

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

by  
**Danne René Rasmussen, BSc (*Hons*) Syd.**

A thesis submitted for the degree of Doctor of Philosophy  
of The Australian National University



THE AUSTRALIAN  
NATIONAL UNIVERSITY

Research School of Chemistry

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## **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.

Danne René Rasmussen 27 April, 2000

## List of Publications

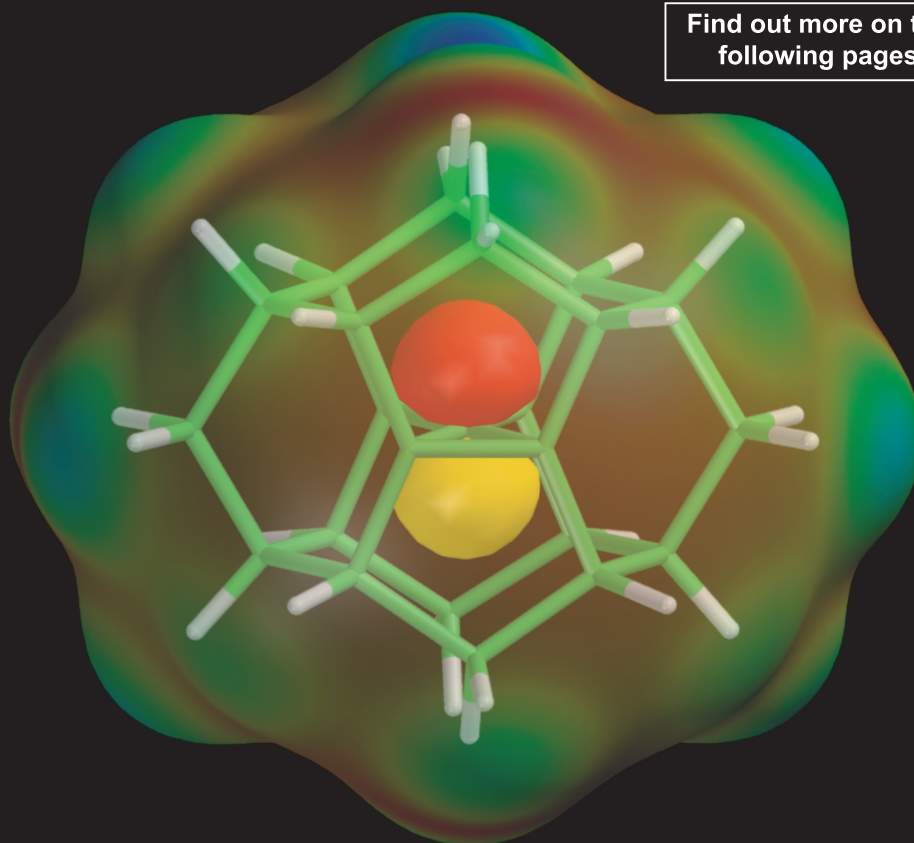
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- (2) Planar Carbon Story  
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- (3) Planar-tetracoordinate carbon in a neutral saturated hydrocarbon: Theoretical design and characterization  
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- (4) Hemispiroalkaplanes: Hydrocarbon cage systems with a pyramidal tetracoordinate carbon atom and remarkable basicity  
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- (5) The theoretical design of planar tetracoordinate carbon in neutral, saturated hydrocarbon systems  
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A neutral saturated hydrocarbon with  
a planar tetracoordinate carbon atom?

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following pages



A saturated hydrocarbon with an ionization  
energy comparable to that of alkali metals?

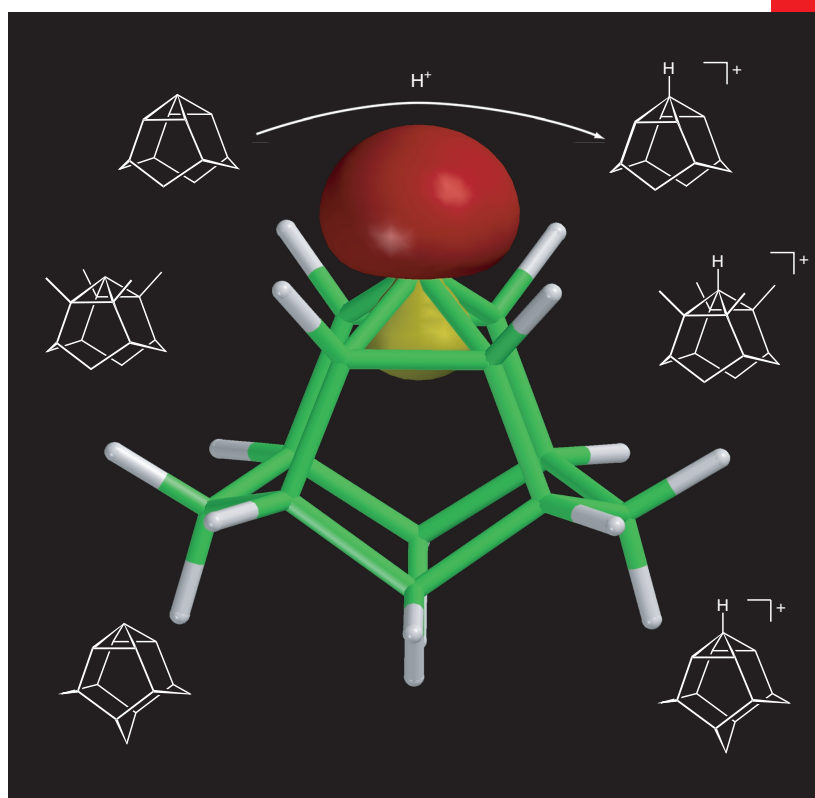
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# CHEMISTRY

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### Concept

Hemispiroalkaplanes: Hydrocarbon cage systems with a pyramidal-tetracoordinate carbon atom and remarkable basicity

D. R. Rasmussen and L. Radom

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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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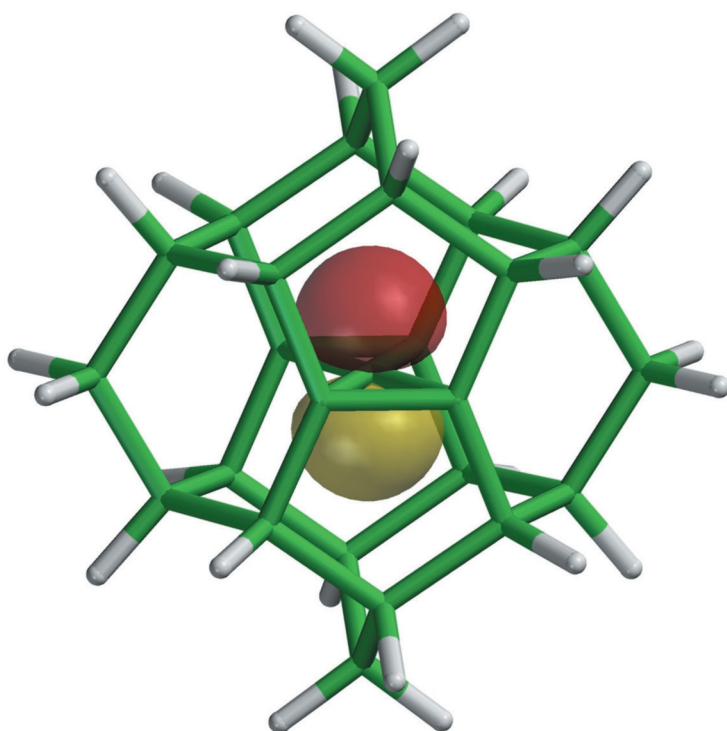
My colleagues at the Research School of Chemistry have been of great support over the years: amongst them are, Dr Tony Scott, the man with endless patience, Dr David Smith, who will always be remembered warmly and whose insight has been of assistance on many occasions, Chris Parkinson, whose cooking ability is only surpassed by his steadfast reliability, Dr James Gault and Dr Athanassios Nicolaides, members of the old guard, Dr Allan L. L. East, who was often frustrated, Dr Andrew Chalk, Dr Anna K. Croft, whose youthful looks and keen attitude will take her far, Dr Hans Heuts, our Dutch drinking partner, Justine and all the other Vacation Scholars, who made working over Christmas far more enjoyable than one would imagine, Dr Stefan Senger, Dr Michael (Micha) Hartmann, who will probably always try to help the down-trodden, however futile it may seem, Dr David Henry, who was certainly born in the wrong century, and is one of the last true gentleman, Dr Theis Sjølling, a kinsman of mine who seems to have boundless energy, Dr Stacey Wetmore, our newest and cheeriest face, who I am sure will publish prolifically, and Emil Mittag, although his time with us was only brief it was quite momentous — did anybody say Tequila?

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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 planar-tetracoordinate 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, hemialkapanes, hemispiroalkapanes, alkapanes, spiroalkapanes and dimethanospiroalkapanes, 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 hemialkapanes and hemispiroalkapanes are constructed from a spiropentane or neopentane subunit, respectively, which is capped by a cyclic hydrocarbon. The hemispiroalkapanes 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 hemispiroalkapanes are calculated to be more than 1170 kJ mol<sup>-1</sup>, even greater than those for the diamine “proton sponges”.

The alkapanes and the spiroalkapanes, 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 dimethanospiroalkapanes, 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 planar-tetracoordinate 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 planar-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 planar-tetracoordinate 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.

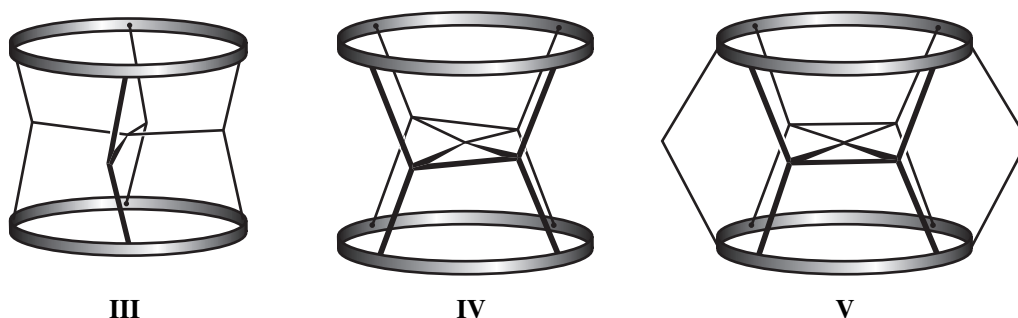
Chapter 2 gives a brief description of the theoretical methods used in the present work and some observations are made concerning the computational resources required.



In Chapter 3 we explore, using *ab initio* molecular orbital calculations at the MP2 and B3-LYP levels, the hemialkapanes (**I**)<sup>†</sup> and hemispiroalkapanes (**II**), which are constructed by capping a spiropentane or neopentane subunit, respectively, with a cyclic hydrocarbon. The hemialkapanes capped by a larger ring are predicted to exert considerable flattening

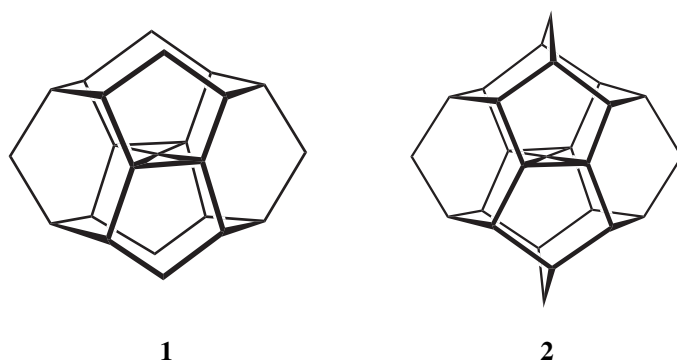
<sup>†</sup> Throughout the present work Roman numerals (e.g. **II**) are used to represent schematic structures while molecules are labelled with Arabic numerals (e.g. **2**).

at the apical carbon atom ( $\alpha_{\text{plan}} = 9.6\text{--}10.0^\circ$ ) but are not expected to be particularly stable due to the presence of overlong C–C bonds (with lengths of 1.7 Å 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 kJ mol<sup>−1</sup>, 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 spiro-pentanes.



Molecules which we have named alkaplanes (**III**), spiroalkaplanes (**IV**) and dimethano-spiroalkaplanes (**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 ( $\alpha_{\text{plan}} = 5\text{--}9^\circ$ , and  $\alpha_{\text{plan}} = 3\text{--}4^\circ$ , respectively). In addition, the spiroalkaplanes with an eight-membered primary-ring cap are calculated to have structures without any particularly long C–C bonds and to have a low barrier to inversion at the central carbon atom ( $\Delta E_{\text{plan}} = 4\text{--}13$  kJ mol<sup>−1</sup>). 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 dimethano-spiroalkaplanes. 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-tetra-coordinate 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.



Some consideration has been given to likely pathways for unimolecular decomposition. The probable existence of a low-lying triplet surface in the alkapanes suggests that these molecules will not be good synthetic targets. On the other hand, the spiroalkapanes and dimethanospiroalkapanes 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 C–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 dimethanospiroalkapanes 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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# List of Molecules

## Chapter 1

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- 1-III** Fenestranes (atom labels)
- 1-IV** Paddlanes
- 1-V** Alkaplanes
- 1-VI** Spiroalkaplanes
- 1-VII** Dimethanospiroalkaplanes

- 1-VIII** Fenestranes (general)
- 1-IX** Fenestranes (three fused rings)
- 1-X** Paddlanes (experimental)
- 1-XI** Hemialkaplanes
- 1-XII** Hemispiroalkaplanes
- 1-XIII** Bridged spiropentanes

### Molecules

- |             |   |             |   |
|-------------|---|-------------|---|
| <b>1-1</b>  | 2,3,4,5-tetraboraspiropentane   | <b>1-40</b> | ( <i>deloc</i> -4,5,6,7,8)-spiro[2.5]octa-1,5,7-trien-4-ylum      |
| <b>1-2</b>  | 1,1-dilithiocyclopropane  | <b>1-41</b> | ( <i>deloc</i> -6,7,8,9,10)-spiro[4.5]deca-1,3,7,9-tetraen-6-ylum |
| <b>1-3</b>  | 3,3-dilithio-1,2-diboracyclopropane   | <b>1-42</b> | spiro[2.5]octadienylum  |
| <b>1-4</b>  | bowlane   | <b>1-43</b> | dimethanospiro[2.2]binonaplane                                    |
| <b>1-5</b>  | octaplane   | <b>1-44</b> | [4.4.4.4]fenestrane   |
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| <b>1-8</b>  | 3,3-dilithiocyclopentene  | <b>1-47</b> | <i>trans,trans</i> -[4.4.4.4]fenestrane                           |
| <b>1-9</b>  | diboracyclopropane  | <b>1-48</b> | all- <i>trans</i> -[4.4.4.4]fenestrane                            |
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| <b>1-16</b> | 1,2-dilithioethene  | <b>1-55</b> | a <i>cis,trans,cis,cis</i> -[4.5.5.5]fenestrane derivative        |
| <b>1-17</b> | 2,3-diboraspiropentane  | <b>1-56</b> | a <i>cis,trans,cis,cis</i> -[4.5.5.5]fenestrane-like derivative   |
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| <b>1-24</b> | [8-(dimethylamino)-1-naphthyl]-lithium•Et <sub>2</sub> O <sub>2</sub>           | <b>1-63</b> | vesiprene   |
| <b>1-25</b> | Cotton's V <sub>2</sub> complex   | <b>1-64</b> | fenestrindan  |
| <b>1-26</b> | Buchwald's Zr <sub>2</sub> Complex  | <b>1-65</b> | [1.1.1.1]paddlane   |
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| <b>1-37</b> | unsaturated [5.6.5.6]fenestrane   |             |   |
| <b>1-38</b> | unsaturated [5.5.6.6]fenestrane   |             |   |
| <b>1-39</b> | porphyrin analogue  |             |   |

- 1-73** tricyclo[4.1.0.0<sup>1,3</sup>]heptane  
**1-74** benztotricyclo[4.1.0.0<sup>1,3</sup>]hept-4-ene  
**1-75** tricyclo[5.1.0.0<sup>1,3</sup>]octane  
**1-76** 7,7-dichloro-2,5,5,8,8-pentamethyl-  
tricyclo[5.1.0.0<sup>1,3</sup>]octane  
**1-77** tetracyclo[6.1.0.0<sup>1,3</sup>.0<sup>4,6</sup>]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-  
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**3-11** [3.3.3]fenestrane (tricyclo[2.1.0.0<sup>1,3</sup>]-  
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heptane)  
**3-13** [3.6.3]fenestrane (tricyclo[5.1.0.0<sup>1,3</sup>]-  
octane)  
**3-14** 4,5-benzototricyclo[4.1.0.0<sup>1,3</sup>]hept-4-ene  
**3-15** pyramidane  
**3-16** Dodziuk's hemidecaplane  
**3-17** Dodziuk's hemiundecaplane  
**3-18** Dodziuk's hemidodecaplane  
**3-19** Fe<sub>4</sub>C core compounds  
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**3-22** C bound to norbornadiene  
**3-23** C bound to bicyclo[2.2.2]octa-2,5-diene  
**3-24** tetramethylhemispirooctaplane  
**3-25** hemibiheptaplane  
**3-26** hemibioctaplane  
**3-27** hemibinonaplane  
**3-28** hemispirobutaplane

- 1-78** Baird's bridged spiropentane (tetracyclo-  
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**1-79** 3-vinyl-7,7-dibromobicyclo[4.1.0]heptane  
**1-80** tricyclo[3.1.0.0<sup>1,3</sup>]hexane-4-ketene  
**1-81** tricyclo[3.1.0.0<sup>1,3</sup>]hexane  
**1-82** tricyclo[2.1.0.0<sup>1,3</sup>]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** hemispirohhexaplane (perp)  
**3-32** hemispirohhexaplane (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<sup>2,5</sup>]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<sup>1,3</sup>]-  
hexane)  
**3-54** tetracyclo[3.3.1.0<sup>2,4</sup>.0<sup>2,8</sup>]nonane (Baird's  
hydrocarbon)  
**3-55** hydrocarbon parent of isodrin  
**3-56** tetrahydrotetraquinane 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** Hemialkapanes

- 4-V** Hemispiroalkapanes  
**4-VI** Alkapanes  
**4-VII** Spiroalkapanes  
**4-VIII** Dimethanospiroalkapanes

### Molecules

- 4-1** 2,3,4,5-tetraboraspiropentane  
**4-2** 1,1-dilithiocyclopropane  
**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** C<sub>3</sub>B<sub>2</sub>H<sub>4</sub> (*cis*-isomer)  
**4-10** C<sub>3</sub>B<sub>2</sub>H<sub>4</sub> (*trans*-isomer)  
**4-11** Chisholm's ditungsten adducts  
**4-12** Siebert's dicobalt complexes  
**4-13** Cotton's V<sub>2</sub> complex  
**4-14** Buchwald's Zr<sub>2</sub> 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  
**4-18** all-*trans*-[4.4.4.4]fenestrane  
**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  
**4-24** hemioctaplane (bowlane)  
**4-25** [3.4.3]fenestrane (tricyclo[3.1.0.0<sup>1,3</sup>]-hexane)  
**4-26** [3.3.3]fenestrane (tricyclo[2.1.0.0<sup>1,3</sup>]-pentane)  
**4-27** octaplane (S<sub>4</sub>)  
**4-28** spiro[2.2]octaplane  
**4-29** dimethanospiro[2.2]octaplane  
**4-30** bihexaplane  
**4-31** hexaplane  
**4-32** biheptaplane  
**4-33** heptaplane  
**4-34** bioctaplane  
**4-35** octaplane (D<sub>2</sub>)  
**4-36** binonaplane  
**4-37** hemibioctaplane  
**4-38** hemibinonaplane  
**4-39** spiro[2.2]hexaplane  
**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<sup>1,3</sup>]heptane  
**4-46** tetracyclo[3.3.1.0<sup>2,4</sup>.0<sup>2,8</sup>]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  
**4-55** tetrahedrane  
**4-56** pyramidane  
**4-57** [1.1.1]propellane  
**4-58** spiropentane  
**4-59** prismane  
**4-60** cubane  
**4-61** tetramethyltetrahedrane  
**4-62** tetra-*tert*-butyltetrahedrane  
**4-63** pagodane  
**4-64** dodecahedrane  
**4-65** bicyclo[2.2.0]hexane  
**4-66** cycloheptane  
**4-67** norbornane  
**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  
**4-71** [2.2.1.1]isopagodane  
**4-72** isodrin  
**4-73** a dibenzo derivative of the isodrin parent hydrocarbon  
**4-74** a *syn* dimeric benzene derivative of bird-cage hydrocarbon  
**4-75** a *syn* dimeric benzene derivative of hemispirobioctaplane

## Appendix A

### Schematics

- A-I** Fenestranes (three rings)

- A-II** Fenestranes (four rings)



## Molecules

<b>A-1</b>	a [4.4.4.5]fenestrane	<b>A-9</b>	biheptaplane
<b>A-2</b>	a [3.5.3.5]fenestrane	<b>A-10</b>	spirooctaplane
<b>A-3</b>	a [4.5.5.5]fenestrene	<b>A-11</b>	spiro[4.4]bihexaplane
<b>A-4</b>	a [5.5.5.5]fenestratetraene	<b>A-12</b>	dimethanospiro[2.2]bioctaplane
<b>A-5</b>	pyramidane	<b>A-13</b>	hemioctaplane
<b>A-6</b>	windowpane	<b>A-14</b>	hemispirobioctaplane (perpendicular)
<b>A-7</b>	staurane	<b>A-15</b>	hemispirobioctaplane (parallel)
<b>A-8</b>	octaplane		