Chapter 3
Hemialkaplanes – Pyramidal Carbon

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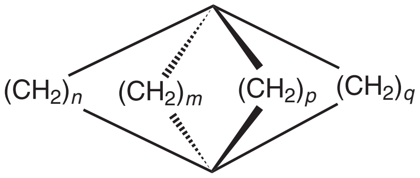
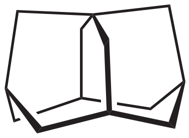
3.1 Introduction

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 (**3-1**) was found by McGrath, Radom and Schaefer[1] to be a local minimum on the



3-I

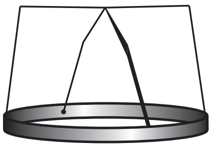


3-1

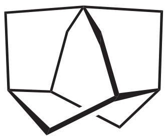
$C_{13}H_{20}$ potential energy surface and to contain a highly-flattened tetracoordinate carbon atom.

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 spiropentane-type) 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 hemi*spiro*-alkaplanes (see **3-V** and **3-4** – **3-6**), members of a new class of saturated hydrocarbons.[†] All the hemispiroalkaplanes are predicted to have an apical, pyramidal-tetracoordinate carbon atom.

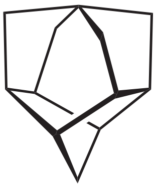
3-II



3-III

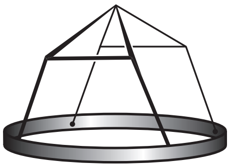


3-2 (C_2)



3-3 (C_2)

3-IV



3-V

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

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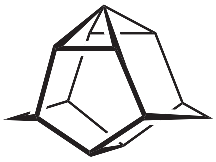
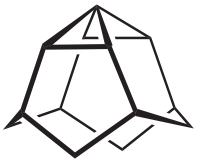
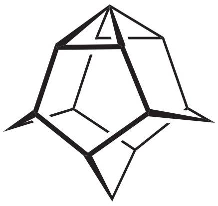
[†] For a description of the nomenclature of these molecules, see Appendix A.



3-4 (C_{2v})

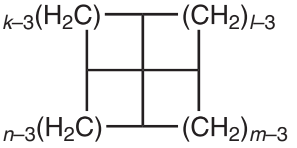


3-5 (C_{2v})

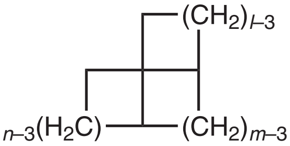


3-6 (C_{2v})

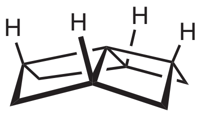
posal by Liebman and Greenberg[6] that the tetracoordinate, central carbon of all-*trans*-[4.4.4.4]fenestrane (**3-7**) should prefer a pyramidal over a planar arrangement, a contention supported by model calculations on methane (see Section 1.2 on page 4 and Section 1.3 on page 6).[7] Keese, Agosta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



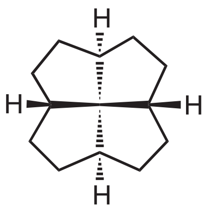
3-VI ($k,l,m,n \geq 4$)



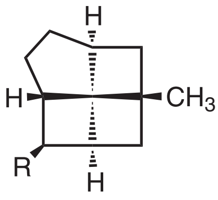
3-VII ($l,m,n \geq 3$)



3-7 (C_{2v})

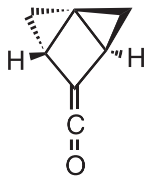


3-8 (D_{2d})

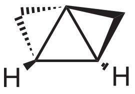


3-9 (R = $COOCH_3$

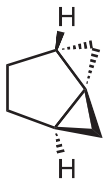
[3.4.3]fenestrane derivative (**3-10**),[9a,d] which is expected to have a butterfly or half-planar geometry,[10] and [3.3.3]fenestrane (**3-11**),[9e] which is expected to have a pyramidal-tetracoordinate carbon atom.[9h] Prior to Wiberg's work, considerable success had also been achieved by Brinker, 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 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).



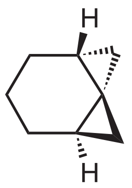
3-10 (C_2)



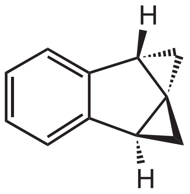
3-11 (C_1)



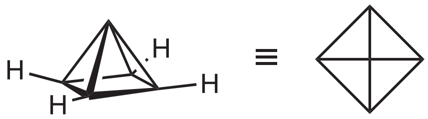
3-12 (C_2)



3-13 (C_2)



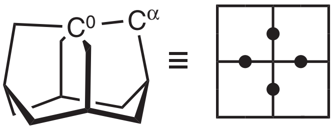
3-14 (C_2)



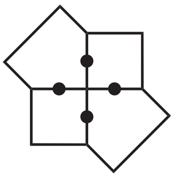
3-15 (C_{4v})

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 C_5H_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.[1b,c] However, *ab initio* calculations indicate that the apical carbon atom (C^0) in **3-1** is not pyramidal[1a] 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.

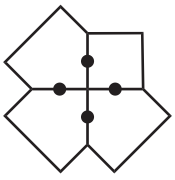
Particularly striking have been recent discoveries in both iron-cluster and gold chemistry. Compounds with an Fe_4C core[10,15] are found to have a butterfly geometry (**3-**



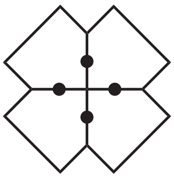
3-1 (C_{2v})



3-16

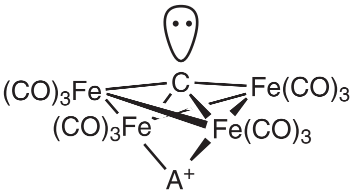


3-17

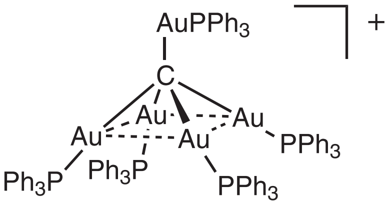


3-18

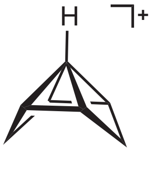
19) in which the tetracoordinate carbon atom is bound to four Fe atoms in the one hemisphere. A number of unusual ruthenium cluster compounds have also been observed, in which carbon is bound on the face of the ruthenium core and is therefore ‘exposed’ or almost planar-tetracoordinate.[15c,d] Schmidbaur has found that the as-yet-unisolated compound $[(Ph_3PAu)_4C]$ prefers to bind a fifth ligand and form $[(Ph_3PAu)_5C]^+$,[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 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.



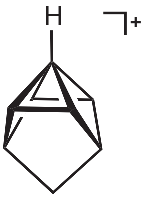
3-19 (A = H or CO)



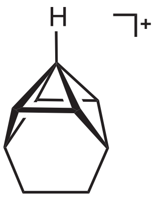
3-20 (C_{4v})



3-21-H$^+$



3-22-H$^+$



3-23-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 C–C σ-bonds (six bonding electrons spread over four bonds). As

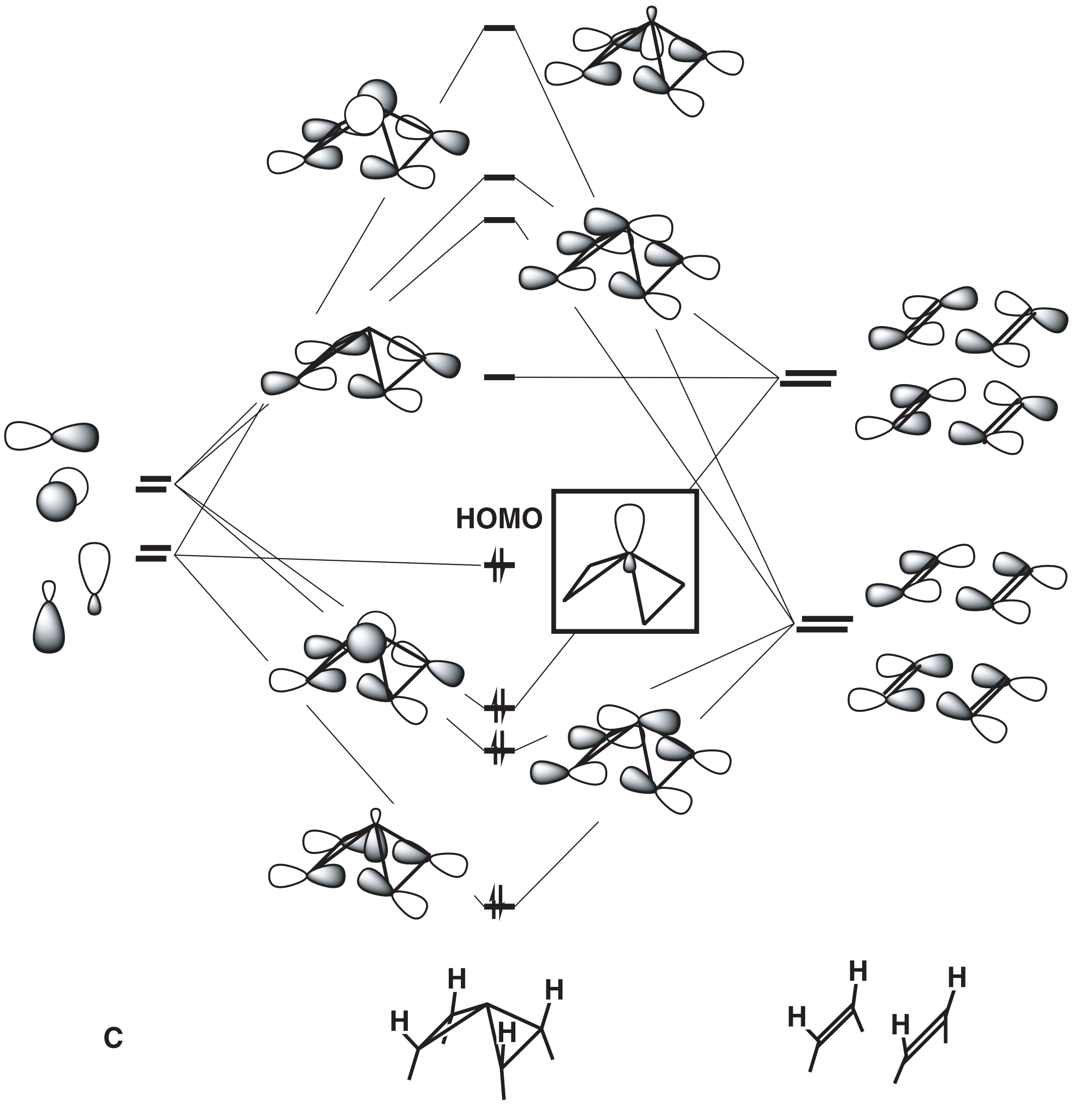


Figure 3-1. Orbital interaction diagram showing the molecular orbitals in pyramidal-tetracoordinate carbon formed from the interaction of a carbon atom with a pair of C=C double bonds.

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 kJ mol^{-1} for the proton affinity[18c] of the pyramidal isomer of [$(H_3PAu)_4C$].[†] Both Jemmis and Schleyer[19] and Minkin, Minyaev and coworkers[14a] 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

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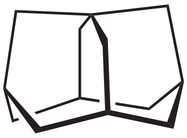
[†] Pyykkö's calculations predict that the preferred isomer has a tetrahedral-type geometry (C_{3v} symmetry) but that this isomer also has a very large proton affinity (1166 kJ mol^{-1}).

calculated the proton affinity of **3-15** to be 1060 kJ mol^{-1} at the HF/3-21G level. The resulting $C_5H_5^+$ 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 **3-21-H$^+$**, **3-22-H$^+$** and **3-23-H$^+$**, have been observed in superacid media.[20,21d,h,j]

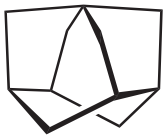
Given the wealth of experimental support both for distorted spiropentanes and for pyramidal carbocations, we have embarked on an examination of the hemialkaplanes and hemispiroalkaplanes as attractive, prototypical hydrocarbon examples of such species, and as possible synthetic targets.

3.2 Methods

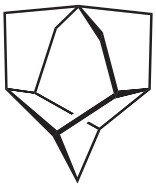
Standard *ab initio* molecular orbital calculations[23] were carried out using the Gaussian 98 system of programs.[24] All structures[†] were optimized initially without symmetry constraints at the B3-LYP/6-31G(d) level. Structures of interest were then re-optimized with the preferred symmetry, and either 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 **3-5**, and the protonated species **3-1-H$^+$**, **3-4-H$^+$**, **3-5-H$^+$**, **3-6-H$^+$** and **3-24-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 initially 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



3-1 (C_{2v})



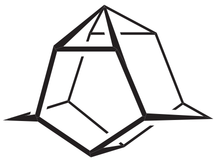
3-2 (C_2)



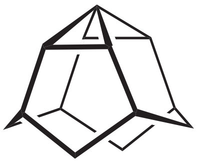
3-3 (C_2)

[†] Throughout this chapter, bond lengths are given in Ångstrom (Å) and bond angles are in degrees (°).

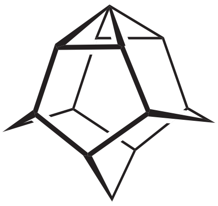
standard statistical thermodynamics and the same frequencies scaled by 0.9989.[25] For a



3-4 (C_{2v})



3-5 (C_{2v})



3-6 (C_{2v})

selection of molecules, reaction enthalpies were also computed at the MP2/6-311+G(2d,p)//MP2/6-31G(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 6-31G(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:

3-III + 8 ethane → cap + neopentane + 4 isobutane (3-1)

We have defined the apical strain energy (*ApSE*) for a hemialkaplane as $-\Delta H$ for Reaction 3-1. This strain energy includes contributions from the strain in the highly distorted apical C_5H_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:

3-V + 4 propane + 10 ethane → cap + neopentane + 8 isobutane (3-2)

Values of the *ApSE* = $-\Delta H$(Reaction 3-2) are given in Table 3-4 on page 108. As a special 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:

$$\textbf{3-24} + 4\ \text{propane} + 10\ \text{ethane} \rightarrow \text{cyclooctane} + 5\ \text{neo}^{\dagger} + 4\ \text{isobutane} \qquad (3\text{-}3)$$

The calculated *ApSE* for **3-24**, –Δ*H*(Reaction 3-3), is also included in Table 3-4.

Conventional total strain energies (*SE*) 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:

$$\textbf{3-5} + 16\ \text{ethane} \rightarrow \text{neopentane} + 4\ \text{isobutane} + 8\ \text{propane} \qquad (3\text{-}4)$$

The total strain energy for hemispirooctaplane (**3-5**) is then defined as –Δ*H*(Reaction 3-4). The heat of formation (ΔH_f) of the hydrocarbon in question (e.g. hemispirooctaplane (**3-5**)) is calculated using the computed enthalpy of the appropriate homodesmic reaction (e.g. Δ*H*(Reaction 3-4)) and the experimental values for the heats of formation of the small unstrained hydrocarbons: ethane (–83.9 kJ mol^{-1}), propane (–104.7 kJ mol^{-1}), isobutane (–134.2 kJ mol^{-1}) and neopentane (–167.9 kJ mol^{-1}).[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 (–Δ*H*(Reaction 3-5)) in the reaction:

$$\text{spiropentane} + 6\ \text{ethane} \rightarrow \text{neopentane} + 4\ \text{propane} \qquad (3\text{-}5)$$

Even with B3-LYP/6-311+G(3df,2p), the computed *SE* differs from the experimental value by approximately 50 kJ 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 (–22.8 kJ mol^{-1}), neopentane (–38.1 kJ mol^{-1}), propane (–5.5

[†] The abbreviation “neo” indicates neopentane.

kJ mol^{-1}) and ethane (+2.5 kJ mol^{-1}).[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 *SE* for spiropentane (one of the worst cases) computed via a homodesmic scheme differs from experiment by approximately 15 kJ 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 3-5.

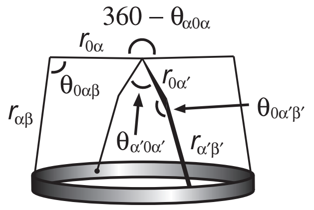
Gas–phase proton affinities were determined as the negative of the enthalpy change in the protonation reactions, $B_{(g)} + H^+_{(g)} \rightarrow BH^+_{(g)}$, obtained using MP2/6-311+G(2d,p)// MP2/ 6-31G(d) energies, corrected for *ZPVE* and to 298 K using MP2/6-31G(d) analytic frequencies and the same scaling factors mentioned above. The ideal gas value of 2.5*RT* 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 CH_4, NH_3, and H_2O, giving values of 530, 852 and 687 kJ mol^{-1}, respectively, which may be compared with experimental values[31] of 552, 854 and 697 kJ mol^{-1}, respectively.

The total energies, scaled *ZPVE*s, 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 C-18 – C-20 of Appendix C.

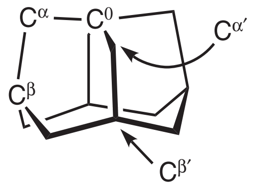
3.3 Results and Discussion

3.3.1 Structures of Hemialkaplanes

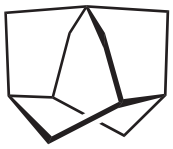
The hemialkaplanes (**3-III**) are constructed formally by capping a neopentane-type unit with a cycloalkane. We examined structures which result from using the following eight cyclic hydrocarbons as the basis for the capping unit: cyclobutane, cyclopentane, bicyclo[2.2.0]hexane, cyclohexane, norbornane (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**),



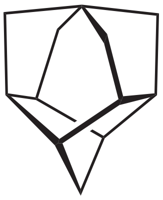
3-VIII



3-1 (C_{2v})

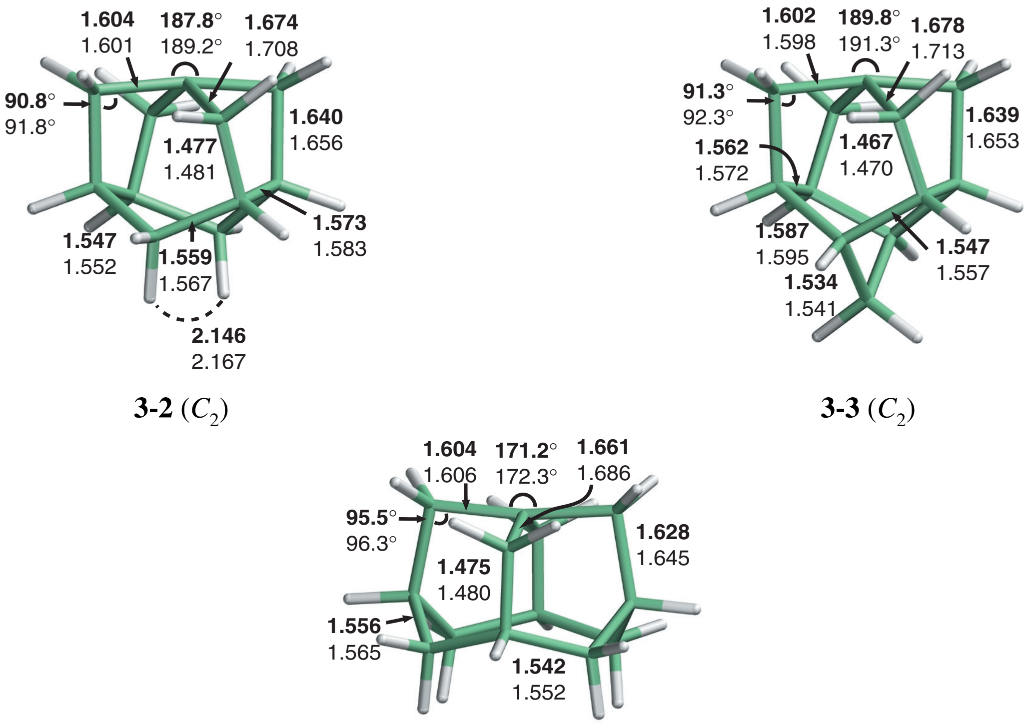


3-2 (C_2)



3-3 (C_2)

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 (**3-2**), hemibiheptaplane (**3-3**) and hemioctaplane (**3-1**) are displayed in Figure 3-2.



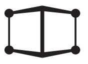
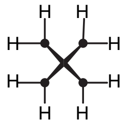
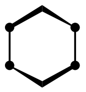
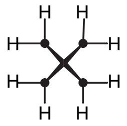
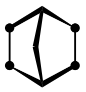
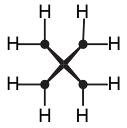
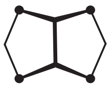
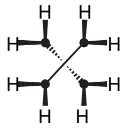
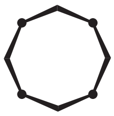
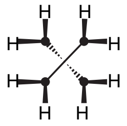
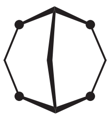
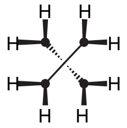
3-2 (C_2)

3-3 (C_2)

3-1 (C_2)

Figure 3-2. 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 hemihexaplane (**3-2**), hemibiheptaplane (**3-3**) and hemioctaplane (**3-1**). The apical angle is $\theta_{\alpha 0\alpha}$, i.e. $\angle C^{\alpha}C^{0}C^{\alpha}$; the other angle indicated is $\theta_{0\alpha\beta}$ i.e. $\angle C^{0}C^{\alpha}C^{\beta}$.

Table 3-1. General structural features of the hemialkaplanes.[a]

Molecule		Sym.[b]	Cap Formula	Cap Structure[c]	Apical C_5H_8 Subunit[c]	Molecular Formula
hemibihexaplane	**3-25**	C_2	*bicyclo*-C_6H_6			$C_{11}H_{14}$
hemihexaplane	**3-2**	C_2	*cyclo*-C_6H_8			$C_{11}H_{16}$
hemibiheptaplane	**3-3**	C_2	*bicyclo*-C_7H_8			$C_{12}H_{16}$
hemibioctaplane	**3-26**	C_2	*bicyclo*-C_8H_{10}			$C_{13}H_{18}$
hemioctaplane	**3-1**	C_{2v}	*cyclo*-C_8H_{12}			$C_{13}H_{20}$
hemibinonaplane	**3-27**	C_2	*bicyclo*-C_9H_{12}			$C_{14}H_{20}$

[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. [b] The symmetry of the equilibrium structure. [c] The carbon atoms with unfilled valences, which form C–C bonds between the cap and the apical C_5H_8 subunit, are marked •.

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 (*ApSE*) and apical structural parameters for the hemialkaplanes.[a,b]

			Apical Parameters[c]							
			lengths				angles			
Molecule		*ApSE*[d]	$r_{0\alpha}$	$r_{\alpha\beta}$	$r_{0\alpha'}$	$r_{\alpha'\beta'}$	$\theta_{\alpha0\alpha}$[e]	$\theta_{\alpha'0\alpha'}$	$\theta_{0\alpha\beta}$	$\theta_{0\alpha'\beta'}$
hemibihexaplane	**3-25**	687	1.585	1.586	1.730	1.469	185.7	141.1	91.3	101.2
hemihexaplane	**3-2**	726 **716**	1.601 **1.604**	1.656 **1.640**	1.708 **1.674**	1.481 **1.477**	189.2 **187.8**	139.9 **140.2**	91.8 **90.8**	100.9 **101.0**
hemibiheptaplane	**3-3**	717 **706**	1.598 **1.602**	1.653 **1.639**	1.713 **1.678**	1.470 **1.467**	191.3 **189.8**	140.7 **141.2**	92.3 **91.3**	101.2 **101.3**
hemibioctaplane	**3-26**	673	1.578	1.653	1.728	1.489	174.2	145.8	93.8	111.6
hemioctaplane	**3-1**	642 **623**	1.606 **1.604**	1.645 **1.628**	1.686 **1.661**	1.480 **1.475**	172.3 **171.2**	148.7 **148.8**	96.3 **95.5**	112.8 **113.1**
hemibinonaplane	**3-27**	696	1.581	1.659	1.704	1.477	172.9	148.7	95.0	112.7

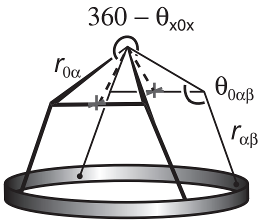
[a] B3-LYP/6-31G(d) values are given in plain text. MP2/6-311+G(2d,p)//MP2/6-31G(d) and MP2/6-31G(d) values are given in bold type. [b] Bond lengths are given in Å, bond angles in degrees, and energies in kJ mol^{-1}. [c] See structure **3-VIII** for a description of the geometrical parameters. [d] *ApSE* is the apical strain energy, the negative of the enthalpy change at 298 K for Reaction 3-1 on page 98. [e] Values for $\theta_{\alpha0\alpha}$ greater than 180.0° 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 C(CH$_2$)$_4$ moiety: (i) there is a pair of elongated C–C bonds to the apical carbon atom, C^0, i.e. with lengths $r_{0\alpha}$ in the range 1.58–1.60 Å; (ii) these two elongated C–C bonds are attached to the apical carbon in an almost linear arrangement ($\theta_{\alpha0\alpha}$ = 170–190°); (iii) associated with this pair of elongated C–C bonds is another long C–C bond between C$^\alpha$ and C$^\beta$ whose length, $r_{\alpha\beta}$, is considerably greater than 1.60 Å in all but **3-25**; (iv) in all cases these two elongated bonds form a tight angle, $\theta_{0\alpha\beta} = \angle C^0C^\alpha C^\beta$, which is close to 90.0°; (v) there is a second pair of very long C–C bonds to C^0 which have a bond length, $r_{0\alpha'}$, around 1.70 Å at B3-LYP/6-31G(d) and greater than 1.65 Å at MP2/6-31G(d); and (vi) associated with this pair of very long C–C bonds is a pair of compressed C–C bonds between C$^{\alpha'}$ and C$^{\beta'}$ which are in the range 1.47–1.49 Å at both levels of theory. We suspect that the presence of four

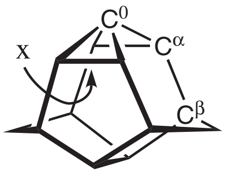
C–C bonds with lengths greater than 1.65 Å, found in all the hemialkaplanes except **3-25**, will make the hemialkaplanes somewhat susceptible to internal rearrangement/ isomerization to lower energy species.

3.3.2 Structures of Hemispiroalkaplanes

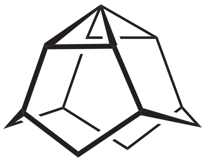
The hemi*spiro*alkaplanes (**3-V**) are constructed formally by capping a spiropentane-type unit with a cycloalkane. We examined structures which result from using the following seven cyclic hydrocarbons as the basis for the capping unit: cyclobutane, bicyclo[2.2.0]hexane, cyclohexane, norbornane (bicyclo[2.2.1]heptane), 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 B3-LYP/6-31G(d) level. A tetramethyl derivative of **3-5** in which the C^{α} hydrogens are replaced with methyl groups, tetramethylhemispirooctaplane (**3-24**), was also examined. Structures of particular interest were then re-optimized at the MP2/6-31G(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.



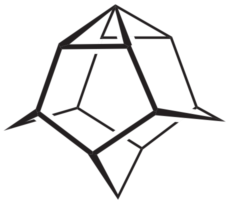
3-IX[32]



3-4 (C_{2v})



3-5 (C_{2v})



3-6 (C_{2v})

The spiropentane-type C_5H_4 apical subunit (in hemispiroalkaplanes) lacks the fourfold symmetry of the neopentane-type C_5H_8 apical subunit (in hemialkaplanes). As a consequence, there are two possible structural isomers for each of the hemispiroalkaplanes 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.

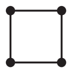
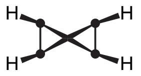
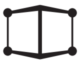
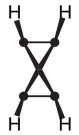
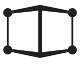
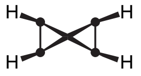
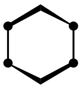
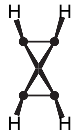
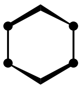
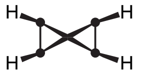
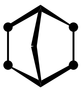
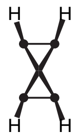
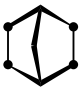
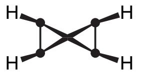
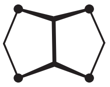
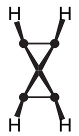
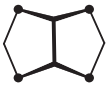
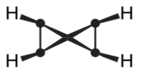
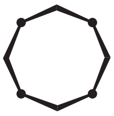
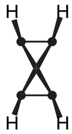
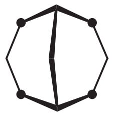
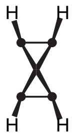
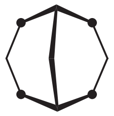
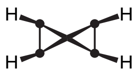
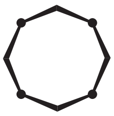
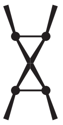
Molecule		Sym.[a]	Cap Formula	Cap Structure[b]	Apical C_5H_4 Subunit[b]	Molecular Formula
hemispirobutaplane	**3-28**	C_{2v}	*cyclo*-C_4H_4			C_9H_8
hemispirobihexaplane (perpendicular)	**3-29**	C_{2v}	*bicyclo*-C_6H_6			$C_{11}H_{10}$
hemispirobihexaplane (parallel)	**3-30**	C_2	*bicyclo*-C_6H_6			$C_{11}H_{10}$
hemispirohexaplane (perpendicular)	**3-31**	C_{2v}	*cyclo*-C_6H_8			$C_{11}H_{12}$
hemispirohexaplane (parallel)	**3-32**	C_{2v}	*cyclo*-C_6H_8			$C_{11}H_{12}$
hemispirobiheptaplane (perpendicular)	**3-33**	C_{2v}	*bicyclo*-C_7H_8			$C_{12}H_{12}$
hemispirobiheptaplane (parallel)	**3-34**	C_{2v}	*bicyclo*-C_7H_8			$C_{12}H_{12}$
hemispirobioctaplane (perpendicular)	**3-4**	C_{2v}	*bicyclo*-C_8H_{10}			$C_{13}H_{14}$
hemispirobioctaplane (parallel)	**3-35**	C_{2v}	*bicyclo*-C_8H_{10}			$C_{13}H_{14}$

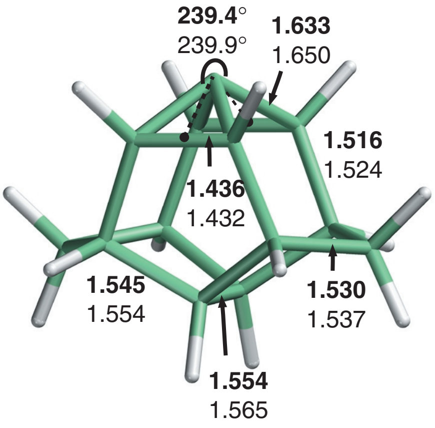
Table 3-3. (Continued) General structural features for the hemispiroalkaplanes.

Molecule		Sym.[a]	Cap Formula	Cap Structure[b]	Apical C_5H_4 Subunit[b]	Molecular Formula
hemispirooctaplane	**3-5**	C_{2v}	*cyclo*-C_8H_{12}			$C_{13}H_{16}$
hemispirobinonaplane (perpendicular)	**3-6**	C_{2v}	*bicyclo*-C_9H_{12}			$C_{14}H_{16}$
hemispirobinonaplane (parallel)	**3-36**	C_{2v}[c]	*bicyclo*-C_9H_{12}			$C_{14}H_{16}$
tetramethyl-hemispirooctaplane	**3-24**	C_{2v}	*cyclo*-C_8H_{12}			$C_{17}H_{24}$

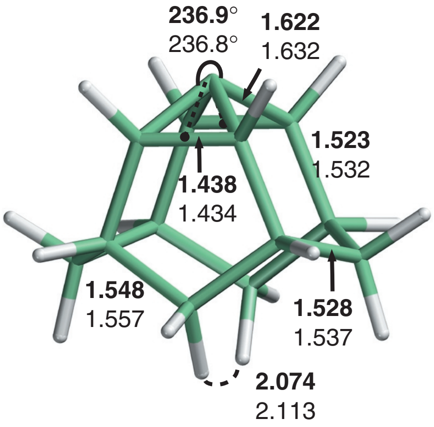
[a] The symmetry of the equilibrium structure. [b] The carbon atoms with unfilled valences, which form C–C bonds between the cap and the apical C_5H_4 subunit, are marked •. The relative orientation of the cap and apical subunit is as shown. [c] The C_{2v} structure of hemispirobinonaplane (parallel) (**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).

ular isomer is favoured in all cases (see below).

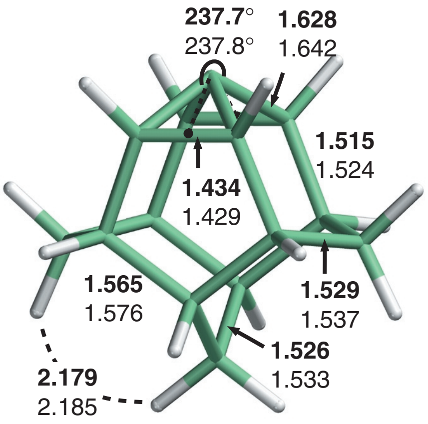
An examination of the structures of the hemispiroalkaplanes that we have considered reveals that they all prefer a pyramidal arrangement at the apical, tetracoordinate carbon atom. There is one relatively long C–C bond ($r_{0\alpha}$ = 1.61–1.67 Å) from C^0 to C^α while all other C–C bonds are unremarkable. 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**) (θ_{x0x} = 107–108°)[32] and those with a wider angle (**3-30**, **3-32**, **3-34**) (θ_{x0x} = 121–124°) 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 C_5H_4 unit and the cap. Interestingly, it is these structures with the wider value for θ_{x0x} that have shorter C^0–C^α bonds ($r_{0\alpha}$ =



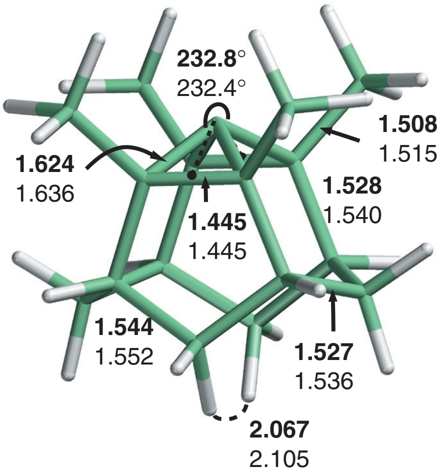
3-4 (C_{2v})



3-5 (C_{2v})



3-6 (C_{2v})



3-24 (C_{2v})

Figure 3-3. 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 hemispirobioctaplane (**3-4**), hemispirooctaplane (**3-5**), hemispirobinonaplane (**3-6**), and tetramethylhemispirooctaplane (**3-24**). The apical angle shown is 360 – θ_{x0x}, i.e. the outer angle made by x, C^0 and x.[32]

1.62 Å for **3-32** and **3-34**, $r_{0\alpha}$ = 1.65 Å and 1.59 Å for **3-30**[†]). Hemispirobutaplane (**3-28**) is a special case as it is the only hemispiroalkaplane with a four-membered primary-

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[†] The structure of **3-30** has C_2 symmetry and as a result has two distinct C^0–C^α lengths ($r_{0\alpha}$ and $r_{0\alpha}'$).

Table 3-4. Calculated apical strain energies (*ApSE*) and structural parameters for the hemispiroalkaplanes.[a,b]

			Apical Parameters[c]			
			lengths		angles	
Molecule		*ApSE*[d]	$r_{0\alpha}$ $r_{0\alpha}'$ [e]	$r_{\alpha\beta}$ $r_{\alpha\beta}'$ [e]	θ_{x0x} [f]	$\theta_{0\alpha\beta}$ $\theta_{0\alpha\beta}'$ [e]
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	1.646 *1.586*[e]	1.563 *1.531*[e]	124.3	117.2 *117.7*[e]
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 (perpendicular)	**3-4**	504 **547**	1.650 **1.633**	1.524 **1.516**	120.1 **120.6**	121.1 **121.2**
hemispirobioctaplane (parallel)	**3-35**	618	1.631	1.542	120.6	125.2
hemispirooctaplane	**3-5**	527 **572**	1.632 **1.622**	1.532 **1.523**	123.2 **123.1**	123.5 **123.6**
hemispirobinonaplane (perpendicular)	**3-6**	499 **550**	1.642 **1.628**	1.524 **1.515**	122.2 **122.3**	122.3 **122.4**
hemispirobinonaplane (parallel)	**3-36**	662	1.609	1.546	120.0	127.4
tetramethylhemispiro-octaplane	**3-24**	480 **516**	1.636 **1.624** 1.515[g] **1.508**[g]	1.540 **1.528**	127.6 **127.2**	120.6 **120.9**

[a] B3-LYP/6-31G(d) values are given in plain text. MP2/6-311+G(2d,p)//MP2/6-31G(d) and MP2/6-31G(d) values are given in bold type. [b] Bond lengths are given in Å, bond angles in degrees, and energies in kJ mol^{-1}. [c] See structure **3-IX** for a description of the geometrical parameters. [d] *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 **3-24**, for Reaction 3-3 on page 99. [e] The lower symmetry (C_2, see Table 3-3 on page 105) gives two unique bond lengths in the apical unit. [f] See Ref. 32. [g] The methyl C–C bond length.

ring cap. Hemispirobutaplane has both a steep angle at the pyramidal carbon (θ_{x0x} = 109.7°) 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 (θ_{x0x} = 120–123°) and intermediate values for the C^0–C^α bond length ($r_{0\alpha}$ = 1.61–1.65 Å). Although these C–C bonds are longer than normal C–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_{2v} 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 H–H close contacts. The shortest H–H contact is found in the C_{2v} structure for the parallel-type hemispirobinonaplane (**3-36**) where the H–H distance is calculated at the B3-LYP/ 6-31G(d) level to be 1.864 Å. 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 H–H distance is increased to 1.954 Å. All other H–H close approaches, in all structures, are greater than 2.0 Å.

The tetramethyl derivative of **3-5** (i.e. **3-24**), shows slightly greater widening of the θ_{x0x} angle at the pyramidal carbon than in **3-5** (θ_{x0x} = 127°). The only other notable feature is that the C^α–CH_3 bond (1.51 Å) is somewhat shorter than a standard C–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 (*ApSE*) is effectively the total strain energy (*SE*) 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 carbon atom. Secondly, although the *ApSE*s 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 *ApSE*, 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 *ApSE*s 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 (ΔH_f) for systems for which we have calculated MP2/6-311+G(2d,p)// MP2/6- 31G(d) energies are given in Table 3-5.

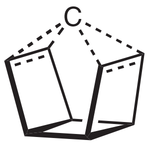
The calculated *ApSE*s for the hemialkaplanes range from about 620–730 kJ mol^{-1} (Table 3-2 on page 103). A comparison of the B3-LYP/6-31G(d) and MP2/6-311+G(2d,p)//MP2/6-31G(d) values shows that the B3-LYP values tend to be higher by about 10–20 kJ mol^{-1}. Strain in the smaller systems with a six-membered primary-ring cap (**3-2**, **3-3**, **3-25**) is generally higher than in the larger systems which have an eight-membered 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 kJ mol^{-1}), **3-3** (768 kJ mol^{-1}) and **3-1** (674 kJ mol^{-1}). Hemioctaplane (**3-1**) stands out clearly as the least-strained hemialkaplane, being the only system to have an *ApSE* lower than 650 kJ mol^{-1} and an *SE* less than 700 kJ mol^{-1}.

The hemispiroalkaplanes give directly-calculated *ApSE*s that lie between 480 and 760 kJ 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 kJ mol^{-1}.[†] In the discussion that follows, the *ApSE*s have consequently been adjusted by 40 kJ 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** – **3-34**) clearly form two groups: the parallel-type isomers (**3-30**, **3-32**, **3-34**) which all have very high *ApSE*s (around 720–800 kJ mol^{-1} after correction) and their perpendicular-type counterparts (**3-29**, **3-31**, **3-33**) which have more modest *ApSE*s (580–620

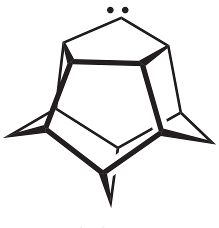
[†] Comparing the B3-LYP/6-31G(d) and MP2/6-311+G(2d,p)//MP2/6-31G(d) calculated values for the *ApSE*s of the hemialkaplanes (Table 3-2 on page 103) and the hemispiroalkaplanes (Table 3-4 on page 108) shows that the B3-LYP values are systematically too high by approximately 20 kJ mol^{-1} and too low by approximately 40 kJ mol^{-1}, respectively. In the discussion of the *ApSE*s of the hemispiroalkaplanes, the B3-LYP values have therefore been adjusted accordingly.

kJ 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 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 *ApSE* for **3-28** (776 kJ mol^{-1} 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 (*ApSE*s greater than 650 kJ mol^{-1}) than the other four structures in this group (**3-4** – **3-6**, **3-24**) (*ApSE*s in the range 515–575 kJ 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 perpendicular-type counterparts (**3-4** and **3-6**), from an unfavorable placement of the C$^{\alpha}$ atoms. The hemispiroalkaplanes can also be thought of as a carbon atom stabilized over 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**)).[14d] 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 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



3-38 (C_{2v})



3-37 (C_s)

parallel-type hemispirobinonaplane (**3-36**), the H–H close contacts mentioned earlier also contribute to the *ApSE*. As a result, the C_{2v} structure for **3-36** 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 C^{α} atoms and relieving much of the strain associated with keeping the opposing C^{α} atoms at a non-bonding distance.

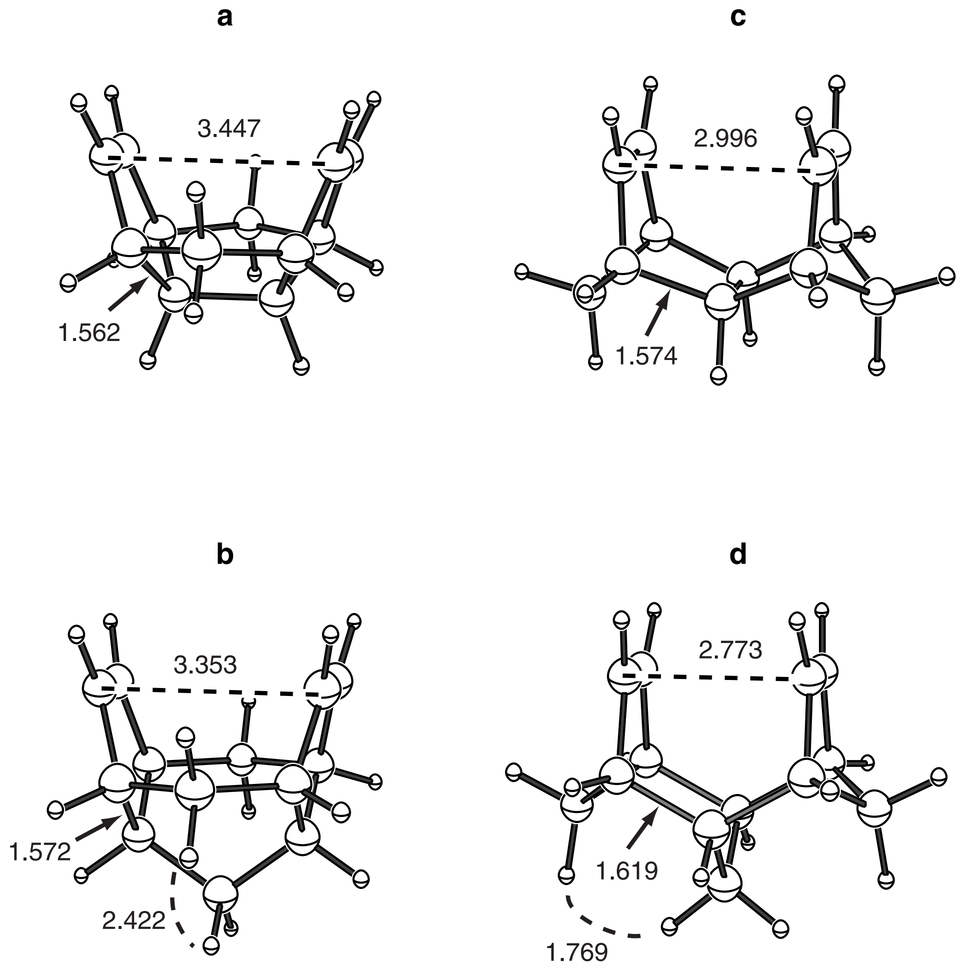


Figure 3-4. The polycyclic diene 'half–cage' frameworks for **3-4** (a), **3-6** (b), **3-35** (c) and **3-36** (d). The olefinic carbon atoms in (c) and (d) (which correspond to C^{α} in **3-35** and **3-36**) are forced into a close-contact situation. MP2/6-31G(d) optimized lengths are given in Å.

The non-parallel-type hemispiroalkaplanes (**3-4** – **3-6**, **3-24**) have the lowest *ApSE*s of the hemispiroalkaplanes studied. Further, both their *ApSE*s and *SE*s are 50–100 kJ mol^{-1} lower than the *ApSE* and *SE* of hemioctaplane. Tetramethylhemispirooctaplane (**3-24**) is of particular interest. It appears that methylation at C^{α} helps to reduce the strain in the hemispiroalkaplanes considerably. The total strain energy of tetramethylhemispirooctaplane (**3-24**) (SE = 567 kJ mol^{-1}) is almost 50 kJ mol^{-1} lower than the strain in hemispirooctaplane (**3-5**) (SE = 623 kJ mol^{-1}).

In order to probe more widely the effect of alkylation on strain, we have also calculated the strain energies for tetrahedrane (**3-40**) (SE = 601 kJ mol^{-1}) and tetrakis(*tert*-butyl)tetrahedrane (**3-45**) (SE = 535 kJ 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 **3-45**, it is likely that alkylation of the C^{α} atoms with bulky alkyl groups like *tert*-butyl, or perhaps isopropyl, would have a beneficial effect on kinetic stability by protecting the ‘sensitive’ C–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 kJ mol^{-1}) is quite large but comparable to the *SE* of cubane (**3-44**) (708 kJ mol^{-1}) or prismane (**3-43**) (639 kJ 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) C–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 *ApSE* (623 kJ mol^{-1} in **3-1**), which in the hemialkaplanes is mainly distributed over the five apical carbon atoms and approximately eight C–C bonds (the four C^0–C^{α} and four C^{α}–C^{β} bonds), suggesting a greater strain per carbon or per C–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 kJ 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 C–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 (*SE*)[a] and calculated and experimental heats of formation (ΔH_f) at 298 K (kJ mol^{-1}).

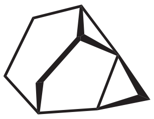
Molecule	Homodesmic reaction[b]	*SE* (calc)[c]	ΔH_f (calc)	ΔH_f (exp)[d]
cyclopropane	**3-39** + 3 ethane → 3 propane	125	62	53.3 ± 0.6
tetrahedrane	**3-40** + 6 ethane → 4 isobutane	601	567	(535 ± 4)[e]
pyramidane	**3-15** + 8 ethane → neopentane + 4 isobutane	645	611	
spiropentane	**3-41** + 6 ethane → neopentane + 4 propane	284	200	185.1 ± 0.8
[1.1.1]propellane	**3-42** + 7 ethane → 2 neopentane + 3 propane	432	369	351 ± 4[f]
prismane	**3-43** + 9 ethane → 6 isobutane	639	589	
cubane	**3-44** + 12 ethane → 8 isobutane	708	641	622.2 ± 3.7
tetra-*tert*-butyl-tetrahedrane	**3-45** + 10 ethane → 8 neopentane	535	30	25.9 ± 8.8[g]
cyclobutane	**3-46** + 4 ethane → 4 propane	115	32	28.5 ± 0.6
bicyclo[2.2.0]-hexane	**3-47** +7 ethane → 2 isobutane + 4 propane	238	138	125[f]
cyclohexane (twistboat)	**TB-3-48** + 6 ethane → 6 propane	27	–98	
cyclohexane (chair)	**C-3-48** + 6 ethane → 6 propane	1	–124	–123.1 ± 0.8
norbornane	**3-49** + 8 ethane → 2 isobutane + 5 propane	62	–59	–54.9 ± 4.7
cis-bicyclo[3.3.0]-octane (*cis*-octahydropental-ene)	**3-50** + 9 ethane → 2 isobutane + 6 propane	49	–93	–93.3 ± 1.5
cyclooctane (boat–chair)	**BC-3-51** + 8 ethane → 8 propane	41	–125	–124.4 ± 1.0
cyclooctane (crown)	**Crown-3-51** + 8 ethane → 8 propane	51	–116	
bicyclo[3.3.1]nonane (chair–chair)	**CC-3-52** + 10 ethane → 2 iso + 7 propane	27	–135	–127.5 ± 2.3
bicyclo[3.3.1]nonane (twistboat–twistboat)	**TBTB-3-52** + 10 ethane → 2 iso + 7 propane	63	–100	

Table 3-5. (Continued) Calculated strain energies (*SE*)[a] and calculated and experimental heats of formation (ΔH_f) at 298 K (kJ mol^{-1}).

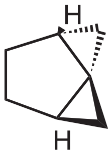
Molecule	Homodesmic reaction[b]	*SE* (calc)[c]	ΔH_f (calc)	ΔH_f (exp)[d]
[3.3.3]fenestrane	**3-11** + 7 ethane → neo + 2 iso + 2 propane	586	528	
[3.4.3]fenestrane	**3-53** + 8 ethane → neo + 2 iso + 3 propane	499	420	
[3.5.3]fenestrane	**3-12** + 9 ethane → neo + 2 iso + 4 propane	355	255	
tetracyclo-[3.3.1.0^{2,4}.0^{2,8}]nonane	**3-54** + 12 ethane → neo + 4 iso + 4 propane	426	309	
hemihexaplane	**3-2** + 14 ethane → neo + 4 iso + 6 propane	743	584	
hemibiheptaplane	**3-3** + 16 ethane → neo + 6 iso + 5 propane	768	613	
hemioctaplane	**3-1** + 16 ethane → neo + 4 iso + 8 propane	674	473	
hemispirobioctaplane (perpendicular)	**3-4** + 19 ethane → neo + 10 iso + 2 propane	595	469	
hemispirooctaplane	**3-5** + 18 ethane → neo + 8 iso + 4 propane	623	472	
hemispirobinonaplane (perpendicular)	**3-6** + 20 ethane → neo + 10 iso + 3 propane	613	466	
tetramethyl-hemispirooctaplane	**3-24** + 18 ethane → 5 neo + 4 iso + 4 propane	567	281	

[a] MP2/6-311+G(2d,p)//MP2/6-31G(d) values corrected to 298 K (kJ mol^{-1}). [b] The abbreviations "neo" and "iso" indicate neopentane and isobutane, respectively. [c] The strain energy (*SE*) is determined as the negative of the enthalpy change for the given homodesmic reaction. [d] Taken from Ref. 28b unless otherwise noted. [e] G2 calculated value from Ref. 28d. [f] From Ref. 28c. [g] From Ref. 28a.

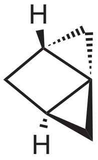
The situation for the hemispiroalkaplanes is more promising. In the first place, *ApSE*s for the hemispiroalkaplanes are generally lower than for the hemialkaplanes. Again, strain is concentrated mainly in the apical unit and is distributed mostly over these five carbon atoms and the ten associated C–C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



3-53



3-12

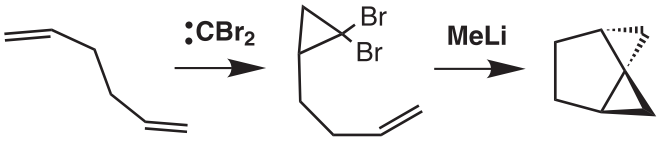


3-54

(**3-53**, **3-12** and **3-54**) (499, 355 and 426 kJ mol^{-1}, respectively) that have been observed experimentally.[11] Although these strains are somewhat lower than the *ApSE*s for the hemispiroalkaplanes **3-4** – **3-6**, the strain in **3-53** is comparable to the *ApSE* for the tetramethyl derivative of **3-5** (i.e. **3-24**) (516 kJ mol^{-1}). We also expect that the tetramethyl derivatives of **3-4** and **3-6** will have *ApSEs* around 500 kJ 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 C=C double bond.[11] For example, both the tricycloheptane **3-12**[11a] and the tetracyclononane **3-54**[11c] have been synthesized in this manner (see Scheme 1).[†] An analogous reaction pathway for the synthesis of the hemispiroalkaplanes would involve, as principle reactant, a polycyclic diene[‡] such as **3-55** (the hydrocarbon parent of the well-known insecticide isodrin) or **3-56** (the tetraquinane isomer of **3-55**, which is thermally



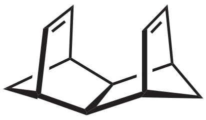
3-12

Scheme 1

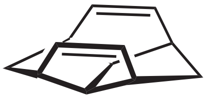
[†] It is worth noting that Brinker found this reaction could not be relied upon in general and he therefore developed a different procedure to synthesize the tricyclooctane analogue of **3-12**, which might also be labelled [3.6.3]fenestrane (**3-13**).[11g,h]

[‡] Compounds **3-55** and **3-56** and other similar species are involved in the synthesis of pagodanes and isopagodanes.[35]

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

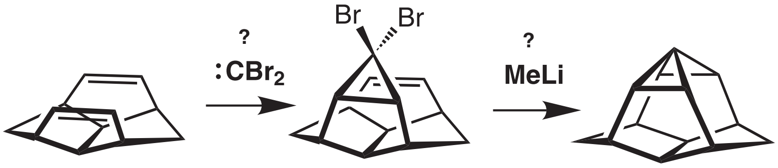


3-55



3-56

For cases where this type of cyclization reaction was found to be successful, Skattebøl observed that methylation at the C=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.



3-56 **3-4**

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_{2v} symmetry and are found to be minima on their respective potential

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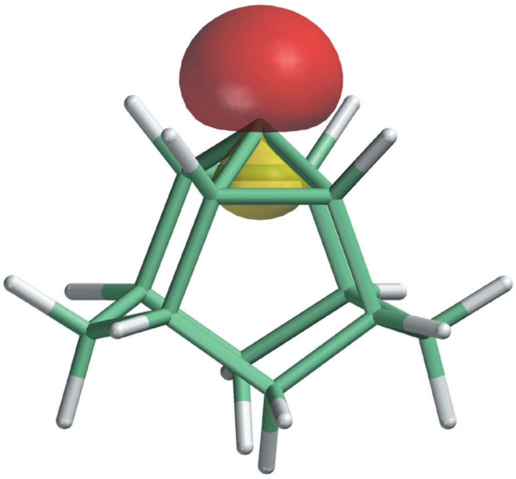
[†] It is expected that the *exo*-isomer would result initially from carbene attack on the polycyclic dienes **3-55** or **3-56**. Obtaining *endo*-isomers may prove difficult and a ‘cation route’, in which a protonated hemispiroalkaplane is formed first via a carbocation rearrangement and then deprotonated with a very strong base, may be worth considering.



3-5 (C_{2v})

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 eÅ^{-3}.

energy surfaces. Once again, the longest bonds are found to be the C^0–C^α bonds ($r_{0\alpha}$ = 1.73 Å for **3-1-H$^+$**, $r_{0\alpha}$ = 1.61–1.62 Å for **3-4-H$^+$**, **3-5-H$^+$**, **3-6-H$^+$** and **3-24-H$^+$**). These structures appear to be typical pyramidal carbocations, although the angle at the apex (θ_{x0x} = 131–138°)[32] is somewhat flatter than in known pyramidal carbocations like **3-21-H$^+$**, **3-22-H$^+$** and **3-23-H$^+$** (θ_{x0x} = 93–94°) (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 kJ mol^{-1} (Table 3-6)! The non-pyramidal hemialkaplane **3-1**, as would be expected, has the lowest *PA* (1119 kJ mol^{-1}) while **3-24** has a slightly greater proton affinity (1193 kJ mol^{-1}) than the non-alkylated hemispiroalkaplanes **3-4** – **3-6** (1172–1179 kJ mol^{-1}). These values are considerably larger than the *PA*s of any of the organic systems listed in a recent compendium,[31] including the renowned superbase, 'proton sponge' (1,8-bis(dimethylamino)naphthalene) (1028 kJ 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 $[(Ph_3PAu)_4C]$ (which does not, however, adopt a pyramidal structure) to attract a fifth ligand and form $[(Ph_3PAu)_5C]^+$.[16] In addition, calculations by

Table 3-6. Calculated gas-phase proton affinities (*PA*) at 298 K (kJ mol^{-1}) for selected molecules[a] and selected geometrical parameters (Å or degrees) for the protonated species.[b]

Molecule	*PA*[c]	$r_{0\alpha}$	θ_{x0x}[d]
pyramidane (**3-15**)	965	1.646	58.6
3-21[e]	1094	1.623	92.9
3-22[e]	1096	1.619	94.1
3-23[e]	1102	1.620	93.1
hemioctaplane (**3-1**)	1119	1.732	138.1
hemispirobioctaplane (**3-4**)	1172	1.620	131.4
hemispirooctaplane (**3-5**)	1175	1.613	133.5
hemispirobinonaplane (**3-6**)	1179	1.617	132.7
tetramethylhemispirooctaplane (**3-24**)	1193	1.620	137.1

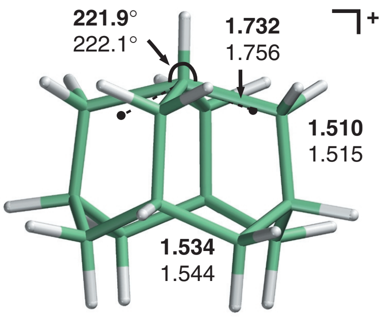
[a] MP2/6-311+G(2d,p)//MP2/6-31G(d) values corrected to 298 K as described in the text. [b] MP2/6-31G(d) values. [c] *PA* is determined as the negative of the enthalpy change for reaction (6). [d] See Ref 32. [e] The conjugate bases of **3-21-H$^+$**, **3-22-H$^+$** and **3-23-H$^+$**.

Pyykkö indicate that both the pyramidal and tetrahedral-like isomers of [$(H_3PAu)_4C$] have proton affinities comparable to those of the hemispiroalkaplanes.[18c] We have recalculated the proton affinity of pyramidane (**3-15**) (965 kJ mol^{-1}), and find it to be somewhat less than that predicted by Jemmis and Schleyer[19] (1060 kJ mol^{-1}) and considerably less than the *PA*s of the hemispiroalkaplanes **3-4** – **3-6** and **3-24**.

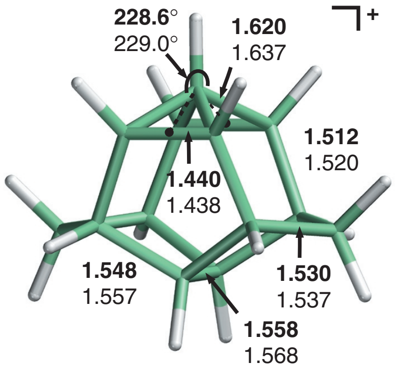
Once again, the effects of methylation appear to be beneficial. Thus the greater *PA* for **3-24** over **3-5** indicates that methylation, as well as reducing the strain in the unprotonated species (see above), also reduces the relative energy of the protonated molecule. This advantageous effect of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

3.3.6 Stabilities

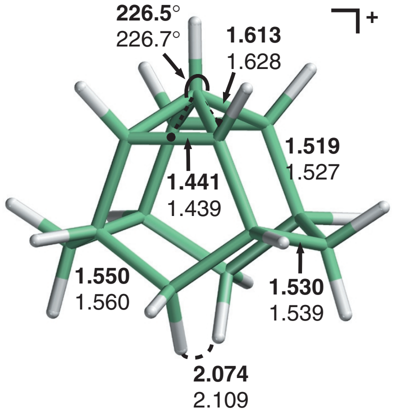
Determining the kinetic stability of prospective synthetic targets is not a simple task, yet the absence of low-lying transition states, leading to potential decomposition pathways, is essential to their eventual isolation. An exhaustive search of all the possi-



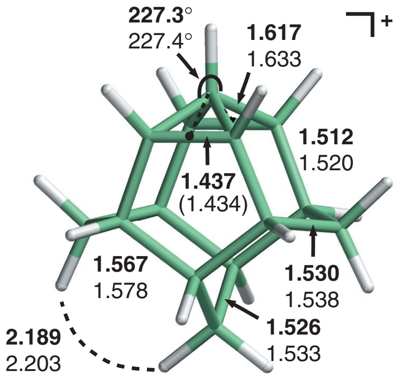
3-1-H$^+$ (C_{4v})



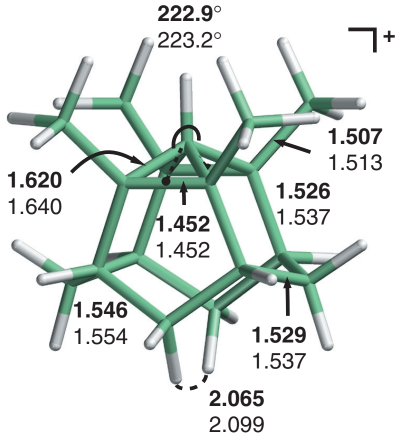
3-4-H$^+$ (C_{2v})



3-5-H$^+$ (C_{2v})



3-6-H$^+$ (C_{2v})



3-24-H$^+$ (C_{2v})

Figure 3-6. 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 protonated hemioctaplane (**3-1-H**$^+$), hemispirobioctaplane (**3-4-H**$^+$), hemispirooctaplane (**3-5-H**$^+$), hemispirobinonaplane (**3-6-H**$^+$), and tetramethylhemispirooctaplane (**3-24-H**$^+$). The apical angle shown is 360 – θ_{x0x}, i.e. the outer angle made by x, C^0 and 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[8c] 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.[8c] 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 C–C bond lengths) should give an indication of any particularly weak bonds that may have low dissociation barriers. The pair of elongated C^0–C^α bonds in the hemialkaplanes (**3-III**), that are approximately 1.67 Å 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 Å 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 C–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 C^0–C^α bonds are, in general, considerably shorter (approximately 1.63 Å 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 C^0–C^α bonds (1.49–1.52 Å) can readily rearrange via what is thought to be either initial C–C cleavage at one of the C^0–C^α 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-benzotricyclo-[4.1.0.0^{1,3}]hept-4-ene (**3-14**) and find a good correlation between the energy of homolytic dissociation at the inner C^0–C^α bond and the rate of thermal rearrangement. Initial calculations on the cleavage at one of the C^0–C^α bonds in hemispirooctaplane (**3-5**) indicate that this process is exothermic (rather than endothermic, as is customary for C–C bond cleavage). However, we do find a barrier to C–C bond cleavage which varies from approximately 20 kJ mol^{-1}, as calculated with UB3-LYP/6-31G(d), to 60 kJ 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 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 cm^{-1}, correspond to a symmetric and an anti-symmetric C–C stretch of the C^0–C^α bonds and a scissor-like motion which causes inversion at the apical carbon atom, C^0. Hemioctaplane (**3-1**) is unusual because of its C_{2v} symmetry. In this case, there are a few low frequencies that correspond to twisting motions, especially of the cap. The scissor-like motion at C^0 appears at about 250 cm^{-1}, the lowest C^0–C^α stretching motion (antisymmetric) appears at about 350 cm^{-1}, and the symmetric C^0–C^α stretch is found at about 550 cm^{-1}. It appears from the relatively low frequencies for C^0–C^α stretching, coupled with the rather long C^0–C^α bonds, that initial cleavage of the C^0–C^α 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 C^0–C^α bonds (see Figure 3-7). One of these modes (**A**) leads to ring opening at C^0 (with C–C bond formation between $C^{\alpha,2}$ and $C^{\alpha,3}$) to give a cyclopentylidene structure, while the other mode (**B**) represents a symmetric stretching of the opposing C^0–C^α bonds and is likely to lead to homolytic C^0–C^α bond cleavage. The ring opening mode (**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_{2v} 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 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 cm^{-1}. Even in the hemispirooctaplanes **3-5** and **3-24**, the frequency associated with this mode is quite small (100 and 200 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

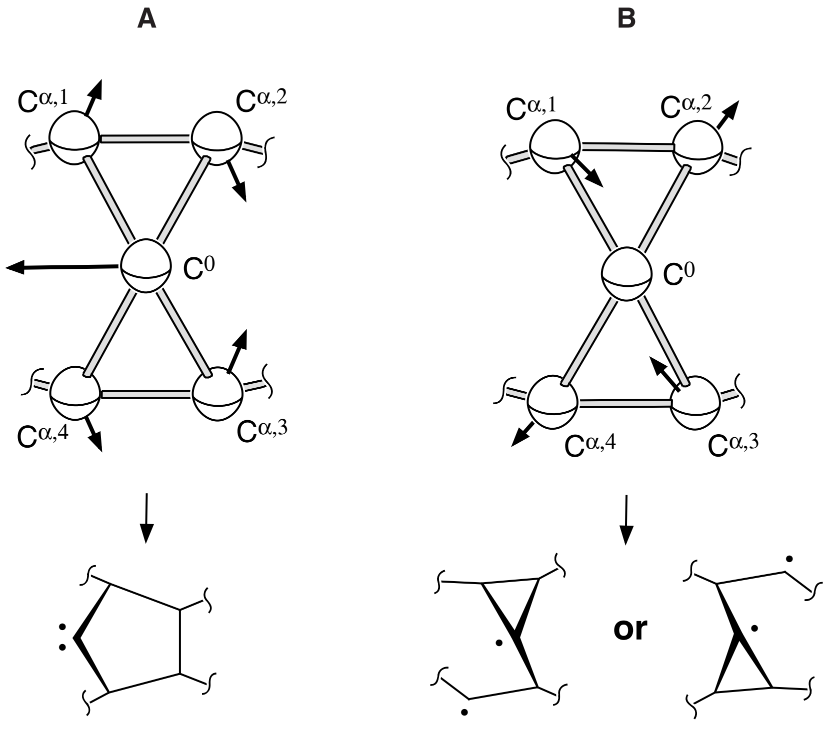


Figure 3-7. The two lowest vibrational modes, **A** and **B**, which may lead to ring opening at the apical carbon atom in the hemispiroalkaplanes. The apical carbon atom, C^0, is above the plane of the C^α atoms.

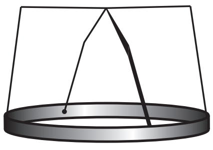
vibrational profiles of the protonated hemispiroalkaplanes in this low-frequency region are similar to those we calculate for the experimentally-observed pyramidal carbocations **3-21-H$^+$**, **3-22-H$^+$** and **3-24-H$^+$**. These observations suggest that this particular vibration, despite being 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 C^0–C^α 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 cm^{-1}) and the perpendicular-type hemispiroalkaplanes with an eight-membered primary-ring cap (**3-4** – **3-6**) (190–240 cm^{-1}). The value of the corresponding frequency in the parallel-type hemispiroalkaplanes (**3-30**, **3-32** and **3-34** – **3-36**) is somewhat lower (100–200 cm^{-1}). However, this same mode corresponds to a much larger frequency (approximately 300–400 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 C^0–C^α bond cleavage will be one of the preferred modes of rearrangement in the hemispiroalkaplanes, and an accurate determination of the barrier to this C–C bond cleavage is required if we are to establish the stability of these molecules with respect to unimolecular rearrangement.

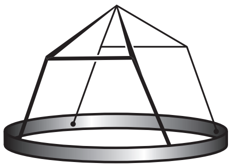
3.4 Concluding Remarks

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 (*ApSE*), the shortest C^0–C^α bonds, and probably the greatest (albeit small) barrier to C^0–C^α bond cleavage (and subsequent rearrangement). We expect, however, that the hemi*spiro*alkaplanes will generally have

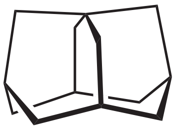


3-III

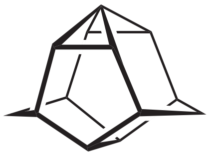


3-V

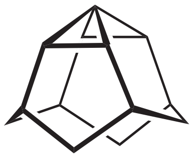
better prospects of synthesis. Alkylated derivatives of hemispirobioctaplane (**3-4**), hemispirooctaplane (**3-5**) and hemispirobinonaplane (**3-6**) are predicted to be the best target molecules. These molecules are the least strained hemispiroalkaplanes, and the amount of strain associated with the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



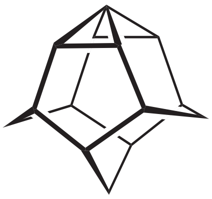
3-1



3-4 (C_{2v})



3-5 (C_{2v})



3-6 (C_{2v})

We find that methylation (or perhaps alkylation with larger groups like isopropyl or *tert*-butyl) at the C^α atoms reduces the total strain and the *ApSE* 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 C^α 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.

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