A Theoretical Approach to Molecular Design: Planar-Tetracoordinate Carbon

by
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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

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
   Lyons, J. E.; Rasmussen, D. R.; McGrath, M. P.; Nobes, R. H.; Radom, L.

(2) Planar Carbon Story
   Radom, L.; Rasmussen, D. R.

(3) Planar-tetracoordinate carbon in a neutral saturated hydrocarbon: Theoretical design and characterization
   Rasmussen, D. R.; Radom, L.

(4) Hemispiroalkaplanes: Hydrocarbon cage systems with a pyramidal tetracoordinate carbon atom and remarkable basicity
   Rasmussen, D. R.; Radom, L.

(5) The theoretical design of planar tetracoordinate carbon in neutral, saturated hydrocarbon systems
   Rasmussen, D. R.; McGrath, M. P.; Radom, L.

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).
A neutral saturated hydrocarbon with a planar tetracoordinate carbon atom?

Find out more on the following pages

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

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Professor Mark Gordon ran the first of the large MP2 frequency calculations on the dimethanospiroalkaplanes which was the final proof that was needed to establish without doubt that the ‘planar’ structure for dimethanospirooctaplane is indeed an equilibrium structure on the MP2 potential energy surface. This calculation would have been difficult, if not impossible, using local resources alone. His assistance in making this calculation possible is much appreciated. I would like to thank Professor Denis Evans and Dr Ryan Bettens for their help in solving the least-squares problem that enabled me to define a simple, ubiquitous definition of planarity ($\alpha_{\text{plan}}$).

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The people who have been involved in proof-reading are my parents (especially my mother, who is almost unique in her ability to proof on screen), Dr Anthony Scott, Professor Denis Evans and my supervisor. I would especially like to thank Leo for his extensive proofing. Hopefully there are not too many misplaced hyphens.

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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, 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 kJ 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 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 $n = 3\text{–}4$) 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 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.

\(^\dagger\) 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\(^{-1}\), 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 ($\alpha_{\text{plan}} = 5\text{–}9^\circ$, 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\(^{-1}\)). 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 (I) 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.

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 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 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.

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Figure 4-4. The four possible orientations of the methyl groups in ‘planar’ neopentane (A, B, C and 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 (\(\sigma\)).

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 \(S_{4h}\) symmetry octaplane (4-27). All unique bond lengths and H–H close contacts (Å) are shown. The most highly distorted CCC angles and the distortion from planarity, \(\alpha_{\text{plan}}\) (°) 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 Å or degrees) for spirohexaplane (4-39), spiroheptaplane (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 \(C_0\), \(\alpha_{\text{plan}}\) are given. The angles and bond lengths around the central C(C\(_4\)) subunit for 4-42 are also shown.

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 Å or degrees) for spirobioxaplane (4-43), spirooctaplane (4-28) and spirobinonaplane (4-44). All unique bond lengths, any H–H close contacts, and the most distorted CCC angles are shown. The distortion from planarity at \(C_0\), \(\alpha_{\text{plan}}\) (°), 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 Å or
degrees) for dimethanospirobiotaplane (4-47), dimethanospirooctaplane (4-29), and dimethanospirobinonaplane (4-48). All unique bond lengths and some close-contact distances (Å) are shown. CCC angles significantly distorted from the tetrahedral ideal and the distortion from planar-tetracoordination at $C^0$, $\alpha_{\text{plan}}$ (°), are also given.

Figure 4-9. Calculated potential energy curves for inversion at $C^0$ determined at the MP2/6-311+G(2d,p)//MP2/6-311+G(2d,p)(red) level are given as relative energy, $E_{\text{rel}}$ (kJ mol$^{-1}$) against angle of distortion from planarity at $C^0$, $\alpha_{\text{plan}}$ (°), for the three species typifying the three alkaplane families: ● – octaplane (4-27), O – spiro[2.2]octaplane (4-28), and ■ – dimethanospiro[2.2]octaplane (4-29). In all cases, this inversion mode corresponds to the lowest-energy vibrational mode.

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 $e\text{-Å}^3$).

Figure 4-11. Structural parameters (MP2/6-31G(d) values in bold type, B3-LYP/6-31G(d) values in plain text, all values in Å or degrees) for octaplane radical cation (4-27$^+$), spirooctaplane radical cation (4-28$^+$), and dimethanospirooctaplane (4-29$^+$). All unique bond lengths and some close-contact distances (Å) are shown. Angles significantly distorted from the tetrahedral ideal are also given.

Figure 4-12. Structural parameters (MP2/6-31G(d) values in bold type, B3-LYP/6-31G(d) values in plain text, all values in Å 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 $C(C)$4 and $C(CH)$4 regions.

Figure 4-13. Calculated potential energy curves for homolytic $C^0$–$C^\alpha$ bond cleavage in dimethanospirooctaplane (4-29) determined at the O – UMP2(fc)/6-31G(d) and ■ – UB3-LYP/6-31G(d) levels are given as relative energy, $E_{\text{rel}}$ (kJ mol$^{-1}$) against $C^0$–$C^\alpha$ bond length, $r(C^0$–$C^\alpha$) (Å). Optimized geometries at fixed values of $r(C^0$–$C^\alpha$) were determined at the UB3-LYP/6-31G(d) level.
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1-10 difluorodilithiethane
1-11 dilithiethane
1-12 CB₂H₄ (preferred isomer)
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1-17 2,3-diborasiropentane
1-18 1,2-diborabicyclo[1.1.0]butane
1-19 1,2-diborasirop[2.2]pent-4-ene
1-20 C₂B₂H₄ (cis-isomer)
1-21 C₂B₂H₄ (trans-isomer)
1-22 phenyllithium dimer
1-23 [(2,6-dimethoxyphenyl)lithium]₂
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     lithium•Et₂O]₂
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1-33 [WRe₃(C₃Me₅)(O)(CO)₆(CPh)]
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1-36 unsaturated [3.5.5.5]fenestrane
1-37 unsaturated [5.6.5.6]fenestrane
1-38 unsaturated [5.6.6.6]fenestrane
1-39 porphyrin analogue

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1-XI Hemialkaplanes
1-XII Hemispiroalkaplanes
1-XIII Bridged spiropentanes

1-40 (deloc-4,5,6,7,8)-spiro[2.5]octa-1,5,7-
     trien-4-ylum
1-41 (deloc-6,7,8,9,10)-spiro[4.5]deca-1,3,7,9-
     tetraen-6-ylum
1-42 spiro[2.5]octadienylium
1-43 dimethanospiro[2.2]binonaplane
1-44 [4.4.4.4]fenestrane
1-45 cis-bicyclo[2.2.0]hexane
1-46 trans-bicyclo[2.2.0]hexane
1-47 trans,trans-[4.4.4]fenestrane
1-48 all-trans-[4.4.4]fenestrane
1-49 all-cis-[4.4.4]fenestrane
1-50 trans,trans,cis-[4.4.4]fenestrane
1-51 trans,cis,cis-[4.4.4]fenestrane
1-52 all-cis-[5.5.5.5]fenestrane
1-53 all-trans-[5.5.5.5]fenestrane
1-54 a cis,trans,cis-[4.5.5.5]fenestrane
     derivative
1-55 a cis,trans,cis-[4.5.5.5]fenestrane
     derivative
1-56 a cis,trans,cis-[4.5.5.5]fenestrane-like
     derivative
1-57 Wender’s trans,cis,cis-[5.5.5.5]-
     fenestrane
1-58 unsaturated bridgehead [4.5.5.5]fenestrane
1-59 unsaturated bridgehead [5.5.5.5]fenestrane
1-60 all-cis-[5.5.5.5]fenestratetraene
1-61 a [4.4.4.5]fenestrane derivative
1-62 pyramide
1-63 vespiprene
1-64 fenestrinand
1-65 [1.1.1.1]paddlane
1-66 [2.2.2.2]paddlane
1-67 hexa-3-ene-1,5-diynye
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
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none
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2-1 dimethanospiro[2.2]octaplane
2-2 spiro[2.2]octaplane

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3-III Hemiakaplanes
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3-V Hemispiroakaplanes

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3-2 hemihexaplane
3-3 hemibiheptaplane
3-4 hemispirooctaplane (perp)
3-5 hemispiroctaplane (perp)
3-6 hemispirobinonaplane (perp)
3-7 all-trans-[4.4.4.4]fenestranne
3-8 all-cis-[5.5.5.5]fenestranne
3-9 all-cis-[4.4.4.5]fenestranne derivative
3-10 [3.4.3]fenestranne-ketene (tricyclo[3.1.0.01,3]hexane-ketene)
3-11 [3.3.3]fenestranne (tricyclo[2.1.0.01,3]pentane)
3-12 [3.5.3]fenestranne (tricyclo[4.1.0.01,3]heptane)
3-13 [3.6.3]fenestranne (tricyclo[5.1.0.01,3]octane)
3-14 4,5-benzotricyclo[4.1.0.13]hept-4-ene
3-15 pyramidane
3-16 Dodziuk’s hemidecaplane
3-17 Dodziuk’s hemundecaplane
3-18 Dodziuk’s hemidodecaplane
3-19 Fe₄C core compounds
3-20 [(Ph₃PAu)₅C]+
3-21 C bound to cyclohexa-1,4-diene
3-22 C bound to norbornadiene
3-23 C bound to bicyclo[2.2.2]octa-2,5-diene
3-24 tetramethyl/hemispirooctaplane
3-25 hemihexaplane
3-26 hemibiheptaplane
3-27 hemibinonaplane
3-28 hemispirobutaplane
3-29 hemispirohexaplane (perp)
3-30 hemispirohexaplane (par)
3-31 hemispirohexaplane (perp)
3-32 hemispirohexaplane (par)
3-33 hemispirohexaplane (perp)
3-34 hemispirohexaplane (par)
3-35 hemispirohexaplane (par)
3-36 hemispirohexaplane (par)
3-37 syn-tricyclo[4.2.0.02,5]octa-3,7-diene
3-38 ring opened hemispirobinonaplane
3-39 cyclopropane
3-40 tetrahedrane
3-41 spirotetrahedrane
3-42 [1.1.1]propellane
3-43 prismane
3-44 cubane
3-45 tetakis(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]fenestranne (tricyclo[3.1.0.01,3]hexane)
3-54 tetracyclo[3.3.1.02,4.02,8]nonane (Baird’s hydrocarbon)
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3-56 tetradehydrotetraquinane isomer of the hydrocarbon parent of isodrin
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Schematics

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4-IV Hemialkaplanes
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4-VI Alkaplanes
4-VII Spiroalkaplanes
4-VIII Dimethanospiroalkaplanes

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 \(\text{C}_3\text{B}_2\text{H}_4\) \((\text{cis}-\text{isomer})\)
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4-18 all-\(\text{trans}\)-[4.4.4.4]fenestrane
4-19 \([5.5.5.5]\) fenestrane
4-20 an unsaturated fenestrane \(([5.6.5.6]-\text{fenestraoctaene})\)
4-21 another unsaturated fenestrane \(([5.5.5.5]\text{fenestrahexaene})\)
4-22 \([2.2.2.2]\) paddlane
4-23 an unsaturated paddlane
4-24 hemioctaplane (bowlane)
4-25 \([3.4.3]\) fenestrane \((\text{tricyclo}[3.1.0.0^{2,4}]\text{-hexane})\)
4-26 \([3.3.3]\) fenestrane \((\text{tricyclo}[2.1.0.0^{2,5}]\text{-pentane})\)
4-27 octaplane \((S_5)\)
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 biocylaplane
4-35 octaplane \((D_2)\)
4-36 binonaplane
4-37 hemibiotaplane
4-38 hemibionaplane

Appendix A

Schematics

A-I Fenestranes (three rings)
A-II Fenestranes (four rings)
<table>
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<th>Formula</th>
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<tbody>
<tr>
<td>A-1</td>
<td>a [4.4.4.5]fenestrane</td>
</tr>
<tr>
<td>A-2</td>
<td>a [3.5.3.5]fenestrane</td>
</tr>
<tr>
<td>A-3</td>
<td>a [4.5.5.5]fenestrane</td>
</tr>
<tr>
<td>A-4</td>
<td>a [5.5.5.5]fenestratetraene</td>
</tr>
<tr>
<td>A-5</td>
<td>pyramidane</td>
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<td>windowpane</td>
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<td>A-10</td>
<td>spirooctaplane</td>
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<td>spiro[4.4]bihexaplane</td>
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<td>A-12</td>
<td>dimethanospiro[2.2]biocaplane</td>
</tr>
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<td>A-13</td>
<td>hemioctaplane</td>
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<tr>
<td>A-14</td>
<td>hemispirobioctaplane (perpendicular)</td>
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<tr>
<td>A-15</td>
<td>hemispirobioctaplane (parallel)</td>
</tr>
</tbody>
</table>