Chapter 4
Alkaplanes – Planar Carbon

4.1 Introduction

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

The possibility of the existence of planar-tetracoordinate carbon has aroused much interest since the seminal work by Hoffmann, Alder and Wilcox in 1970.¹ In this work Hoffmann et al. challenged the long-standing tenet of organic chemistry, established by van’t Hoff and le Bel in 1870,² which supposes that tetracoordinate carbon will have a tetrahedral geometry. However, Hoffmann suggested that because molecules with a simple chiral center at carbon do not racemize we should expect that an achiral geometry, such as a planar one, will lie at least 250 kJ mol⁻¹ above the tetrahedral form. Model calculations on methane³ showed that the preference for a tetrahedral over a square-
planar bonding arrangement, at least in methane, was much greater than this proposed lower limit; computed estimates went as high as 1000 kJ mol\(^{-1}\). This preference for the tetrahedral geometry appeared so strong that it was considered unlikely that a simple carbon compound could be found that actually prefers a planar arrangement.

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

It has since been shown by both Gordon \textit{et al.}\(^{4a}\) and Pepper \textit{et al.}\(^{4b}\) that the lowest-energy path for the hypothetical classical inversion of methane is not via a planar structure but via a pyramidal-type structure (with \(C_3\) or possibly \(C_{4v}\) symmetry).\(^4\) Both groups also found that the lowest-energy planar structure for methane does not have four equivalent hydrogen atoms, as had been supposed, but has \(C_{2v}\) symmetry and a structure that resembles a complex between \(\text{CH}_2\) and \(\text{H}_2\) (reminiscent of the structure for \(\text{CH}_4^{2+}\)).\(^5\) Further, the energy of the \(C_{2v}\) (\(D_{4h}\)) symmetry planar structure relative to the tetrahedral geometry is about 500 (600) kJ mol\(^{-1}\). This is significantly higher than the homolytic dissociation energy of the C–H bond in methane (435 kJ mol\(^{-1}\))\(^6\) and suggests that pla-
The problem of overcoming this strong preference for the tetrahedral geometry at a tetracoordinate carbon can be approached in one of two ways. The method that has received most attention and success to date is best described as electronic. This approach tries to reduce the destabilization of the planar arrangement relative to the tetrahedral arrangement by replacing hydrogen with substituents that afford relative electronic stabilization to a planar or near-planar arrangement. An examination of the electronic structure of $D_{4h}$ methane (Figure 4-1) shows a lone–pair $p$-type HOMO and four electron-deficient $\sigma$-bonds. It would thus be expected that substitution of hydrogen by groups with $\sigma$-donor/$\pi$-acceptor characteristics (e.g. Li, BH$_2$ or SiH$_3$) should favor a planar bonding arrangement at carbon. Such ligands afford electronic stabilization to the planar geometry (relative to the tetrahedral geometry) by delocalizing the electrons in the lone pair $p$-type orbital and increasing the electron density in the $\sigma$-bonds to carbon. It has also been found that placing the target carbon atom in small rings (particularly three-membered rings) also greatly helps in stabilizing the planar geometry over the tetrahedral-like geometry (see Section 1.5.1 on page 23).

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

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1. For a detailed discussion of the electronic approach to forming planar-tetracoordinate carbon see Section 1.4 on page 9.
2. A more complete discussion of the electronic structure of square-planar methane and its consequences is given in Section 1.3 on page 6.
3. They identified a number of other molecules that were also found to prefer a planar-tetracoordinate geometry but these molecules have been since found not to be minima on their respectively potential energy surfaces. For more information, see Section 1.4.1 on page 9.
Much of their ground-breaking work has been subsequently re-examined at higher levels of theory and extended to include other similar, small polarorganometallic molecules. More recently, Sorger and Schleyer\(^7\) have examined a range of small, lithium- and boron-containing compounds with up to ten heavy atoms. They found seven molecules that are predicted to have a planar-tetracoordinate carbon atom (4-1 – 4-7). Most recently, Gribanova, Minyaev and Minkin\(^7\) have identified three isomers of \(\text{C}_2\text{B}_2\text{H}_4\) (4-8 – 4-10) as preferring a planar geometry at the central tetracoordinate carbon atom.

None of these molecules (4-1 – 4-10) has yet been synthesized. Further, synthesis of the lithium-containing species may be complicated both by the tendency for lithium compounds to aggregate and by the tendency of donor solvent molecules to coordinate to the lithium centers and disrupt planar-tetracoordination at carbon.\(^8\) There is, however,
a growing list of compounds that have been synthesized which have one or more planar-tetracoordinate carbon atoms.\textsuperscript{9,12} These compounds can be broadly classified into two groups. The first\textsuperscript{9} (e.g. $4\text{-}11$ and $4\text{-}12$) are polarorganometallics which owe the stability of the planar-tetracoordinate carbon solely to strong electronic stabilization afforded by one or more metal centers. The others\textsuperscript{12} are also polarorganometallics which rely on strong electronic stabilization from one or more metal centers, but also depend on the planar-tetracoordinate carbon atom being included in a $\pi$-bonding system (e.g. $4\text{-}13$, $4\text{-}14$ and $4\text{-}15$).\textsuperscript{†} Including the carbon atom of interest in a $\pi$-system is clearly a very effective way of reducing the energy of the otherwise lone-pair $\rho$-type HOMO. In fact, in these compounds, the $\sigma^2\pi^2$ electronic configuration of square-planar methane becomes $\sigma^n\pi^1$, where $n \approx 3–4$ (a drastic reduction of $\pi$-electron density). However, this

\begin{equation*}
\begin{array}{c}
\text{Cp}_2\text{M}^1 \quad \text{C} \quad \text{R}^2 \\
\text{R}^1 \quad \text{L} \quad \text{M}^2\text{R}_2^3
\end{array}
\end{equation*}

\text{M}^1 = \text{Ti, Zr, Hf}; \text{R}^1, \text{R}^2 = \text{Alkyl, Aryl, SiMe}_3 \\
\text{M}^2\text{R}_2^3 = \text{BEt}_2, \text{AlBu}_2, \text{AlMe}_2, \text{AlEt}_2, \text{GaMe}_2 \\
\text{L} = \text{Me, Et, CCMe, CCPh, CCcHex, Cl}

\text{4-15}

\text{†} \text{Note that 4-4 and 4-5 also involve the planar-tetracoordinate carbon atom in a $\pi$-system.}
leaves some ambiguity as to the nature of the planar-tetracoordinate carbon atom which, although tetracoordinate, is clearly not derived from a saturated carbon atom.†

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

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

directed towards finding molecules with structurally imposed planarizing distortions at a tetracoordinate carbon atom, has centered mostly on this very broad class of hydrocarbons (e.g. tetracyclo[4.2.1.0²⁹,⁰]nonane or [3.5.3.5]fenestrane (4-16),16 an all-cis-[4.4.4.5]fenestrane derivative (4-17),15 all-trans-[4.4.4.4]-fenestrane (all-trans-4-18),13,18

† For an in depth discussion of this matter, see Section 1.4 on page 9 and Section 1.6 on page 38.
and [5.5.5.5]fenestrane (4-19)$^{13,14}$. However, these molecules at best show only moderate distortions from the tetrahedral ideal. The most flattened tetracoordinate carbon reported to date for an isolable molecule can be found in the all-cis-[4.4.4.5]fenestrane derivative 4-17,$^{13d,15e}$ which has opposing CCC angles ($\angle C^{\alpha,1}C^{\alpha,3}$ and $\angle C^{\alpha,2}C^{\alpha,4}$) (see 4-II) of approximately 130° (which is not greatly disturbed from the tetrahedral ideal of 109.5°).

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

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

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

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

\(^\dagger\) Discussion of a number of compounds of this type and further details concerning the paddlanes are presented in Section 1.5.4 on page 31.
However, while the hemispiroalkaplanes (4-V) are all found to have a highly pyramidalized, tetracoordinate carbon, the larger hemialkaplanes, e.g. hemioctaplane or bowlane (4-24), are found to have a tetrahedral-like, but considerably flattened, apical carbon atom. For example, hemioctaplane is found to have CCC angles across the apical carbon atom (C<sup>0</sup>) of 171.0° and 148.8°.

Recently, Wiberg has had good success in achieving large distortions at a tetracoordinate carbon center through binding spiropentane with very short bridges (e.g. 4-25-ketene and 4-26). These experimentally observed compounds have a CCC angle across C<sup>0</sup> of close to 180°. Although this work is not directed explicitly towards the synthesis of a planar-tetracoordinated carbon, it gives an indication of just how much distortion is possible at a C(C)<sub>4</sub> center. However, although these compounds exhibit very large distortions at the quaternary carbon they are not particularly flattened. The angle between the two cyclopropane rings which are spiro-bound at C<sup>0</sup> is around 80° for 4-25 and 50° for 4-26 (for a planar-tetracoordinate geometry this angle needs to be 0°).

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

In the following sections of this chapter, we will begin by accurately determining the energy required to flatten the central, tetracoordinate carbon atom in a number of small, prototypical saturated hydrocarbon systems — methane, neopentane and spiro-pentane. A complete examination of the lower-lying states of planar methane with a range of methods (up to the most advanced techniques available) will provide us with valuable information on the accuracy of these methods in describing the unusual bonding situation found in a planar-tetracoordinate carbon atom. Neopentane and spiro-pentane serve as good model quaternary systems (they are two of the simplest systems which posses a C(C)₄ substructure), and will provide some insight into the level of theory necessary to adequately describe a planar C(C)₄ moiety.

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

4.2 Methods

\textit{Ab initio} molecular orbital calculations\textsuperscript{25} were carried out using the \textsc{gau}ussian 98\textsuperscript{26} and \textsc{molpro}\textsuperscript{27,28} programs.

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

\textsuperscript{†} For a discussion of our nomenclature for these molecules, see Appendix A.
CCSD(T) optimized structures. Optimized geometries are listed in Table 4-2. Relative energies are given in Table 4-3 and Figure 4-3. Total energies are given in Tables C-5 and C-6 of Appendix C.

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

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

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

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\footnote{We refer to this basis set as 6-311+G(2d,p)(red). Approximate linear dependency problems led to difficulty calculating accurate gradients with both GAUSSIAN 94 and GAUSSIAN 98 when using this 6-311+G(2d,p)(red) basis for dimethanospirooctaplane (4-29). The approximate linear dependency problems were found to be resolved by removing the $s$-component of the diffuse functions at the C\textsuperscript{o} atoms for this molecule.}
stationary points we had located. Improved relative energies were then determined from MP2(fc)/6-311+G(2d,p) single point energy calculations on the resulting structures.

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

![Figure 4-2](Image)

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

Calculations on methane have shown\(^4\) that an accurate description of the planar-tetracoordinate carbon moiety requires at least a second set of \(d\)-functions and a set of
diffuse functions on carbon. Without these components in the basis set, energies for planar structures are overestimated relative to distorted geometries. We find a similar result (see Table 4-3 on page 153), although we also find that the need for very large basis sets is somewhat less important for C(C)_4 planar carbon moieties (i.e., a quaternary carbon) and when the B3-LYP method is being used (see Table 4-5 on page 158). Choosing an adequate basis set to properly describe the planar carbon electronic structure becomes critical for alkaplanes where the structures being examined approach planarity at the central quaternary carbon. Essentially, as the barrier to inversion at the central carbon atom (which occurs via a ‘planar’ geometry) becomes small, the relative increase in energy around the ‘planar’ structure, which results from not including two sets of \(d\)-functions nor diffuse functions, becomes important. This effect can artificially raise the barrier to inversion and shift the equilibrium to a more distorted geometry when too small a basis set is employed. In extreme cases, it can even introduce a barrier where no barrier should exist. As an example, we find that MP2(fc)/6-31G(d) and B3-LYP/6-31G(d) optimized geometries for dimethanospiro[2.2]octaplane (4-29) prefer a slight distortion away from planar-tetracoordination at \(C^0\), giving a \(D_2\) symmetry structure. However, when optimized at the MP2(fc)/6-311+G(2d,p)(red) level, dimethanospiro[2.2]octaplane (4-29) optimizes to a \(D_{2h}\) symmetry structure. An examination of the lowest-energy vibrational mode of 4-29 (see Figure 4-2), which normally corresponds to the pathway for inversion at \(C^0\) for the spiroalkaplanes (4-VII), shows no barrier to inversion at both the MP2(fc)/6-311+G(2d,p) and MP2(fc)/6-311+G(2d,p)(red) levels and a very small (0.35 kJ mol\(^{-1}\)), probably artificial, barrier at the MP2(fc)/6-31G(d) level. Our 6-311+G(2d,p)(red) basis, which adds extra \(d\)-functions and diffuse functions to the central region only, gives good agreement with the full 6-311+G(2d,p) basis.

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

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

$$4-28 + 30 \text{ ethane} \rightarrow 5 \text{ neopentane} + 8 \text{ isobutane} + 8 \text{ propane} \quad (4-1)$$

The strain energy (SE) for spiro[2.2]octaplane (4-28) is then defined as $-\Delta H(\text{Reaction 4-1})$. The heat of formation ($\Delta H_f$) of the hydrocarbon in question (in this case spirooctaplane (4-28)) is calculated using the computed enthalpy of the appropriate homodesmic reaction (e.g. $\Delta H_f(\text{Reaction 4-1})$ for 4-28) 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$^{-1}$). Total energies were calculated at the MP2(fc)/6-311+G(2d,p) level and geometries were determined at the MP2(fc)/6-311+G(2d,p)(red) level for the majority of the alkaplanes (4-VI, 4-VII and 4-VIII), except where otherwise noted. The geometries for other
hydrocarbons, whose geometries are not expected to show the same basis set dependency as the alkaplanes, were calculated at the MP2/6-31G(d) level. Zero-point vibrational energy (ZPVE) corrections were determined using the B3-LYP/6-31G(d) calculated frequencies scaled by 0.9806, and corrections to 298 K ($H_{298}^0$) for the resulting enthalpies were determined using the same frequencies but scaled by 0.9989. Calculated total strain energies (SE) and heats of formation for a variety of hydrocarbons (including the novel systems described herein) are given in Tables 4-12 to 4-15. Total energies, ZPVEs and the values of the temperature corrections ($H_{298}^0$) are given in Tables C-11 – C-15 of Appendix C. Optimized geometries are given in Tables C-22 – C-26 of Appendix C.

The first adiabatic ionization energies have been determined at the MP2/6-311+G(2d,p)//MP2/6-311+G(2d,p)(red) level for a few representative molecules (4-27\(^+\), 4-28\(^+\) and 4-29\(^+\)), taken from each of the alkaplane classes (4-VI, 4-VII and 4-VIII, respectively). We have used the stationary electron (or ion) convention. Calculated values are determined at 0 K and zero-point vibrational energy (ZPVE) corrections were determined using B3-LYP/6-31G(d) calculated frequencies scaled by 0.9806. Thus, for the reaction, $A \rightarrow A^{\ddagger} + e^-$, the ionization energy is calculated as,

$$IE_a[A] = (E[A^{\ddagger}] + ZPVE[A^{\ddagger}]) - (E[A] + ZPVE[A])$$  \hspace{1cm} (4-2)

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

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

4.3 Results and Discussion

4.3.1 How hard is it to flatten methane?

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

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

Firstly, we examined relative energies for structures with the highest possible symmetry, i.e. $D_{4h}$ symmetry. The three lowest-lying states of square-planar methane are $^1A_g$, $^1B_{2u}$ and $^3B_{2u}$. Our best estimates, indicate clearly that the lowest of these three
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The closed-shell singlet (1\text{Ag}) is found to lie 573 kJ mol\(^{-1}\) above the tetrahedral ground-state. The \(D_{4h}\) triplet (\(^3\text{B}_{2u}\)) lies considerably higher in energy than the \(D_{4h}\) closed-shell singlet (\(\Delta \Delta E_{\text{PT}} [^3\text{B}_{2u} - 1\text{Ag}] = 106 \text{ kJ mol}^{-1}\)), while the open-shell singlet (\(^1\text{B}_{2u}\)) is slightly lower in energy than the triplet (\(\Delta \Delta E_{\text{PT}} [^1\text{B}_{2u} - 1\text{Ag}] = 100 \text{ kJ mol}^{-1}\)).

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

• 

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geometry (reminiscent of the situation for CH_4^{2+} which has a ‘CH_2^{2+} + H_2’-like structure) which is a minimum with respect to in-plane distortion. This structure is considerably lower in energy (by 51 kJ mol\(^{-1}\)) than the \(D_{4h}\) geometry (\(\Delta E_{PT} = 522\) kJ mol\(^{-1}\)). The two planar open-shell states (\(^3B_{2u}\) and \(^1B_{2u}\)) are not well bound; relaxation in \(C_s\) symmetry leads to homolytic C–H bond cleavage giving CH_3\(^+\) + H\(^-\) which lies 469 kJ mol\(^{-1}\) above the tetrahedral ground state of methane. Clearly, planar methane prefers the \(C_{2v}\) closed-shell singlet and single excitations to the \(B_{2u}\) states will lead to exothermic dissociation into CH_3\(^+\) + H\(^-\).

We have explored methane at a variety of levels in order to gain some information on how well lower level calculations perform relative to the most sophisticated, and accurate, methods available to us (in this case MRCI+Q/AV5Z//UCCSD(T)(full)/6-311+G-(3df,2p)). We find that the UCCSD(T)(fc)/AVQZ//UCCSD(T)(full)/

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

<table>
<thead>
<tr>
<th>method</th>
<th>nbf</th>
<th>(D_{4h})</th>
<th>(D_{4h})</th>
<th>(D_{4h})</th>
<th>(C_{2v})</th>
</tr>
</thead>
<tbody>
<tr>
<td>UB3-LYP/6-31G(d)</td>
<td>23</td>
<td>660.3</td>
<td>650.2</td>
<td>629.6</td>
<td>606.1</td>
</tr>
<tr>
<td>UB3-LYP/6-311+G(2d,p)</td>
<td>51</td>
<td>647.2</td>
<td>639.6</td>
<td>562.4</td>
<td>525.2</td>
</tr>
<tr>
<td>UB3-LYP/6-311+G(3df,2p)</td>
<td>75</td>
<td>647.2</td>
<td>639.8</td>
<td>555.7</td>
<td>517.0</td>
</tr>
<tr>
<td>UMP2(full)/6-31G(d)</td>
<td>23</td>
<td>707.6</td>
<td>694.6</td>
<td>668.6</td>
<td>630.9</td>
</tr>
<tr>
<td>UMP2(full)/6-311+G(2d,p)</td>
<td>51</td>
<td>691.1</td>
<td>689.3</td>
<td>582.4</td>
<td>536.6</td>
</tr>
<tr>
<td>UMP2(full)/6-311+G(3df,2p)</td>
<td>75</td>
<td>689.6</td>
<td>690.7</td>
<td>568.0</td>
<td>522.4</td>
</tr>
<tr>
<td>UCCSD(T)(fc)/AVQZ</td>
<td>264</td>
<td>678.3(^d)</td>
<td>675.3(^c)</td>
<td>573.4</td>
<td>522.3</td>
</tr>
<tr>
<td>MRCI+Q/AV5Z</td>
<td>447</td>
<td>678.8</td>
<td>672.8</td>
<td>573.0</td>
<td>522.1</td>
</tr>
</tbody>
</table>

\(^a\) A UHF reference wavefunction was used for single-determinant calculations on the open-shell systems except as noted in footnote \(d\). \(^b\) Number of basis functions. \(^c\) Calculated at UCCSD(T)(full)/6-311+G(3df,2p) optimized geometries. \(^d\) Calculated with MOLPRO’s URCCSD(T) algorithm. \(^e\) Calculated with GAUSSIAN 98’s UCCSD(T) algorithm.
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The 6-311+G(3df,2p) level performs essentially as well as our best method. We also find that small basis sets do not give an adequate description of the closed-shell singlet (both $D_{4h}$ and $C_{2v}$). The energy of the planar closed-shell singlet drops considerably relative to the ground-state as the basis set size is increased. This is most evident in the progression of the MP2 relative energies given in the final column of Table 4-3, but the same effect is also seen in the B3-LYP calculations. This effect has been noted by Gordon and Schmidt with respect to MCSCF calculations and is also evident in the calculations of Pepper and co-workers. Our calculations indicate that diffuse functions at the central atom are very helpful in obtaining a good estimate of $\Delta E_{PT}$ and that the 6-311+G(2d,p) basis appears to be the smallest basis set which adequately approaches the basis set limit for $\Delta E_{PT}$. We also note that both B3-LYP and MP2 perform quite well for the closed-shell singlet state provided an adequate basis set is used.

The only significant difference between the two methods (UCCSD(T) and MRCI+Q) is found for the value for $\Delta E_{PT}$ of the open-shell singlet state. The UCCSD(T) result is found to lie between the $^1B_{2u}$ and $^3B_{2u}$ MRCI+Q values for $\Delta E_{PT}$, as might well have been expected in such a case where the single-reference wavefunction gives $<S^2> = 1.0$ (i.e. an equal mixture of the open-shell singlet and triplet wavefunctions).

Figure 4-3. The lowest-energy planar methane structure is found to have $C_{2v}$ symmetry. Open-shell $D_{4h}$ structures have downhill in-plane modes that lead to dissociation into CH$_3^+$ + H'. MRCI+Q/AV5Z//UCCSD(T)/6-311+G(3df,2p) energies (in kJ mol$^{-1}$) are relative to the tetrahedral ground-state singlet. Where appropriate, the number of imaginary frequencies ($n_i$) is indicated.
Methane provides some valuable insights into the electronic structure of a general planar-tetracoordinate carbon moiety. Accepting that in a hydrocarbon a hydrogen substituent is a special case, it would appear that even in molecules where all four substituents are identical, it may be necessary to consider geometries in which the four central bonding distances vary. Further, the use of three-membered rings or bonding between substituents may aid in reducing the energy of a planar-tetracoordinate carbon moiety by providing a more favorable interaction at the central carbon.\(^1\) Essentially, distortions from a square geometry are expected to be advantageous to achieving planar-tetracoordinate carbon.

The predicted 522 kJ mol\(^{-1}\) preference for tetrahedral bonding in methane is about 1.2 times the energy required to break the CH\(_3\)-H bond homolytically.\(^6\) Overcoming this huge penalty for distorting the bonding arrangement at a saturated carbon atom is clearly a formidable task and it seems likely that any successful attempt to design a molecule with a planar-tetracoordinate carbon atom will need to protect or enclose the sensitive central bonds to carbon, preventing the highly exothermic homolytic dissociation.

### 4.3.2 Flattening Neopentane and Spiropentane

Our strategy for achieving planar-tetracoordinate carbon through incorporation into a rigid hydrocarbon cage system relies on the ability to constrain the positioning of the four atoms attached to the central carbon atom. In general, this will require a quaternary central carbon because it is only through covalent bonds to the four coordinating atoms that we can restrict the positioning of these atoms (i.e. hydrogen positions cannot be constrained). For this reason we have examined the ‘flattening’ of both neopentane and spiropentane — two of the simplest saturated hydrocarbon systems containing the necessary C(C)\(_4\) central substructure. Information on the performance of our methods and the electronic structure of these species will serve as a guide for calculations on larger systems.

There are four geometries for neopentane that give a plane of symmetry through the five carbon atoms of the central C(C)\(_4\) substructure. These structures have \(D_{2h}\), \(C_{4h}\), \(C_{2v}\) and \(C_s\) symmetry depending on the orientation of the four methyl groups (see Figure 4-\(^1\) For more detail, see the discussion in Section 1.5.1 on page 23.
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We have calculated optimized structures (some geometric parameters are given in Table 4-4) and energies (see Table 4-5) for the closed-shell singlet states relative to the ground-state tetrahedral geometry. Remarkably, we find that all these structures have similar energies (i.e. all lie within 3 kJ mol\(^{-1}\) of one another). It appears that the adverse energetics which result from the different types of H–H close contacts (such as the difference between the six very tight contacts in the \(D_{2h}\) structure versus the eight weaker contacts in the \(C_{4h}\) structure) are balanced by preferential electronic effects (see Table 4-4 for details of the H–H close-contact distances). Alternatively, it may simply be that the energetic consequences of the difference between the various degrees of H–H close contact in the four structures are relatively small and fall within this 3 kJ mol\(^{-1}\) difference.

At our best level of theory, CCSD(T)(fc)/6-311+G(3df,2p)//MP2(full)/6-311+G-(2d,p), we determine the energy difference between the planar and tetrahedral-like structures for closed-shell singlet neopentane to be approximately 880 kJ mol\(^{-1}\) (see Table 4-
Table 4-4. Some geometrical parameters for ‘planar’ neopentane and ‘planar’ spiropentane closed-shell singlet species.\(^a\)

<table>
<thead>
<tr>
<th>method</th>
<th>A ((C_{\text{ib}}))</th>
<th>B ((D_{2\text{h}}))</th>
<th>C ((C_{\text{v}}))</th>
<th>D ((C_{\text{s}}))</th>
<th>(D_{2\text{h}})</th>
</tr>
</thead>
<tbody>
<tr>
<td>B3-LYP/6-31G(d)</td>
<td>(C^0-C^\text{at} = 1.639)</td>
<td>(H^\text{1}-H^\text{0} = 2.053)</td>
<td>(C^0-C^\text{at} = 1.644)</td>
<td>(H^\text{1}-H^\text{0} = 1.978)</td>
<td>(H^\text{1}-H^\text{0} = 1.707)</td>
</tr>
<tr>
<td>B3-LYP/6-311+G(2d,p)</td>
<td>(C^0-C^\text{at} = 1.649)</td>
<td>(H^\text{1}-H^\text{0} = 2.049)</td>
<td>(C^0-C^\text{at} = 1.652)</td>
<td>(H^\text{1}-H^\text{0} = 1.974)</td>
<td>(H^\text{1}-H^\text{0} = 1.703)</td>
</tr>
<tr>
<td>MP2(full)/6-31G(d)</td>
<td>(C^0-C^\text{at} = 1.622)</td>
<td>(H^\text{1}-H^\text{0} = 2.036)</td>
<td>(C^0-C^\text{at} = 1.627)</td>
<td>(H^\text{1}-H^\text{0} = 1.962)</td>
<td>(H^\text{1}-H^\text{0} = 1.692)</td>
</tr>
<tr>
<td>MP2(full)/6-311+G(2d,p)</td>
<td>(C^0-C^\text{at} = 1.637)</td>
<td>(H^\text{1}-H^\text{0} = 2.031)</td>
<td>(C^0-C^\text{at} = 1.640)</td>
<td>(H^\text{1}-H^\text{0} = 1.953)</td>
<td>(H^\text{1}-H^\text{0} = 1.685)</td>
</tr>
</tbody>
</table>

\(^a\) \(C^0\) indicates the central carbon atom. \(H^\text{1}\) indicates an in-plane hydrogen. \(H^\text{0}\) indicates an out-of-plane hydrogen. See Figure 4-4 on page 156 for a graphical representation of the structures.

5). This is about 2.6 times the tert-C<sub>4</sub>H<sub>9</sub>-CH<sub>3</sub> bond dissociation energy,\(^6\) and clearly rules out the existence of any neutral acyclic saturated hydrocarbon containing a planar carbon, however fleetingly.

The situation for flattening spiropentane appears to be quite different to that of neo-
pentane. Our best estimate indicates that the $\Delta E_{PT}$ is less than 440 kJ mol$^{-1}$, which is half the size of $\Delta E_{PT}$ for neopentane. Incorporation of the central carbon atom into a pair of three-membered rings has reduced $\Delta E_{PT}$ by more than 80 kJ mol$^{-1}$ compared with methane and by more than 440 kJ mol$^{-1}$ compared with neopentane. However, $\Delta E_{PT}$ for spiropentane is still 1.9 times the expected bond strength for the weakest bond in the tetrahedral-like spiropentane (the central C–C bonds are expected to have a dissociation energy$^{37}$ less than 230 kJ mol$^{-1}$).

Once again, we have repeated our calculations over a range of levels in order to assess the accuracy of the lower level methods to which we will be restricted when examining larger molecules (see Table 4-5). Of particular note, we find that the MP2/6-31G(d) level predicts much better values for $\Delta E_{PT}$ for spiropentane and neopentane than

### Table 4-5. Energies, $\Delta E_{PT}$ (kJ mol$^{-1}$), for ‘planar’ neopentane and ‘planar’ spiropentane closed-shell singlet species relative to their respective tetrahedral-like ground states.

<table>
<thead>
<tr>
<th>method</th>
<th>'planar' neopentane$^a$</th>
<th>'planar' spiropentane$^b$</th>
</tr>
</thead>
<tbody>
<tr>
<td>A ($C_{4v}$)</td>
<td>B ($D_{2h}$)</td>
<td>C ($C_{2v}$)</td>
</tr>
<tr>
<td>B3-LYP/6-31G(d)</td>
<td>881.7</td>
<td>878.9</td>
</tr>
<tr>
<td>B3-LYP/6-311+G(2d,p)</td>
<td>858.1</td>
<td>858.8</td>
</tr>
<tr>
<td>B3-LYP/6-311+G(3df,2p)</td>
<td>854.7</td>
<td>855.9</td>
</tr>
<tr>
<td>MP2(full)/6-31G(d)$^c$</td>
<td>927.4</td>
<td>930.2</td>
</tr>
<tr>
<td>MP2(full)/6-311+G(2d,p)(red)$^{cd}$</td>
<td>888.5</td>
<td>892.3</td>
</tr>
<tr>
<td>MP2(full)/6-311+G(2d,p)$^d$</td>
<td>869.8</td>
<td>872.5</td>
</tr>
<tr>
<td>MP2(full)/6-311+G(3df,2p)$^c$</td>
<td>866.9</td>
<td>869.2</td>
</tr>
<tr>
<td>CCSD(T)(fc)/6-311+G(2d,p)$^e$</td>
<td>879.8</td>
<td>883.0</td>
</tr>
<tr>
<td>CCSD(T)(fc)/6-311+G(3df,2p)$^f$</td>
<td>880.1</td>
<td>882.7</td>
</tr>
<tr>
<td>CCSD(T)(fc)/AVTZ$^g$</td>
<td>–</td>
<td>–</td>
</tr>
</tbody>
</table>

$^a$ Neopentane energies are calculated relative to the $T_d$ closed-shell singlet state ($^1A_1$).

$^b$ Spiropentane energies are calculated relative to the $D_{2d}$ closed-shell singlet state ($^1A_1$).

$^c$ Calculated at the MP2(full)/6-31G(d) optimized geometries.

$^d$ Our reduced 6-311+G(2d,p)(red) basis set is detailed in Section 4.2 on page 145.

$^e$ Calculated at MP2(full)/6-311+G(2d,p) optimized geometries.

$^f$ Calculated at MP2(full)/6-311+G(3df,2p) optimized geometries.
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159 was the case with methane; at worst, $\Delta E_{\text{pt}}$ values are over-estimated by 50 kJ mol$^{-1}$. MP2/6-311+G(2d,p) gives consistently low values (compared with our best estimates) for the energy required to flatten the bonding to the central carbon atom, but the underestimation at both this level and MP2/6-311+G(2d,p)(red)$^{38}$ is less than 10 kJ mol$^{-1}$. B3-LYP calculations all under-estimate $\Delta E_{\text{pt}}$. For large basis sets this error becomes quite significant (up to 25 kJ mol$^{-1}$).

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

A simple examination of the problem at hand leads us to stipulate the following design parameters. Firstly, we desire a saturated hydrocarbon. This should remove any ambiguity as to the coordination of the planar-tetracoordinate carbon atom. Secondly, we only want a single planar-tetracoordinate carbon atom. All other carbons should have, as far as possible, tetrahedral-like bonding. Considering the energy required to flatten just a single carbon atom, this is the only approach that is likely to lead to viable molecules. Finally, we desire a structure that has an identical bonding arrangement both above and below the plane of the central C(C)$_4$ substructure, a necessary requirement for exact planarity at the central carbon atom. Clearly, the only way to achieve planar-tetra-coordination in a saturated hydrocarbon is to build a cage system. But any design without an implicit plane of symmetry which coincides with the central C(C)$_4$ substructure can only hope to achieve near or coincidental planarity. With these design parameters in mind we set about designing novel saturated hydrocarbon cage systems that might afford planar-tetracoordinate carbon.

### 4.3.3 Alkaplane Structures

Our first attempt at designing a saturated hydrocarbon with a planar-tetracoordinate carbon involves molecules which are built up by bicapping planar C$_5$H$_4$ (a neopen-tane subunit) with identical cyclic hydrocarbon caps both above and below the plane, resulting in a family of molecules that we have labelled the alkaplanes (4-VI). Initial work on these molecules by McGrath and Radom$^{24}$ in which they obtained HF/6-31G(d) structures and HF/3-21G frequencies showed great promise. Unlike previous attempts, this design has the advantage that the environment around the central carbon
atom is such that a plane of symmetry through the central C(C)4 subunit is possible without requiring multiple planar-tetracoordinate carbon atoms (cf. [4.4.4.4]fenestrane (4-18)). We examined structures for molecules designed using the following cyclic hydrocarbon caps: bicyclo[3.3.1]nonane (bicyclo-C9H12), cyclooctane (cyclo-C8H12), bicyclo[3.3.0]octane (bicyclo-C7H8), bicyclo[2.2.1]heptane or norbornane (bicyclo-C7H8), cyclohexane (cyclo-C6H8), and bicyclo[2.2.0]hexane (bicyclo-C6H6). Each pair of caps was combined with a neopentane subunit corresponding to one of the three neo-pentane structures, A (C4h), B (D2h), or C (C2v), of Figure 4-4 on page 156. The resulting structures were examined initially using the AM1 method for local minima. The molecules identified by this process as worthy of further examination, named bihexaplane (4-30), hexaplane (4-31), biheptaplane (4-32), heptaplane (4-33), bioctaplane (4-34), octaplane (4-27 and 4-35) and binonaplane (4-36), were re-optimized at the HF/6-31G(d), B3-LYP/6-31G(d) and, in the case of 4-27, 4-31 and 4-33, at the MP2/ 6-311+G(2d,p)(red)38 levels. General structural features of these molecules are listed in Table 4-6 on page 161. The symmetry of the equilibrium structure, the degree of distortion from planarity at C0, and the barrier to inversion at C0 are listed in Table 4-7 on page 163. More complete structural information (all bond lengths and selected bond angles) for hexaplane (4-31), heptaplane (4-33) and the S4 symmetry isomer of octaplane (4-27) are given in Figure 4-5 on page 165.

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

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1 Note that, as with the hemispiroalkaplanes (see Section 3.3.2 on page 104), structural isomers result from changing the orientation of the cap relative to the central moiety, where either the cap or the central moiety do not have four-fold symmetry. Where necessary we have chosen the isomer that gave the least strained structure.
below) that were guaranteed to give an exactly planar-tetracoordinate central carbon atom. Alkaplanes constructed from neopentane subunits based on the neopentane structures \( A \), \( B \) or \( C \) (which we refer to as \( A \)-, \( B \)- and \( C \)-type templates) were thus constrained to \( C_{4h} \), \( D_{2h} \) or \( C_{2v} \) symmetry, respectively. In almost all cases we find that these

<table>
<thead>
<tr>
<th>Molecule</th>
<th>Sym.</th>
<th>Cap Formula</th>
<th>Cap Structure</th>
<th>( C_nH_4 ) Subunit</th>
<th>Molecular Formula</th>
</tr>
</thead>
<tbody>
<tr>
<td>bihexaplane</td>
<td>( D_2 )</td>
<td>( bicyclo-C_6H_6 )</td>
<td>![diagram]</td>
<td></td>
<td>( C_{16}H_{16} )</td>
</tr>
<tr>
<td>hexaplane</td>
<td>( D_2 )</td>
<td>( cyclo-C_6H_8 )</td>
<td>![diagram]</td>
<td></td>
<td>( C_{15}H_{20} )</td>
</tr>
<tr>
<td>biheptaplane</td>
<td>( D_2 )</td>
<td>( bicyclo-C_7H_8 )</td>
<td>![diagram]</td>
<td></td>
<td>( C_{19}H_{20} )</td>
</tr>
<tr>
<td>heptaplane</td>
<td>( C_2 )</td>
<td>( cyclo-C_7H_{10} )</td>
<td>![diagram]</td>
<td></td>
<td>( C_{19}H_{24} )</td>
</tr>
<tr>
<td>bioctaplane</td>
<td>( D_2 )</td>
<td>( cyclo-C_8H_{10} )</td>
<td>![diagram]</td>
<td></td>
<td>( C_{21}H_{24} )</td>
</tr>
<tr>
<td>octaplane (A-type)</td>
<td>( S_4 )</td>
<td>( cyclo-C_8H_{12} )</td>
<td>![diagram]</td>
<td></td>
<td>( C_{21}H_{28} )</td>
</tr>
<tr>
<td>octaplane (B-type)</td>
<td>( D_2 )</td>
<td>( cyclo-C_8H_{12} )</td>
<td>![diagram]</td>
<td></td>
<td>( C_{21}H_{28} )</td>
</tr>
<tr>
<td>binonaplane</td>
<td>( D_2 )</td>
<td>( bicyclo-C_9H_{12} )</td>
<td>![diagram]</td>
<td></td>
<td>( C_{23}H_{28} )</td>
</tr>
</tbody>
</table>

\( a \) The symmetry of the equilibrium structure. \( b \) The carbon atoms with unfilled valences, which form C–C bonds to the planar unit, are marked \( \bullet \). The caps and planar units are bound in the orientation given.
structures are second-order saddle points (see Table 4-7 on page 163). The only exception is the MP2/6-311+G(2d,p)(red) force constant analysis for 4-31. At this level of theory, the $D_{2h}$ symmetry structure for 4-31 is found to be a first-order saddle point (and the transition structure for inversion at C0). Equilibrium geometries for the alkaplanes 4-27 and 4-30 – 4-36 result from a small distortion toward a tetrahedral-like arrangement of bonds at the central carbon atom (C0), giving structures with $S_4$, $D_2$ and $C_2$ symmetry from molecules built on A-, B- and C-type neopentane subunits, respectively. We have determined $\alpha_{\text{plan}}$ values (an average of the distortions of each of the four C atoms from the best-fit plane) as a measure of the degree of distortion from planarity at the central quaternary carbon atom (C0).† These values are listed in Table 4-7.

The alkaplanes with the most flattened central quaternary carbon atom are hexaplane (4-31), biheptaplane (4-32), heptaplane (4-33) and the $S_4$ symmetry isomer of octaplane (4-27), all of which have $\alpha_{\text{plan}}$ values of about 5°. Calculated values for $\alpha_{\text{plan}}$ vary between the methods we have used by at most 0.8°. The alkaplanes with the largest deviations from planar-tetracoordination at the central carbon atom are bioctaplane (4-34) and binonaplane (4-36) which have $\alpha_{\text{plan}}$ values around 8 or 9°. The other two alkaplanes we examined, bihexaplane (4-30) and the $D_2$ symmetry isomer of octaplane (4-35) fall in between with $\alpha_{\text{plan}}$ values of around 6°.

As a family of structures, the alkaplanes (4-VI) exhibit an impressive degree of flattening at a quaternary carbon atom ($\alpha_{\text{plan}} = 5–9°$). Although the distortion from planarity at C0 is clearly non-negligible, the only saturated hydrocarbon previously predicted to show this degree of flattening at a tetracoordinate carbon atom is the all-trans isomer of [5.5.5.5]-fenestrane (all-trans-4-19) ($\alpha_{\text{plan}}[\text{MP2/6-31G(d)}] = 7.9°$). The three hemi-alkaplanes, hemibioctaplane (4-37), hemioctaplane (4-24) and hemibinonaplane (4-38),

† For a more complete descriptions of $\alpha_{\text{plan}}$ see Section 4.2 on page 145 and Appendix B.
Table 4-7. Structural information, the angle of deviation from planarity, $\alpha_{\text{plan}}$ (°), and the inversion barrier at $C^0$, $\Delta E_{\text{plan}}$ (kJ mol$^{-1}$), for the alkaplanes.

<table>
<thead>
<tr>
<th>Molecule</th>
<th>Sym.</th>
<th>$n_i$</th>
<th>$\alpha_{\text{plan}}$</th>
<th>$\Delta E_{\text{plan}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>bihexaplane</td>
<td>4-30</td>
<td>$D_2$</td>
<td>6.2°</td>
<td>(63.3) 78.7</td>
</tr>
<tr>
<td>hexaplane</td>
<td>4-31</td>
<td>$D_2$</td>
<td>4.5°</td>
<td>41.5</td>
</tr>
<tr>
<td>biheptaplane</td>
<td>4-32</td>
<td>$D_2$</td>
<td>5.0°</td>
<td>(34.8) 55.9</td>
</tr>
<tr>
<td>heptaplane</td>
<td>4-33</td>
<td>$C_2$</td>
<td>5.0°</td>
<td>67.7</td>
</tr>
<tr>
<td>bioctaplane</td>
<td>4-34</td>
<td>$D_2$</td>
<td>8.4°</td>
<td>(135.5) 137.5</td>
</tr>
<tr>
<td>octaplane (A-type)</td>
<td>4-27</td>
<td>$S_4$</td>
<td>5.1°</td>
<td>58.6</td>
</tr>
<tr>
<td>octaplane (B-type)</td>
<td>4-35</td>
<td>$D_2$</td>
<td>6.3°</td>
<td>(59.7) 76.6</td>
</tr>
<tr>
<td>binonaplane</td>
<td>4-36</td>
<td>$D_2$</td>
<td>7.5°</td>
<td>(98.1) 102.1</td>
</tr>
</tbody>
</table>

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

However, the fact that all alkaplanes built on a \textbf{B}-type neopentane subunit (\textit{4-30, 4-31, 4-32, 4-34, 4-35 and 4-36}) give two imaginary frequencies when optimized in $D_{2h}$ symmetry (see Table 4-6 on page 161), indicates that inversion for these molecules does not proceed via this highly symmetric structure. A closer examination of the imaginary frequencies reveals that in all cases one corresponds to an in-plane vibrational mode and the other to an out-of-plane mode. The out-of-plane, downhill mode leads to the $D_2$ symmetry equilibrium structure but the in-plane, downhill mode, in all cases, leads to a much lower-energy $C_s$ symmetry equilibrium structure in which one of the C–C\textsubscript{α} bonds is lengthened beyond 2.0 Å. This suggests that homolytic cleavage of one of the C–C\textsubscript{α} bonds will result. The correct transition structure for inversion at C\textsubscript{0} is expected to have either $C_1$ or $C_2$ symmetry and the barrier to inversion will necessarily be less than $\Delta E_{\text{plan}}$, the difference in energy between the $D_2$ symmetry equilibrium structure and the $D_{2h}$ structure, also referred to as the ‘planar’ structure (for $\Delta E_{\text{plan}}$ values see Table 4-7 on page 163). The true barrier to inversion must be lower than $\Delta E_{\text{plan}}$ for these alkaplanes because the $D_{2h}$ symmetry structure is a second-order saddle point in which one of the downhill modes corresponds to the inversion mode. However, the presence of the sec-

\textsuperscript{†} B3-LYP and MP2 optimized values for $\alpha_{\text{plan}}$ usually vary by a few tenths of a degree. For examples see Table 4-7 on page 163.

\textsuperscript{‡} This is purely a formal argument. As discussed later, instability may of course arise from other exit channels which lead to stable isomers/decomposition products of lower symmetry.
Results and Discussion

•

Second downhill mode in the $D_{2h}$ symmetry structure suggests that inversion may not be observed because of competition from a highly exothermic and irreversible channel that leads to bond cleavage. The barrier to this decomposition pathway is also expected to be lower than the $\Delta E_{\text{plan}}$ values quoted in Table 4-7 on page 163.

We have examined two structures which are not based on a B-type neopentane subunit, heptaplane (4-33) and the A-type octaplane (4-27). The ‘planar’ structures for both 4-27 and 4-33 have only a single imaginary frequency. This frequency corresponds to the vibrational mode connecting the two identical equilibrium structures. The $C_{4h}$ ($C_{2v}$) structure for 4-27 (4-33) is the transition structure for inversion at $C^0$. This suggests that, for these molecules, the transition structure leading to $C^0$–C$\alpha$ cleavage is higher-

**Figure 4-5.** Structural parameters (MP2/6-311+G(2d,p)(red)$^{38}$ values in bold type, B3-LYP/6-31G(d) values in plain text) for hexaplane (4-31), heptaplane (4-33), and $S_4$ symmetry octaplane (4-27). All unique bond lengths and H–H close contacts (Å) are shown. The most highly distorted CCC angles and the distortion from planarity, $\alpha_{\text{plan}}$, (°) are also given.
lying than in the B-type alkaplanes (4-30, 4-31, 4-32, 4-34, 4-35 and 4-36). Although we have not explicitly searched for possible rearrangement or decomposition pathways, it is likely that 4-27 and 4-33 will have greater kinetic stability than the B-type alkaplanes.

A closer examination of the structures of hexaplane (4-31), heptaplane (4-33) and the $S_4$ symmetry octaplane (4-27) (Figure 4-5) reveals that the distortion at the central carbon atom is largely the result of alternation of bond lengths between pairs of $C^\alpha-C^\beta$ bonds, although some twisting of the cage is also evident. The MP2 optimized values for these bond pairs are 1.61/1.52 for hexaplane (4-31), 1.73/1.55 and 1.54/1.49 for heptaplane (4-33), and 1.60/1.51 for $S_4$ octaplane (4-27) (see Table 4-8 on page 167 for details and a comparison with B3-LYP/6-31G(d) values). We also note that the cyclohexane caps of hexaplane have considerable bond length strain as the MP2 calculated bond lengths of four of the C–C bonds have increased to 1.60 Å from 1.53 Å in the boat conformer of cyclohexane. The bond lengths of the C–C bonds in the heptaplane caps are all only slightly higher than the standard length of 1.54 Å, indicating little bond-length strain in the caps. However, the stability of heptaplane is likely to be affected adversely by the very long $C^\alpha-C^\beta$ bond ($r(C^\alpha-C^\beta) = 1.73$ Å at MP2/6-311+G(2d,p)(red)). The accompanying $C^\beta C^\alpha C^\beta$ angle of 158.4°, and the very short H–H distance of 1.77 Å also indicate that there is considerable strain associated with this region of the molecule (as well as with the central carbon atom). The $S_4$ symmetry octaplane structure (4-27) shows some bond lengthening in the cyclooctane cap (MP2 calculated C–C bonds lengths are in the range 1.54–1.58 Å) over the MP2 calculated bond lengths of crown cyclooctane (1.53 Å). Of all the alkaplanes we examined, 4-27 has the smallest $C^\beta C^\alpha C^\beta$ angle (146.4° at MP2/6-311+G(2d,p)(red)) and, because of the orientation of the central methine (CH) groups, no H–H close contacts.

Octaplane (4-27) appears to be the best candidate for attempts at synthesis, of all the parent alkaplanes (4-VI) we have examined. However, the large degree of angle strain present at the relatively exposed C$^\alpha$ atoms suggests that these centers will need to be protected. The orientation of the C$^\alpha$ hydrogens in octaplane is well placed to allow substitution, and methylation at these positions may prove advantageous. A brief examination of possible alkyl protecting groups using the AM1 method indicated that tert-butyl groups will be too bulky but methyl groups fit well and form a complete protec-
Table 4-8. Selected structural parameters, $r(C^\alpha-C^\beta)$ (Å) and $\angle C^\beta C^\alpha C^\beta$ (°), for the alkaplanes.

<table>
<thead>
<tr>
<th>Molecule</th>
<th>Sym. $^a$</th>
<th>$r(C^\alpha-C^\beta)^b$</th>
<th>$\angle C^\beta C^\alpha C^\beta$</th>
</tr>
</thead>
<tbody>
<tr>
<td>bihexaplane</td>
<td>4-30</td>
<td>$D_2$</td>
<td>1.599/1.505 142.9°</td>
</tr>
<tr>
<td>hexaplane</td>
<td>4-31</td>
<td>$D_2$</td>
<td>1.609/1.519 148.5°</td>
</tr>
<tr>
<td>biheptaplane</td>
<td>4-32</td>
<td>$D_2$</td>
<td>1.616/1.520 153.9°</td>
</tr>
<tr>
<td>heptaplane$^c$</td>
<td>4-33</td>
<td>$C_2$</td>
<td>1.536/1.488 1.734/1.551 134.9° 158.4°</td>
</tr>
<tr>
<td>biocaplane</td>
<td>4-34</td>
<td>$D_2$</td>
<td>1.636/1.527 153.0°</td>
</tr>
<tr>
<td>octaplane (A-type)</td>
<td>4-27</td>
<td>$S_4$</td>
<td>1.604/1.512 146.4°</td>
</tr>
<tr>
<td>octaplane (B-type)</td>
<td>4-35</td>
<td>$D_2$</td>
<td>1.618/1.520 153.9°</td>
</tr>
<tr>
<td>binonaplane</td>
<td>4-36</td>
<td>$D_2$</td>
<td>1.627/1.513 150.3°</td>
</tr>
</tbody>
</table>

$^a$ The symmetry of the equilibrium structure. $^b$ Values given are calculated at MP2/6-311+G(2d,p)(red) (bold text) and B3-LYP/6-31G(d) (plain text) optimized geometries. $^c$ Lower symmetry in this $C_2$ structure results in two long/short $C^\alpha-C^\beta$ bond pairs and two $C^\beta-C^\alpha-C^\beta$ angles.

tive ring about the $C^\alpha$ carbons.

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

As might be expected, the size of $\Delta E_{\text{plan}}$ correlates fairly well with values for $\alpha_{\text{plan}}$.

The alkaplanes, 4-27, 4-30 – 4-33 and 4-35, which have $\alpha_{\text{plan}}$ values in the range 5–6°, require the least work to achieve planarity ($\Delta E_{\text{plan}} = 35–80$ kJ mol$^{-1}$), while the alkaplanes, 4-34 and 4-36, which exhibit the least flattening ($\alpha_{\text{plan}} \geq 7°$), have the largest values for $\Delta E_{\text{plan}}$ (100–140 kJ mol$^{-1}$).

The values for $\Delta E_{\text{plan}}$ for the alkaplanes are remarkably small (ca. 35–140 kJ mol$^{-1}$)
when compared with the barrier for inversion at the central carbon atom in neopentane (\(ca. 880 \text{ kJ mol}^{-1}\)) (see Section 4.3.2 on page 155). Clearly, the alkaplanes (4-VI) are a family of molecules that show remarkable flattening of the central tetracoordinate carbon atom (having overcome most of the 880 kJ mol\(^{-1}\) preference for tetrahedral bonding), achieved through purely structural means. However, our survey of many possible capping subunits suggests that such modifications alone will not lead to planar-tetracoordinate carbon and that further reduction of the degree of distortion at the central C(CH)\(_4\) subunit will probably require modification to the central C\(_5\) moiety. It seems likely that steric effects resulting from attempts to force four carbon atoms not bonded to each other into a plane\(^\dagger\) are such that they contribute strongly to the preferential, alternate lengthening and compression of the C\(^\alpha\)–C\(^\beta\) bond pairs, which results in distortion from planar-tetracoordination at C\(^0\) despite the overall rigidity of the cage structure. One way to overcome this problem is to replace the four central methine (C\(^{\alpha\prime}\)H) groups with two C–C bonded pairs, i.e. to form bonds between adjacent pairs of C\(^\alpha\) atoms. This leads to the spiroalkaplanes (4-VII), which are discussed in the next section.

4.3.4 Spiroalkaplane Structures

The spiro[2.2]alkaplanes (4-VII) are constructed in a similar fashion to the alkaplanes (4-VI), by bicapping a planar C(C)\(_4\) subunit with cyclic hydrocarbons from both above and below the plane. In the case of the spiroalkaplanes, the planar neopentane subunit used in the alkaplanes is replaced with a spiropentane subunit (C\(^0\)(C\(^{\alpha\prime}\))\(_4\)). This effectively replaces the four in-plane methine groups (CH) with two pair of bonded quaternary carbon atoms. By bonding adjacent pairs of C\(^\alpha\) atoms, a large degree of the repulsive non-bonding interaction is removed and we expect the in-plane crowding to be significantly relieved; the target, planar-tetracoordinate carbon atom has been incorporated into a pair of three-membered rings, a characteristic which is present in all planar-tetracoordinate carbon containing species synthesized to date (see Section 1.5.1 on page 23). Further, like the alkaplanes, the spiroalkaplanes are designed in a manner that allows (but does not require) a plane of symmetry through the central C(C)\(_4\) moiety.

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

\(^\dagger\) For a discussion of these effects see Section 1.5.1 on page 23.
Bicyclo[3.3.1]nonane (bicyclo-C₉H₁₂), cyclooctane (cyclo-C₈H₁₂), bicyclo[3.3.0]octane (bicyclo-C₈H₁₀), bicyclo[2.2.1]heptane or norbornane (bicyclo-C₇H₈), and cyclohexane (cyclo-C₆H₈) were used in identical pairs as capping hydrocarbons in an initial search, performed using the AM1 method, designed to locate promising spiroalkaplane structures. Seven spiro[2.2]alkaplanes were identified as worthy of further investigation† and structures for these molecules, spiro[2.2]hexaplane (4-39), spiro[2.2]biheptaplane (4-40), two spiro[2.2]heptaplane isomers (4-41 and 4-42), spiro[2.2]bioctaplane (4-43), spiro[2.2]octaplane (4-28) and spiro[2.2]binonaplane (4-44), were determined by optimization at the B3-LYP/6-31G(d) and MP2/6-311+G(2d,p)(red) levels. General structural features of the seven spiroalkaplanes listed above are given in Table 4-9 on page 170. The symmetry of the equilibrium structure, the degree of distortion from planarity at C⁰, the number of imaginary frequencies for the structure constrained to have a

† Again we note that, as with the hemispiroalkaplanes (see Section 3.3.2 on page 104), spiroalkaplane structural isomers result from changing the orientation of the cap relative to the central moiety, where the cap does not have four-fold symmetry. Where appropriate we have chosen the isomer that gave the least strained structure, except for spiroheptaplane (4-41 and 4-42) for which we have examined both isomers.
planar-tetracoordinate carbon atom, and the barrier to inversion at \( C^0 \) (\( \Delta E_{\text{plan}} \)) are also included in Table 4-9. More complete structural information (all bond lengths and

<table>
<thead>
<tr>
<th>Molecule</th>
<th>Sym.</th>
<th>Cap</th>
<th>Cap Structure</th>
<th>Molecular Formula</th>
<th>nf</th>
<th>( \alpha_{\text{plan}} ) (°)</th>
<th>( \Delta E_{\text{plan}} ) (kJ mol(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>spiro[2.2]hexaplane</td>
<td>4-39</td>
<td>( D_2 ) cyclo-</td>
<td>( C_6H_8 )</td>
<td>( C_{17}H_{16} )</td>
<td>1</td>
<td>3.8°</td>
<td>9.0</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>4.1°</td>
<td>18.9</td>
</tr>
<tr>
<td>spiro[2.2]biheptaplane</td>
<td>4-40</td>
<td>( D_2 ) bicyclo-</td>
<td>( C_7H_8 )</td>
<td>( C_{19}H_{16} )</td>
<td>1</td>
<td>3.5°</td>
<td>4.7</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>3.8°</td>
<td>16.1</td>
</tr>
<tr>
<td>spiro[2.2]heptaplane</td>
<td>4-41</td>
<td>( C_2 ) cyclo-</td>
<td>( C_7H_{10} )</td>
<td>( C_{19}H_{20} )</td>
<td>1</td>
<td>3.6°</td>
<td>12.0</td>
</tr>
<tr>
<td></td>
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<td></td>
<td></td>
<td></td>
<td>3.9°</td>
<td>18.9</td>
</tr>
<tr>
<td>spiro[2.2]heptaplane</td>
<td>4-42</td>
<td>( C_2 ) cyclo-</td>
<td>( C_7H_{10} )</td>
<td>( C_{19}H_{20} )</td>
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<td>3.0°</td>
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<td>3.3°</td>
<td>18.7</td>
</tr>
<tr>
<td>spiro[2.2]bioctaplane</td>
<td>4-43</td>
<td>( D_2 ) bicyclo-</td>
<td>( C_8H_{10} )</td>
<td>( C_{21}H_{20} )</td>
<td>1</td>
<td>3.4°</td>
<td>12.9</td>
</tr>
<tr>
<td></td>
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<td></td>
<td></td>
<td></td>
<td>3.7°</td>
<td>21.7</td>
</tr>
<tr>
<td>spiro[2.2]octaplane</td>
<td>4-28</td>
<td>( D_2 ) cyclo-</td>
<td>( C_8H_{12} )</td>
<td>( C_{21}H_{24} )</td>
<td>1</td>
<td>3.1°</td>
<td>7.4</td>
</tr>
<tr>
<td></td>
<td></td>
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<td></td>
<td></td>
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<td>3.5°</td>
<td>15.0</td>
</tr>
<tr>
<td>spiro[2.2]binonaplane</td>
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<td>( C_{12}H_{12} )</td>
<td>( C_{23}H_{24} )</td>
<td>1</td>
<td>2.7°</td>
<td>4.4</td>
</tr>
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<td></td>
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<td></td>
<td></td>
<td></td>
<td></td>
<td>3.2°</td>
<td>11.7</td>
</tr>
</tbody>
</table>

\( ^a \) The symmetry of the equilibrium structure. \( ^b \) In all cases the central \( C(C)_4 \) subunit is a spiropentane subunit in the following orientation \( \mathcal{C} \). The carbon atoms with an unfilled valence, which form C–C bonds to the central \( C(C)_4 \) subunit, are marked \( \bullet \). \( ^c \) The number of imaginary vibrational frequencies for the structure constrained to contain a planar tetracoordinate carbon atom calculated at the B3-LYP/6-31G(d) level. \( ^d \) Calculated at MP2/6-311+G(2d,p)(red) (bold text) and B3-LYP/6-31G(d) (plain text) optimized geometries. \( ^e \) Calculated at the MP2/6-311+G(2d,p)/MP2/6-311+G(2d,p)(red) (bold text) and B3-LYP/6-311+G(2d,p)//B3-LYP/6-31G(d) levels (plain text).
selected bond angles) for spirohexaplane (4-39), spiroheptaplane (4-40), and the two spiroheptaplane isomers (4-41 and 4-42) are given in Figure 4-6 on page 174, and for spirobiocaplane (4-43), spirooctaplane (4-28) and spirobinonaplane (4-44) are given in Figure 4-7 on page 175.

Initially, we examined structures for the spiroalkaplanes in which the bonding at the central, quaternary carbon atom was constrained to be exactly planar-tetracoordinate. For spiroalkaplanes 4-39, 4-40, 4-43 and 4-44, these ‘planar’ structures had $D_{2h}$ symmetry, while for spiroalkaplanes 4-41 and 4-42 the ‘planar’ structures had $C_{2v}$ symmetry. In all cases, analysis of the analytic force constant matrix indicated that these ‘planar’ structures are transition structures, with a single imaginary frequency, and that the mode corresponding to this imaginary frequency leads to a distortion in the direction of tetrahedral-like bonding at $C_0$. This distortion leads to $D_2$ symmetry equilibrium structures for 4-39, 4-40, 4-43 and 4-44 (see Figure 4-6), and to $C_2$ symmetry equilibrium structures for the spiroheptaplane isomers, 4-41 and 4-42 (see Figure 4-7). Thus, the ‘planar’ structures are the transition structures for inversion at $C_0$, a process which connects a pair of identical equilibrium structures. This suggests that the spiro[2.2]-alkaplanes (4-VII) will be less susceptible than the alkaplanes (4-VI) (especially the $D_2$ symmetry alkaplanes) to potential kinetic instability from ring opening at the central carbon atom.

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

\textsuperscript{†} We note that our measure of planarity can be somewhat misleading in certain low symmetry molecules because it is an average of four angles. For example, the pyramidal tetracoordinate structure of 4-26, which has $C_1$ symmetry, results in a best-fit plane where three of the atoms coordinated to the apical carbon atom lie above the plane and one below the plane, with angles to this best-fit plane of 2.0$^\circ$, 14.5$^\circ$, 16.7$^\circ$ and 19.7$^\circ$ giving an average value of 13.2$^\circ$. 
also considerably more flattened than the most flattened \([k.l.m.n]\text{fenestrane synthesized to date, an all-}\text{cis-}[4.4.4.5]\text{fenestrane derivative (4-17), which we have determined to have }\alpha_{\text{plan}} = 24.3^\circ \text{ (MP2/6-31G(d) optimized geometry). In fact, our measure for planarity suggests that spiropentane itself exhibits some flattening at the central carbon atom (}\alpha_{\text{plan}} = 21.4^\circ). This is entirely consistent with what is observed. In the fenestrane derivative 4-17\text{ the opposite CCC angles} are 128.3^\circ \text{ and 129.2}^\circ \text{ (see Section 1.5.2 on page 24), while in spiropentane the opposite CCC angles are both 137.2}^\circ. \text{ These opposite CCC angles are 109.5}^\circ \text{ in an ideal tetrahedral structure and 180.0}^\circ \text{ for planar-tetra-}

\[\text{coordinate. Clearly, spiropentane should be considered more flattened than 4-17. We also note that, 4-25-ketene, 4-26, 4-45 and 4-46, although considerably bent from the parent spiropentane structure, exhibit only slightly greater flattening at the central carbon atom over spiropentane (for a more detailed discussion of bending, which leads to pyramidal carbon, versus twisting, which leads to planar carbon, in these bridged spiropentanes, see Section 1.5.5 on page 35). Much of the considerable strain in spiropentane arises from angle strain, and some of this angle strain can be thought of as contributing to flattening at the central carbon atom.}

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

Further examination of the structures of the spiroalkaplanes reveals a number of interesting features. Firstly, there are no extraordinarily long C–C bonds.\text{\footnote{For a clearer indication of which angle is referred to here, see the fenestrane discussion in Section 4.1.}} The longest

\[\text{\footnote{\text{C–C bonds as long as 1.60 \AA\ in strained saturated hydrocarbons have been observed. The most distorted fenestrane synthesized to date, the [4.4.4.5]fenestrane derivative 4-17, has internal bonds to the central carbon atom which are about 1.50 \AA\ while some peripheral bonds are as long as 1.60 \AA.}}\text{ Bonds longer than this in hydrocarbon compounds have been observed but are rare and are usually found only in unsaturated systems.}}\]
C–C bonds are found in the smallest spiroalkaplanes (4-39–4-42) (see Figure 4-6). Both 4-39 and 4-40 have six-membered primary-ring caps\(^1\) and each of these molecules has a C\(^\alpha\)–C\(^\beta\) bond of 1.64 Å and a C\(^\beta\)–C\(^\beta\) bond of 1.62 Å.\(^2\) The spiroheptaplane isomer 4-41 has an unusually long C\(^\beta\)–C\(^\beta\) bond in the seven-membered ring caps of 1.65 Å and a C\(^\alpha\)–C\(^\beta\) bond of 1.61 Å. The other spiroheptaplane isomer (4-42) also has an elongated C\(^\beta\)–C\(^\beta\) bond of 1.60 Å. In the larger-ring spiroalkaplanes 4-28, 4-43 and 4-44, all the C–C bonds are less than 1.60 Å. As a consequence, there are no obvious sources of kinetic instability in these molecules, due to overlong C–C bonds. We also note that in all the spiroalkaplanes examined, the C\(^0\)–C\(^\alpha\) bonds vary in length from 1.45 to 1.51 Å, and are thus generally similar in length to, or slightly shorter than, the equivalent bonds in spiropentane (1.47 Å).

One structural aspect that is of particular interest is the origin of the distortion from planar-tetracoordination at C\(^0\). When examining the alkaplanes (4-VI) (see Section 4.3.3), it was seen that a large proportion of the distortion of the C\(^\alpha\) atoms from the plane is a consequence of the alternate lengthening and compression of pairs of C\(^\alpha\)–C\(^\beta\) bonds.\(^3\) This bond alternation must be overcome if true planar-tetracoordination is to be achieved. The central spiropentane subunit of the spiroalkaplanes does appear to reduce this effect. However, the alternate lengthening and compression is still evident (see Table 4-10 on page 176 for details). Pairs of C\(^\alpha\)–C\(^\beta\) bond lengths for spirohexaplane (4-39) (1.64/1.53 Å), spirobiheptaplane (4-40) (1.64/1.53 Å), the spiroheptaplane isomer 4-41 (1.58/1.53 and 1.61/1.52 Å), the spiroheptaplane isomer 4-42 (1.58/1.52 and 1.58/1.52 Å), spirobiocaplane (4-43) (1.56/1.50 Å), spirooctaplane (4-28) (1.55/1.50), and spirobinaoctaplane (4-44) (1.55/1.50) differ by at most 0.11 Å in the case of the small spiroalkaplanes 4-39 and 4-40, and by 0.05–0.06 Å for the larger spiroalkaplanes with an eight-membered primary-ring cap, 4-28, 4-43 and 4-44. The equivalent C\(^\alpha\)–C\(^\beta\) bond-length differences for hexaplane (4-31) and S\(_4\) octaplane (4-27) are 0.11

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\(^1\) Bonding constraints in the alkaplane families are determined primarily by the size of the major ring in the cyclic hydrocarbon cap. As a result, geometric features of spirohexaplane (4-39) and spirobiheptaplane (4-40), both of which have a six-membered primary ring, are similar. The term n-membered primary-ring cap refers to this situation.

\(^2\) Throughout this discussion, we refer to bond lengths from MP2/6-311+G(2d,p)(red)\(^3\) optimized structures.

\(^3\) The degree of distortion in the caps was not quantified in that discussion but we found it to be less than the degree of distortion at the central moiety.
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Clearly, for species based on cyclohexane there has been no reduction in the alternation effect while for the species based on cyclooctane the effect has been almost halved.

Figure 4-6. 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 spirohexaplane (4-39), spirobiheptaplane (4-40) and the two spiroheptaplane isomers (4-41 and 4-42). All unique bond lengths are shown. The most distorted CCC angles and the distortion from planarity at C₀, α_plan, are given. The angles and bond lengths around the central C(C)₄ subunit for 4-42 are also shown.

and 0.09 Å, respectively. Clearly, for species based on cyclohexane there has been no reduction in the alternation effect while for the species based on cyclooctane the effect has been almost halved.
One possible cause for the alternate lengthening and compression of the C\(_{\alpha}\)–C\(_{\beta}\) bonds may be that these bonds are weakened as a consequence of the significant angle strain introduced at C\(_{\alpha}\) by the geometric constraints which are the result of a bicapped structure. In fact, there is a reasonably good correlation between the size of the C\(_{\beta}\)C\(_{\alpha}\)C\(_{\beta}\) angles and the differences in length of the C\(_{\alpha}\)–C\(_{\beta}\) bond-pairs (see Table 4-8 on page 167 and Table 4-10); the difference in length of the C\(_{\alpha}\)–C\(_{\beta}\) bond-pairs is larger when \(\angle C_{\beta}C_{\alpha}C_{\beta}\) is large. In the spiroalkaplanes in particular, very large C\(_{\beta}\)C\(_{\alpha}\)C\(_{\beta}\) angles (greater than 170°) are present in the two smallest molecules, 4-39 and 4-40, and these
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Planar Carbon molecules have by far the largest alternation in $C^\alpha-C^\beta$ bond lengths (and consequently the largest values for $\alpha_{\text{plan}}$). On the other hand, the largest spiroalkaplanes we have examined, 4-28 and 4-44 have the least pronounced bond length alternation and the smallest values for $\angle C^\beta C^\alpha C^\beta$ (138° and 137°, respectively, compared with an MP2/6-31G(d) calculated angle of 115° for the equivalent angle in octamethylspiropentane). This suggests that a cage which would reduce the $\angle C^\beta C^\alpha C^\beta$ angle may help in achieving absolute planarity.

The spiroalkaplanes (4-VII) are also found to have a remarkably low barrier to inversion at the central carbon atom ($C^0$). Values for $\Delta E_{\text{plan}}$ calculated at the MP2/6-311+G(2d,p)//MP2/6-311+G(2d,p)(red) level for 4-28 and 4-39 – 4-44 are in the range 5–15 kJ mol$^{-1}$ while the B3-LYP/6-311+G(2d,p)//B3-LYP/6-31G(d) values are in the range 10–20 kJ mol$^{-1}$ (see Table 4-9 on page 170). Rapid conversion between the two equivalent isomers is expected to occur at room temperature.

The pair of cyclic hydrocarbon caps introduced in the spiroalkaplanes has resulted in an almost complete reduction in the 437 kJ mol$^{-1}$ barrier to planar-tetracoordination.

<table>
<thead>
<tr>
<th>Molecule</th>
<th>Sym.$^a$</th>
<th>$r(C^\alpha-C^\beta)^b$</th>
<th>$\angle C^\beta C^\alpha C^\beta$ $^b$</th>
</tr>
</thead>
<tbody>
<tr>
<td>spiro[2.2]hexaplane 4-39</td>
<td>$D_2$</td>
<td>1.635/1.532</td>
<td>174.1°</td>
</tr>
<tr>
<td>spiro[2.2]biheptaplane 4-40</td>
<td>$D_2$</td>
<td>1.640/1.531</td>
<td>173.2°</td>
</tr>
<tr>
<td>spiro[2.2]heptaplane$^c$ 4-41</td>
<td>$C_2$</td>
<td>1.579/1.521 1.583/1.515 1.598/1.523 1.602/1.526</td>
<td>135.3° 142.3° 135.1° 142.2°</td>
</tr>
<tr>
<td>spiro[2.2]octaplane 4-28</td>
<td>$D_2$</td>
<td>1.551/1.499</td>
<td>137.9°</td>
</tr>
<tr>
<td>spiro[2.2]binonaplane 4-44</td>
<td>$D_2$</td>
<td>1.547/1.497</td>
<td>137.0°</td>
</tr>
</tbody>
</table>

$^a$ The symmetry of the equilibrium structure. $^b$ Calculated at MP2/6-311+G(2d,p)(red) (bold text) and B3-LYP/6-31G(d) (plain text) optimized geometries. $^c$ Lower symmetry in these $C_2$ structure results in two long/short $C^\alpha-C^\beta$ bond pairs and two $C^\beta C^\alpha C^\beta$ angles.
in spiropentane (see Section 4.3.2). Work towards overcoming the final impediment to planarity is detailed in the next section.

### 4.3.5 Dimethanospiroalkaplane Structures

Further flattening at the central tetracoordinate carbon atom (C\(^0\)) can be achieved by strapping together the cyclic hydrocarbon caps of a spiroalkaplane (4-VII) with hydrocarbon bridges. In particular, we have used methylene bridges to link pairs of methylene groups between the caps of spiroalkaplanes built with caps of at least eight carbon atoms (specifically spiro[2.2]bioctaplane (4-43), spiro[2.2]octaplane (4-28), and spiro[2.2]binonaplane (4-44)). This modification to the spiroalkaplane structures is expected to make the cage more rigid by preventing the linked pair of methylene groups from twisting in an anti fashion. It is also expected to help in reducing the C\(^\beta\)-C\(^\alpha\)-C\(^\beta\) angles and thereby reduce the bond-length alternation in the C\(^\alpha\)-C\(^\beta\) bonds. We refer to the resulting molecules, dimethanospiro[2.2]bioctaplane 4-47, dimethanospiro[2.2]octaplane 4-29 and dimethanospiro[2.2]binonaplane 4-48, collectively as dimethanospiroalkaplanes (4-VIII). Initial structures were determined using the AM1 method.
without symmetry constraints. In all three cases a $D_2$ symmetry structure resulted. These structures were then re-optimized in $D_2$ symmetry at the B3-LYP/6-31G(d) and MP2/6-31+G(2d,p)(red) levels. In the case of both 4-29 and 4-48 the MP2 optimization resulted in a $D_{2h}$ symmetry structure. Structures for all molecules with $D_{2h}$ symmetry imposed were also determined by optimization at the B3-LYP/6-31G(d) and MP2/6-31+G(2d,p)(red) levels. The nature of the resulting B3-LYP stationary points were examined by analytic force constant analysis. The extremely challenging task† of determining second derivatives for the $D_{2h}$ symmetry MP2/6-31+G(2d,p)(red) optimized structures was also undertaken in order to establish without doubt the nature of these stationary points. Where appropriate, improved energy differences were calculated at the MP2/6-31+G(2d,p)/MP2/6-31+G(2d,p)(red) and B3-LYP/6-31+G(2d,p)//B3-LYP/6-31G(d) levels. General structural features, the symmetry of equilibrium structures, the number of imaginary vibrational frequencies for the $D_{2h}$ symmetry structures, the distortion from planar-tetracoordination at $C^0$, $\alpha_{\text{plan}}$, and the values for $\Delta E_{\text{plan}}$, the barrier to inversion at $C^0$, for the three dimethanospiroalkaplanes explored in this work, 4-47, 4-29 and 4-48, are given in Table 4-11. More detailed structural data (all bond lengths and the most distorted CCC angles) are given in Figure 4-8 on page 180.

Optimizations at the MP2/6-31+G(2d,p)(red) level, which are substantiated by numerical force constant analyses which give no imaginary frequencies, predict quite conclusively that the dimethanospiroalkaplanes, dimethanospiro[2.2]octaplane (4-29) and dimethanospiro[2.2]binonaplane (4-48) have an exactly planar-tetracoordinate central carbon atom ($\alpha_{\text{plan}} = 0.0^\circ$). The third dimethanospiroalkaplane examined here, dimethanospiro[2.2]binonaplane (4-47), is predicted from the MP2 calculations to have a $D_2$ symmetry equilibrium structure. However, although the MP2 predicted distortion from planar-tetracoordination at $C^0$ is $2.2^\circ$, the difference between the energies of the distorted ($D_2$) and ‘planar’ ($D_{2h}$) structures, $\Delta E_{\text{plan}}[\text{MP2}]$, is almost negligible (0.4 kJ mol$^{-1}$). Calculations at the B3-LYP/6-31G(d) level differ in that they predict $D_2$ symmetry equilibrium structures for all three molecules, 4-47, 4-29 and 4-48. However, the B3-LYP/6-31+G(2d,p)//B3-LYP/6-31G(d) calculated difference in the energy of the $D_2$ and $D_{2h}$ symmetry structures ($\Delta E_{\text{plan}}$) is remarkably small for 4-29 and 4-48 (0.6 and 0.2

† With current computer technology, these calculations require about 30,000 node-hours on a CRAY-T3E or 3 months of CPU time on a Fujitsu VPP-300 (for more details see Section 2.11.3 on page 81).
Results and Discussion

179 kJ mol\(^{-1}\), respectively). It seems likely that the B3-LYP predicted distortions from planar-tetracoordination at C\(_0\) in \(4-29\) and \(4-48\) are an artifact of the B3-LYP/6-31G(d) calculations. Dimethanospirooctaplane (\(4-29\)) and dimethanospirobinonaplane (\(4-48\)) are the first neutral saturated hydrocarbons predicted to contain an exactly planar-tetracoordinate carbon atom.

<table>
<thead>
<tr>
<th>Molecule</th>
<th>Sym.(^a)</th>
<th>Cap Structure(^b)</th>
<th>Molecular Formula</th>
<th>(n)(^c)</th>
<th>(\alpha_{\text{plan}})(^d)</th>
<th>(\Delta E_{\text{plan}})(^e)</th>
</tr>
</thead>
<tbody>
<tr>
<td>dimethanospiro[2.2]biocaplane</td>
<td>(D_2/D_2)</td>
<td>(\circlearrowleft)</td>
<td>C(<em>{23})H(</em>{20})</td>
<td>1/1</td>
<td>2.2(^a)</td>
<td>2.6(^b)</td>
</tr>
<tr>
<td>dimethanospiro[2.2]ocaplane</td>
<td>(D_{2h}/D_2)</td>
<td>(\circlearrowright)</td>
<td>C(<em>{23})H(</em>{24})</td>
<td>0/1</td>
<td>0.0(^d)</td>
<td>0.0(^f)</td>
</tr>
<tr>
<td>dimethanospiro[2.2]capplane</td>
<td>(D_{2h}/D_2)</td>
<td>(\circlearrowright)</td>
<td>C(<em>{25})H(</em>{24})</td>
<td>0/1</td>
<td>0.0(^d)</td>
<td>0.0(^f)</td>
</tr>
</tbody>
</table>

\(^a\) The symmetry of the MP2 (bold type) and B3-LYP (plain text) equilibrium structures. \(^b\) In all cases the central C(C)\(_4\) unit is a spiropentane subunit in the following orientation. The carbon atoms with an empty valence, which form C–C bonds to the central C(C)\(_4\) subunit, are marked •. The position of methano bridges between the caps are marked by an open circle (\(\bigcirc\)) which represents a CH\(_2\) unit lying in the ‘plane’ of the central C\(_5\) subunit. \(^c\) The number of imaginary vibrational frequencies for the structure constrained to contain a planar tetracoordinate carbon atom, MP2/6-311+G(2d,p)-(red) \(^3\) and B3-LYP/6-31G(d) levels, respectively. \(^d\) Calculated at MP2/6-311+G(2d,p)(red) (bold text) and B3-LYP/6-31G(d) (plain text) optimized geometries. \(^e\) Calculated from MP2/6-311+G(2d,p)//MP2/6-311+G(2d,p)(red) (bold text) and B3-LYP/6-311+G(2d,p)//B3-LYP/6-31G(d) (plain text) energies. \(^f\) No distortion from planarity, no barrier to planarity.

\(^\dagger\) Further B3-LYP calculations using larger basis sets (6-311+G(3df,2p), AVTZ and beyond) indicate that both \(\alpha_{\text{plan}}\) and \(\Delta E_{\text{plan}}\) are reduced somewhat as the basis set is increased in size.
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C_3^0C_6^0C_6^0 angles in 4-47, 4-29 and 4-48 (135.5°, 134.2° and 134.4°, respectively) are slightly reduced from those in the parent spiroalkaplanes, 4-43, 4-28 and 4-44 (138.7°, 137.9° and 137.0°, respectively). This is consistent with the expectation that bond-

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

\( 4-47 (D_2h/D_2) \)

\[ \alpha_{\text{plan}} = 0.0/1.8 \]

\( 4-29 (D_{2d}/D_2) \)

\[ \alpha_{\text{plan}} = 0.0/1.7 \]

\( 4-48 (D_{2d}/D_2) \)

Figure 4-8. 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 dimethanospirobioctaplane (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.

\[ ^\dagger \] MP2/6-311+G(2d,p)(red) optimized values are quoted in the text. For the corresponding B3-LYP/6-31G(d) optimized values see Figure 4-8 on page 180.

\[ ^\ddagger \] MP2/6-311+G(2d,p)(red) optimized values are quoted in the text. For the corresponding B3-LYP/6-31G(d) optimized values see Figure 4-7 on page 175.
length alternation in the Cα–Cβ bond pairs will be decreased by a reduction in the CβCαCβ angle.

Very long carbon–carbon bonds can indicate a potential source of kinetic instability via facile C–C cleavage or molecular rearrangement. Examination of the calculated C–C bond lengths for 4-47, 4-29 and 4-48 reveals no bonds longer than 1.60 Å (see Figure 4-8 on page 180). It is worth noting, however, that, with the exception of the shortest C–C bond in 4-48 (1.525 Å compared with 1.534 Å in twistboat–twistboat bicyclo[3.3.1]nonane (TBTB-4-54)), the C–C bonds of the capping units (derived from cis-bicyclo[3.3.0]octane, crown cyclooctane and bicyclo[3.3.1]nonane) are all longer than the corresponding bonds of the unincorporated cyclic hydrocarbons.† It appears that the entire cage surrounding C0 is slightly expanded. This is consistent with our intention to design a cage that ‘clamps down’ the bonding at C0 to give planar-tetracoordination.

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

Finally, it can also be seen that the MP2/6-31G(d) optimized structures for cis-bicyclo[3.3.0]octane (4-68), crown cyclooctane (Cr-4-53) and twistboat–twistboat bicyclo[3.3.1]nonane (TBTB-4-54) give C–C bond lengths of 1.538, 1.533 and 1.567 Å for 4-68, 1.533 Å for Cr-4-53, and 1.534, 1.554, 1.543, 1.542 and 1.531 Å for TBTB-4-54.

† MP2/6-31G(d) optimized structures for cis-bicyclo[3.3.0]octane (4-68), crown cyclooctane (Cr-4-53) and twistboat–twistboat bicyclo[3.3.1]nonane (TBTB-4-54) give C–C bond lengths of 1.538, 1.533 and 1.567 Å for 4-68, 1.533 Å for Cr-4-53, and 1.534, 1.554, 1.543, 1.542 and 1.531 Å for TBTB-4-54.
atom in a neutral saturated hydrocarbon. Dimethanospirooctaplane (4-47) is predicted to have a substantial degree of flattening at C° (α_plan = 2.2°) and an almost negligible barrier to inversion at C° (ΔE_plan = 0.4 kJ mol⁻¹), which is expected to be below the zero-point energy for the inversion mode, suggesting that this molecule might be best described as pseudo-planar-tetracoordinate.

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

4.3.6 Strain Energies and Heats of Formation

Determining the total strain energies ($SE$s) of our novel hydrocarbons allows for a comparison with other strained hydrocarbons.$^{43}$ We have chosen to use a method of calculating strain energies which has been used to great effect by Schulman and Disch.$^{32}$ This method determines the strain energy as the negative of the calculated enthalpy change of a homodesmic reaction in which the number of quaternary (C), tertiary (CH) and secondary (CH$_2$) carbons present in the target hydrocarbon are balanced with product neopentane, isobutane and propane molecules. The number of primary (CH$_3$) carbons on each side of the reaction is then balanced using ethane. This preserves the number and type of C–C bonds on each side of the reaction and is found to give good cancellation of errors when the MP2 method is used to calculate energies (see also Section 3.2 on page 97). If these product molecules are defined as being strain free (which is usual), the enthalpy change of this homodesmic reaction gives the total strain of the target hydrocarbon. The resulting reaction enthalpy change can then be used in conjunction with experimental heats of formation for ethane, propane, isobutane and neopentane to give calculated heats of formation ($\Delta H_f^{\text{calc}}$) for the target hydrocarbon.

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