SCF=(VSHIFT,NOVARACC,DIRECT) NAME=RASMUSSEN GUESS=CHECK GEOM=(CHECK,NODISTANCE,NOANGLE,NODIHEDRAL) <br>Dimethanospiro[2.2]octaplane D2<br>0,1\C,0.,0.,0.\C,-0.7191839521,-0.0 $469287695,-1.3191144063 \backslash C, 0.7191839521,0.0469287695,-1.3191144063 \backslash \mathrm{C}, 0$. 7191839521,-0.0469287695,1.3191144063\C,-0.7191839521,0.0469287695,1.3 $191144063 \backslash \mathrm{C},-1.3089729688,-1.4166741729,-1.3380523577 \backslash \mathrm{C}, 1.3089729688,1$ .4166741729,-1.3380523577\C,1.3089729688,-1.4166741729,1.3380523577\C, $-1.3089729688,1.4166741729,1.3380523577 \backslash \mathrm{C},-1.3172568181,1.3519419981,-$
$1.3031776458 \backslash C, 1.3172568181,-1.3519419981,-1.3031776458 \backslash C, 1.3172568181$ , 1. $3519419981,1.3031776458 \backslash C,-1.3172568181,-1.3519419981,1.3031776458 \backslash$ $C,-2.1716483589,-1.3759029675,-0.0115655369 \backslash C, 2.1716483589,1.375902967$ $5,-0.0115655369 \backslash C, 2.1716483589,-1.3759029675,0.0115655369 \backslash C,-2.1716483$ 589,1.3759029675,0.0115655369\C, -0.028641231,2.267537116,-1.522052298\ $C,-0.028641231,-2.267537116,1.522052298 \backslash C, 0.028641231,2.267537116,1.52$ $2052298 \backslash C, 0.028641231,-2.267537116,-1.522052298 \backslash C,-2.9979635374,0 ., 0 . \backslash$ C, 2. $9979635374,0.0 . \backslash \mathrm{H},-1.99201834,-1.6414935319,-2.1767422262 \backslash \mathrm{H}, 1.992$ 01834, 1. $6414935319,-2.1767422262 \backslash \mathrm{H}, 1.99201834,-1.6414935319,2.17674222$ $62 \backslash \mathrm{H},-1.99201834,1.6414935319,2.1767422262 \backslash \mathrm{H}, 2.0116041885,-1.524601081$ , - 2. $141248613 \backslash \mathrm{H}, 2.0116041885,1.524601081,2.141248613 \backslash \mathrm{H},-2.0116041885$, $1.524601081,2.141248613 \backslash \mathrm{H},-2.0116041885,1.524601081,-2.141248613 \backslash \mathrm{H},-2$. $8963977218,-2.2002995987,0.0072837085 \backslash \mathrm{H}, 2.8963977218,2.2002995987,0.00$ $72837085 \backslash \mathrm{H}, 2.8963977218,-2.2002995987,-0.0072837085 \backslash \mathrm{H},-2.8963977218,2$. $2002995987,-0.0072837085 \backslash \mathrm{H},-0.041977571,2.5817512981,-2.5741924732 \backslash \mathrm{H}$, -$0.0534763635,3.1913968011,-0.9416585675 \backslash \mathrm{H},-0.041977571,-2.5817512981,2$ $.5741924732 \backslash \mathrm{H},-0.0534763635,-3.1913968011,0.9416585675 \backslash \mathrm{H}, 0.041977571,2$ $.5817512981,2.5741924732 \backslash \mathrm{H}, 0.0534763635,3.1913968011,0.9416585675 \backslash \mathrm{H}, 0$. $041977571,-2.5817512981,-2.5741924732 \backslash \mathrm{H}, 0.0534763635,-3.1913968011,-0$. $9416585675 \backslash \mathrm{H},-3.6571535514,-0.013391157,0.8785590834 \backslash \mathrm{H},-3.6571535514,0$ $.013391157,-0.8785590834 \backslash \mathrm{H}, 3.6571535514,-0.013391157,-0.8785590834 \backslash \mathrm{H}, 3$ $.6571535514,0.013391157,0.8785590834 \backslash \backslash V e r s i o n=I B M-R S 6000-G 94 R e v E .2 \backslash$ Sta te=1-A $\backslash H F=-890.548503 \backslash R M S D=9.112 e-09 \backslash R M S F=2.879 e-06 \backslash D i p o l e=0 ., 0 ., 0 . \backslash P G$ =D02 [O(C1), C2" (C1.C1), X (C20H24)] <br>@

## $\mathrm{C}-\mathrm{C}=1.600 \AA$

$1 \backslash 1 \backslash G I N C-P A L O \backslash F O p t \backslash U B 3 L Y P \backslash 6-31 G(d) \backslash C 23 H 24 \backslash R A S M U S S E N \backslash 13-F e b-2000 \backslash 0 \backslash \backslash \# P$ UB3LYP/6-31G* 5D NAME=RASMUSSEN OPT=MODREDUNDANT GEOM= (CHECK, NODISTANC E,NOANGLE,NODIHEDRAL) GUESS=CHECK<br>dimethanospiro[2.2]octaplane C1 5D Surface: 1.6 dist $\backslash \backslash 0,1 \backslash C, 0.0200120213,-0.0104236056,-0.0225039584 \backslash C, 0$. $6393638643,-0.0467184621,1.3361874857 \backslash C,-0.8013052768,0.0451292405,1.3$ $494849106 \backslash \mathrm{C},-0.6532246304,-0.0453420673,-1.3436478248 \backslash \mathrm{C}, 0.7935362429,0$ $.0472962406,-1.303285463 \backslash C, 1.2397174195,-1.4137715564,1.3956019368 \backslash C$, $1.373146044,1.4184244949,1.2814808099 \backslash C,-1.2436046809,-1.4151367488,-1$ $.3967642772 \backslash C, 1.3767892749,1.4210207432,-1.2825588746 \backslash C, 1.2476564162,1$ $.3498214883,1.3583643531 \backslash C,-1.3808260114,-1.3553972972,1.2498281458 \backslash C$, $-1.251584391,1.3530210648,-1.3598996176 \backslash C, 1.3835303144,-1.3556915354$, $1.2496427643 \backslash C, 2.166601706,-1.3752144745,0.1119462839 \backslash C, 2.1679150906,1$ $.3759251912,0.0887783851 \backslash C,-2.1652182855,-1.372425718,-0.1107245419 \backslash C$, $-2.1669128415,1.374120424,-0.087364508 \backslash C,-0.1002268603,-2.268772036,1$. $5196064993 \backslash \mathrm{C},-0.044452703,2.2686876792,1.5183959343 \backslash \mathrm{C}, 0.1012503941,-2$. $2660003979,-1.5258013874 \backslash C, 0.0456487886,2.2681574216,-1.5247388625 \backslash C, 2$ $.9924426471,0.0002856764,0.1420314936 \backslash C,-2.9914116693,0.0009296442,-0$. $1400307308 \backslash \mathrm{H}, 1.8822012289,-1.629140358,2.2687017024 \backslash \mathrm{H},-2.0988787026,1$. $6665269075,2.077154028 \backslash \mathrm{H},-1.8906968646,-1.6404104531,-2.2640056299 \backslash \mathrm{H}, 2$ $.1000911126,1.6609078358,-2.0824288362 \backslash \mathrm{H},-2.1187154334,-1.5517771127,2$ $.0442872373 \backslash \mathrm{H},-1.9094130923,1.5267139897,-2.2268308194 \backslash \mathrm{H}, 2.1199168023$, $-1.5447692216,-2.0483769672 \backslash \mathrm{H}, 1.9001448338,1.5128486738,2.2312204071 \backslash \mathrm{H}$ , 2. $8919818537,-2.1990095656,0.1339749721 \backslash H, 2.8905484592,2.2002479785,0$ $.1491159505 \backslash \mathrm{H},-2.8911500195,-2.1963738702,-0.1237552328 \backslash \mathrm{H},-2.890112111$ $6,2.1990325357,-0.1371233084 \backslash H,-0.1031273033,-3.1885524451,0.932649873$ $2 \backslash \mathrm{H},-0.1577505901,-2.5887890174,2.5687853973 \backslash \mathrm{H}, 0.0007865037,3.18734297$
$6,0.9315534429 \backslash \mathrm{H},-0.0754973135,2.591354899,2.5675308448 \backslash \mathrm{H}, 0.1010633533$ $,-3.1924294078,-0.9484413779 \backslash \mathrm{H}, 0.1585222043,-2.5768164254,-2.577775392$ $9 \backslash \mathrm{H},-0.0030590505,3.1950803237,-0.9502313275 \backslash \mathrm{H}, 0.0764144588,2.57822794$ $2,-2.5777115129 \backslash \mathrm{H}, 3.6951273308,-0.0129635621,-0.7021712981 \backslash \mathrm{H}, 3.6063532$ $269,0.0137132166,1.0528557281 \backslash \mathrm{H},-3.6951744343,-0.0123324144,0.70351890$ $84 \backslash \mathrm{H},-3.6048811659,0.0138141172,-1.0509573556 \backslash \backslash V e r s i o n=S u n-S V R 4-U n i x-G$ $98 \mathrm{RevA} .7 \backslash \mathrm{HF}=-890.5457736 \backslash \mathrm{~S} 2=0 . \backslash \mathrm{S} 2-1=0 . \backslash \mathrm{S} 2 \mathrm{~A}=0 . \backslash \mathrm{RMSD}=8.765 \mathrm{e}-09 \backslash \mathrm{RMSF}=3.19$ 1e-03\Dipole=-0.071681,0.0245877,0.1073591 \PG=C01 [X(C23H24)] <br>@

## $\mathrm{C}-\mathrm{C}=1.700 \AA$

$1 \backslash 1 \backslash G I N C-P A L O \backslash F O p t \backslash U B 3 L Y P \backslash 6-31 G(d) \backslash C 23 H 24 \backslash R A S M U S S E N \backslash 13-F e b-2000 \backslash 0 \backslash \backslash \# P$ UB3LYP/6-31G* 5D NAME=RASMUSSEN OPT=MODREDUNDANT GEOM = (CHECK, NODISTANC E,NOANGLE,NODIHEDRAL) GUESS=CHECK<br>dimethanospiro[2.2]octaplane C1 5D Surface: 1.7 dist <br>0,1\C,0.042802226,-0.0277192191,-0.0467915387\C,0.6 $213321304,-0.0506525026,1.3173862779 \backslash C,-0.821257276,0.047577403,1.4153$ $073701 \backslash C,-0.6506707512,-0.0480196208,-1.3375406404 \backslash C, 0.8069843235,0.05$ $24653168,-1.3246069581 \backslash C, 1.2346308108,-1.4128403597,1.3949291973 \backslash C,-1$. $375808362,1.4219547225,1.2908045693 \backslash C,-1.2432197617,-1.4165939305,-1.3$ $973525726 \backslash \mathrm{C}, 1.3828956226,1.4292117706,-1.2923834262 \backslash \mathrm{C}, 1.2406205691,1.3$ $44706617,1.3495988576 \backslash \mathrm{C},-1.3849918628,-1.3549703812,1.2607650552 \backslash \mathrm{C},-1$. $2486671435,1.3514809192,-1.3527003294 \backslash \mathrm{C}, 1.3903965173,-1.357070771,-1.2$ $581412995 \backslash \mathrm{C}, 2.1649695594,-1.3749213931,0.1114603676 \backslash \mathrm{C}, 2.1658907461,1.3$ $766505349,0.0848509766 \backslash C,-2.1609954915,-1.367786766,-0.1079148549 \backslash C,-2$ $.164027956,1.3725787955,-0.0818587177 \backslash \mathrm{C},-0.1028738273,-2.269198102,1.5$ $213055656 \backslash \mathrm{C},-0.044033011,2.2695826873,1.5155398001 \backslash \mathrm{C}, 0.1042833464,-2.2$ $64806061,-1.5323911051 \backslash C, 0.0455833449,2.2696751096,-1.5262803229 \backslash C, 2.9$ $900320209,0.0009607478,0.142413109 \backslash \mathrm{C},-2.9879488882,0.0025778726,-0.138$ $9519437 \backslash \mathrm{H}, 1.8753844683,-1.6188627665,2.2721147926 \backslash \mathrm{H},-2.1050013953,1.69$ $5863565,2.0748683464 \backslash \mathrm{H},-1.8945207079,-1.6457875336,-2.2612494102 \backslash \mathrm{H}, 2.1$ $060609886,1.6869858569,-2.0864964446 \backslash \mathrm{H},-2.1285720353,-1.5736193349,2.0$ $43321798 \backslash \mathrm{H},-1.9108677721,1.5234647062,-2.2161319559 \backslash \mathrm{H}, 2.1302525047$, -1. $560721,-2.0510139118 \backslash \mathrm{H}, 1.8918111494,1.4935918535,2.2253713105 \backslash \mathrm{H}, 2.8917$ 147995,-2.1974813933,0.1381856964 \H, 2. $8879574759,2.2008240619,0.154322$ $9821 \backslash \mathrm{H},-2.8878299469,-2.1913355245,-0.1172623774 \backslash \mathrm{H},-2.8866694846,2.198$ $3894376,-0.1312094204 \backslash H,-0.1138102774,-3.1852443839,0.929069678 \backslash \mathrm{H},-0.1$ $550300677,-2.5937077607,2.5695255041 \backslash H,-0.0048275124,3.1836763205,0.92$ $18310855 \backslash \mathrm{H},-0.0672264279,2.5989628377,2.5624273862 \backslash \mathrm{H}, 0.1084156479,-3.1$ $927658721,-0.9571703018 \backslash \mathrm{H}, 0.157241342,-2.5732946766,-2.5855329491 \backslash \mathrm{H},-0$ $.0014721893,3.1991476456,-0.9554084291 \backslash \mathrm{H}, 0.0683172921,2.5756354357,-2$. $5803662441 \backslash \mathrm{H}, 3.6961612835,-0.0135436308,-0.6989666905 \backslash \mathrm{H}, 3.6003013308,0$ $.0163131017,1.0556775571 \backslash \mathrm{H},-3.695489213,-0.0116290096,0.7015941751 \backslash \mathrm{H},-$ 3.5978625687,0.0160777255,-1.0521868001 <br>Version=Sun-SVR4-Unix-G98RevA $.7 \backslash H F=-890.5394337 \backslash S 2=0 . \backslash S 2-1=0 . \backslash S 2 A=0 . \backslash R M S D=4.686 e-09 \backslash R M S F=4.530 e-03 \backslash$ Dipole $=-0.1413282,0.0637281,0.1892768 \backslash \mathrm{PG}=\mathrm{CO} \quad[\mathrm{X}(\mathrm{C} 23 \mathrm{H} 24)] \backslash \backslash @$

## $\mathbf{C}-\mathbf{C}=\mathbf{1 . 8 0 0} \AA$

$1 \backslash 1 \backslash G I N C-V P P 03 \backslash F O p t \backslash U B 3 L Y P \backslash 6-31 G(d) \backslash C 23 H 24 \backslash R A S M U S S E N \backslash 12-F e b-2000 \backslash 0 \backslash \backslash \# P$ UB3LYP/6-31G* 5D NAME=RASMUSSEN OPT= (READFC, MODREDUNDANT) GEOM= (CHECK , NODISTANCE, NOANGLE, NODIHEDRAL) GUESS=CHECK<br>dimethanospiro[2.2]octapl ane C1 5D Surface: 1.8 dist $\backslash \backslash 0,1 \backslash C, 0.0687126253,-0.0564494347,-0.07180$ $53784 \backslash C, 0.5821955344,-0.0532486126,1.3056216536 \backslash C,-0.8611440486,0.0566$ $783914,1.4652598231 \backslash C,-0.6282699084,-0.0546617626,-1.3439313827 \backslash C, 0.84$
$0612661,0.0553456159,-1.3330516306 \backslash C, 1.2061855713,-1.409756468,1.41827$ $0988 \backslash C,-1.3964452618,1.4302343471,1.2764877027 \backslash \mathrm{C},-1.2247294183,-1.4207$ $630459,-1.4154460286 \backslash C, 1.410901134,1.4334023636,-1.2849230713 \backslash C, 1.2141$ $429529,1.3408398474,1.3536905218 \backslash C,-1.4103699316,-1.3466694507,1.25557$ $68452 \backslash C,-1.2221843769,1.3478866704,-1.3656001273 \backslash C, 1.414221654,-1.3632$ $847156,-1.2404103023 \backslash C, 2.1598692048,-1.377499881,0.1489058178 \backslash C, 2.1640$ 5206, 1. $3755257084,0.1093554032 \backslash \mathrm{C},-2.1561098391,-1.3591457114,-0.134789$ $1533 \backslash \mathrm{C},-2.1571929393,1.374497108,-0.1116971496 \backslash \mathrm{C},-0.1331396844,-2.2644$ 19009, 1. 5291616428\C, -0.0640634243,2.2743146803, 1.5067993777\C, 0. 12736 $13634,-2.2680563126,-1.5322514392 \backslash \mathrm{C}, 0.0717731802,2.2680539437,-1.53172$ $07221 \backslash \mathrm{C}, 2.9849892105,-0.0015176755,0.18794596 \backslash \mathrm{C},-2.9816271898,0.009053$ $6071,-0.1831656647 \backslash \mathrm{H}, 1.8300066802,-1.6028316963,2.310995149 \backslash \mathrm{H},-2.14005$ $57894,1.7328685711,2.0357463328 \backslash \mathrm{H},-1.8664916959,-1.6555191351,-2.28586$ $28594 \backslash \mathrm{H}, 2.1446888919,1.7044441614,-2.0636786776 \backslash \mathrm{H},-2.172603486,-1.5844$ $020557,2.0130060815 \backslash \mathrm{H},-1.8741914556,1.5137898969,-2.2368048489 \backslash \mathrm{H}, 2.168$ $6811311,-1.5817205116,-2.0162800707 \backslash \mathrm{H}, 1.8500669237,1.4729894447,2.2420$ $00838 \backslash \mathrm{H}, 2.8866889449,-2.1993461266,0.192533575 \backslash \mathrm{H}, 2.8851502732,2.198859$ 5254, 0.1970659509\H, -2.8845827339,-2.1814702672,-0.1485646391 \H, -2. 876 $219676,2.2028004718,-0.1753356816 \backslash \mathrm{H},-0.1442476211,-3.1798894867,0.9360$ $975587 \backslash \mathrm{H},-0.1965727108,-2.5879759981,2.5771444774 \backslash \mathrm{H},-0.019716422,3.184$ $4026656,0.9077395254 \backslash \mathrm{H},-0.0935234153,2.6098071442,2.5509481637 \backslash \mathrm{H}, 0.125$ $2601145,-3.1952279218,-0.9555898257 \backslash \mathrm{H}, 0.1932232736,-2.5774090482,-2.58$ $46418143 \backslash \mathrm{H}, 0.0183592659,3.2012467483,-0.9675607638 \backslash \mathrm{H}, 0.1022812634,2.56$ $64607332,-2.5872443894 \backslash \mathrm{H}, 3.7068909834,-0.0209152395,-0.6399006528 \backslash \mathrm{H}, 3$. $5779576628,0.0183898883,1.1124748402 \backslash \mathrm{H},-3.7051797613,-0.0032750079,0.6$ $437543817 \backslash \mathrm{H},-3.5743174156,0.0217620231,-1.1077447647 \backslash \backslash$ Version=Fujitsu-VP-Unix-G98RevA. $7 \backslash \mathrm{HF}=-890.5322056 \backslash \mathrm{~S} 2=0 . \backslash \mathrm{S} 2-1=0 . \backslash \mathrm{S} 2 \mathrm{~A}=0 . \backslash \mathrm{RMSD}=7.563 \mathrm{e}-09 \backslash$ $\mathrm{RMSF}=4.341 \mathrm{e}-03 \backslash \mathrm{Dipole}=-0.179382,0.1174548,0.2109523 \backslash \mathrm{PG}=\mathrm{CO1} \quad[\mathrm{X}(\mathrm{C} 23 \mathrm{H} 24)]$ <br>@

## $\mathrm{C}-\mathrm{C}=1.850 \AA$

$1 \backslash 1 \backslash G I N C-F R 3 N 05 \backslash F O p t \backslash U B 3 L Y P \backslash 6-31 G(d) \backslash C 23 H 24 \backslash R A S M U S S E N \backslash 11-F e b-2000 \backslash 0 \backslash \backslash \#$ P UB3LYP/6-31G* 5D NAME=RASMUSSEN OPT= (NEWESTMFC, MODREDUNDANT) GEOM= (C HECK, NODISTANCE, NOANGLE, NODIHEDRAL) SCF=RESTART<br>dimethanospiro[2.2]oc taplane C1 5D Surface: 1.85 dist $\backslash 0,1 \backslash C, 0.0742929554,-0.0353761528,-0$. $0698847668 \backslash C, 0.5893229,-0.0434929285,1.2797495302 \backslash C,-0.8399009316,0.03$ $22924987,1.5370194751 \backslash C,-0.6511683559,-0.0387518858,-1.3157417819 \backslash C, 0$. $8266709254,0.0470716715,-1.3587942266 \backslash C, 1.2272841861,-1.3995122117,1.3$ $812620596 \backslash C,-1.379649662,1.4058375161,1.2969237479 \backslash C,-1.2478025575,-1$. $4074284016,-1.3922278517 \backslash \mathrm{C}, 1.3954241603,1.4306061133,-1.3039176679 \backslash \mathrm{C}, 1$ $.2289296038,1.3453256115,1.3363304264 \backslash \mathrm{C},-1.3874128421,-1.3592655951,1$. $2815092607 \backslash \mathrm{C},-1.2437652883,1.3582287467,-1.3486212064 \backslash \mathrm{C}, 1.3967459783$, -$1.3678816468,-1.2715083568 \backslash C, 2.1617743159,-1.3758848615,0.1067731449 \backslash C$ , 2. 1633805507,1.3798698296, 0.0797891846\C,-2.1513728262,-1.3604028609, $-0.1014026677 \backslash C,-2.1547550784,1.3690103372,-0.0802418658 \backslash C,-0.09946481$ $61,-2.2708757488,1.5206984709 \backslash C,-0.0555602102,2.2683716945,1.509876235$ $6 \backslash C, 0.0965529889,-2.2643325626,-1.5384043275 \backslash \mathrm{C}, 0.0551009909,2.27298551$ $74,-1.5304690619 \backslash \mathrm{C}, 2.9855358803,0.001981511,0.1387159981 \backslash \mathrm{C},-2.97950207$ $93,0.0048504361,-0.1384617822 \backslash \mathrm{H}, 1.8588641337,-1.5642105689,2.271113644$ $4 \backslash \mathrm{H},-2.1198258053,1.7186490085,2.0530772986 \backslash \mathrm{H},-1.8955493634,-1.6164111$ $328,-2.2619738183 \backslash H, 2.117436742,1.7020734782,-2.0919529137 \backslash \mathrm{H},-2.140606$ $1375,-1.632776977,2.034482764 \backslash \mathrm{H},-1.8982218257,1.5131960248,-2.21853065$
$81 \backslash \mathrm{H}, 2.1335267782,-1.5926148586,-2.0588086792 \backslash \mathrm{H}, 1.8698428457,1.4643527$ $278,2.2215231273 \backslash \mathrm{H}, 2.8883014812$, $-2.197976317,0.1440436012 \backslash \mathrm{H}, 2.88558963$ $58,2.2031448651,0.1574490296 \backslash \mathrm{H},-2.8775830165,-2.1847839732,-0.10918978$ $48 \backslash H,-2.8744027668,2.1980215624,-0.1214632364 \backslash H,-0.1104130966,-3.19066$ $40246,0.934403599 \backslash \mathrm{H},-0.137773113,-2.5856140324,2.5711578868 \backslash \mathrm{H},-0.03045$ $0673,3.1834242394,0.9173640806 \backslash \mathrm{H},-0.0703581836,2.5929240408,2.55668050$ $46 \backslash \mathrm{H}, 0.0974865456,-3.1968272607,-0.9714777918 \backslash \mathrm{H}, 0.1416550878,-2.559319$ $9506,-2.5945012247 \backslash \mathrm{H}, 0.0169799206,3.2060623316,-0.9657506445 \backslash \mathrm{H}, 0.07084$ $8882,2.5678928835,-2.5863608373 \backslash H, 3.6955181848,-0.011312155,-0.6998393$ $434 \backslash \mathrm{H}, 3.592105608,0.0156044179,1.0545666538 \backslash \mathrm{H},-3.6869497873,-0.0057654$ $287,0.7022327837 \backslash \mathrm{H},-3.5899868046,0.0135713349,-1.052077867 \backslash \backslash$ Version=IB M-RS6000-G98RevA. $7 \backslash \mathrm{HF}=-890.5309591 \backslash \mathrm{~S} 2=0.627281 \backslash \mathrm{~S} 2-1=0 . \backslash \mathrm{S} 2 \mathrm{~A}=0.022755 \backslash \mathrm{RM}$ $S D=1.787 e-09 \backslash \mathrm{RMSF}=2.703 \mathrm{e}-03 \backslash \mathrm{Dipole}=-0.0452999,0.059176,0.0106252 \backslash \mathrm{PG}=\mathrm{C} 0$ 1 [X(C23H24)] <br>@

## $\mathrm{C}-\mathrm{C}=1.875$ £

$1 \backslash 1 \backslash G I N C-V P P 12 \backslash F O p t \backslash U B 3 L Y P \backslash 6-31 G(d) \backslash C 23 H 24 \backslash R A S M U S S E N \backslash 14-F e b-2000 \backslash 0 \backslash \backslash \# P$ UB3LYP/6-31G* 5D NAME=RASMUSSEN OPT= (NEWESTMFC, MODREDUNDANT) GEOM= (CH ECK, NODISTANCE, NOANGLE, NODIHEDRAL) GUESS=CHECK<br>dimethanospiro[2.2]oct aplane C1 5D Surface: 1.875 dist $\backslash \backslash 0,1 \backslash C, 0.0732542722,-0.0105795509,-0$. $0652858101 \backslash C, 0.5933908181,-0.0243639287,1.2670402493 \backslash C,-0.8208641508,0$ $.0021451922,1.582737332 \backslash C,-0.667100245,-0.0050579527,-1.2988309773 \backslash C, 0$ $.8149832291,0.0238376592,-1.3743368719 \backslash C, 1.2372573479,-1.3896032721,1$. $3404531122 \backslash C,-1.3644931694,1.3799603526,1.31322221 \backslash \mathrm{C},-1.2643521788,-1$. $3798551976,-1.3737823344 \backslash C, 1.3865262574,1.4155686301,-1.3014124398 \backslash C, 1$ $.2422811256,1.3504427238,1.3405782184 \backslash \mathrm{C},-1.372199235,-1.3760425891,1.2$ $932285783 \backslash C,-1.2571295241,1.3831979716,-1.3426043783 \backslash C, 1.38137515,-1.3$ $822979297,-1.3053482694 \backslash C, 2.1594509042,-1.3812118902,0.0663358526 \backslash C, 2$. $1649407105,1.3749813076,0.072492039 \backslash C,-2.1515341012,-1.3571943517$, - 0.0 $813943873 \backslash C,-2.1476709254,1.3687246651,-0.0587879522 \backslash C,-0.0743865839$, $2.2797224374,1.5017952243 \backslash C,-0.0515079457,2.2603788644,1.5243112837 \backslash C$, $0.0629556305,-2.2582694638,-1.549850697 \backslash C, 0.0568786962,2.2796614638$, -1 $.5213608732 \backslash \mathrm{C}, 2.9852758497,-0.0048118812,0.1055409553 \backslash \mathrm{C},-2.9771988931$, $0.0077539968,-0.1084874322 \backslash H, 1.8756127121,-1.5311618582,2.226266144 \backslash H$, -2.1046563044,1.6877083058,2.0679292824 \H,-1.91689244, -1.5540368952,-2 $.2445177028 \backslash \mathrm{H}, 2.1045684072,1.6766832463,-2.0946813132 \backslash \mathrm{H},-2.1176724289$, $-1.6774753136,2.0433582219 \backslash H,-1.911018559,1.5494666474,-2.211578382 \backslash H$, $2.1033478732,-1.619371138,-2.1014419396 \backslash \mathrm{H}, 1.884514774,1.4634248623,2.2$ $257403728 \backslash \mathrm{H}, 2.8828091382,-2.2058643161,0.1059739511 \backslash \mathrm{H}, 2.8900653872,2.1$ $966598352,0.1368490296 \backslash \mathrm{H},-2.8762944836,-2.1826391432,-0.0943427246 \backslash \mathrm{H},-$ $2.8668261639,2.1989551099,-0.0732811609 \backslash \mathrm{H},-0.0797587811,-3.1977615894$, $0.9129122194 \backslash \mathrm{H},-0.0929136483,-2.5967769166,2.5508686752 \backslash \mathrm{H},-0.041463361$ $5,3.1832770781,0.9434658395 \backslash \mathrm{H},-0.0614316483,2.5690163821,2.5755390117 \backslash$ H, 0.0547215292,-3.1956592552, -0. $9918263372 \backslash \mathrm{H}, 0.0874738277,-2.541735272$ $9,-2.6085948842 \backslash \mathrm{H}, 0.0379492966,3.2105108987,-0.9527256394 \backslash \mathrm{H}, 0.07204326$ $04,2.575934072,-2.5764235282 \backslash \mathrm{H}, 3.6866183117,-0.0059572818,-0.740581091$ $4 \backslash \mathrm{H}, 3.6013583785,-0.0064063053,1.0152021177 \backslash \mathrm{H},-3.67243681,0.0005861027$ , 0.7422161798 \H,-3.6005165007,0.0167684525,-1.0138421335 \VVersion=Fuji tsu-VP-Unix-G98RevA. $7 \backslash \mathrm{HF}=-890.5329399 \backslash \mathrm{~S} 2=0.973354 \backslash \mathrm{~S} 2-1=0 . \backslash \mathrm{S} 2 \mathrm{~A}=0.085022$ $\backslash \mathrm{RMSD}=5.299 \mathrm{e}-09 \backslash \mathrm{RMSF}=7.414 \mathrm{e}-03 \backslash \mathrm{Dipole}=0.0482129,0.0172196,-0.1311011 \backslash \mathrm{P}$ $\mathrm{G}=\mathrm{C01}[\mathrm{X}(\mathrm{C} 23 \mathrm{H} 24)] \backslash \backslash @$

## $\mathrm{C}-\mathrm{C}=1.900$ Å

$1 \backslash 1 \backslash G I N C-P A L O \backslash F O p t \backslash U B 3 L Y P \backslash 6-31 G(d) \backslash C 23 H 24 \backslash R A S M U S S E N \backslash 11-F e b-2000 \backslash 0 \backslash \ \# P$ UB3LYP/6-31G* 5D NAME=RASMUSSEN OPT=MODREDUNDANT GEOM= (NODISTANCE,NOAN GLE,NODIHEDRAL) GUESS=CHECK <br>dimethanospiro[2.2]octaplane C1 5D Surfac e: 1.9 dist $\backslash \backslash 0,1 \backslash C, 0.0780045297,-0.0012351027,-0.0714742731 \backslash C, 0.573659$ $28,0.0000628708,1.2693446606 \backslash C,-0.839289971,0.0002778965,1.5924153758 \backslash$ $C,-0.6532842767,-0.000106978,-1.3079222022 \backslash C, 0.831291926,0.0001551336$, $-1.3693665451 \backslash C, 1.2234931022,-1.3683593202,1.351365376 \backslash C,-1.38190815,1$ . $3777402115,1.2925207047 \backslash C,-1.2462973301,-1.3818775169,-1.3715747263 \backslash C$ ,1.3985373171,1.3998731297,-1.2912105665\C,1.2233953576,1.3684189661,1 $.3508173027 \backslash C,-1.3818447596,-1.3773944035,1.2923455003 \backslash C,-1.2462096602$ ,1.381636966,-1.3709781546\C,1.3986466039,-1.3996926249,-1.2911782623\} C, 2.1603922397,-1.3779333555,0.0909270782\C,2.1602938967,1.3780279821, $0.0906718228 \backslash C,-2.1462302035,-1.3615284911,-0.0908032507 \backslash C,-2.14631076$ $68,1.3615228599,-0.0905189756 \backslash C,-0.0791161072,-2.2700515124,1.51292826$ $8 \backslash C,-0.0790656965,2.2703277627,1.5126908293 \backslash C, 0.0763444012,-2.26937391$ $2,-1.5360953692 \backslash C, 0.076167741,2.2693297446,-1.5358069675 \backslash C, 2.983074299$ $, 0.0000699416,0.135649813 \backslash C,-2.9738011005,-0.0000221901,-0.1385282802 \backslash$ H, 1. $8540133283,-1.4906886418,2.2444222514 \backslash \mathrm{H},-2.1335536013,1.6880097578$ , 2. $033274107 \backslash \mathrm{H},-1.8918114997,-1.5532475562,-2.2467735776 \backslash \mathrm{H}, 2.126775499$ ,1.6509436006,-2.0776537696\H,-2.1336218246,-1.6874507373,2.0330750885 \H,-1.8917524958,1.5527239451,-2.2461695239\H,2.1270514165,-1.65070373 83,-2.0775235219\H,1.8539158059,1.4905417499,2.2438652595\H, 2.88381857 93,-2.2012739503,0.1522646908\H,2.883630755,2.2014386368,0.1520893705\} H,-2.8676755891,-2.1897125834,-0.1112223521 \H, -2.8677541935, 2.18970736 $48,-0.1113078308 \backslash \mathrm{H},-0.0716860993,-3.1904959373,0.9280383522 \backslash \mathrm{H},-0.10201$ 9688,-2.5826664244,2.5629280746\H,-0.0716030602,3.1908542825,0.9279180 $391 \backslash \mathrm{H},-0.1016751533,2.582824684,2.5627271403 \backslash \mathrm{H}, 0.0573509816,-3.2033234$ 864,-0.972681146\H, 0.1064181405,-2.5592789388,-2.5927118121 \H, 0.057151 8882,3.2034018426,-0.9726000035\H, 0.1059433609,2.5589912658,-2.5924852 $549 \backslash \mathrm{H}, 3.693423842,-0.0000081521,-0.7029287511 \backslash \mathrm{H}, 3.5893338522,0.0002213$ $1,1.0518811391 \backslash \mathrm{H},-3.6778982107,-0.0001925593,0.7048273117 \backslash \mathrm{H},-3.5874320$ 663, 0.000175918,-1.05056823<br>Version=Sun-SVR4-Unix-G98RevA.7\HF=-890.5 $360422 \backslash S 2=1.01152 \backslash S 2-1=0 . \backslash S 2 A=0.092347 \backslash \mathrm{RMSD}=6.859 \mathrm{e}-09 \backslash \mathrm{RMSF}=7.725 \mathrm{e}-03 \backslash \mathrm{D}$ ipole=0.0585585,0.0010561,-0.1481145\PG=C01 [X(C23H24)]<br>@

## $\mathrm{C}-\mathrm{C}=2.000 \AA$

$1 \backslash 1 \backslash G I N C-F R 3 N 09 \backslash F O p t \backslash U B 3 L Y P \backslash 6-31 G(d) \backslash C 23 H 24 \backslash R A S M U S S E N \backslash 11-F e b-2000 \backslash 0 \backslash \backslash \#$ P UB3LYP/6-31G* 5D OPT=MODREDUNDANT NAME=RASMUSSEN GEOM=(CHECK,NODISTA NCE,NOANGLE,NODIHEDRAL) GUESS=CHECK <br>dimethanospiro[2.2]octaplane C1 5 D Surface: 2.0 dist $\backslash \backslash 0,1 \backslash C, 0.1012280837,-0.0001361862,-0.1105865616 \backslash C$, $0.5462538612,0.000036275,1.2517098655 \backslash C,-0.8524291258,0.0000303849,1.6$ $47405626 \backslash C,-0.6510302622,-0.0000477262,-1.3280814919 \backslash C, 0.8427475076,0$. $0000172221,-1.381816582 \backslash C, 1.2119721474,-1.3629366095,1.3449551665 \backslash C,-1$ $.3860164921,1.3776008878,1.3106207748 \backslash C,-1.2424432393,-1.3840481309,-1$ $.3695411906 \backslash C, 1.4063428462,1.4054395969,-1.3000193417 \backslash \mathrm{C}, 1.2118303467,1$ .3631459097,1.3448643588\C,-1.385906142,-1.3776714495,1.3107186476\C, -$1.2425889046,1.3838432409,-1.3695766855 \backslash C, 1.4064965995,-1.4053568176,-$ $1.2999954287 \backslash \mathrm{C}, 2.1570237671,-1.3775333174,0.0891494387 \backslash \mathrm{C}, 2.1568570875$, $1.3777666968,0.0891243864 \backslash C,-2.1378327216,-1.3559632383,-0.0817452506 \backslash$ C, $-2.1379482472,1.3557617648,-0.0818131306 \backslash C,-0.0830966122,-2.27046599$ $66,1.5161861855 \backslash C,-0.0832869892,2.2705621886,1.5159802744 \backslash C, 0.08060351$
$56,-2.2704223577,-1.53976776 \backslash C, 0.080465549,2.2703371095,-1.539924114 \backslash C$ , 2. $9796134871,0.0001678015,0.1373675419 \backslash \mathrm{C},-2.9664523573,-0.0001385147$, $-0.1352162053 \backslash \mathrm{H}, 1.8418337368,-1.4683732255,2.2403619019 \backslash \mathrm{H},-2.142342720$ $5,1.7057182085,2.0379469849 \backslash \mathrm{H},-1.8973774051,-1.5704504995,-2.234745564$ $2 \backslash H, 2.1361655971,1.6658909869,-2.0817789666 \backslash \mathrm{H},-2.1422244776,-1.7058136$ $034,2.0380317726 \backslash \mathrm{H},-1.8974970079,1.5701860525,-2.2348248488 \backslash \mathrm{H}, 2.136297$ 8451, - $1.6658375478,-2.081774114 \backslash H, 1.8416500411,1.468617449,2.240302317$ $5 \backslash \mathrm{H}, 2.8799640725,-2.2006356976,0.1596838436 \backslash \mathrm{H}, 2.8797277489,2.200947953$ $5,0.1595774231 \backslash \mathrm{H},-2.8584012303,-2.1851682029,-0.1019615764 \backslash \mathrm{H},-2.858574$ 8508, 2. 1849080469,-0.1020636588 \H, - 0.0833645361, -3.1866682848, 0.924480 $4259 \backslash \mathrm{H},-0.0950927075,-2.5910222381,2.5640761004 \backslash \mathrm{H},-0.0835647632,3.1866$ $459528,0.9241027003 \backslash \mathrm{H},-0.0953275135,2.5913440931,2.5638014131 \backslash \mathrm{H}, 0.0644$ $068034,-3.2049296589,-0.976841212 \backslash \mathrm{H}, 0.1053306576,-2.5595313709,-2.5968$ $750014 \backslash \mathrm{H}, 0.0640225835,3.2049858598,-0.977228068 \backslash \mathrm{H}, 0.1050994892,2.55922$ $30429,-2.5971032151 \backslash H, 3.6937659821,0.0001778729,-0.697889577 \backslash \mathrm{H}, 3.58120$ $46101,0.0002169436,1.0565572575 \backslash \mathrm{H},-3.6746824142,-0.0001682669,0.704586$ $0138 \backslash \mathrm{H},-3.5754417715,-0.0001962691,-1.0504134932 \backslash \backslash V e r s i o n=1 B M-R S 6000-G$ 98RevA. $7 \backslash \mathrm{HF}=-890.5469888 \backslash \mathrm{~S} 2=1.009312 \backslash \mathrm{~S} 2-1=0 . \backslash \mathrm{S} 2 \mathrm{~A}=0.074645 \backslash \mathrm{RMSD}=4.987 \mathrm{e}-$ $09 \backslash \mathrm{RMSF}=5.854 \mathrm{e}-03 \backslash \mathrm{Dipole}=0.0423858,0.0000994,-0.1339591 \backslash \mathrm{PG}=\mathrm{C01} \quad[\mathrm{X}(\mathrm{C} 23 \mathrm{H}$ 24)]<br>@

## $\mathbf{C}-\mathbf{C}=2.100 \AA$

$1 \backslash 1 \backslash$ MHPCC-FR31N05 \FOpt \UB3LYP\6-31G(d) \C23H24\RASMUSSEN $\backslash 10-$ Feb-2000 \0 <br>\#P UB3LYP/6-31G* 5D OPT= (NEWESTMFC, MODREDUNDANT) NAME=RASMUSSEN GEOM = (CHECK, NODISTANCE, NOANGLE, NODIHEDRAL) SCF=RESTART<br>dimethanospiro[2. 2 ]octaplane C1 5D Surface: 2.1 dist <br>0,1\C,-0.1146477989,0.1567477225,0 $.0000052134 \backslash \mathrm{C},-0.5776381285,-1.2073146581,0.0000014898 \backslash \mathrm{C}, 0.7863724181$, $-1.7401441775,0.0000034745 \backslash C, 0.7104218305,1.3195387656,-0.0000020255 \backslash C$ ,-0.7891398111, 1.4436879906, 0.0000009241 \C, -1.2619856852,-1.2802487166 , 1.357329092\C, 1.3268109508, -1.3966051802,-1.3788403825\C,1.3012564453 , 1.3071427458,1.386036417\C, -1.3510506674,1.3753258254,-1.4111566169\C , -1. $2619881371,-1.2802519709,-1.3573242541 \backslash \mathrm{C}, 1.3268160679,-1.396596393$ $3,1.3788429436 \backslash C, 1.3012507299,1.3071385917,-1.3860426845 \backslash C,-1.35104835$ $05,1.3753265951,1.4111591886 \backslash C,-2.1545953668,0.0148374832,1.3769021353$ $\backslash C,-2.1545926472,0.0148361402,-1.3769029555 \backslash C, 2.1298572438,-0.02930927$ $76,1.3500407181 \backslash C, 2.1298458605,-0.0293158031,-1.350052006 \backslash C, 0.01547760$ $69,-1.5238280123,2.2705606896 \backslash C, 0.0154701125,-1.5238531623,-2.27055381$ $35 \backslash C,-0.0121037685,1.5455183519,2.2716201345 \backslash C,-0.0121099519,1.5455284$ $974,-2.2716189779 \backslash C,-2.9787957662,0.0020340172,-0.0000013612 \backslash C, 2.96133$ $52541,-0.0093073451,-0.000009295 \backslash \mathrm{H},-1.9331704158,-2.1469093688,1.44637$ $33255 \backslash \mathrm{H}, 2.0529406565,-2.1446377884,-1.7263644205 \backslash \mathrm{H}, 2.0059585219,2.1287$ $821435,1.5890885946 \backslash \mathrm{H},-2.0458361527,2.1838041842,-1.6857188848 \backslash \mathrm{H}, 2.052$ $9416158,-2.1446312077,1.7263710794 \backslash \mathrm{H}, 2.005958385,2.1287727525,-1.58909$ $58929 \backslash \mathrm{H},-2.0458283908,2.1838085646,1.6857254563 \backslash \mathrm{H},-1.933180454,-2.1469$ $075117,-1.4463592429 \backslash \mathrm{H},-2.8797914867,-0.0301630014,2.19992152 \backslash \mathrm{H},-2.879$ $7865924,-0.0301644718,-2.1999241779 \backslash \mathrm{H}, 2.8494125489,-0.0418691873,2.180$ $3920994 \backslash \mathrm{H}, 2.8493940335,-0.0418777104,-2.1804094551 \backslash \mathrm{H}, 0.0526142441,-0.9$ $266028726,3.1825216079 \backslash \mathrm{H},-0.0344412051,-2.5682695658,2.5989191114 \backslash \mathrm{H}, 0$. $052605654,-0.9266544049,-3.1825325881 \backslash H,-0.0344525231,-2.5683040695,-2$ $.598881583 \backslash \mathrm{H},-0.0258071021,0.9816701726,3.2058169311 \backslash \mathrm{H}, 0.0192632097,2$. $6024035048,2.5613737667 \backslash \mathrm{H},-0.0258165425,0.9817025906,-3.2058297023 \backslash \mathrm{H}, 0$ $.0192577554,2.6024203946,-2.5613474532 \backslash \mathrm{H},-3.6564613021,0.8670638485,-0$
$.000002628 \backslash \mathrm{H},-3.6187667059,-0.8907646431,-0.0000014718 \backslash \mathrm{H}, 3.6338927262$, $-0.877889237,-0.000010117 \backslash \mathrm{H}, 3.6077888753,0.8798887063,-0.0000141629 \backslash \backslash \mathrm{~V}$ ersion=IBM-RS6000-G98RevA. $7 \backslash \mathrm{HF}=-890.5542349 \backslash \mathrm{~S} 2=1.008183 \backslash \mathrm{~S} 2-1=0 . \backslash \mathrm{S} 2 \mathrm{~A}=0$. $065606 \backslash \mathrm{RMSD}=5.698 \mathrm{e}-09 \backslash \mathrm{RMSF}=3.200 e-03 \backslash \mathrm{Dipole}=-0.0142432,0.1085466,-0.00$ $00059 \backslash \mathrm{PG}=\mathrm{C} 01$ [X(C23H24)]<br>@

## dissociated equilibrium

## $C_{s}$

$1 \backslash 1 \backslash G I N C-P A L O \backslash F O p t \backslash U B 3 L Y P \backslash 6-31 G(d) \backslash C 23 H 24 \backslash R A S M U S S E N \backslash 09-F e b-2000 \backslash 4 \backslash \backslash \# P$ UB3LYP/6-31G* 5D OPT=NEWESTMFC SCF= (NOVARACC) NAME=RASMUSSEN GEOM= (NOD ISTANCE, NOANGLE , NODIHEDRAL) GUESS=ALTER<br>dimethanospiro[2.2] octaplane C1 5D Surface: singlet diradical<br>0,1\C,-0.1338419083,0.2027242745,0.0 $000128961 \backslash C,-0.5491126804,-1.1885966783,0.000005505 \backslash C, 0.8025464866,-1$. $7976031819,0.0000124772 \backslash C, 0.7068719333,1.3476856642,0.0000016491 \backslash C,-0$. $804110107,1.4745842306,0.0000073102 \backslash C,-1.2483055398,-1.273724985,1.350$ $9496324 \backslash C, 1.3327315716,-1.4223924231,-1.3811028534 \backslash C, 1.2953440283,1.30$ $46236726,1.3881892216 \backslash \mathrm{C},-1.3597720744,1.3870918112,-1.4174287402 \backslash \mathrm{C},-1$. $2483017277,-1.2737480284,-1.3509373168 \backslash C, 1.332745853,-1.4223580358,1.3$ $811139795 \backslash C, 1.295332017,1.304640073,-1.3881900724 \backslash C,-1.3597774097,1.38$ $70671994,1.4174408603 \backslash C,-2.1498091727,0.0170515929,1.3758841749 \backslash C,-2.1$ $497722458,0.0170539513,-1.375917972 \backslash C, 2.1189926339,-0.0407190985,1.343$ $6871523 \backslash C, 2.1189494494,-0.0407289715,-1.3437297704 \backslash C, 0.0203155994,-1.5$ $311040161,2.2704963237 \backslash C, 0.0203040581,-1.5312555607,-2.270470362 \backslash C,-0$. $0175451349,1.549049293,2.2731074832 \backslash C,-0.0175487325,1.5491825626,-2.27$ $30848685 \backslash \mathrm{C},-2.9741848553,0.0002229311,-0.0000304629 \backslash \mathrm{C}, 2.9520367655,-0$. $0142881829,-0.0000368445 \backslash \mathrm{H},-1.9190345238,-2.1423792024,1.4226878646 \backslash \mathrm{H}$, $2.0641995177,-2.1539569414,-1.7503678428 \backslash \mathrm{H}, 2.0104784099,2.1128192909,1$ $.6101684649 \backslash H,-2.0579686272,2.1867512282,-1.709169439 \backslash \mathrm{H}, 2.0641913087$, $2.1539263762,1.7504162677 \backslash \mathrm{H}, 2.0104928219,2.1128211173,-1.6101356193 \backslash \mathrm{H}$, $-2.0579485904,2.1867354663,1.7092193134 \backslash \mathrm{H},-1.9190627781,-2.142381075$, $1.4226275511 \backslash \mathrm{H},-2.8745673113,-0.0373219158,2.1988395247 \backslash \mathrm{H},-2.874509510$ $2,-0.03731804,-2.1988914801 \backslash \mathrm{H}, 2.8369609528,-0.0506696864,2.1754630377 \backslash$ $\mathrm{H}, 2.8368942022,-0.0506833548,-2.1755257956 \backslash \mathrm{H}, 0.0675559572,-0.927451605$ , $3.1778859735 \backslash \mathrm{H},-0.0442346025,-2.5722381954,2.6069859672 \backslash \mathrm{H}, 0.067540752$ $5,-0.9277478247,-3.1779516777 \backslash \mathrm{H},-0.0442520213,-2.5724389477,-2.6068069$ $025 \backslash \mathrm{H},-0.0351400312,0.9827198454,3.2059452655 \backslash \mathrm{H}, 0.0208292063,2.6051834$ $382,2.565192927 \backslash \mathrm{H},-0.0351465155,0.9829973585,-3.2060061288 \backslash \mathrm{H}, 0.0208273$ $624,2.6053580582,-2.5650205006 \backslash \mathrm{H},-3.6563042517,0.8616768473,-0.0000400$ $894 \backslash \mathrm{H},-3.6089706341,-0.8961417949,-0.0000407528 \backslash \mathrm{H}, 3.6301737481,-0.8784$ $937331,-0.0000460086 \backslash \mathrm{H}, 3.5924623104,0.8793374777,-0.0000512321 \backslash \backslash 81,82 \backslash$ $\backslash \backslash V e r s i o n=S u n-S V R 4-U n i x-G 98 R e v A .7 \backslash H F=-890.5569735 \backslash S 2=1.007561 \backslash S 2-1=0 . \$ $S 2 A=0.060625 \backslash R M S D=6.896 e-09 \backslash R M S F=9.133 e-06 \backslash D i p o l e=0.0095939,0.0760739$, $-0.0000174 \backslash \mathrm{PG}=\mathrm{C} 01 \quad[\mathrm{X}(\mathrm{C} 23 \mathrm{H} 24)] \backslash \backslash @$


[^0]:    ${ }^{\dagger}$ Throughout the present work Roman numerals (e.g. II) are used to represent schematic structures while

[^1]:    ${ }^{\dagger}$ Van't Hoff's proposal was general but was born of the problem of uniting the structural theory and experimental evidence for the isomers (both structural and "physical") of the fatty acids.

[^2]:    ${ }^{\dagger}$ O. T. Benfey gives some details of this affair in his translation of van't Hoff's article. ${ }^{1}$

[^3]:    ${ }^{\dagger}$ However, as is explained later (see Section 1.4.2.2 on page 14), there is some ambiguity as to the nature of the planar-tetracoordinate carbon in these compounds, which might be better considered as a tricoordinate, planar, $\mathrm{sp}^{2}$-hybridized carbon (typical of olefins), with a fourth, partially-bonded, in-plane ligand, than as a planarized, tetracoordinate carbon.

[^4]:    ${ }^{\dagger}$ Bolton, Laidig, Schleyer and Schaefer ${ }^{32}$ have examined the $\mathrm{Li}_{2} \mathrm{C}_{2} \mathrm{H}_{2}$ potential energy surface in great detail at the CCSD/DZP(+ZPVE) level and find a number of local minima (at least three) that exhibit pla-nar-tetracoordinate carbon. The global minimum, which is considerably lower in energy (about 120 $\mathrm{kJ} \mathrm{mol}^{-1}$ ), was found to be a complex between LiH and HCCLi . Barriers to rearrangement of the species with a planar-tetracoordinate carbon to the global minimum are, in general, quite large ( $40-80 \mathrm{~kJ} \mathrm{~mol}^{-1}$ ).

[^5]:    ${ }^{\dagger}$ Cotton and Millar were, in fact, mostly interested in the triple-bond between the two vanadium atoms.

[^6]:    ${ }^{\dagger}$ Not all permutations of the given substituents have been synthesized. More detailed descriptions of the compounds that have been made can be found elsewhere. ${ }^{38}$
    ${ }^{\ddagger}$ The list of compounds of this type is over 50 and growing.

[^7]:    ${ }^{\dagger}$ Bowlane and a number of closely related molecules will be examined in detail in Chapter 3.

[^8]:    ${ }^{\dagger}$ Octaplane and many related molecules will be discussed in detail in Chapter 4.

[^9]:    ${ }^{\dagger}$ For an explanation of the nomenclature of all the alkaplane families, see Appendix A.

[^10]:    ${ }^{\dagger}$ [4.4.4.4]fenestrane has also been called windowpane.

[^11]:    ${ }^{\dagger}$ The system of nomenclature for expressing the various isomers of the fenestranes can also be given by specifying the orientation of the hydrogen at the bridgehead carbon $\mathrm{C}^{\alpha}$ as either $\alpha$ 'above' or $\beta$ 'below' the projection plane. Thus, trans,trans-[4.4.4]fenestrane (1-47) is $1 \beta, 3 \alpha-[4.4 .4]$ fenestrane. This nomenclature is less clear as to the degree of strain in the system and will not be used here. Some further discussion of fenestrane nomenclature is given in Appendix A.
    ${ }^{*}$ The all-trans isomer of $[4.4 .4 .4]$ fenestrane has also (somewhat confusingly) been called cis[4.4.4.4]fenestrane. The latter nomenclature ${ }^{64}$ refers to the fact that all hydrogens at $\mathrm{C}^{\alpha}$ are on the same side of the 'plane' of the molecule.

[^12]:    ${ }^{\dagger}$ Total energies are given in Table C-1 and optimized geometries are given in Table C-17 of Appendix C.

[^13]:    ${ }^{\dagger}$ Total energies are given in Table C-1 and optimized geometries are given in Table C-17 of Appendix C.

[^14]:    ${ }^{\dagger}$ For a detailed discussion of pyramidal-tetracoordinate bonding at carbon, see Chapter 3.

[^15]:    ${ }^{\dagger}$ Interestingly, Wiberg considered the possibility of a carbon atom approaching square-planar through structural imposition some years before Hoffmann's original paper ${ }^{4}$ on the electronic structure of squareplanar methane and design of planar-tetracoordinate carbon-containing systems.
    ${ }^{\ddagger}$ The name paddlane comes from the resemblance of the structures to the paddles of the paddle-steamers on the Mississippi River.

[^16]:    ${ }^{\dagger}$ A recent report of the synthesis and isolation of [1.1.1.1]paddlane from [1.1.1]propellane has appeared. ${ }^{73}$ The product they report (with two ${ }^{13} \mathrm{C}-\mathrm{NMR}$ signals with a $2: 1$ ratio and a single hydrogen environment) is not likely to be [1.1.1.1]paddlane; allene may be a possible product and is suggested from our calculations to be the preferred breakdown product of a short-lived [1.1.1.1]paddlane species.

[^17]:    ${ }^{\dagger}$ Further details of our own calculations are provided in Chapter 3.

[^18]:    ${ }^{\dagger}$ For example, Cotton's dimethoxyphenyldivanadium complex (1-25) was not recognized as containing a planar-tetracoordinate carbon until some time after the X-ray crystal structure was published.

[^19]:    ${ }^{\dagger}$ Keese has also expressed his preference for the structural approach to planar-tetracoordinate carbon. ${ }^{6 b}$

[^20]:    ${ }^{\dagger}$ This is obviously not the case in all situations. Solvation has the effect of blurring the boundary between a discrete molecule and its environment. However, rather than attempting to treat the entire system as one large quantum system, ways are being developed to treat the boundary and apply the effects of the environment as a continuum or other non-quantum system.

    * The term "ab initio" was first used in this context by Emeritus Professor David Craig of the Australian National University. ${ }^{6}$
    ${ }^{\S}$ Density functional methods (see Section 2.7 on page 71 ) are often considered a rather special category of $a b$ initio calculation because they either use some parameters which are not truly fundamental or the design of functionals is not truly rigorous because the 'true' form of the functional is not known with the result that terms included in the functional are often chosen for empirical reasons.

[^21]:    ${ }^{\dagger}$ Moore's Law is named after one of the founders of the computer-chip-making giant Intel and states that computer processing power will double every 6-12 months.

[^22]:    ${ }^{\dagger}$ Examination of the electronic structure of the experimentally unknown, structurally-imposed planartetracoordinate carbon indicates a pair of low-lying non-degenerate orbitals which suggests an open-shell (or diradical) configuration might be preferred in some cases.

[^23]:    ${ }^{\dagger}$ There has been much discussion as to the applicability of gaussian-type functions compared with Slatertype functions (which have the correct form for hydrogenic orbitals). Recent work suggests that gaussians (which allow for much simpler integral evaluation) may even be superior in molecular systems.
    ${ }^{\ddagger}$ Size consistency and extensivity require that relative errors increase more or less in proportion with the size of the system. This is particularly important when comparisons between systems of various sizes are required. Size consistency refers to the problem of differing results from calculations on a pair of noninteracting systems (at say $100 \AA$ separation) are treated individually and as a whole. Size extensivity implies that a method scales properly with the number of particles. ${ }^{1-4}$

[^24]:    ${ }^{\dagger}$ It is worth noting that the traditional definition of correlation energy defines the RHF solution as the reference and all techniques that lower the energy in some way as accounting for electron correlation to some degree.

[^25]:    ${ }^{\dagger}$ As an example, the $6-311+G(2 d, p)$ basis with spherical polarization functions gives for dimethanospiro[2.2]octaplane $\left(\mathrm{C}_{21} \mathrm{H}_{24}\right)(\mathbf{2 - 1})$ a basis set of 765 functions. However, the mixed basis set which we have termed $6-311+G(2 d, p)(r e d)$, in which $6-311+G(2 d, p)$ is used on the central atom and $6-311+G(d, p)$ is used on the four $\beta$-carbon atoms and $6-31 \mathrm{G}(\mathrm{d})$ is used elsewhere, affords a good approximation to the full $6-311+G(2 d, p)$ basis for the alkaplanes but includes 'only' 415 basis functions.

[^26]:    ${ }^{\dagger}$ Although there are a number of parameters in both the Becke three-parameter model and the LYP correlation functional which are fitted to experimental data, these methods are not usually referred to as semiempirical. For a discussion of the semi-empirical methods used in this work see Section 2.8 on page 74.

[^27]:    ${ }^{\dagger}$ Note that it is the product of basis functions and not the integral over these products that is set to zero. * A good overview of currently available semi-empirical methods along with some indication of their deficiencies is available elsewhere. ${ }^{1}$

[^28]:    ${ }^{\dagger}$ The calculation of the numerical force constants for dimethanospiro[2.2]binonaplane (2-3) (see Section 2.11 on page 80 ) provides one example of the savings possible from the use of symmetry. If the $D_{2 \mathrm{~h}}$ symmetry of the molecule had not been used to reduce the number of gradients needed to calculate the numerical second derivatives (by double-differencing), then 294 gradients would have been required (instead of only 59) and the time to complete the calculation would have been almost six times greater, or 18 months!

[^29]:    ${ }^{\dagger}$ This is quite variable and actually depends on the three-dimensional shape of a system. The initial set-up cost for such linear-scaling calculations is least for linear systems (like all- $E$-dodecahexaene), greater for planar systems (for example a graphite fragment) and greatest for globular systems (like the alkaplanes or proteins).

[^30]:    ${ }^{\dagger}$ For a description of the nomenclature of these molecules, see Appendix A.

[^31]:    ${ }^{\dagger}$ Pyykkö's calculations predict that the preferred isomer has a tetrahedral-type geometry ( $C_{3 \mathrm{v}}$ symmetry) but that this isomer also has a very large proton affinity $\left(1166 \mathrm{~kJ} \mathrm{~mol}^{-1}\right)$.

[^32]:    ${ }^{\dagger}$ Throughout this chapter, bond lengths are given in Ångstrom $(\AA)$ and bond angles are in degrees $\left({ }^{\circ}\right)$.

[^33]:    " The abbreviation "neo" indicates neopentane.

[^34]:    ${ }^{\text {a }}$ The only cyclobutane- and cyclopentane-capped structures that we could find which preserve the bonding integrity, correspond to high-order saddle points on their respective potential energy surfaces. ${ }^{\text {b }}$ The symmetry of the equilibrium structure. ${ }^{\text {c }}$ The carbon atoms with unfilled valences, which form $\mathrm{C}-\mathrm{C}$ bonds between the cap and the apical $\mathrm{C}_{5} \mathrm{H}_{8}$ subunit, are marked $\bullet$.

[^35]:    ${ }^{\text {a }}$ The symmetry of the equilibrium structure. ${ }^{\mathrm{b}}$ The carbon atoms with unfilled valences, which form $\mathrm{C}-\mathrm{C}$ bonds between the cap and the apical $\mathrm{C}_{5} \mathrm{H}_{4}$ subunit, are marked $\bullet$. The relative orientation of the cap and apical subunit is as shown. ${ }^{\mathrm{c}}$ The $C_{2 \mathrm{v}}$ structure of hemispirobinonaplane (parallel) (3-36) is a first-order saddle point. Optimization with reduced symmetry constraints leads to ring opening at the apex to give a cyclopentylidene-type structure (3-38) (see Section 3.3.3 on page 109).

[^36]:    ${ }^{\dagger}$ The structure of 3-30 has $C_{2}$ symmetry and as a result has two distinct $\mathrm{C}^{0}-\mathrm{C}^{\alpha}$ lengths ( $r_{0 \alpha}$ and $r_{0 \alpha}{ }^{\prime}$ ).

[^37]:    ${ }^{\text {a }}$ B3-LYP/6-31G(d) values are given in plain text. MP2/6-311+G(2d,p)//MP2/6-31G(d) and MP2/ $6-31 \mathrm{G}(\mathrm{d})$ values are given in bold type. ${ }^{\mathrm{b}}$ Bond lengths are given in $\AA$, bond angles in degrees, and energies in $\mathrm{kJ} \mathrm{mol}^{-1}$. ${ }^{\mathrm{c}}$ See structure 3-IX for a description of the geometrical parameters. ${ }^{\mathrm{d}} \mathrm{ApSE}$ is the apical strain energy, the negative of the enthalpy change at 298 K for Reaction 3-2 on page 98 , or in the case of $\mathbf{3 - 2 4}$, for Reaction $3-3$ on page 99 . ${ }^{\mathrm{e}}$ The lower symmetry ( $C_{2}$, see Table 3-3 on page 105) gives two unique bond lengths in the apical unit. ${ }^{\text {f }}$ See Ref. 32. ${ }^{\text {g }}$ The methyl $\mathrm{C}-\mathrm{C}$ bond length.

[^38]:    ${ }^{\dagger}$ Comparing the B3-LYP/6-31G(d) and MP2/6-311+G(2d,p)//MP2/6-31G(d) calculated values for the ApSEs of the hemialkaplanes (Table 3-2 on page 103) and the hemispiroalkaplanes (Table 3-4 on page 108) shows that the B3-LYP values are systematically too high by approximately $20 \mathrm{~kJ} \mathrm{~mol}^{-1}$ and too low by approximately $40 \mathrm{~kJ} \mathrm{~mol}^{-1}$, respectively. In the discussion of the $A p S E s$ of the hemispiroalkaplanes, the B3-LYP values have therefore been adjusted accordingly.

[^39]:    ${ }^{\dagger}$ It is worth noting that Brinker found this reaction could not be relied upon in general and he therefore developed a different procedure to synthesize the tricyclooctane analogue of 3-12, which might also be labelled [3.6.3]fenestrane (3-13). ${ }^{11 \mathrm{~g}, \mathrm{~h}}$
    ${ }^{*}$ Compounds 3-55 and 3-56 and other similar species are involved in the synthesis of pagodanes and isopagodanes. ${ }^{35}$

[^40]:    ${ }^{\dagger}$ It is expected that the exo-isomer would result initially from carbene attack on the polycyclic dienes 3-55 or 3-56. Obtaining endo-isomers may prove difficult and a 'cation route', in which a protonated hemispiroalkaplane is formed first via a carbocation rearrangement and then deprotonated with a very strong base, may be worth considering.

[^41]:    ${ }^{\dagger}$ For a detailed discussion of the electronic approach to forming planar-tetracoordinate carbon see Section 1.4 on page 9.
    A more complete discussion of the electronic structure of square-planar methane and its consequences is given in Section 1.3 on page 6.
    ${ }^{\text {§ }}$ They identified a number of other molecules that were also found to prefer a planar-tetracoordinate geometry but these molecules have been since found not to be minima on their respectively potential energy surfaces. For more information, see Section 1.4.1 on page 9 .

[^42]:    ${ }^{\dagger}$ Note that 4-4 and 4-5 also involve the planar-tetracoordinate carbon atom in a $\pi$-system.

[^43]:    ${ }^{\dagger}$ For an in depth discussion of this matter, see Section 1.4 on page 9 and Section 1.6 on page 38.

[^44]:    ${ }^{\dagger}$ Discussion of a number of compounds of this type and further details concerning the paddlanes are presented in Section 1.5.4 on page 31.

[^45]:    ${ }^{\dagger}$ For a discussion of our nomenclature for these molecules, see Appendix A.

[^46]:    ${ }^{\dagger}$ We refer to this basis set as $6-311+\mathrm{G}(2 \mathrm{~d}, \mathrm{p})(\mathrm{red})$. Approximate linear dependency problems led to difficulty calculating accurate gradients with both GaUSSIAN 94 and GAUSSIAN $98^{26}$ when using this 6$311+G(2 d, p)(r e d)$ basis for dimethanospirooctaplane (4-29). The approximate linear dependency problems were found to be resolved by removing the $s$-component of the diffuse functions at the $\mathrm{C}^{\alpha}$ atoms for this molecule.

[^47]:    ${ }^{\dagger}$ In fact, the best-fit plane is chosen as the plane that minimizes the sum of the squared distances $(d)$ from the plane. But the four distances from the plane are calculated from the unit vectors to the four atoms so the distances from the plane are equal to the sines of the angles to the plane $\left(\sin \alpha_{i}\right)$. Thus we actually minimize the squared sum of sines of the angles $\left(d^{2}=\Sigma \sin ^{2} \alpha_{i}\right.$ for all atoms $\mathrm{C}^{\alpha, i}$, where $\left.i=1,2,3,4\right)$. The deviation from planarity, $\alpha_{\text {plan }}$, is the average of the angles to this best-fit plane $\left(\alpha_{\text {plan }}=\left(\alpha_{1}+\alpha_{2}+\alpha_{3}+\alpha_{4}\right) /\right.$ 4). For more details see Appendix B.
    ${ }^{\ddagger}$ Note that this measure assigns some degree of flattening to spiropentane. Although the two threemembered rings are perpendicular, the best-fit plane will be at $45^{\circ}$ to each of these rings and the resulting value for $\alpha_{\text {plan }}$ is $21.4^{\circ}$ (for the MP2/6-31G(d) optimized geometry).

[^48]:    ${ }^{\dagger}$ The only significant difference between the two methods $(\operatorname{UCCSD}(\mathrm{T})$ and MRCI+Q) is found for the value for $\Delta \mathrm{E}_{\mathrm{PT}}$ of the open-shell singlet state. The $\operatorname{UCCSD}(\mathrm{T})$ result is found to lie between the ${ }^{1} \mathrm{~B}_{2 \mathrm{u}}$ and ${ }^{3} \mathrm{~B}_{2 \mathrm{u}} \mathrm{MRCI}+\mathrm{Q}$ values for $\Delta \mathrm{E}_{\mathrm{PT}}$, as might well have been expected in such a case where the single-reference wavefunction gives $\left\langle S^{2}\right\rangle=1.0$ (i.e. an equal mixture of the open-shell singlet and triplet wavefunctions).

[^49]:    ${ }^{\dagger}$ For more detail, see the discussion in Section 1.5.1 on page 23.

[^50]:    ${ }^{a} \mathrm{C}^{0}$ indicates the central carbon atom. $\mathrm{H}^{\mathrm{i}}$ indicates an in-plane hydrogen. $\mathrm{H}^{0}$ indicates an out-of-plane hydrogen. See Figure 4-4 on page 156 for a graphical representation of the structures.

[^51]:    ${ }^{\dagger}$ Note that, as with the hemispiroalkaplanes (see Section 3.3 .2 on page 104 ), structural isomers result from changing the orientation of the cap relative to the central moiety, where either the cap or the central moiety do not have four-fold symmetry. Where necessary we have chosen the isomer that gave the least strained structure.

[^52]:    ${ }^{\dagger}$ For a more complete descriptions of $\alpha_{\text {plan }}$ see Section 4.2 on page 145 and Appendix B.

[^53]:    ${ }^{\dagger}$ B3-LYP and MP2 optimized values for $\alpha_{\text {plan }}$ usually vary by a few tenths of a degree. For examples see Table 4-7 on page 163.
    ${ }^{\ddagger}$ This is purely a formal argument. As discussed later, instability may of course arise from other exit channels which lead to stable isomers/decomposition products of lower symmetry.

[^54]:    ${ }^{\dagger}$ For a discussion of these effects see Section 1.5.1 on page 23.

[^55]:    ${ }^{\dagger}$ Again we note that, as with the hemispiroalkaplanes (see Section 3.3.2 on page 104), spiroalkaplane structural isomers result from changing the orientation of the cap relative to the central moiety, where the cap does not have four-fold symmetry. Where appropriate we have chosen the isomer that gave the least strained structure, except for spiroheptaplane (4-41 and 4-42) for which we have examined both isomers.

[^56]:    ${ }^{\text {a }}$ The symmetry of the equilibrium structure. ${ }^{\mathrm{b}}$ In all cases the central $\mathrm{C}(\mathrm{C})_{4}$ subunit is a spiropentane subunit in the following orientation . The carbon atoms with an unfilled valence, which form $\mathrm{C}-\mathrm{C}$ bonds to the central $\mathrm{C}(\mathrm{C})_{4}$ subunit, are marked $\bullet .^{\mathrm{c}}$ The number of imaginary vibrational frequencies for the structure constrained to contain a planar tetracoordinate carbon atom calculated at the B3-LYP/6-31G(d) level. ${ }^{\text {d }}$ Calculated at MP2/6-311+G(2d,p)(red) (bold text) and B3-LYP/6-31G(d) (plain text) optimized geometries. ${ }^{\mathrm{e}}$ Calculated at the MP2/6-311+G(2d,p)//MP2/6-311+G(2d,p)(red) (bold text) and B3-LYP/ 6-311+G(2d,p)//B3-LYP/6-31G(d) levels (plain text).

[^57]:    ${ }^{\dagger}$ We note that our measure of planarity can be somewhat misleading in certain low symmetry molecules because it is an average of four angles. For example, the pyramidal tetracoordinate structure of 4-26, which has $C_{1}$ symmetry, results in a best-fit plane where three of the atoms coordinated to the apical carbon atom lie above the plane and one below the plane, with angles to this best-fit plane of $2.0^{\circ}, 14.5^{\circ}, 16.7^{\circ}$ and $19.7^{\circ}$ giving an average value of $13.2^{\circ}$.

[^58]:    ${ }^{\dagger}$ For a clearer indication of which angle is referred to here, see the fenestrane discussion in Section 4.1.
    ${ }^{\ddagger} \mathrm{C}-\mathrm{C}$ bonds as long as $1.60 \AA$ in strained saturated hydrocarbons have been observed. The most distorted fenestrane synthesized to date, the [4.4.4.5]fenestrane derivative 4-17, has internal bonds to the central carbon atom which are about $1.50 \AA$ while some peripheral bonds are as long as $1.60 \AA .{ }^{15}$ Bonds longer than this in hydrocarbon compounds have been observed but are rare and are usually found only in unsaturated systems. ${ }^{42}$

[^59]:    ${ }^{\dagger}$ Bonding constraints in the alkaplane families are determined primarily by the size of the major ring in the cyclic hydrocarbon cap. As a result, geometric features of spirohexaplane (4-39) and spirobiheptaplane (440), both of which have a six-membered primary ring, are similar. The term $n$-membered primary-ring cap refers to this situation.
    ${ }^{*}$ Throughout this discussion, we refer to bond lengths from MP2/6-311+G(2d,p)(red) ${ }^{38}$ optimized structures.
    ${ }^{8}$ The degree of distortion in the caps was not quantified in that discussion but we found it to be less than the degree of distortion at the central moiety.

[^60]:    ${ }^{\text {a }}$ The symmetry of the equilibrium structure. ${ }^{\text {b }}$ Calculated at MP2/6-311+G(2d,p)(red) (bold text) and B3-LYP/6-31G(d) (plain text) optimized geometries. ${ }^{\text {c }}$ Lower symmetry in these $C_{2}$ structure results in two long/short $\mathrm{C}^{\alpha}-\mathrm{C}^{\beta}$ bond pairs and two $\mathrm{C}^{\beta} \mathrm{C}^{\alpha} \mathrm{C}^{\beta}$ angles.

[^61]:    ${ }^{\dagger}$ With current computer technology, these calculations require about 30,000 node-hours on a CRAY-T3E or 3 months of CPU time on a Fujitsu VPP-300 (for more details see Section 2.11.3 on page 81).

[^62]:    ${ }^{\text {a }}$ The symmetry of the MP2 (bold type) and B3-LYP (plain text) equilibrium structures. ${ }^{\text {b }}$ In all cases the central $\mathrm{C}(\mathrm{C})_{4}$ unit is a spiropentane subunit in the following orientation . The carbon atoms with an empty valence, which form $\mathrm{C}-\mathrm{C}$ bonds to the central $\mathrm{C}(\mathrm{C})_{4}$ subunit, are marked $\bullet$. The position of methano bridges between the caps are marked by an open circle $(\mathrm{O})$ which represents a $\mathrm{CH}_{2}$ unit lying in the 'plane' of the central $\mathrm{C}_{5}$ subunit. ${ }^{\mathrm{c}}$ The number of imaginary vibrational frequencies for the structure constrained to contain a planar tetracoordinate carbon atom, MP2/6-311+G(2d,p)-(red) ${ }^{38}$ and B3-LYP/6-31G(d) levels, respectively. ${ }^{\text {d }}$ Calculated at MP2/6-311+G(2d,p)(red) (bold text) and B3-LYP/6-31G(d) (plain text) optimized geometries. ${ }^{e}$ Calculated from MP2/6-311+G(2d,p)//MP2/ $6-311+G(2 d, p)($ red $)$ (bold text) and B3-LYP/6-311+G(2d,p)//B3-LYP/6-31G(d) (plain text) energies. ${ }^{f}$ No distortion from planarity, no barrier to planarity.

[^63]:    ${ }^{\dagger}$ Further B3-LYP calculations using larger basis sets $(6-311+G(3 \mathrm{df}, 2 \mathrm{p})$, AVTZ and beyond) indicate that both $\alpha_{\text {plan }}$ and $\Delta \mathrm{E}_{\text {plan }}$ are reduced somewhat as the basis set is increased in size.

[^64]:    ${ }^{\dagger}$ MP2/6-311+G(2d,p)(red) optimized values are quoted in the text. For the corresponding B3-LYP/6$31 \mathrm{G}(\mathrm{d})$ optimized values see Figure 4-8 on page 180.
    ${ }^{\ddagger}$ MP2/6-311+G(2d,p)(red) optimized values are quoted in the text. For the corresponding B3-LYP/6$31 \mathrm{G}(\mathrm{d})$ optimized values see Figure 4-7 on page 175.

[^65]:    ${ }^{\dagger}$ MP2/6-31G(d) optimized structures for cis-bicyclo[3.3.0]octane (4-68), crown cyclooctane ( $\mathbf{C r}-\mathbf{4 - 5 3}$ ) and twistboat-twistboat bicyclo[3.3.1]nonane (TBTB-4-54) give $\mathrm{C}-\mathrm{C}$ bond lengths of $1.538,1.533$ and $1.567 \AA$ for 4-68, $1.533 \AA$ for Cr-4-53, and 1.534, 1.554, 1.543, 1.542 and $1.531 \AA$ for TBTB-4-54.

[^66]:    ${ }^{\text {a }}$ MP2/6-311+G(2d,p)//MP2/6-31G(d) values corrected to $298 \mathrm{~K}\left(\mathrm{~kJ} \mathrm{~mol}^{-1}\right)$. ${ }^{\mathrm{b}}$ The abbreviations "eth", "pro", "iso" and "neo" indicate ethane, propane, isobutane and neopentane, respectively. ${ }^{\text {c }}$ The strain energy ( $S E$ ) is determined as the negative of the enthalpy change for the given homodesmic reaction. ${ }^{\mathrm{d}}$ Taken from Ref. 33b unless otherwise noted. ${ }^{\mathrm{e}} \mathrm{G} 2$ calculated value from Ref. 33d. ${ }^{\mathrm{f}}$ From Ref. 33c. ${ }^{\mathrm{g}}$ From Ref. 33a. ${ }^{\text {h }}$ From Ref. 33e. ${ }^{\mathrm{i}}$ Calculated from an experimental determination of $\Delta H_{\mathrm{f}}$ for the diester, see Ref. 33g.

[^67]:    ${ }^{\dagger}$ Although tetra-tert-butyl tetrahedrane has been isolated, the parent tetrahedrane is not known experimentally and this comparison is with a G2 calculated $\Delta H_{\mathrm{f}}{ }^{33 \mathrm{~d}}$

[^68]:    ${ }^{\dagger}$ For details concerning the observation of tricyclo[2.1.0.0 $0^{1,3}$ ]pentane, see Chapter 1 and Section 4.1.
    ${ }^{\ddagger}$ We note, however, that the discussion of bond lengths in Section 4.3.4 indicated that there is some bond elongation in the alkaplane caps and that this, along with some angle strain in the caps, is likely to make a sizeable contribution to the total strain.

[^69]:    ${ }^{\text {a }}$ MP2/6-311+G(2d,p)//MP2/6-311+G(2d,p)(red) ${ }^{38}$ values corrected to $298 \mathrm{~K}\left(\mathrm{~kJ} \mathrm{~mol}^{-1}\right) .{ }^{\mathrm{b}}$ The abbreviations "eth", "pro", "iso" and "neo" indicate ethane, propane, isobutane and neopentane, respectively. ${ }^{c}$ The strain energy $(S E)$ is determined as the negative of the enthalpy change for the given homodesmic reaction. ${ }^{\mathrm{d}}$ For these molecules MP2/6-311+G(2d,p) energies were calculated at the HF/6-31G(d) optimized equilibrium geometry.

[^70]:    ${ }^{\dagger}$ For details, see Section 4.2 on page 145.

[^71]:    ${ }^{\dagger}$ It is worth noting that removing an electron from a spiro[2.2] carbon aids flattening in general. Spiropentane radical cation exhibits further flattening at the central carbon atom compared with the neutral spiropentane species (4-58). In the ion the two cyclopropane rings are twisted with an angle of about $60.0^{\circ}$ (compared with the exactly perpendicular, $90.0^{\circ}$ angle in the parent). This leads to a reduction of $\alpha_{\text {plan }}$ from $21.4^{\circ}$ in the parent $(\mathbf{4 - 5 8})$ to $13.7^{\circ}$ in spiropentane radical cation (for the UMP2/6-31G(d) optimized structure).

[^72]:    ${ }^{\text {a }}$ 'Planar' singlet energies are taken from Table 4-5 on page $158 .{ }^{\text {b }}$ Calculated at the UMP2(full)/631G(d) optimized geometries. ${ }^{\text {c }}$ Triplet energies were calculated with MoLPRO's URCCSD(T) method at the UMP2(full)/6-311+G(2d,p) optimized geometries.

[^73]:    ${ }^{\dagger}$ We note that the open-shell singlet and triplet are very close in energy, consequently, for the majority of this section, we will restrict our discussion of the open-shell configurations to the triplet because it is better described by the single determinant methods used primarily in this work.

[^74]:    ${ }^{\text {a }}$ Particular T-S differences are labelled as triplet symmetry - singlet symmetry. For example, $C_{\mathrm{s}}$ triplet $-S_{4}$, refers to the difference in energy between the $C_{\mathrm{s}}$ symmetry stationary point on the triplet surface and the $S_{4}$ symmetry stationary point on the singlet surface.

[^75]:    ${ }^{\dagger}$ For basis set considerations, see Section 4.2 on page 145.
    ${ }^{\ddagger}$ Not surprisingly, the geometry and energy of the biradical C-C dissociation product was found to be close to the corresponding triplet geometry and energy.
    ${ }^{\S}$ Preliminary calculations on spirooctaplane (4-28) indicate that the barrier height for $\mathrm{C}^{0}-\mathrm{C}^{\alpha}$ cleavage in this molecule is slightly larger than for 4-29.

[^76]:    ${ }^{\dagger}$ These are the original alkaplanes and the nomenclature of these molecules was devised by McGrath and Radom: McGrath, M. P.; Radom, L. "Alkaplanes: A class of neutral hydrocarbons containing a potentially planar tetracoordinate carbon," J. Am. Chem. Soc. 1993, 115, 3320-3321.

[^77]:    ${ }^{\dagger}$ Previously, this molecule was given the trivial name bowlane: Dodziuk, H. "Bowlane (tetracyclo[3.3.3.1 $\left.{ }^{3,10} \cdot 1^{7,10}\right]$ tridecane): a new hypothetical molecule possessing a pyramidal tetracoordinated carbon atom in the ground state," J. Mol. Struct., Theochem. 1990, 239, 167-172.

[^78]:    ${ }^{\dagger}$ Hemispiroalkaplanes based on cyclobutane or cyclooctane do not exhibit this form of structural isomerism.

[^79]:    ${ }^{\text {a }}$ Our $6-31 \mathrm{G}(\mathrm{d})$ basis uses a set of five spherical $d$-functions rather than the usual six Cartesian functions.
    ${ }^{\mathrm{b}}$ The thermochemical corrections are calculated from the B3-LYP/6-31G(d) frequencies and scaled by $0.9806(Z P V E)$ or $0.9989\left(H^{298}-H^{0}\right)$.

[^80]:    ${ }^{\text {a }}$ We have used a set of five spherical $d$-functions rather than the usual six Cartesian functions for the 6$31 \mathrm{G}(\mathrm{d})$ basis set. ${ }^{\mathrm{b}}$ Calculated at the MP2(full)/6-31G(d) optimized geometries. Here the usual set of six Cartesian $d$-functions were used. ${ }^{c}$ Our reduced $6-311+\mathrm{G}(2 \mathrm{~d}, \mathrm{p})($ red $)$ basis set is detailed in Section 4.2 on page 145. ${ }^{\text {d }}$ Calculated at MP2(full)/6-311+G(2d,p) optimized geometries.

