dramatically reduces the barrier to inversion (ΔE_{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 (ΔE_{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 (ΔH_f(calc)) for the target hydrocarbon.

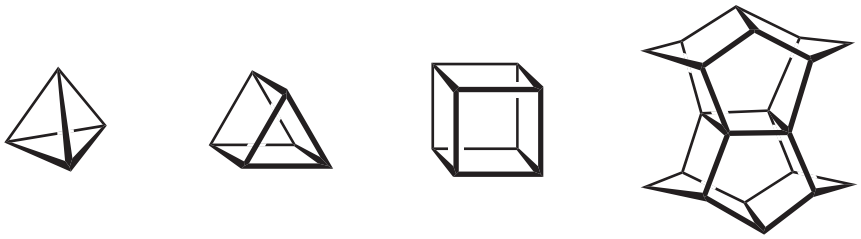
Previous work, using MP2/6-31G(d)//HF/6-31G(d) calculated energies, has shown this type of approach to yield heats of formation for a number of hydrocarbons, some with significant strain energies, to within 13 kJ mol^{-1}. We have used MP2/6-311+G(2d,p) energies (calculated at MP2/6-311+G(2d,p), MP2/6-31G(d)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

Table 4-12. Calculated strain energies (*SE*)[a] and strain per carbon atom (*SE*/C), and calculated and experimental heats of formation (ΔH_f) at 298 K (kJ mol^{-1}) for a variety of known and previously explored hydrocarbons.

Molecule	Homodesmic reaction[b]	*SE* (calc)[c]	*SE*/C (calc)	ΔH_f (calc)	ΔH_f (exp)[d]
	Simple Alicyclic Hydrocarbons				
cyclopropane	**4-49** + 3 eth → 3 pro	124	41.5	62	53.3 ± 0.6
cyclobutane	**4-50** + 4 eth → 4 pro	115	28.7	32	28.5 ± 0.6
cyclopentane	**4-51** + 5 eth → 5 pro	29	5.9	–75	–76.4
cyclohexane (chair)	**C-4-52** + 6 eth → 6 pro	1	0.1	–124	–123.1 ± 0.8
cyclooctane (boat–chair)	**BC-4-53** + 8 eth → 8 pro	42	5.3	–125	–124.4 ± 1.0
bicyclo[3.3.1]nonane (chair–chair)	**CC-4-54** + 10 eth → 7 pro + 2 iso	28	3.1	–135	–127.5 ± 2.3
	Strained Hydrocarbons				
tetrahedrane	**4-55** + 6 eth → 4 iso	602	150.5	568	(535.0 ± 4.0)[e]
pyramidane	**4-56** + 8 eth → neo + 4 iso	644	128.8	610	
[1.1.1]propellane	**4-57** + 7 eth → 2 neo + 3 pro	429	85.9	366	351.0 ± 4.0[f]
spiropentane	**4-58** + 6 eth → neo + 4 pro	282	56.4	198	185.1 ± 0.8
prismane	**4-59** + 9 eth → 6 iso	640	106.7	589	
cubane	**4-60** + 12 eth → 8 iso	712	89.0	644	622.2 ± 3.7
tetramethyl-tetrahedrane	**4-61** + 6 eth → 4 neo	593	74.1	425	
tetra-*tert*-butyl-tetrahedrane	**4-62** + 10 eth → 8 neo	527	26.3	22	25.9 ± 8.8[g]
pagodane	**4-63** + 30 eth → 4 pro + 12 iso + 4 neo	348	17.4	163	200.3 ± 3.8[h]
dodecahedrane	**4-64** + 30 eth → 20 iso	245	12.3	77	76.1 ± 4.2[i]

[a] MP2/6-311+G(2d,p)//MP2/6-31G(d) values corrected to 298 K (kJ mol^{-1}). [b] The abbreviations "eth", "pro", "iso" and "neo" indicate ethane, propane, isobutane and neopentane, respectively. [c] The strain energy (*SE*) is determined as the negative of the enthalpy change for the given homodesmic reaction. [d] Taken from Ref. 33b unless otherwise noted. [e] G2 calculated value from Ref. 33d. [f] From Ref. 33c. [g] From Ref. 33a. [h] From Ref. 33e. [i] Calculated from an experimental determination of ΔH_f for the diester, see Ref. 33g.

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



4-55 (T_d) **4-59** (D_{3h}) **4-60** (O_h) **4-63** (D_{2h})

A comparison of calculated and experimental heats of formation for the simple cyclic and bicyclic hydrocarbons listed in Table 4-12 (**4-49**, **4-50**, **4-51**, **C-4-52**, **BC-4-53** and **CC-4-54**) shows that for these relatively unstrained molecules our method gives ΔH_fs in good agreement with experiment, with results to within 12 kJ mol^{-1} (and to within 7 kJ mol^{-1} if cyclopropane is excluded). For the capping hydrocarbons listed in Table 4-13 for which we have experimental heats of formation (**4-65** – **4-68**), this impressive agreement is maintained. However, for experimentally-known, highly-strained hydrocarbons (**4-57**, **4-58**, **4-60**, **4-62**, **4-63** and **4-64**), the differences between theory and experiment appear to be somewhat larger (see Table 4-12). The largest difference is associated with the calculated ΔH_f of [1.1.1.1]pagodane (**4-63**[44]), which differs from the experimental value[33e] by 37 kJ mol^{-1}. Relatively large discrepancies between the calculated and experimental ΔH_fs are also found for cubane (**4-60**) (22 kJ mol^{-1}) and tetrahedrane (**4-55**)[†] (33 kJ mol^{-1}).

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

[†] Although tetra-*tert*-butyl tetrahedrane has been isolated, the parent tetrahedrane is not known experimentally and this comparison is with a G2 calculated ΔH_f.[33d]

Table 4-13. Calculated strain energies (*SE*)[a] and strain per carbon atom (*SE*/C) and calculated and experimental heats of formation (ΔH_f) at 298 K (kJ mol^{-1}) for the capping hydrocarbons.

Molecule	Homodesmic reaction[b]	*SE* (calc)[c]	*SE*/C (calc)	ΔH_f (calc)	ΔH_f (exp)[d]
	Capping Hydrocarbons				
bicyclo[2.2.0]hexane	**4-65** +7 eth → 4 pro + 2 iso	238	39.7	138	125.[e]
cyclohexane (twistboat)	**TB-4-52** + 6 eth → 6 pro	28	4.6	–97	
cycloheptane	**4-66** + 7 eth → 7 pro	27	3.9	–119	–118.1 ± 1.0[f]
norbornane	**4-67** + 8 eth → 5 pro + 2 iso	62	8.9	–59	–54.9 ± 4.7
cis-bicyclo-[3.3.0]octane	**4-68** + 9 eth → 6 pro + 2 iso	49	6.1	–93	–93.3 ± 1.5
cyclooctane (crown)	**Cr-4-53** + 8 eth → 8 pro	52	6.4	–115	
bicyclo[3.3.1]nonane (twistboat–twistboat)	**TBTB-4-54** + 10 eth → 7 pro + 2 iso	63	7.0	–100	

[a] MP2/6-311+G(2d,p)//MP2/6-31G(d) values corrected to 298 K (kJ mol^{-1}). [b] The abbreviations "eth", "pro", "iso" and "neo" indicate ethane, propane, isobutane and neopentane, respectively. [c] The strain energy (*SE*) is determined as the negative of the enthalpy change for the given homodesmic reaction. [d] Taken from Ref. 33b unless otherwise noted. [e] From Ref. 33c. [f] From 33h.

capping units based on **TB-4-52**, **Cr-4-53**, **TBTB-4-54**, **4-66**, **4-67** and **4-68** of approximately 60–120 kJ mol^{-1}, while a pair of caps based on **4-65** will contribute 480 kJ mol^{-1}. The examination of bond lengths in Sections 4.3.3 – 4.3.5, indicates that the strain attributable to the caps will in fact be greater than this, particularly in the case of molecules like spirohexaplane (**4-39**) where a number of cyclohexane C–C bond lengths are significantly lengthened after incorporation into the alkaplane.

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

Table 4-14. Calculated strain energies (*SE*),[a] strain per carbon atom (*SE*/C) and calculated heats of formation (ΔH_f) at 298 K (kJ mol^{-1}) for a number of bridged spiropentanes and fenestranes.

Molecule	Homodesmic reaction[b]	*SE* (calc)[c]	*SE*/C (calc)	ΔH_f (calc)
	Bridged Spiropentanes			
[3.3.3]fenestrane	**4-26** + 7 eth → neo + 2 iso + 2 pro	585	116.9	526
[3.4.3]fenestrane	**4-25** + 8 eth → neo + 2 iso + 3 pro	498	83.0	418
[3.5.3]fenestrane	**4-45** + 9 eth → neo + 2 iso + 4 pro	354	50.5	253
tetracyclo-[3.3.1.0^{2,4}.0^{2,8}]nonane	**4-46** + 12 eth → neo + 4 pro + 4 iso	424	47.1	307
	Fenestranes			
trans,cis,cis,cis-[4.4.4.4]fenestrane	***C*$_s$-4-18** + 12 eth → neo + 4 iso + 4 pro	663	73.7	546
all-*cis*-[4.4.4.4]fenestrane	***D*$_{2d}$-4-18** + 12 eth → neo + 4 iso + 4 pro	719	79.9	602
all-*trans*-[4.4.4.4]fenestrane	***C*$_{2v}$-4-18** + 12 eth → neo + 4 iso + 4 pro	735	81.7	618
trans,cis,trans,cis-[4.4.4.4]fenestrane	***C*$_2$-4-18** + 12 eth → neo + 4 iso + 4 pro	1098	122.0	981
[5.5.5.5]fenestrane	**all-*cis*-4-19** + 16 eth → neo + 4 iso + 8 pro	59	4.5	–142
[5.5.5.5]fenestrane	**all-*trans*-4-19** + 16 eth → neo + 4 iso + 8 pro	637	49.0	436

[a] MP2/6-311+G(2d,p)//MP2/6-31G(d) values corrected to 298 K (kJ mol^{-1}). [b] The abbreviations "eth", "pro", "iso" and "neo" indicate ethane, propane, isobutane and neopentane, respectively. [c] The strain energy (*SE*) is determined as the negative of the enthalpy change for the given homodesmic reaction.

bons. The least strained of all the alkaplanes we have examined are amongst those based on eight-membered primary-ring caps, **4-28**, **4-29**, **4-43**, **4-44**, **4-47** and **4-48** (*SE* = 875–1065 kJ mol^{-1}). Of these, spirooctaplane (**4-28**) (*SE* = 873 kJ mol^{-1}), which is approximately 160 kJ mol^{-1} more strained than cubane, is the least strained alkaplane. However, strain accumulates and cubane is only a C_8H_8 hydrocarbon while spirooctaplane is $C_{21}H_{24}$. As such, comparisons between molecules often examine strain per carbon (*SE*/C) or strain per C–C bond in order to introduce some size consistency. We have calculated that prismane (**4-59**) has the highest strain per carbon atom of all isolated hydro-

carbons (*SE*/C = 107 kJ mol^{-1}), while, as far we are aware, [3.3.3]fenestrane (or tricyclo[2.1.0.0^{1,3}]pentane)[16] (**4-26**), has the highest strain per carbon of any observed[†] hydrocarbon (117 kJ mol^{-1}). In comparison, the least strained alkaplanes (**4-28**, **4-29**, **4-43**, **4-44**, **4-47** and **4-48**) have strain energies per carbon of only 39–46 kJ mol^{-1}. Comparison of *SE*/C of the alkaplanes with cubane (*SE* = 89 kJ mol^{-1}) or prismane is somewhat misleading because in **4-59** and **4-60** the strain is quite clearly, equally distributed throughout the molecule, whereas the alkaplanes have a very highly strained central region and considerably less strained caps.[‡] Comparison with bridged spiropentanes (**4-25**, **4-26**, **4-45**, **4-46**) (*SE*/C = 47–117 kJ mol^{-1}) is likely to be more meaningful (see Table 4-14). Like the alkaplanes, the bridged spiropentanes contain a highly distorted spiro[2.2] carbon and a progressively less strained surrounding structure. Interestingly, the least strained alkaplanes (**4-28**, **4-29**, **4-43**, **4-44**, **4-47** and **4-48**) are found to have lower strain per carbon than the synthetically-isolable bridged spiropentanes **4-45** (*SE*/C = 50.5 kJ mol^{-1}) and **4-46** (*SE*/C = 47.1 kJ mol^{-1}). However, this is almost certainly affected by the fact that the alkaplanes concerned have from 21 to 25 carbon atoms, compared with only 7 and 9 carbon atoms in **4-45** and **4-46**.

Of the parent alkaplanes (**4-VI**), the S_4 symmetry isomer of octaplane (**4-27**) is clearly the least strained (*SE* = 1179 kJ mol^{-1}). All the **B**-type (D_2 symmetry) structures (**4-31**, **4-32**, **4-34**, **4-35** and **4-36**) are very highly strained with *SE*s around 1500 kJ mol^{-1}, indicating that the **B**-type orientation of the central $C(CH)_4$ moiety is unfavorable. Bihexaplane (**4-30**) (also a **B**-type alkaplane), has the highest strain of all the alkaplanes (*SE* = 1772 kJ mol^{-1}), reflecting in part the much greater strain inherent in the bicyclo[2.2.0]hexane caps.

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

[†] For details concerning the observation of tricyclo[2.1.0.0^{1,3}]pentane, see Chapter 1 and Section 4.1.

[‡] We note, however, that the discussion of bond lengths in Section 4.3.4 indicated that there is some bond elongation in the alkaplane caps and that this, along with some angle strain in the caps, is likely to make a sizeable contribution to the total strain.

Table 4-15. Calculated strain energies (*SE*),[a] strain per carbon atom (*SE*/C) and calculated heats of formation (ΔH_f) at 298 K (kJ mol^{-1}) for the alkaplanes.

Molecule	Homodesmic reaction[b]	*SE* (calc)[c]	*SE*/C (calc)	ΔH_f (calc)
	Alkaplanes			
bihexaplane[d]	**4-30** + 26 eth → neo + 16 iso	1772	104.2	1637
hexaplane	**4-31** + 24 eth → neo + 12 iso + 4 pro	1467	86.3	1282
biheptaplane[d]	**4-32** + 28 eth → neo + 16 iso + 2 pro	1519	79.9	1342
heptaplane	**4-33** + 26 eth → neo + 12 iso + 6 pro	1285	67.6	1058
bioctaplane[d]	**4-34** + 30 eth → neo + 16 iso + 4 pro	1480	70.5	1262
octaplane (**A**-type)	**4-27** + 28 eth → neo + 12 iso + 8 pro	1179	56.1	910
octaplane (**B**-type)[d]	**4-35** + 28 eth → neo + 12 iso + 8 pro	1486	70.7	1218
binonaplane[d]	**4-36** + 32 eth → neo + 16 iso + 6 pro	1533	66.7	1273
	Spiroalkaplanes			
spirohexaplane	**4-39** + 26 eth → 5 neo + 8 iso + 4 pro	1625	95.6	1473
spirobiheptaplane	**4-40** + 30 eth → 5 neo + 12 iso + 2 pro	1742	91.7	1598
spiroheptaplane (isomer a)	**4-41** + 28 eth → 5 neo + 8 iso + 6 pro	1302	68.5	1109
spiroheptaplane (isomer b)	**4-42** + 28 eth → 5 neo + 8 iso + 6 pro	1166	61.4	972
spirobioctaplane	**4-43** + 32 eth → 5 neo + 12 iso + 4 pro	977	46.5	791
spirooctaplane	**4-28** + 30 eth → 5 neo + 8 iso + 8 pro	873	41.6	638
spirobinonaplane	**4-44** + 34 eth → 5 neo + 12 iso + 6 pro	904	39.3	677
	Dimethanospiroalkaplanes			
dimethanospirobioctaplane	**4-47** + 36 eth → 5 neo + 16 iso + 2 pro	1040	45.2	862
dimethanospirooctaplane	**4-29** + 34 eth → 5 neo + 12 iso + 6 pro	1064	46.2	836
dimethanospirobinonaplane	**4-48** + 38 eth → 5 neo + 16 iso + 4 pro	980	39.2	760

[a] MP2/6-311+G(2d,p)//MP2/6-311+G(2d,p)(red)[38] values corrected to 298 K (kJ mol^{-1}). [b] The abbreviations "eth", "pro", "iso" and "neo" indicate ethane, propane, isobutane and neopentane, respectively. [c] The strain energy (*SE*) is determined as the negative of the enthalpy change for the given homodesmic reaction. [d] For these molecules MP2/6-311+G(2d,p) energies were calculated at the HF/6-31G(d) optimized equilibrium geometry.

primary-ring caps (**4-28**, **4-43** and **4-44**) have calculated *SE*s of about 900–1000 kJ mol^{-1}.

Adding methylene bridges to the three spiroalkaplanes **4-28**, **4-43** and **4-44** to give the dimethanospiroalkaplanes (**4-VIII**) has the effect of increasing the strain energy by approximately 80–190 kJ mol^{-1}. The smallest increase (76 kJ mol^{-1}) is for dimethanospirobinonaplane (**4-48**) which is also the least strained dimethanospiroalkaplane (*SE* = 980 kJ mol^{-1}). The introduction of a very short H–H close contact in dimethanospirooctaplane (r(H–H) = 1.84 Å) (which was noted in Section 4.3.5 on page 177) probably contributes significantly to the much greater (190 kJ mol^{-1}) difference between the *SE*s of **4-28** and **4-29**. The considerably lower strain in **4-48** suggests that while both **4-29** and **4-48** are predicted to contain a planar-tetracoordinate carbon atom, **4-48** is likely to be a more viable target.

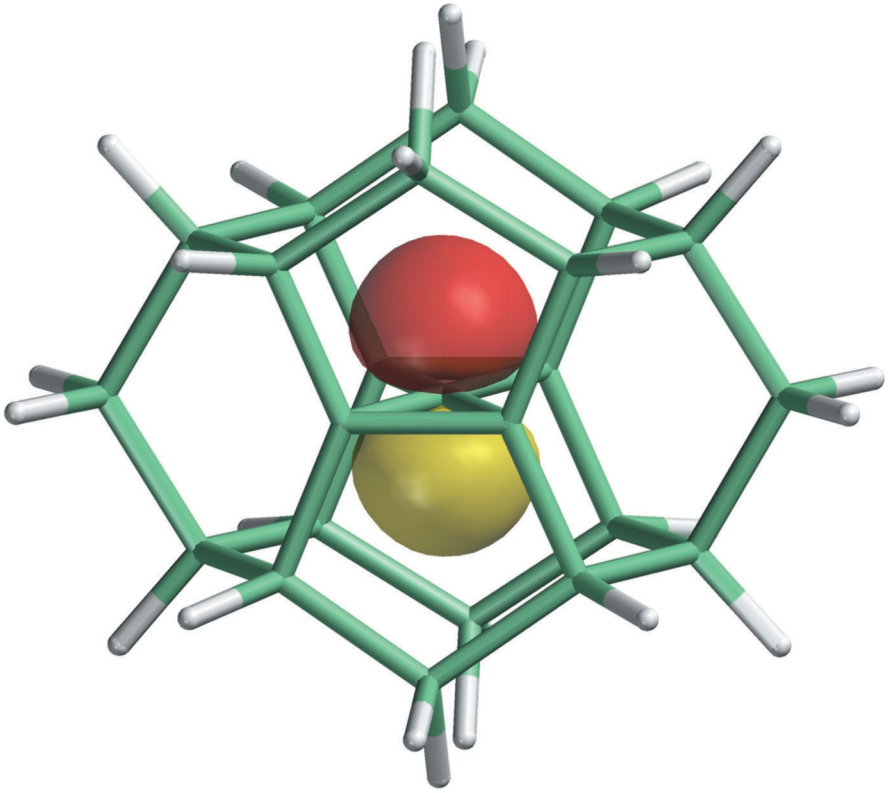
The total strain energies and heats of formation of a number of isomers of [4.4.4.4]- and [5.5.5.5]fenestrane (**4-18** and **4-19**) are given in Table 4-14 on page 187. Despite considerable effort on the part of synthetic chemists, only the least strained of all of these structures, **all-*cis*-4-19**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

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

4.3.7 Ionization Energies

A striking feature of all the alkaplane families (**4-VI**, **4-VII** and **4-VIII**) is that the highest occupied molecular orbital (HOMO) is basically a *p*-type lone pair orbital local-

ized on the central quaternary carbon atom (see Figure 4-10). This should give the alkaplanes interesting chemical and physical properties unlike those of other saturated hydrocarbons. As an example of such properties, we have calculated the adiabatic ion-



4-29 (D_{2h})

Figure 4-10. An iso-surface of the highest occupied molecular orbital (HOMO) of dimethanospiro[2.2]octaplane (**4-29**) (the iso-surface is drawn at 0.080 eÅ^{-3}).

ization energy for octaplane (**4-27**)[45], spirooctaplane (**4-28**) and dimethanospirooctaplane (**4-29**) at the UMP2/6-311+G(2d,p)//UMP2/6-31G(d) level. This yields values for the IE_a of 5.23, 4.97 and 4.96 eV, respectively. Test calculations on small molecules for which accurate experimental data[36] are available (including NH_3, H_2O, $^3CH_2$ and CH_4)[†] suggest that the calculated IE_as will be too low by about 0.1–0.2 eV. The corrected values of just above 5 eV are considerably lower than the ionization energy of tetra-*tert*-butyltetrahedrane, which has an IE_a equal to 7.1 eV (the lowest experimental value for a saturated hydrocarbon from a recent compendium[36]). In fact, the alkaplanes are pre-

[†] For details, see Section 4.2 on page 145.

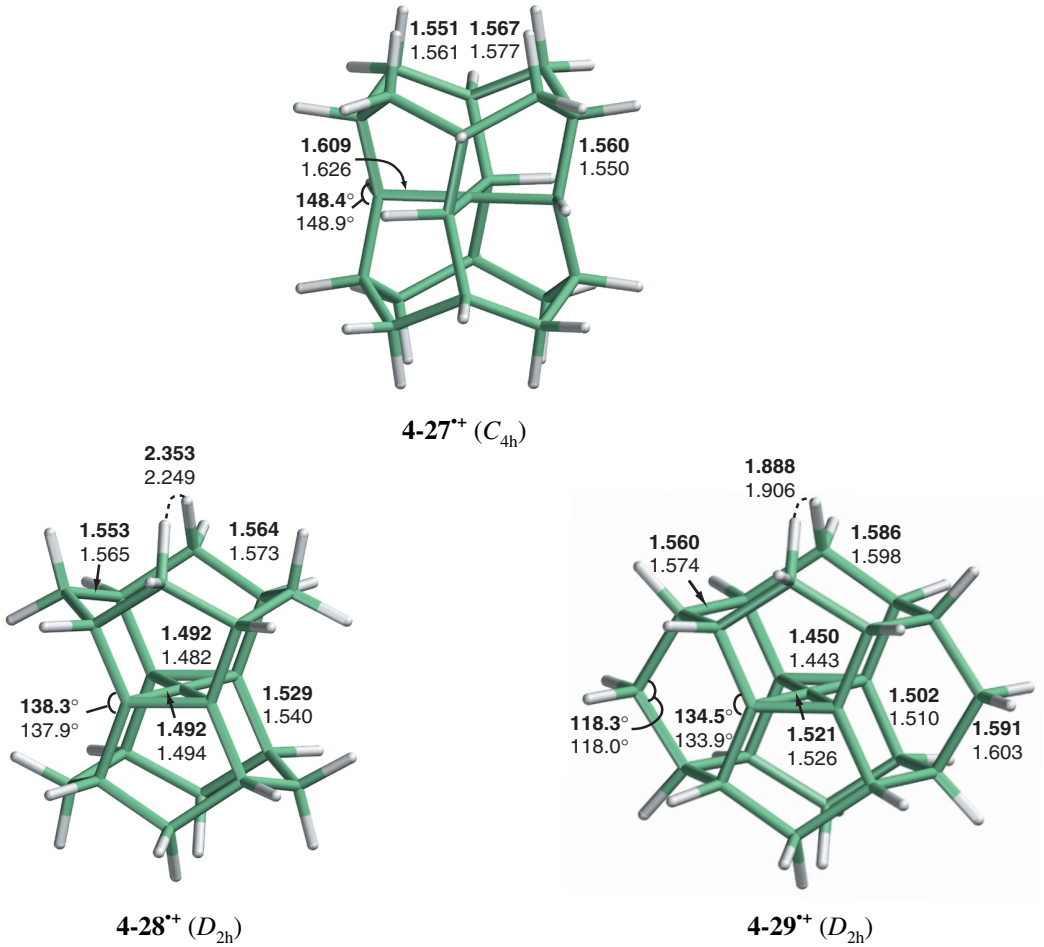


Figure 4-11. Structural parameters (MP2/6-311+G(2d,p)(red)[38] values in bold type, B3-LYP/6-31G(d) values in plain text, all values in Å or degrees) for octaplane radical cation (**4-27**$^{\bullet+}$), spirooctaplane radical cation (**4-28**$^{\bullet+}$), and dimethanospirooctaplane (**4-29**$^{\bullet+}$). All unique bond lengths and some close-contact distances (Å) are shown. Angles significantly distorted from the tetrahedral ideal are also given.

dicted to have an ionization energy comparable to that of the alkali metals lithium and sodium (5.39 and 5.14 eV, respectively[36]).

The radical cations which result from ionization of octaplane, spirooctaplane and dimethanospirooctaplane, **4-27**$^{\bullet+}$, **4-28**$^{\bullet+}$ and **4-29**$^{\bullet+}$, respectively, are predicted to contain an exactly planar-tetracoordinate carbon atom. High symmetry structures (C_{4h}, D_{2h} and D_{2h}, respectively) for **4-27**$^{\bullet+}$, **4-28**$^{\bullet+}$ and **4-29**$^{\bullet+}$, calculated at the HF/6-31G(d) and B3-LYP/6-31G(d) levels, were found via analytic force constant analysis to have no imaginary frequencies.

A comparison of the structures of these radical cations with the corresponding neu-

tral species reveals only minor structural changes (see Figure 4-11 on page 192). The central C^0–C^α bonds are lengthened by about 0.02 Å (from 1.59 to 1.61 Å for **4-27**, from 1.48 to 1.49 for **4-28**, and from 1.50 to 1.52 Å for **4-29**). For both **4-27**$^{\bullet+}$ and **4-28**$^{\bullet+}$, where the neutral species is distorted from planar-tetracoordination at C^0, the C^α–C^β bonds are alternately lengthened and shortened in the ions to values that correspond roughly to the average of the two lengths in the neutral molecules (from 1.60/1.51 to 1.56 for **4-27**, and from 1.55/1.50 to 1.53 for **4-28**). The C^α–C^β bond lengths are relatively unchanged for **4-29**$^{\bullet+}$ (1.50 Å). In all the radical cation structures examined (Figure 4-11), the central carbon atom (C^0) has an exactly planar-tetracoordinate bonding environment.

Removing one of the electrons from the high-energy HOMO appears to significantly reduce the preference for a tetrahedral-like bonding arrangement.[†] The result is that the bicapped alkaplane cage structures now exert easily enough pressure on the bonding arrangement at C^0 to impose planar-tetracoordination. These molecules (**4-27**$^{\bullet+}$, **4-28**$^{\bullet+}$ and **4-29**$^{\bullet+}$) are the *first saturated hydrocarbon radical cations* found to contain a planar-tetracoordinate-carbon atom.

4.3.8 Triplets and Stability

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

[†] It is worth noting that removing an electron from a spiro[2.2] carbon aids flattening in general. Spiropentane radical cation exhibits further flattening at the central carbon atom compared with the neutral spiropentane species (**4-58**). In the ion the two cyclopropane rings are twisted with an angle of about 60.0° (compared with the exactly perpendicular, 90.0° angle in the parent). This leads to a reduction of α_{plan} from 21.4° in the parent (**4-58**) to 13.7° in spiropentane radical cation (for the UMP2/6-31G(d) optimized structure).

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

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

Table 4-16. Energies of the 'planar' neopentane and spiropentane triplets relative to their respective tetrahedral and tetrahedral-like ground state singlets, ΔE_{PT}(triplet) (kJ mol^{-1}), and the energy difference between the 'planar' singlet and triplet, T–S (kJ mol^{-1}).[a]

	'planar' neopentane (C_{4h})		'planar' spiropentane (D_{2h})	
method	ΔE_{PT}(triplet)	T–S	ΔE_{PT}(triplet)	T–S
UB3-LYP/6-31G(d)	764.8	–116.8	482.4	51.2
UB3-LYP/6-311+G(2d,p)	756.2	–101.8	477.5	56.1
UB3-LYP/6-311+G(3df,2p)	756.5	–98.2	479.4	59.9
UMP2(full)/6-31G(d)[b]	836.1	–91.3	536.8	77.8
UMP2(full)/6-311+G(2d,p)[b]	805.0	–64.8	519.7	89.5
UMP2(full)/6-311+G(3df,2p)[b]	805.6	–57.3	520.8	95.6
URCCSD(T)(fc)/6-311+G(2d,p)[c]	781.2	–98.7	503.7	60.3
URCCSD(T)(fc)/6-311+G(3df,2p)[c]	786.9	–91.2	506.4	66.4
URCCSD(T)(fc)/AVTZ[c]	–	–	505.1	67.6

[a] 'Planar' singlet energies are taken from Table 4-5 on page 158. [b] Calculated at the UMP2(full)/6-31G(d) optimized geometries. [c] Triplet energies were calculated with MOLPRO's URCCSD(T) method at the UMP2(full)/6-311+G(2d,p) optimized geometries.

[†] We note that the open-shell singlet and triplet are very close in energy, consequently, for the majority of this section, we will restrict our discussion of the open-shell configurations to the triplet because it is better described by the single determinant methods used primarily in this work.

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

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

In order to gain some idea of where the alkaplane and spiroalkaplane triplet surfaces lie relative to the singlet surfaces, we began by calculating single point energies for the triplet configuration at both the singlet equilibrium and 'planar' geometries of **4-27** and **4-28** (see Table 4-17). These energies predict quite clearly that the triplet surface lies well above the singlet surface at the equilibrium geometries of all the alkaplanes. However, as might be expected from the calculations on the model systems (neopentane and spiropentane), as S_4 octaplane (**4-27**) approaches planar-tetracoordination at C^0 (C_{4h} symmetry) the triplet and closed-shell singlet surfaces become quite close (T–S(vertical) is expected to be in the range 11 to 44 kJ mol^{-1}).

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

Table 4-17. Vertical triplet energy differences, T–S(vertical) (kJ mol^{-1}), for the 'planar' and equilibrium geometries of octaplane (**4-27**) and spirooctaplane (**4-28**).[a]

structure		T–S(vertical) UB3-LYP/6-311+G(2d,p)// B3-LYP/6-31G(d)	T–S(vertical) UMP2/6-31G(d)// MP2/6-31G(d)
octaplane S_4 (singlet)	$\boldsymbol{S_4}$**-4-27**	168.6	240.1
octaplane C_{4h} (singlet)	$\boldsymbol{C_{4h}}$**-4-27**	11.4	44.2
spiro[2.2]octaplane D_2 (singlet)	$\boldsymbol{D_2}$**-4-28**	193.6	285.6
spiro[2.2]octaplane D_{2h} (singlet)	$\boldsymbol{D_{2h}}$**-4-28**	129.3	187.5

[a] Energy differences between the singlet and triplet electronic configurations are calculated at singlet optimized stationary points.

except that one of the C^0–C^α bonds has undergone homolytic cleavage. This distortion is barrier-less and considerably exothermic. As a result, excitation to the triplet surface is likely to lead to homolytic cleavage. For the alkaplanes to be stable, a relatively large singlet–triplet separation is required. An indication of the proximity of the optimized triplet surface to the closed-shell singlet surface can be gleaned from the relative energy differences listed in Table 4-18.

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

molecule	T–S difference[a]	UB3-LYP/6-311+G(2d,p)// UB3-LYP/6-31G(d)	UMP2/6-31G(d)// UMP2/6-31G(d)
octaplane (**4-27**)	C_s triplet – S_4	–182.9	–101.9
	C_{4h} triplet – S_4	55.6	97.3
	C_{4h} triplet – C_{4h}	–16.9	27.3
spirooctaplane (**4-28**)	C_s triplet – D_2	18.1	83.8
	D_{2h} triplet – D_2	128.8	176.8
	D_{2h} triplet – D_{2h}	113.7	164.1

[a] Particular T–S differences are labelled as triplet symmetry – singlet symmetry. For example, C_s triplet – S_4, refers to the difference in energy between the C_s symmetry stationary point on the triplet surface and the S_4 symmetry stationary point on the singlet surface.

Considering octaplane (**4-27**) first, it can be seen that the energy of the optimized C_{4h} triplet (a saddle point) is substantially higher than that for the S_4 symmetry equilibrium structure (between 56 and 97 kJ mol^{-1}). However, the energy of the C_{4h} singlet (the saddle point for inversion between equivalent S_4 symmetry equilibrium structures) is relatively close to the optimized C_{4h} triplet energy. Preliminary calculations on the other alkaplanes (**4-VI**) indicate that this is a general trend. This, in combination with results from calculations on the 'planar' neopentane and the fact that the triplet surface leads, without barrier, in a highly exothermic process, to C^0–C^α cleavage, suggests strongly that no structures based on a neopentane subunit can achieve planar-tetracoordination.

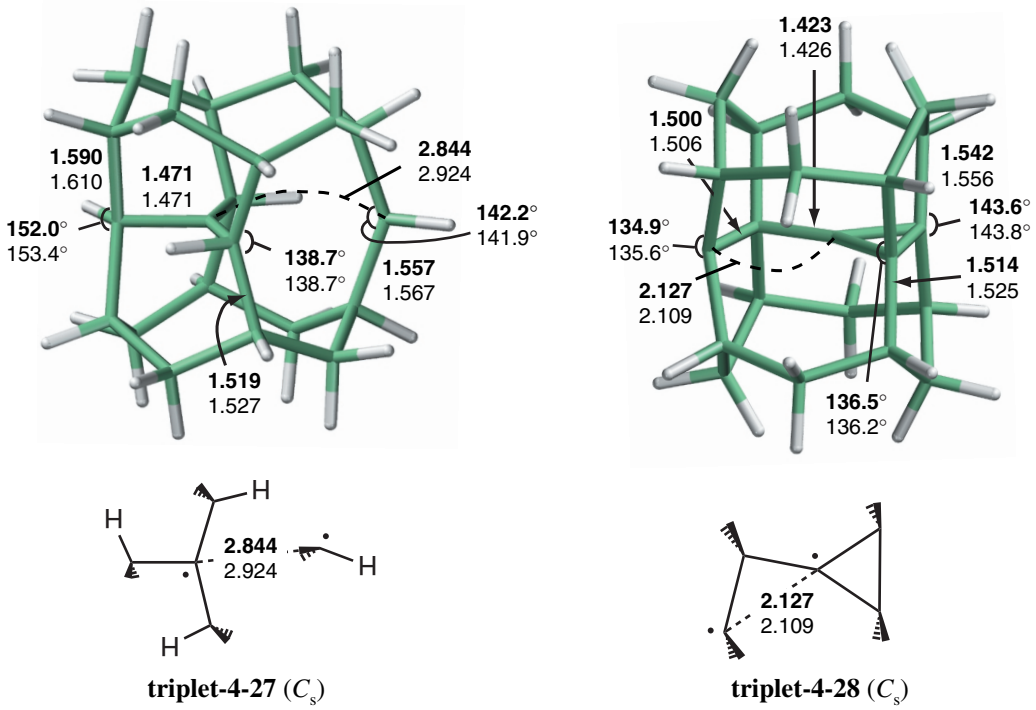


Figure 4-12. Structural parameters (MP2/6-31G(d) values in bold type, B3-LYP/6-31G(d) values in plain text, all values in Å or degrees) for triplet octaplane (**triplet-4-27**) and triplet spirooctaplane (**triplet-4-28**). Selected bond lengths and the dissociated CC distance are shown. Selected angles are also given. The two-dimensional structural elements show a top-down view of a slice of the molecule through the central $C(C)_4$ and $C(CH)_4$ regions.

Spirooctaplane (**4-28**) is entirely different. The energy difference between the D_{2h} symmetry triplet geometry and the D_2 and D_{2h} singlet structures of spirooctaplane sug-

gest that the triplet surface in spirooctaplane lies well above the singlet surface for geometries close to the singlet equilibrium structure (by greater than 100 kJ mol^{-1} at least). Only at the triplet equilibrium geometry, a geometry that can only be reached from the singlet equilibrium structure after inversion at one of the C^{α} atoms and cleavage of the corresponding C^0–C^{α} bond (see Figure 4-12), does the triplet energy approach the singlet energy. As a result, we expect the spiroalkaplanes (**4-VII**) and closely related dimethanospiroalkaplanes (**4-VIII**) not to suffer from triplet instability problems.

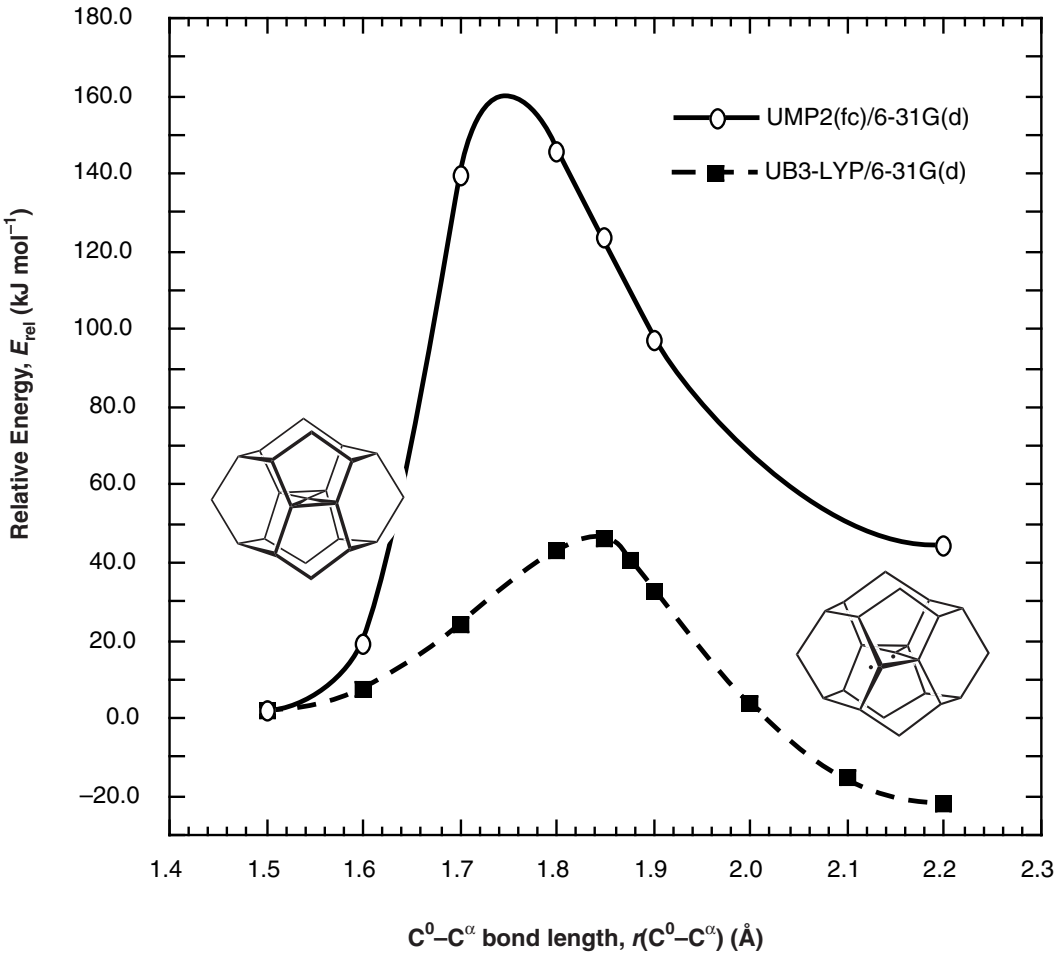


Figure 4-13. Calculated potential energy curves for homolytic C^0–C^{α} bond cleavage in dimethanospirooctaplane (**4-29**) determined at the ○ – UMP2(fc)/6-31G(d) and ■ – UB3-LYP/6-31G(d) levels are given as relative energy, E_{rel}, (kJ mol^{-1}) against C^0–C^{α} bond length, r(C^0–C^{α}) (Å). Optimized geometries at fixed values of r(C^0–C^{α}) were determined at the UB3-LYP/6-31G(d) level.

Calculations on the triplets suggest that one of the lowest-energy routes to decom-

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

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

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

[†] For basis set considerations, see Section 4.2 on page 145.

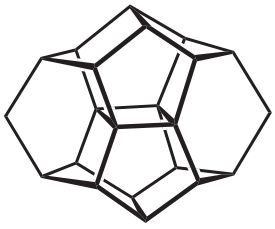
[‡] Not surprisingly, the geometry and energy of the biradical C–C dissociation product was found to be close to the corresponding triplet geometry and energy.

[§] Preliminary calculations on spirooctaplane (**4-28**) indicate that the barrier height for C^0–C^α cleavage in this molecule is slightly larger than for **4-29**.

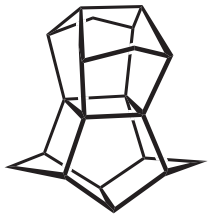
been identified. Spiro[2.2]octaplane (**4-28**), dimethanospiro[2.2]octaplane (**4-29**) and dimethanospiro[2.2]binonaplane (**4-48**) are expected to be good synthetic targets.

4.3.9 Synthetic Considerations

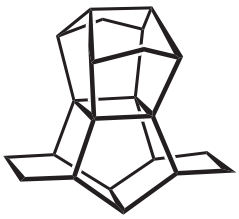
Design of a viable and complete synthetic strategy is beyond the scope of this work and best left to the ingenuity of the synthetic organic chemists. A number of observations are, however, of value.



4-69 (D_{2h})



4-70 (D_{2d})

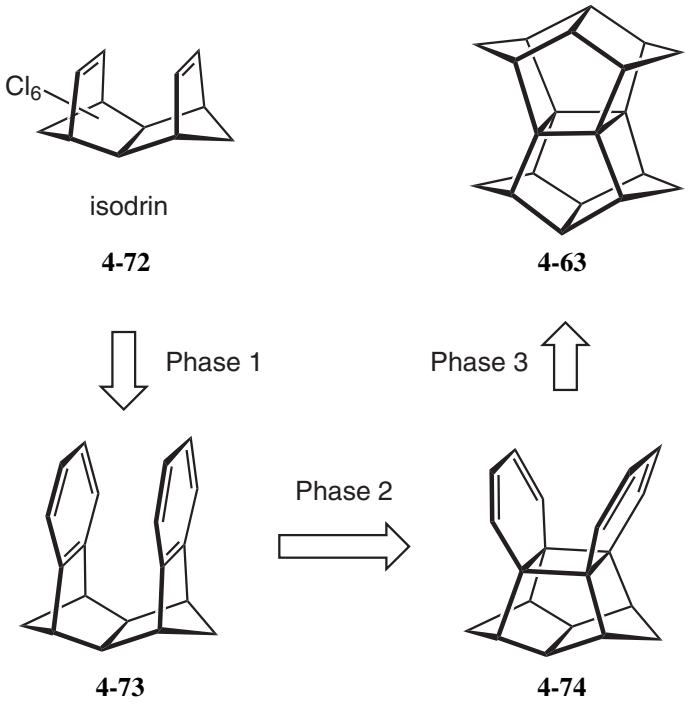


4-71 (C_{2v})

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

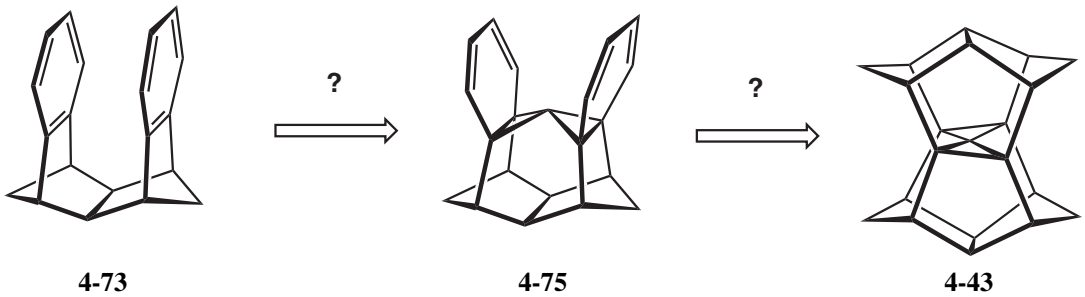
One suggestion[48] has been to fire positively charged carbon atoms at a pagodane cage and hope that some are included in much the same way the cations are inserted into buckminsterfullerenes. The problem here is that the very rigid, inflexible cages do not have the same ability to disperse localized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

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



Scheme 1

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



Scheme 2

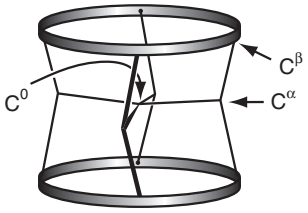
spiropentanes, which we have already referred to in Section 3.3.4 as a potential route to hemispiroalkaplanes (**4-V**), might be employed. However, the success of these approaches all depend on the ability to achieve carbene insertion to give an *endo* isomer at the appropriate aromatic C–C bonds in **4-73.** This is not likely to be an easy task. However, if this can be achieved, the synthesis could proceed with formation of the

upper cap, probably via Diels–Alder condensations as is usual when synthesizing pagodanes.

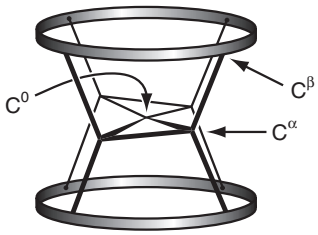
Clearly, this discussion has been purely speculative, but it does serve to indicate that complex, rigid cage compounds of an analogous nature to the spiroalkaplanes and dimethanospiroalkaplanes are well-known and might indeed be synthetically achievable.

4.4 Concluding Remarks

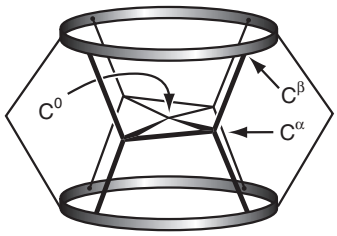
The successful synthesis of rigid saturated hydrocarbon systems such as tetracyclo[3.3.1.$0^{2,4}$.$0^{2,8}$]nonane (**4-46**), prismane (**4-59**), cubane (**4-60**), pagodane (**4-63**) and the bis-methano-bridged [1.1.1.1]pagodane **4-69** reflects the skills of organic chemists in synthesizing systems of this nature today. For this reason, we might be optimistic that if we can design a saturated cage-type hydrocarbon containing a planar-tetracoordinate carbon there would be a reasonable prospect of its successful synthesis. What is needed is a good target molecule for attempts at synthesis. Molecular orbital techniques allow us to examine, relatively straightforwardly, a range of potential target molecules in order to identify the one that is most suitable. The challenging synthetic task might then be reduced to a (still challenging) single molecule.



4-VI



4-VII



4-VIII

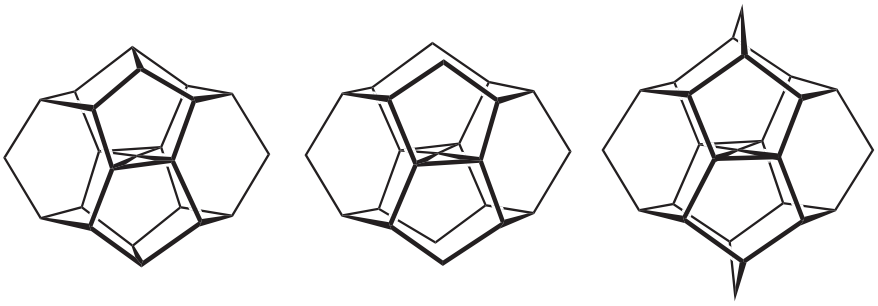
We have examined three families of novel, saturated hydrocarbons, the *alkaplanes* (**4-VI**), the *spiroalkaplanes* (**4-VII**) and the *dimethanospiroalkaplanes* (**4-VIII**), for molecules that would be suitable as synthetic targets in achieving planar-tetracoordinate carbon. The parent alkaplanes based on template **4-VI** are predicted to have a considerable degree of flattening at the central carbon atom (α_{plan} = 5–9°). However, the barrier to inversion through a 'planar' structure is significant (35–140 kJ mol^{-1}) and, of all the novel hydrocarbons studied here, these molecules are the least likely to be good syn-

thetic targets considering their very high strain energies (1180–1770 kJ mol^{-1}), potential problems from a low-lying triplet surface (as seen from the examination of S_4 octaplane (**4-27**)), and, in some cases (in particular **4-33**), elongated C–C bonds.

The spiroalkaplanes (**4-VII**) with an eight-membered primary-ring cap (**4-28**, **4-43** and **4-44**) are much more attractive synthetic targets. They are closer to planarity at the central carbon atom ($\alpha_{plan} \approx 3°$) than the alkaplanes (**4-VI**), and the barrier to inversion is reduced to 5–15 kJ mol^{-1}. Although they are calculated to have quite large total strain energies (873–977 kJ mol^{-1}), taking the size of these structures into consideration ($C_{21}H_{20}$, $C_{21}H_{24}$ and $C_{23}H_{24}$, respectively), these strain energies do not appear to be prohibitive when compared with those for other highly-strained hydrocarbons that have been synthesized (*cf.* cubane (**4-60**), C_8H_8 with $SE = 712$ kJ mol^{-1}, and tetracyclo[3.3.1.$0^{2,4}$.$0^{2,8}$]nonane (**4-46**), C_9H_{12} with $SE = 424$ kJ mol^{-1}). However, the spiroalkaplanes **4-28**, **4-43** and **4-44** do not have the desired property of exact planar-tetracoordination at the central carbon atom. The smaller spiroalkaplanes (**4-39**, **4-40**, **4-41** and **4-42**) look less promising. Although they are also close to planarity at the central carbon atom ($\alpha_{plan} = 3–4°$), they are found to have very strained structures with large values for the $C^{\beta}C^{\alpha}C^{\beta}$ angle (up to 174°) and bond lengths in some of these molecules are calculated to be in excess of 1.60 Å. Consequently, they have very high strain energies (1165–1740 kJ mol^{-1}) and, as a result, are expected to be more difficult to synthesize than the larger spiroalkaplanes (**4-28**, **4-43** and **4-44**).

We have examined three dimethanospiroalkaplanes (**4-VIII**), spiroalkaplanes with a pair of methano-bridges between the caps. Calculations in the present work predict dimethanospiro[2.2]octaplane (**4-29**) and dimethanospiro[2.2]binonaplane (**4-48**) to be exactly planar-tetracoordinate. They are the *first neutral, saturated hydrocarbons to contain an exactly planar-tetracoordinate carbon atom*. Examination of the calculated structures reveals no glaringly long C–C bonds (all bonds are shorter than 1.60 Å) in these molecules that might give an immediate indication of kinetic instability. These two molecules are found to have quite high strain energies (1064 and 980 kJ mol^{-1}, respectively) but preliminary examination of potential decomposition routes suggests that these molecules lie in relatively deep potential energy wells. Provided that these local minima on the $C_{23}H_{24}$ and $C_{25}H_{24}$ potential energy surfaces can be attained, the resulting molecules are expected to be relatively stable. A large proportion of the total

strain energy in these molecules is expected to be concentrated at the central carbon atom (C^0), but this region is well protected by the surrounding hydrocarbon cage. The fairly large $C^\beta C^\alpha C^\beta$ angles of 134–135° suggest that significant strain is also present at the C^α atoms which are quite exposed. It seems likely that a major source of instability in these molecules will result from reactivity at C^α and some protection of these positions may be necessary. This might be achieved by alkyl substitutions at C^β, C^γ (the carbon atoms across a five-membered ring from the C^α–C^α bonds) and possibly at the methano-bridging carbons. The somewhat higher strain energy in **4-29** may be attributed in part to the rather short H–H close contact (1.86 Å), and we therefore suggest dimethanospiro[2.2]binonaplane (**4-48**) as the preferred target.

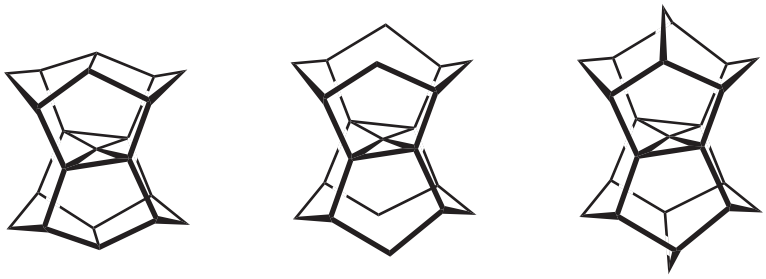


4-47 (D_2) **4-29** (D_2) **4-48** (D_2)

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

The spiroalkaplanes **4-28**, **4-43** and **4-44** and dimethanospiroalkaplanes **4-29**, **4-47** and **4-48** are a remarkable group of molecules that are predicted to have high strain energies but are expected to have good kinetic stability. The extremely planarized coordination at the central tetracoordinate carbon atom of these molecules, imposed in a manner that preserves the $\sigma^2\pi^2$ electronic structure of the planar- or near-planar tetraco-

ordinate carbon, is expected to give these saturated hydrocarbons quite unique properties. As an example, we have calculated the ionization energies (IE_a) of **4-28** and **4-29** to be approximately 5 eV! This is comparable to the ionization energy of the alkali metals lithium and sodium (5.39 and 5.14 eV, respectively). Clearly, successful synthesis of any of these molecules will result in compounds with quite remarkable properties.



4-43 (D_2) **4-28** (D_2) **4-44** (D_2)

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

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