

# Stabilisation of tetrahedrane by fluorination

K. Sudlow, A.A. Woolf\*

Faculty of Applied Sciences, University of the West of England, Bristol BS16 1QY, UK

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## Abstract

The reliability of semi-empirical calculations on tetrahedranes vis-à-vis ab initio ones has been assessed prior to semi-empirical calculations on the geometries and enthalpies of F-, CF<sub>3</sub>- and CF(CF<sub>3</sub>)<sub>2</sub>-substituted tetrahedranes. The tetrahedral skeleton expands on fluorine substitution and slight distortions successively lower the symmetry from *T<sub>d</sub>* to *C<sub>3v</sub>* to *C<sub>2v</sub>* and back again. A much larger expansion occurs with a tetrahedral boron skeleton. Substitution with CF<sub>3</sub> leaves the skeleton intact. This is reflected in the much greater strain energies for fluorine than for CF<sub>3</sub> substitution. The enthalpy increments for F substitution are smaller than Benson's unstrained increment, whereas the CF<sub>3</sub> ones are close to the unstrained value. A single CF<sub>3</sub> substituent produces a greater enthalpy stabilisation than the four t-butyl groups in the only known tetrahedrane. A thermodynamically feasible route to a fluorinated tetrahedrane by halogen elimination from bicyclobutanes is examined.

**Keywords:** Stabilisation; Tetrahedrane; Fluorination; Semi-empirical calculations; Ab initio calculations

## 1. Introduction

There has been continuing interest in closed and cluster compounds over the years accentuated by the recent advent of fullerenes. The smallest closed hydrocarbons of high symmetry, namely tetrahedrane, cubane and dodecahedrane, have carbon skeletons outlining Platonic solids. (Octahedral and icosahedral hydrocarbons are precluded by vertex valencies above four and the requirement of normal two-centre–two-electron bonding.) Tetrahedrane is the most highly strained hydrocarbon in the Baeyer sense, with carbon bond angles a little more than half the normal tetrahedral angle if no allowance is made for bond bending. Nevertheless, a tetrakis(t-butyl) tetrahedrane has been isolated as a stable solid [1]. The reason advanced for its isolation was the ability of the bulky substituents to tightly 'corset' the tetrahedral skeleton and prevent the opening of C–C bonds.

Surprisingly, the possibility of synthesising thermodynamically stable fluorinated tetrahedranes from stable fluorinated precursors, without relying on the steric constraints of bulky tertiary butyl groups, has not been considered; after all, a stable tetrahedral B<sub>4</sub>Cl<sub>4</sub> exists with B–B bonds of less than single-bond order in the absence of a 'corset effect'. There is also evidence for

analogous (BF)<sub>n</sub> clusters [2]. The potential advantage of tetrahedrane syntheses via fluorocarbons is the latter's ability to cyclise more easily and cleanly than hydrocarbons [3,4]. There is also the ability of perfluoroalkyl groups to kinetically stabilise ring structures [5].

In this paper, the stabilities and geometries of fluorinated tetrahedranes are calculated semi-empirically. A previous ab initio calculation at the simplest STO 3G level reported strain energies [6]. Fortunately, many other ab initio calculations on tetrahedranes at higher levels have been made against which we can judge the reliability of the semi-empirical methods employed. The reactivity and preparation of fluorinated tetrahedranes may well differ from those of alkylated derivatives and some reaction possibilities can also be examined semi-empirically.

## 2. Results and discussion

Calculations were performed using the MNDO/PM3 parameters [7] contained in the MOPAC 93 program. All bond lengths are given in Ångstrom and enthalpies in kcal mol<sup>-1</sup> units.

### 2.1. Comparison of semi-empirical PM3 with ab initio calculations

A comprehensive set of calculations on tetrahedrane and its four aza analogues have been made with AM1

\* Corresponding author.

parameters, the predecessor of PM3, and at 3-21G, 4-21G, 6-31G, 6-31G\* and 6-31G\*/MP2 ab initio levels [8]. Abnormally short bonds were found at the penultimate level, which included polarisation, and were only corrected (i.e. brought closer to the first three levels) when MP2 correlation was included.

A comparison of PM3 calculations and the best ab initio ones for enthalpies is given in Table 1. The last values have been computed indirectly by summing ab initio total energies for hypothetical reactions producing triply bonded compounds such as  $C_4H_4 \rightarrow 2HC \equiv CH$  and correcting them with individual zero point energies and  $(H_{298}^\circ - H_0^\circ)$  increments to give standard reaction heats. Finally, these heats combined with experimental enthalpies yielded the requisite tetrahedrane values.

Heats of formation so derived depend both on the basis set and the particular reaction chosen, for example,  $\Delta H_f^\circ(C_4H_4)$  values of 141.3, 155.6 and 132.7 kcal mol<sup>-1</sup> were obtained from three different isodesmic reactions at the same 6-31G\* level. The PM3 value is near the mean of these. An even wider variation (129.3–172.1) was calculated using different basis sets [8]. Although there are no experimental values for direct comparison, it is possible to justify the destabilisation of aza-tetrahedranes independently. Available data show that replacing CH by isoelectronic N stabilises the product when the carbon is sp hybridised. Thus, if  $RC \equiv N$  is compared with  $RC \equiv CH$ , the average stabilisation with R = H, Me, Et,  $CH=CH_2$ , F, Cl and CN is  $23.1 \pm 2.9$ . (This is a probable contributory factor to the interstellar abundance of the nitriles  $H[C \equiv C]_nCN$  where  $n = 1-5$  [9].) However, for non-linear hybridisations there is a destabilisation and this would be expected for similar tetrahedrane carbons with a high p-orbital content.

Deviation of PM3 values from experimental enthalpies of strained cyclic hydrocarbons are not related to strain. (Strain energy is defined as the destabilisation on forming the cyclic system from acyclic 'unstrained' precursors, and compounds were ordered according to the strain energy per carbon.) The most strained closed compound prismane ( $C_6H_6$ ) gave 135.9 kcal mol<sup>-1</sup> with PM3 compared with the experimental value of 136.7. The largest discrepancy occurred with cubane ( $C_8H_8$ ) with 113.8 (PM3) versus 148.7 (expt.). In this instance,

Table 1  
Standard heats of formation (kcal mol<sup>-1</sup>) for gaseous tetrahedranes obtained directly from AM1 or PM3, and indirectly from 6-31G\* calculations [8]

Tetrahedrane	AM1	PM3	6-31G*
$C_4H_4$	159.3	140.2	155.6
$C_3H_2N$	168.5	149.4	159.5
$C_2H_2N_2$	184.7	172.4	173.1
$CHN_3$	207.3	211.0	196.3
$N_4$	234.6	265.7	229.5

the AM1 value (151.2) is much closer. Each closed system has to be assessed separately. With regard to C–C bond lengths in tetrahedranes, the PM3 values of 1.487 Å in  $C_4H_4$  and 1.491 Å in  $C_4Bu_4$  were within the experimental limits found in an X-ray structure of the latter at 1.486(5) Å [10]. This compares favourably with 1.476 Å obtained with the best ab initio calculations (6-31G\*/MP2).

We conclude that PM3 calculations seem no worse than the ab initio ones employed to date with tetrahedranes. Whilst absolute values for enthalpies may be in error, trends in series are likely to be reproduced because enthalpy differences between the related compounds calculated with the same semi-empirical method will tend to cancel individual errors.

## 2.2. Geometries and enthalpies in the $CH_4-C_4F_4$ series

Both  $C_4H_4$  and  $C_4F_4$  have  $T_d$  symmetry with C–H or C–F bonds emerging from the centroids at the requisite 144.7° angles to edges and with faces correctly inclined at 70.5°. The monosubstituted  $C_4H_3F$  is compressed along the  $C_3$  axis, the trisubstituted one elongated. In the disubstituted derivative ( $C_{2v}$ ), the FC–CF bond is compressed while the HC–CH bond is elongated. The bond lengths and enthalpies are collected in Table 2 together with previous ab initio enthalpy values [6]. The sequence of bond lengths  $FC-CF > FC-CH > HC-CH$  might be expected on the basis of decreasing lone pair and bonding pair repulsions. However, the reverse order found is consistent with the atomic charges. Thus the charges on the C–H bond at –0.18 and +0.18 remain constant through the series, but the charges on carbon in the C–F bonds are  $\leq 0.01$  and on fluorine decrease from –0.03 to 0.007. This charge distribution maximizes (C–H) bond repulsions and lengthens HC–CH bonds relative to FC–CF ones. The low polarity on the C–F bond, as compared with the C–H bond, indicated appreciable  $\pi$ -backbonding from the fluorine substituent. In addition, some electron density is inductively withdrawn from the tetrahedral skeleton as evidenced by an averaged C–C bond lengthening.

The enthalpy increments per fluorine decrease slightly with successive fluorines with a mean value of  $35.5 \pm 0.3$ . This is much lower than Benson's  $C(F)(C)_3$  increment of 48.5 [12] for unstrained molecules. The increments in fluorinated benzenes, for example, show a wider variation decreasing linearly from 47.6 to 41.4 from mono- to hexa-fluorobenzenes.

## 2.3. Comparison with ab initio values and calculation of strain energies

Enthalpies for fluorinated tetrahedranes were supplied in a supplement to a comprehensive review of

Table 2  
Bond lengths (Å) and enthalpies (kcal mol<sup>-1</sup>) in the C<sub>4</sub>H<sub>4</sub>–C<sub>4</sub>F<sub>4</sub> tetrahedrane series

Tetrahedrane	C–C	Mean C–C	Mean C–F	ΔH <sub>f</sub> <sup>o</sup> (PM3)	ΔH <sub>f</sub> <sup>o</sup> [6] (STO-3G)
C <sub>4</sub> H <sub>4</sub>		1.487 <sup>a</sup>	–	140.2	141.3 <sup>d</sup>
C <sub>4</sub> H <sub>3</sub> F	1.496 × 3 <sup>a</sup>	1.489	1.315	104.3	99.8
C <sub>4</sub> H <sub>2</sub> F <sub>2</sub>	1.482 × 3 <sup>b</sup>	1.492	1.313	68.9	57.7
	1.505 × 1 <sup>a</sup>				
	1.492 × 4 <sup>b</sup>				
C <sub>4</sub> HF <sub>3</sub>	1.479 × 1 <sup>c</sup>	1.496	1.312	34.1	16.8
	1.502 × 3 <sup>b</sup>				
	1.492 × 3 <sup>c</sup>				
C <sub>4</sub> F <sub>4</sub>		1.500 <sup>c</sup>	1.310	–0.1	–22.7
	Mean increment per F group			35.5 ± 0.3	41.0 ± 0.4

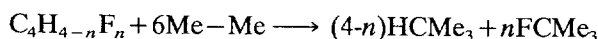
<sup>a</sup> HC–CH.

<sup>b</sup> HC–CF.

<sup>c</sup> FC–CF.

<sup>d</sup> This is a 6-31G\* value [11].

substituent effects on strain energies [13]. It was emphasised that the same basis set had to be maintained in a series in order to cancel out deficiencies in the basis set and neglect of correlation energies. The simplest STO-3G set was used on fluorinated tetrahedranes. However, the tetrahedrane value was inconsistently obtained at the 6-31G\* level via an isodesmic reaction to but-1-yn-3-ene [11]. The total energy for C<sub>4</sub>H<sub>4</sub> calculated with the 6-31G\* basis is less negative than the STO-3G value which renders any ‘same basis’ comparison of C<sub>4</sub>H<sub>4</sub> with C<sub>4</sub>H<sub>4–n</sub>F<sub>n</sub> using the RX + CH<sub>4</sub> → RH + CH<sub>3</sub>X type of reaction invalid. We have recalculated strain energies from the exothermic homodesmotic ring openings, i.e.



with PM3 values and the auxiliary heats ΔH<sub>f</sub><sup>o</sup>(C<sub>2</sub>H<sub>6</sub>) = 20.1, ΔH(HCMe<sub>3</sub>) = –32.35 and ΔH(FCMe<sub>3</sub>) = –79.0 kcal mol<sup>-1</sup> (this last value was estimated using the difference between Benson’s enthalpy increments C(H)(C)<sub>3</sub> = –1.90 and C(F)(C)<sub>3</sub> = –48.5 [12]). The strain energies are compared in Table 3. Both sets indicate increases in strain energy on fluorination.

One can also estimate bond dissociation energies (*D*) in the tetrahedral skeleton by assuming the external C–X bonds have the same strength as in normal bonds. Thus *D*(C–C) in C<sub>4</sub>H<sub>4</sub> is 59 kcal mol<sup>-1</sup>, using *D*(C–H) = 99.4 as in methane, and *D*(C–C) in C<sub>4</sub>F<sub>4</sub> is 49 kcal mol<sup>-1</sup>, using *D*(C–F) = 115.5 as in perfluoroalkane, in agreement with the calculated bond lengthening. This difference in *D*(C–C) values is close to the PM3 difference in strain energies if distributed over the six C–C bonds.

Table 3  
Strain energies in fluorinated tetrahedranes (kcal mol<sup>-1</sup>)

Tetrahedrane	Strain energy/carbon	
	PM3	STO-3G
C <sub>4</sub> H <sub>4</sub>	37.2	37.2 <sup>a</sup>
C <sub>4</sub> H <sub>3</sub> F	40.0	38.3
C <sub>4</sub> H <sub>2</sub> F <sub>2</sub>	42.8	39.3
C <sub>4</sub> HF <sub>3</sub>	45.7	40.4
C <sub>4</sub> F <sub>4</sub>	48.9	41.7
Mean increment per F group	2.9 ± 0.2	1.2 ± 0.2

<sup>a</sup> Calculated with the 6-13G\* basis.

Table 4  
Enthalpies (kcal mol<sup>-1</sup>), bond lengths (Å) and charges in tetrahedral boranes

Borane	B–B	B–X	ΔH <sub>f</sub> <sup>o</sup>	Charge on X
B <sub>4</sub> H <sub>4</sub>	1.661	1.183	126.1	–0.621
B <sub>4</sub> Cl <sub>4</sub>	1.710	1.656	–62.3	–0.081
B <sub>4</sub> F <sub>4</sub>	1.764	1.291	–292.8	–0.143

#### 2.4. Comparison with tetrahedral boranes

The most investigated member of the (BX)<sub>n</sub> series is the stable tetrahedral B<sub>4</sub>Cl<sub>4</sub> [2]. Heats of formation and bond lengths calculated semi-empirically are collected in Table 4.

Unlike in C<sub>4</sub>F<sub>4</sub>, the inductive effect predominates in B<sub>4</sub>F<sub>4</sub> leading to a large negative charge on fluorine and a considerable expansion of the skeleton. The much larger stabilisation on fluorination is partly due to the greater B–F bond strength. A previous ab initio calculation confirmed the stability of B<sub>4</sub>F<sub>4</sub> [14].

Table 5  
Bond lengths (Å) and enthalpies (kcal mol<sup>-1</sup>) in the C<sub>4</sub>H<sub>4</sub>–C<sub>4</sub>(CF<sub>3</sub>)<sub>4</sub> series

Tetrahedrane	Mean C–C	Mean C–C(F <sub>3</sub> )	Mean C–F	ΔH <sub>f</sub> <sup>o</sup>
C <sub>4</sub> H <sub>4</sub>	1.487	–	–	140.2
C <sub>4</sub> H <sub>3</sub> (CF <sub>3</sub> )	1.488	1.485	1.354	–16.0
C <sub>4</sub> H <sub>2</sub> (CF <sub>3</sub> ) <sub>2</sub>	1.488	1.492	1.353	–168.6
C <sub>4</sub> H(CF <sub>3</sub> ) <sub>3</sub>	1.488	1.498	1.351	–318.1
C <sub>4</sub> (CF <sub>3</sub> ) <sub>4</sub>	1.488	1.502	1.350	–464.9
		Mean increment per CF <sub>3</sub> group		153.7 ± 1.4

### 2.5. Geometries and enthalpies in the C<sub>4</sub>H<sub>4</sub>–C<sub>4</sub>(CF<sub>3</sub>)<sub>4</sub> series

In this series the tetrahedral skeleton remains constant but the C–C(F<sub>3</sub>) lengths increase and the C–F lengths decrease slightly on substitution. The latter are close to those of 1.351 Å found in CH<sub>2</sub>F<sub>2</sub>. The external C–C bonds make 144.7° angles to the edges when averaged. The maximum deviation from the 60° face angles is only 0.11° in the disubstituted compound. Again, the formation heats decrease in an almost linear fashion. However, a CF<sub>3</sub> group is about as effective as 4.3 F groups in stabilising tetrahedrane. The results are summarised in Table 5.

A calculation on mono *F*-isopropyltetrahedrane [(CF<sub>3</sub>)<sub>2</sub>CF]C<sub>4</sub>H<sub>3</sub> was made to see if any further enhancement of stability occurred. The point group as expected was C<sub>s</sub>, the mean C–C 1.489, C–C[F(CF<sub>3</sub>)<sub>2</sub>] 1.465, FC–CF<sub>3</sub> 1.601, C–F 1.361 and C–F<sub>3</sub> 1.346 Å. The heat of formation of –216.5 kcal mol<sup>-1</sup>, or stabilisation of 356.7 kcal mol<sup>-1</sup> over C<sub>4</sub>H<sub>4</sub>, is greater than calculated from 2CF<sub>3</sub> + 1F of 337. A CF(CF<sub>3</sub>)<sub>2</sub> group is therefore as effective as 10.2 F groups.

It should be possible to estimate enthalpies of mixed derivatives because of the approximate linearities in series (see Fig. 1). Thus, for C<sub>4</sub>F<sub>2</sub>(CF<sub>3</sub>)<sub>2</sub> the estimate is 140 – 2 × 35.5 – 2 × 153.7 = –238 kcal mol<sup>-1</sup>.

The increment for the CF<sub>3</sub> group of 153.7 ± 1.4 kcal mol<sup>-1</sup> is close to the Benson unstrained increment for C(F)<sub>3</sub>C of 158.4. The strain energies, calculated with ΔH<sub>f</sub><sup>o</sup>(CF<sub>3</sub>CMe<sub>3</sub>) = –188.9, obtained from ΔH<sub>f</sub><sup>o</sup>(HCMe<sub>3</sub>) and the aforementioned Benson increments, were 149.3, 153.2, 160.2 and 169.9 kcal mol<sup>-1</sup>, respectively, for the CF<sub>3</sub> substituted tetrahedranes. Monosubstitution has almost no effect and we can ascribe subsequent increases in strain to *exo* repulsions rather than skeletal change since the tetrahedral C–C bonds lengths remain invariant. The previous value of ΔH<sub>f</sub><sup>o</sup>(CF<sub>3</sub>C<sub>4</sub>H<sub>3</sub>) = 97 [13], using STO-3G total energies, is dubious because the stabilisation for a CF<sub>3</sub> substituent would be only slightly larger than for a single fluorine substituent.

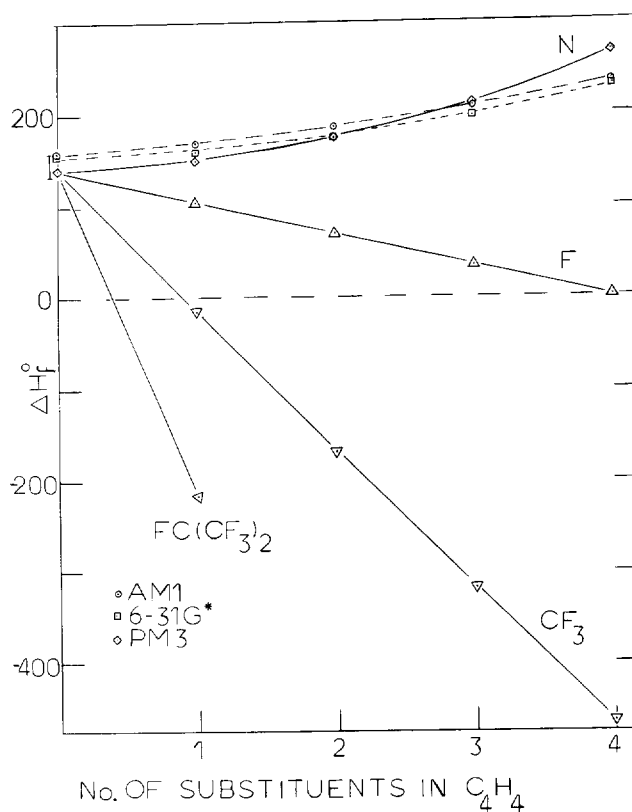


Fig. 1. Variation in the heats of formation for aza- and fluoro-tetrahedranes. (The vertical bar spans 6-31G\* values for C<sub>4</sub>H<sub>4</sub>.)

### 2.6. Tetrahedranes as electron donors

According to Maier [1], all reaction of *t*-butyl tetrahedrane, apart from simple protonation, proceed via oxidation to a radical cation of the cyclobutadiene form. Fluorination would be expected to diminish this propensity. Following Pearson's procedure [15], the fractional electron transfer Δ*N* between A and B can be calculated from Δ*N* = (X<sub>A</sub> – X<sub>B</sub>)/2(n<sub>A</sub> + n<sub>B</sub>) where the X quantities are electronegativities and *n* quantities are hardness values, both derived from ionisation energies (*I*) and electron affinities (*A*), i.e. X = (I + A)/2,

Table 6  
Tetrahydrene electron transfer to dichlorine calculated from absolute electronegativity and hardness [14]

Tetrahydrene	Energies in eV		Hardness ( $n$ ) ( $L-H$ )/2	Electro negativity ( $X$ ) ( $n-L$ )	Electron transfer to dichlorine <sup>a</sup>
	LUMO ( $L$ )	HOMO ( $H$ )			
C <sub>4</sub> H <sub>4</sub>	-10.22	2.48	6.35	3.87	0.143
C <sub>4</sub> H <sub>3</sub> F	-10.41	1.32	5.87	4.54	0.117
C <sub>4</sub> H <sub>2</sub> F <sub>2</sub>	-10.57	0.78	5.68	4.90	0.102
C <sub>4</sub> HF <sub>3</sub>	-10.72	0.44	5.58	5.14	0.091
C <sub>4</sub> F <sub>4</sub>	-10.83	0.12	5.48	5.36	0.081
C <sub>4</sub> H <sub>3</sub> CF <sub>3</sub>	-11.08	0.83	5.96	5.13	0.089
C <sub>4</sub> H <sub>2</sub> (CF <sub>3</sub> ) <sub>2</sub>	-11.82	0.11	5.96	5.85	0.054
C <sub>4</sub> H(CF <sub>3</sub> ) <sub>3</sub>	-13.12	-0.49	6.01	6.50	0.024
C <sub>4</sub> (CF <sub>3</sub> ) <sub>4</sub>	-13.12	-1.03	6.04	7.07	-0.003
C <sub>4</sub> H <sub>3</sub> CF(CF <sub>3</sub> ) <sub>2</sub>	-11.15	-0.33	5.41	5.74	0.063
C <sub>4</sub> <sup>t</sup> Bu <sub>4</sub>	-9.41	2.38	5.89	3.51	0.166

<sup>a</sup>  $(X'-X)/2(n'+n)$  where  $X'$  and  $n'$  for dichlorine are 7.0 and 4.6 derived from the experimental values  $I$  and  $A$ .

Table 7  
Comparison of the enthalpies (kcal mol<sup>-1</sup>) of tetrahydrenes (T) and isomeric cyclobutadienes (CB)

	$\Delta H_f^\circ(T)$	$\Delta H_f^\circ(CB)$	$\Delta H_f^\circ(T) - \Delta H_f^\circ(CB)$
C <sub>4</sub> H <sub>4</sub>	140.2	99.0	41.2 <sup>a</sup>
C <sub>4</sub> F <sub>4</sub>	-0.1	-68.4	68.3
C <sub>4</sub> H <sub>3</sub> (CF <sub>3</sub> )	-16.0	-59.3	43.3
C <sub>4</sub> H <sub>2</sub> (CF <sub>3</sub> ) <sub>2</sub>	-168.6	-214.5 (for 1,2) -215.6 (for 1,3)	45.9 47.0

<sup>a</sup> This difference by PM3 calculation agrees with ab initio values at 4-21G, 4-31G and 6-31G levels but is larger than a 6-31G\* value of 28.

$n = (I - A)/2$ . This is the equivalent of Ohm's law with electronegativity difference replacing electromotive force and hardness the resistance to electron flow. Values of  $\Delta N$  for oxidation by dichlorine are collected in Table 6. The tetrahydrene values were derived from HOMO and LUMO energies assuming Koopmans' theorem to hold for the initial stage of electron-transfer Pearson-related  $\Delta N$  to activation barriers; hence the more positive  $\Delta N$ , the faster the rate.

Table 8  
Bond lengths (Å) and dihedral angles (°) in wing-shaped bicyclo[110]butanes

Bicyclobutane	C(4)–C(2)	Mean of other C–C	C(1)···C(3)	C–F		Dihedral angle
				In CF <sub>2</sub>	In CF <sub>3</sub>	
(CF <sub>2</sub> ) <sub>2</sub> (CCF <sub>3</sub> ) <sub>2</sub>	1.500	1.526	2.307	1.337	1.349	120.6
(CFCl) <sub>2</sub> (CCF <sub>3</sub> ) <sub>2</sub>	1.490	1.519	2.324	1.343 (1.746) <sup>a</sup>	1.350	122.7
(CCl <sub>2</sub> ) <sub>2</sub> (CCF <sub>3</sub> ) <sub>2</sub>	1.488	1.511	2.321	(1.723) <sup>a</sup>	1.351	123.9

<sup>a</sup> C–Cl lengths in brackets (see Fig. 2 for numbering).

Surprisingly, hardness drops on F substitution but is almost constant for CF<sub>3</sub> substitution. This corresponds with skeletal expansion with the former as against skeletal constancy with the latter. (See Tables 2 and 5.) As expected, electron transfer decreases with fluorination and is at a maximum with the <sup>t</sup>Bu derivative.

## 2.7. A possible route to fluorinated tetrahydrenes

The much greater thermodynamic stability of tetrahydrenes with at least one perfluoroalkyl group over that of the tetra(<sup>t</sup>-butyl) derivative is not a guarantee that they can be synthesised in practice. Firstly, the isomeric cyclobutadienes are always more stable than the corresponding tetrahydrenes (see Table 7) so that ring opening is always a possibility on activation, although there is a considerable energy barrier to this symmetry forbidden change.

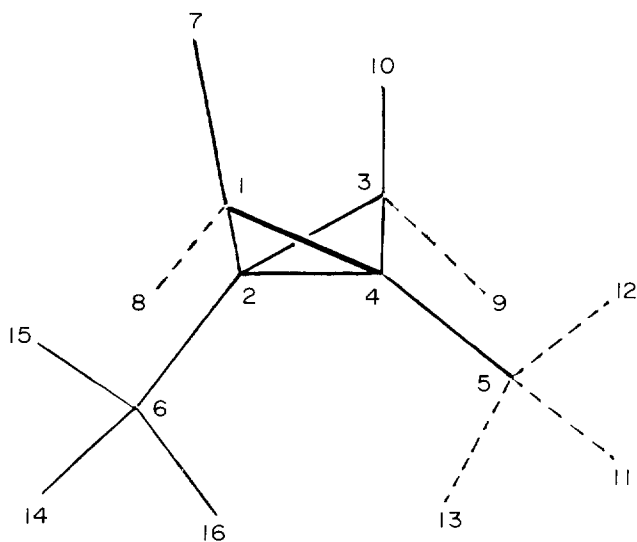
Secondly, the 'corset effect' is not possible with less bulky fluoroalkyl or perfluoroalkyl groups. The original synthesis by UV irradiation of a dienone, matrix-isolated at low temperature, needed a criss-crossing of bonds prior to CO elimination.

Table 9  
Enthalpies (in kcal mol<sup>-1</sup>) of bicyclo[110]butanes and tetrahedranes formed by dehalogenation

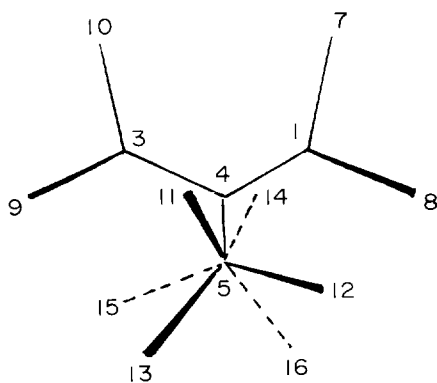
Bicyclobutane	$\Delta H_f^\circ$ (1)	Tetrahedrane	$\Delta H_f^\circ$ (2)	(2-1)	$\Delta H_f^\circ$ [ZnX <sub>2</sub> (s)] <sup>a</sup>
(CF <sub>2</sub> ) <sub>2</sub> (CCF <sub>3</sub> ) <sub>2</sub>	-418.1	(CF <sub>2</sub> ) <sub>2</sub> (CCF <sub>3</sub> ) <sub>2</sub>	-234.6 <sup>b</sup>	183.5	-213.9
(CFCl) <sub>2</sub> (CCF <sub>3</sub> ) <sub>2</sub>	-328.0	(CF) <sub>2</sub> (CCF <sub>3</sub> ) <sub>2</sub>	-234.6	93.4	-124.6
(CCl <sub>2</sub> ) <sub>2</sub> (CCF <sub>3</sub> ) <sub>2</sub>	-249.8	(CCl) <sub>2</sub> (CCF <sub>3</sub> ) <sub>2</sub>	-171.9	77.9	-124.6

<sup>a</sup>  $\Delta H_f^\circ$  for Zn + X<sub>2</sub>(g) → ZnX<sub>2</sub>(s); Zn(s) → Zn(g) is equal to 31.2 kcal mol<sup>-1</sup>.

<sup>b</sup> Compare estimate of -238 kcal mol<sup>-1</sup> given previously.



(a)

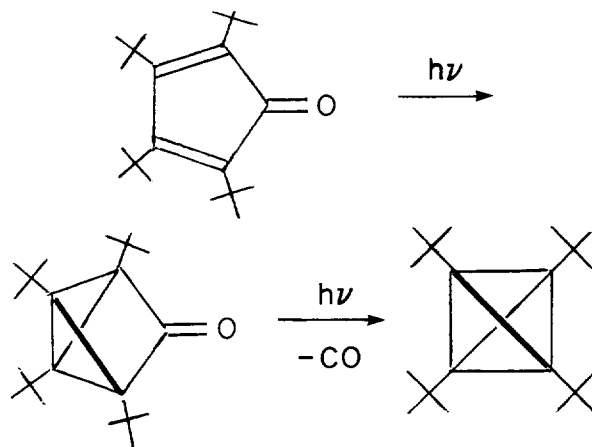


(b)

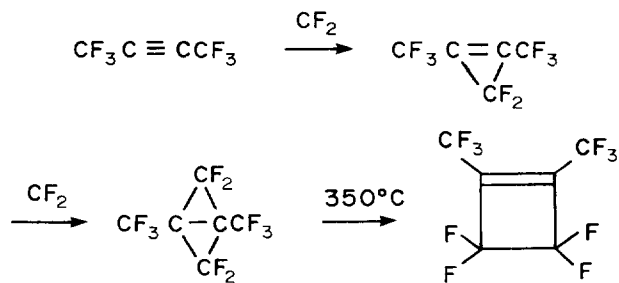
Fig. 2. Calculated wing structure of (CF<sub>2</sub>)<sub>2</sub>(CCF<sub>3</sub>)<sub>2</sub> shown in orthogonal view (atoms 1–6 are carbons). (a) View across wing with CF<sub>2</sub> groups almost eclipsed; (b) view down 5–6 showing the relative orientations of the CF<sub>3</sub> groups.

Room-temperature irradiation yielded di(*t*-butyl)-acetylene. These reactions required *t*-butyl substituents and failed with smaller alkyls and even with the bulky Si(CH<sub>3</sub>)<sub>3</sub> group, and hence are unlikely with a F or

CF<sub>3</sub> substituent on size grounds alone, quite apart from the electronic differences indicated previously. An



alternative route which makes use of a preformed inclined wing structure can be examined. Mahler [16] has already synthesised such a structure by successive additions of difluorocarbene, generated in situ by thermolysis of PF<sub>2</sub>(CF<sub>3</sub>)<sub>3</sub>, to a perfluoroacetylene.



Elimination of a fluorine from each bridging carbon might generate a mixed tetrahedrane if bond switching could be avoided. This seems feasible because the bicyclobutane is kinetically stable. High temperatures were required before it rearranged to the cyclobutene. Calculations on bicyclo compounds with different bridging groups and corresponding tetrahedranes are collected in Tables 8 and 9. The loss in stability on closure to the tetrahedrane has to be more than compensated by the gain in stability on metal halide formation for a reaction to be feasible.

Zinc in polar solvents has been employed for dehalogenation at low temperatures, but metal atom re-

ductions would be much more effective because there is a greater free energy gain on metal halide formation from endoergic metal atoms. Also, reaction is possible at cryogenic temperatures with matrix isolation of intermediates from which products can be controlled by a choice of annealing temperatures. Klabunde et al., for example, have shown that metal atoms interact with methyl halides in matrices kept as low as 10 K [17]. Metals with low ionisation energies can insert in the C–X bond, otherwise weak MeX–M complexes form as with zinc. Timms has described a simple apparatus for carrying out metal atom reactions [18].

The wing would be expected to open if isolated diradicals were formed by elimination of chlorine atoms, and this has been confirmed by calculation. However, the presence of adjoining metal atoms in the matrix would generate polar forces by electron transfer, and tend to close the wing dihedral before the elimination of metal halide. This would be achieved most easily with the dichlorocarbene adduct which also requires the least dimensional change on closure. Four C–C bonds need to shorten by 0.02 Å and the dihedral angle to close to 70.5°. Dechlorination would be the preferred elimination because the C–Cl bond is weaker than the C–F bond.

It seems that C<sub>4</sub>F<sub>4</sub> and the perfluorofullerene C<sub>60</sub>F<sub>60</sub> are at extrema. The former has the maximum internal strain and the minimum external C–F repulsions. The latter has the minimum internal strain and the maximum external C–F repulsions. The C–F bonds in C<sub>60</sub>F<sub>60</sub> are eclipsed and fluorine is easily replaced by nucleophilic attack [19].

For brevity, a limited amount of data is reported. Full print-outs of PM3 calculations on particular compounds can be requested from the authors.

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