PERKIN 2

Isolation and characterisation of two oxahomofullerene derivatives of $C_{60}F_{18}$

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From the products of the reaction of [60]fullerene with K_2PtF_6 under vacuum at 465 °C we have isolated two minor isomers of $C_{60}F_{18}O$, and characterised them by EI mass spectrometry, IR and ^{19}F NMR spectroscopy. Calculations, the NMR spectra, thermal degradation, and the lack of evidence for the existence of precursors for the formation of epoxides indicate that, like the major isomer recently fully characterised, both are ethers. The results emphasise that oxides of fullerene derivatives may be either epoxides or ethers. Calculations show a correlation between length of the FC–CF bonds and heat of formation of the ethers, reinforcing our previous conclusion that the bond length is a driving force for ether formation. Given this, one can anticipate ether formation in other derivatised fullerenes which possess a long α,β-bond.

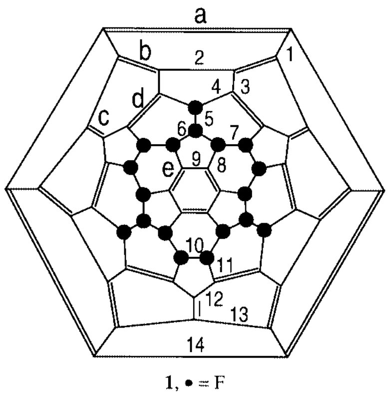
Introduction

The formation of oxides is an important aspect of fullerene chemistry. It is necessary therefore to understand oxide formation more fully if ways to overcome it, when required, are to be found. At present there is no clear information regarding the effect of addends on oxide formation. One area where oxide formation is substantial is in reactions involving halogenofullerenes, the oxides being considered to be epoxides arising from elimination of HX between X and an adjacent OH group (introduced by nucleophilic substitution of X by OH from water). Thus the products of reaction of benzene, bromine, $FeCl_3$ and [60]fullerene contained a number of oxides, presumed to be epoxides.[1] Because of the stronger C–F bond in fluorofullerenes, mass spectroscopic analysis can be used here, the epoxide nature of the oxides C_nF_mO arising from reaction with water being indicated by the presence of precursors such as $C_nF_{m+1}OH$ and C_nF_{m+2}.[2] Where no such corresponding precursor is found (which in the present case would be $C_{60}F_{20}$), the oxides are likely to be in the form of ethers.

A bis-epoxide structure (defined by single crystal X-ray diffraction) has been found in the reaction of $C_{60}Cl_6$ with MeLi–H_2O.[3] Oxide formation is considerable in the products of reaction of either fluorine or metal fluorides with [60]fullerene, especially when fluorine is used.[2,4] In these two reactions water was believed to be absent, implying that direct reaction with oxygen occurs. Nevertheless, after the addition of methanol to a polyfluorinated mixture, molecules containing up to as many as 18 oxygens could be discerned in the mass spectrum, implying involvement of the substitution–elimination pathway in this case.[4]

Previously we described the formation and characterisation of both C_{3v} $C_{60}F_{18}$ (**1**)[5] and C_s $C_{60}F_{18}O$,[6] compounds which were isolated by HPLC (High Pressure Liquid Chromatography) in *ca.* single mg quantities. The ^{19}F NMR was fully consistent with the presence of an epoxide function in the symmetry plane (**2**), but recent single-crystal X-ray diffraction shows that the compound is an ether (**3**)[7] (which would give rise to a similar NMR spectrum). This resolves one problem inherent in the epoxide structure, since not only would it have to be derived from a $C_{60}F_{20}$ precursor present in substantial quantities (which we did not find), but this precursor would require addition of F_2 remote from the other fluorines, contrary to current evidence that fluorine adds regularly in a contiguous manner.[8]

Owing to the availability of much greater amounts of crude material, and a 10 mm diameter Cosmosil Buckyprep column,



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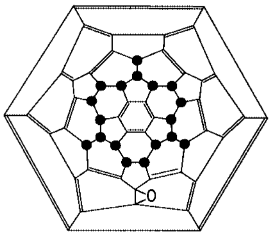

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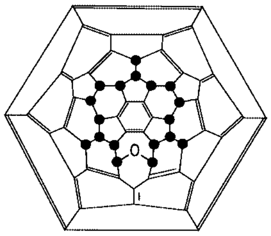

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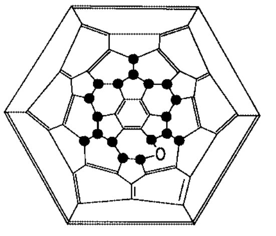

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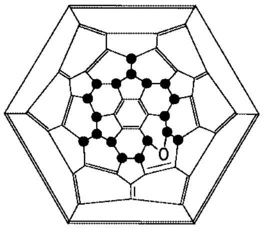

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Table 1 Heats of formation (kcal mol^{-1}) for epoxides calculated by both AM1 and MNDO methods

Epoxide position (see **1**)	Bond	MNDO	AM1	Bond lengths/Å[10]
a	46,47	−122.4	−27.2	1.387
b	28,29	−117.4	−23.2	1.436
c	13,30	−111.7	−18.0	1.386
d	11,12	−113.5	−23.2	1.363
e	5,6	−63.9	17.8	1.372

Table 2 Heats of formation (kcal mol^{-1}) for ethers calculated by both AM1 and MNDO methods

Ether position (see **1**)	Bond	MNDO	AM1	Bond lengths/Å[10]
1	29,47	−128.9	−40.9	1.453
2	27,28	−115.8	−29.2	1.437
3	11,28	−112.7	−27.1	1.435
4	10,11	**−129.2**	**−50.3**	1.524
5	9,10	−122.8	−43.5	1.558
6	1,9	**−142.3**	**−66.2**	1.623
7	1,2	**−129.3**	**−50.5**	1.557
8	1,6	−43.9	−17.9	1.476
9	5,19	−56.7	21.1	1.372
10	2,3	**−150.9**	**−74.5**	1.672
11	2,12	−113.5	−34.2	1.500
12	12,13	−88.3	−18.9	1.428
13	29,30	−120.7	−33.2	1.387
14	47,48	**−130.1**	**−41.7**	1.447

we are now able to describe the isolation and characterisation of two other $C_{60}F_{18}O$ isomers, each of C_1 symmetry. We show that the 1D and 2D ^{19}F NMR data are consistent with ether structures for these compounds (**4**), (**5**), and this is supported by calculations of the heats of formation (Tables 1 and 2).

Experimental

[60]Fullerene (240 mg) was ground in a dry box with K_2PtF_6 (575 mg) and heated to 465 °C at *ca.* 0.01 bar in a glass tube contained within a furnace.[7] The crude fluorofullerene mixture (300 mg, 85%) was partly pre-purified by vacuum sublimation and a sample (*ca.* 280 mg) was dissolved in dry toluene (25 ml) and filtered under conditions which avoided moisture condensation. Purification by HPLC (10 mm × 250 mm Cosmosil Buckyprep column) with toluene elution at a flow rate of 4.7 ml min^{-1} yielded a number of other components in 1–5 mg amounts, together with recovered [60]fullerene (*ca.* 75 mg), $C_{60}F_{18}$[5] (*ca.* 100 mg), and three isomers of $C_{60}F_{18}O$ (**3**),[6] (**4**), and (**5**), in approximate yields of 35, 2, and 2 mg, respectively; each is pale yellow in toluene solution.

The retention times of these components were 37, 58, 44, and 48 min, respectively. Isomer **3** proved very slow to redissolve once toluene solutions of it had evaporated to dryness, indicating close packing in the crystal lattice, a property typical of many fullerenes and derivatives.

Mass spectra (70 eV)

Each component showed the parent ion at 1078 amu [that for **3** has been given previously].[5] Compounds **4** and **5** also showed the presence of a small amount of fluoromethyl derivative, but this did not interfere significantly with the subsequent spectra.

IR spectra (KBr)

The IR spectra for **3**, **4**, and **5** are shown in Fig. 1a–c, respectively. They show strong similarities with each other and to that of $C_{60}F_{18}$,[5] with main bands appearing at (cm^{-1}): 1166, 1136, 1101, 1065, 836 and 590 (**3**); 1180, 1162, 1134, 1101, 1065, 838, 735, and 590 (**4**); 1196, 1165, 1150, 1133, 1103, 1067, 936, 854, 842, 732, and 589 (**5**). On heating the KBr discs to 225 °C for 2 h, each showed the formation of matrix-isolated CO_2 (sharp band at 2334 ± 2 cm^{-1}) and matrix-isolated CO (broad band at 2103 ± 2 cm^{-1}).[9] These bands are shown in Fig. 2a–c, respectively, and it is notable that the most stable isomer **3** (as indicated by its extent of formation) showed less degradation, under the same conditions, than either **4** or **5**.

^{19}F NMR spectra (338.9 MHz)

The spectrum for isomer **3** has been given previously. It consists of 10 lines (8 × 2 F + 2 × 1 F), showing that the compound has C_s symmetry.

The spectrum for isomer **4**, Fig. 3, consists of 18 multiplets of equal intensity, at δ_F −74.6, −77.9, −127.7, −132.7 (coincident peaks), −134.2, −135.1, −137.5, −138.5, −146.1, −146.4, −146.6, −146.8 (coincident peaks), −149.2, −160.8, −163.3, −170.1. This isomer therefore has C_1 symmetry.

The spectrum for isomer **5**, Fig. 4, also consists of 18 multiplets of equal intensity, at δ_F −91.6, −115.8, −127.0, −132.4, −133.0, −133.8, −137.5, −137.7, −139.5, −143.5, −146.1, −146.6, −148.4, −148.9, −150.4, −160.0, −160.5, −162.3. This compound therefore also has C_1 symmetry, and thus we have two asymmetric isomers.

The positions of the most downfield peaks in the three oxides, shown in Fig. 5, are important in determining the structures of **4** and **5**, as shown below.

Discussion

Before considering the possible structures of the oxides, we note that there are five mathematically possible epoxide and 14 possible ether decorations of the C_{3v} $C_{60}F_{18}$ structure, some of which can be ruled out immediately on chemical or spectroscopic grounds.

Of the epoxides, those involving addition across bonds *a*, *c*, and *e* are eliminated since they would have C_s symmetry, and addition across *b* is improbable not only because the precursor fluorines are not contiguous with the rest, but because the oxygen is too far away to produce the observed downfield peaks in the NMR spectra (see Figs. 3 and 4). An epoxide involving addition across bond *d* could be derived from the contiguous addition of two fluorine atoms to $C_{60}F_{18}$, but it has a high heat of formation relative to the ether alternatives, and moreover the oxygen is still two carbon atoms away from any fluorine and thus unlikely to account for the downfield shifts observed in the NMR spectrum.

Of the ethers, those involving insertion into bonds 2, 5, 9, 10, and 14 can be ruled out as they have C_s symmetry; insertion into bond 10 produces the ether isolated previously.[6] For those involving insertion into bonds 1, 3, 12 and 13, the oxygen would be also too far away to cause the observed downfield shifts in the NMR spectra. This leaves ethers involving insertion into bond 4, 6, 7, 8 or 11, of which no. 8 is energetically very unfavourable since it would disrupt the planarity of the central benzenoid ring. Of the remainder, no. 11 is predicted also to have a relatively high heat of formation, so that the choice comes down to nos. 4 (insertion into a FC–C≡ bond), 6 and 7 (insertion into a FC–CF bond).

The calculated heats of formation (MNDO and AM1 semi-empirical Hamiltonians) of all of the possible epoxides and ethers are shown in Tables 1 and 2, together with the experimentally determined bond lengths in the $C_{60}F_{18}$ precursor. These are considered further below.

The structure of the oxides

We have obtained 2D ^{19}F NMR spectra for both of the new oxides but, as in the case of the major isomer reported previously,[6] not all of the connections are seen, attributable

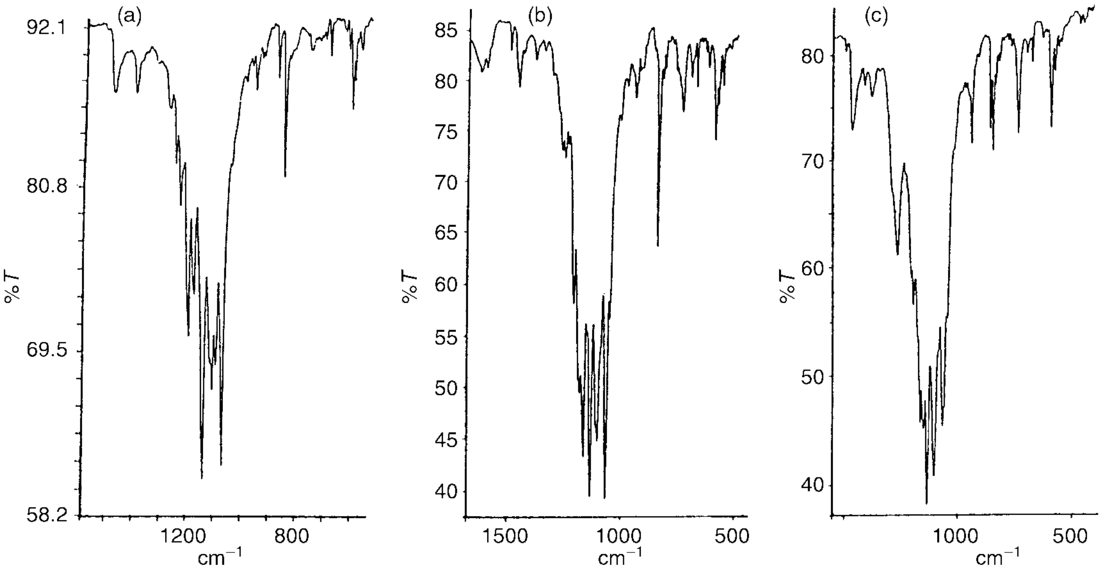

Fig. 1a–c IR spectra (KBr) for isomers **3**, **4**, and **5**, respectively.

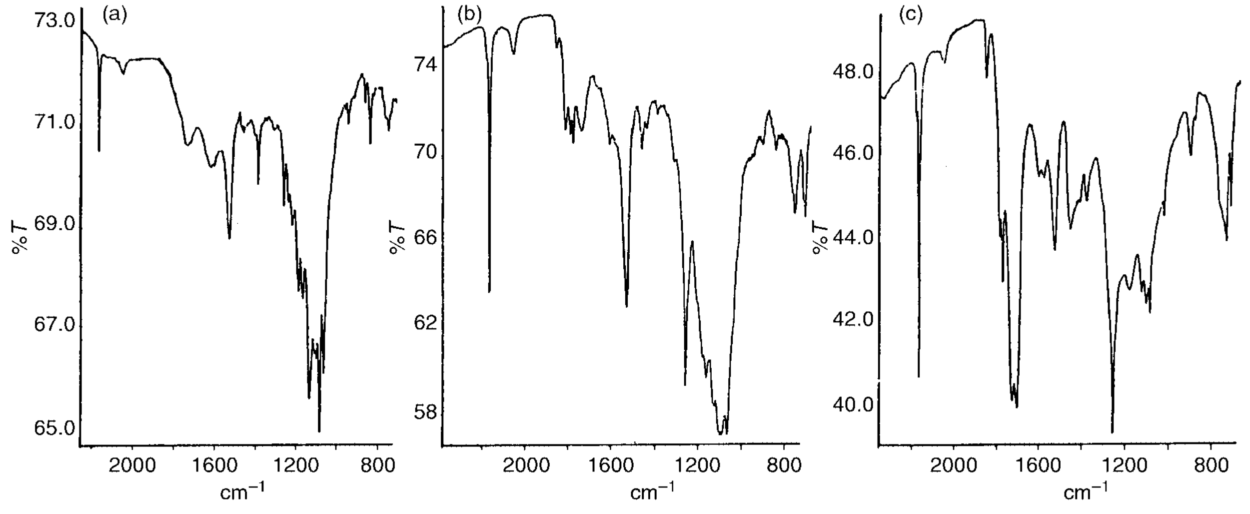

Fig. 2a–c IR spectra (KBr) after heating the discs shown in Fig. 1a–c at 225 °C for 2 h.

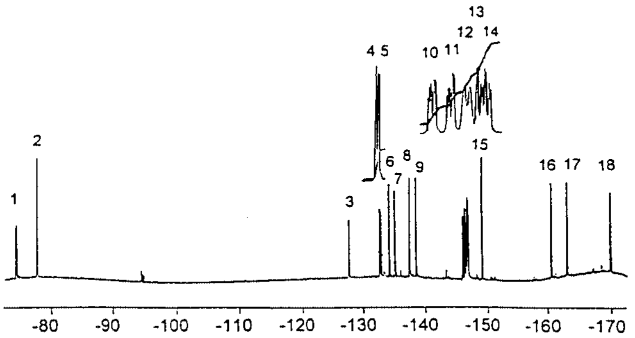

Fig. 3 ^{19}F NMR spectrum for isomer **4**.

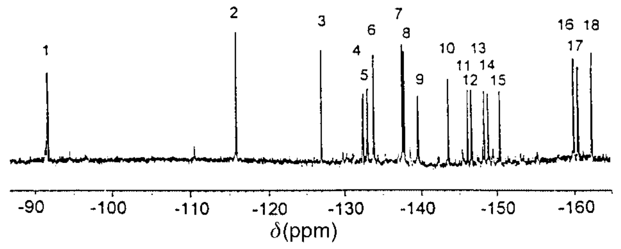

Fig. 4 ^{19}F NMR spectrum for isomer **5**.

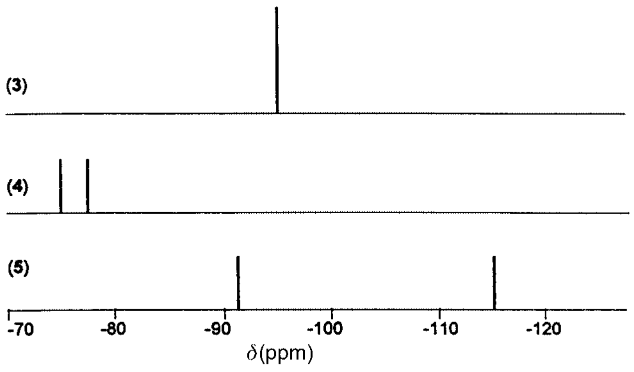

Fig. 5 Comparison of the positions of the downfield peaks for isomers **3**, **4**, and **5**; because of the C_s symmetry the peak shown for isomer **3** is double intensity.

to the weak signals arising from the low concentrations of compounds. Factors involved in interpreting the 2D ^{19}F NMR spectra are those which we have identified from other analyses, and are evident for example in the spectrum of $C_{60}F_{18}$ itself.[5] They are:

1. Fluorine atoms attached to carbons that are surrounded by three sp^3 carbons (less electron-withdrawing than sp^2 carbons) are the most upfield in the spectrum. There are three such fluorines in the $C_{60}F_{18}$ motif.

2. Conversely, fluorine atoms attached to carbons surrounded by one sp^3 and two sp^2 carbons tend (in the absence of other factors) to be the most downfield in the spectrum. There are three such fluorines in the $C_{60}F_{18}$ motif.

3. The other 12 fluorine atoms (attached to carbons neighboured by two sp^3 and one sp^2 carbon) appear in between these positions, but more downfield if adjacent to the central benzenoid ring.

4. Conditions 1–3 will be modified by the effect of the electron-withdrawing oxygens.

5. Observable couplings can be either 1,2-, 1,3-, or 1,4- (if the latter two positions are conjugated).[7]

Although we have applied these features to identify some of the peaks in the 2D spectra (below), the structures can be deduced simply by consideration of the locations of the C–F bonds nearest to the oxide function; these generally are well downfield from the signals due to all the other fluorines. The analysis is clarified by reference to Fig. 5, but first we determine the quantitative effect of the oxygen by comparing the chemical shifts for isomer **3** with those for $C_{60}F_{18}$ itself. In the latter, the shifts for the fluorines attached to the ends of bond 10 (see 1) appear at –143.4 ppm, and in the oxide at −94.6 ppm. There is thus a downfield shift due to the oxygen of 48.8 ppm. This value is of course dependent upon the angle of inclination of the C–O–C bond with cage surface, which may not be identical in each structure. Nevertheless it gives an approximate indication of what to expect.

Identification of isomer 5 (insertion into bond 6). The fluorines which are adjacent to the oxygen appear at −158.1 and −136.0 ppm in $C_{60}F_{18}$, so assuming that the effect of the adjacent oxygen is roughly the same as in **3**, the predicted shifts for isomer **5** would be −109.3 and −87.2, in good agreement with the −115.8 and −91.6 ppm observed. The agreement is sufficiently good for us to be able to identify this isomer with confidence.

Identification of isomer 4 (insertion into bond 7). The same procedure predicts that for isomer **4**, the shifts would be $-(136.0 - 48.8) = -87.2$ ppm and $-(143.4 - 48.8) = -94.6$ ppm. The observed values of the other isolated isomer are −74.6 and −77.9 ppm. Thus although the magnitude of the predicted shifts is too low, the *differences* in the shifts *viz.* 7.43 ppm calculated, 3.3 ppm observed are in good agreement; these differences would not be strongly dependent upon the inclination angle, as noted above.

From this approach we can discount the remaining possible isomer, involving insertion into bond no. 4, since only *one* fluorine atom would exhibit a downfield shift, and to −109.3 ppm, which is not found.

The 2D spectrum for isomer 5

This is shown in Fig. 6, and the peak/atom identification in Fig. 7. Features are:

(i) Peaks 1 and 2 are defined as described above.

(ii) There are three upfield peaks, nos. 16, 17, 18, but only two can be surrounded by three sp^3-hybridised carbons. Peak 17 is coupled to 1, already located, so cannot be surrounded thus. This identifies peaks 16 and 18, and they are coupled to downfield peaks 4 and 5, respectively, the location of these latter being due to their having two sp^2-hybridised neighbours. The peak combinations 16/4 and 18/5 are distinguished under (vi) below.

(iii) Peak 10 is coupled to 2, 3, and 6 (the latter being *para* across the central benzenoid ring).

(iv) Peak 9 is coupled to 1 (*para*, conjugated), and peak 17 is coupled to 15.

(v) Peak 11 is coupled to 12 (1,3 coupling), and peak 13 is coupled to 14 (1,2 coupling). Their position in the spectrum suggests that they are all in a similar environment.

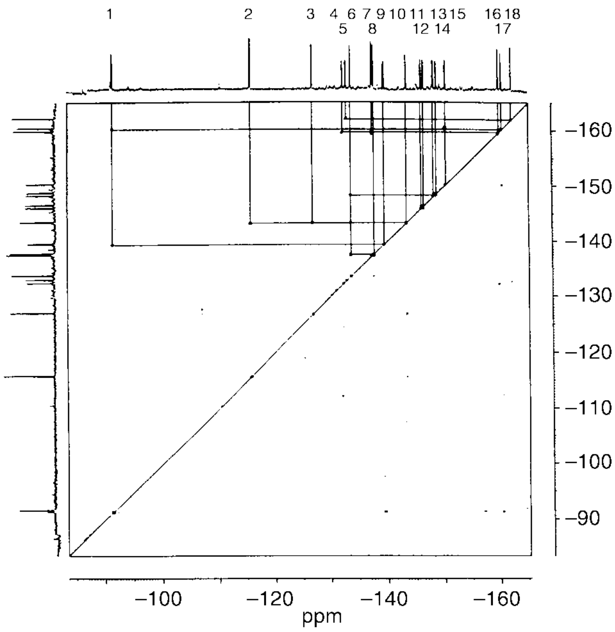

Fig. 6 2D ^{19}F NMR spectrum for isomer **5**.

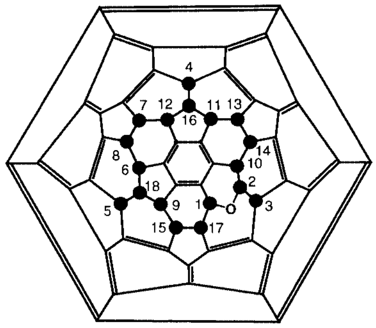

Fig. 7 Assignment of the fluorines in **5**, deduced from the 2D ^{19}F NMR spectrum (Fig. 6).

(vi) Peaks 7 and 8 are precisely located (as a pair) because they are shifted substantially downfield when oxygen is inserted into the carbon atoms bearing the fluorines in a related bis-ether.[11] Since peak 8 is strongly coupled to 6, they are probably in a 1,2-relationship, and since peak 7 couples to 16, this distinguishes peak 16 from 18 (and hence 4 from 5).

(vii) There is one anomaly, *viz.* peak 6 is (weakly) coupled to 13; this can be overcome if peaks 12 and 11 are interchanged with peaks 13 and 14 respectively, but in this case the peak pair nearest to the benzenoid ring would be more upfield. Similar ‘extra’ couplings occur with isomer **4**, below.

Further refinement of the analysis may eventually be possible when higher field ^{19}F NMR instrumentation becomes available.

The 2D spectrum for isomer 4

This (Fig. 8) shows similar features to the above, the peak/atom identification being given in Fig. 9. Features are:

(viii) Peaks 1 and 2 are defined as described above, and 1, being most downfield, should be nearest to the central benzenoid ring. This is consistent with other connectivities below.

(ix) There are three upfield peaks, which should be surrounded by three C–F bonds. Peak 18, coupled to the three most downfield peaks, 1, 2, and 3, is thereby located. Peaks 17 and 16 are coupled to downfield peaks 5 and 4 respectively, and are distinguished by further information as shown below.

(x) Peak 17 also couples to 9 and 7, hence they are closely located.

(xi) Peaks 15 and 10 are coupled to 2, and so are located in the same ring, but since peak 15 is coupled to 7, their relative positions are thus defined. Moreover, peak 10 is nearer to the

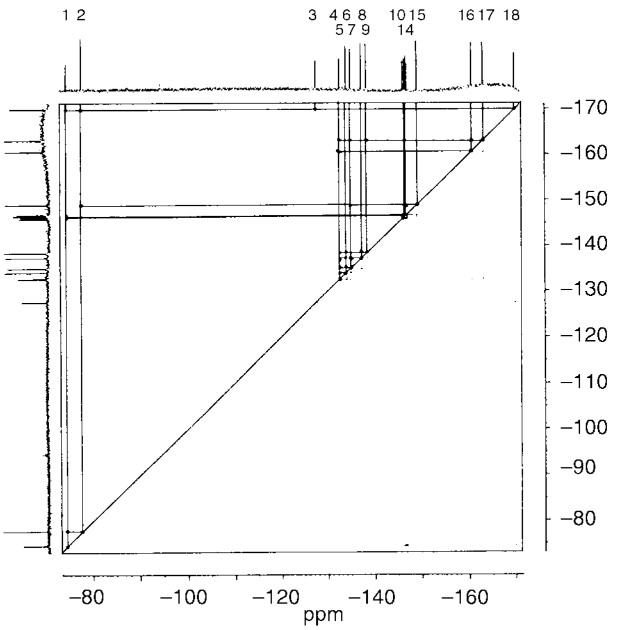

Fig. 8 2D ^{19}F NMR spectrum for isomer **4**.

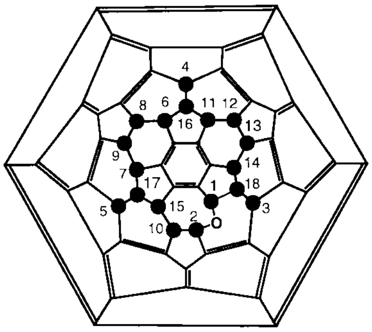

Fig. 9 Assignment of the fluorines in **4**, deduced from the 2D ^{19}F NMR spectrum (Fig. 8).

oxygen than is peak 15, and so should appear more downfield. The location of peak 10 is also consistent with its coupling to peak 1 (not visible from Fig. 8).

(xii) Peaks 11–14 have similar chemical shifts, and are likely to lie in a similar area of the molecule. Peak 1 also couples to one peak in the 11–14 cluster and this is consistent with the location of 11–14 (though the exact order in the hexagon could be different from that shown).

(xiii) Peak 9 couples to 8, and peak 7 couples to 6, and since 9 and 7 are located near to 17 [see (x) above], each of 7–9 may be assigned to a given ring. However, peak 6 is coupled to 4 and peak 7 is coupled to 5 (not visible on Fig. 8), hence their positions in the hexagon containing 6–9 are deduced. Peak 8 also couples to 4, and since peak 9 couples to 7 (see x), the relative positions of peaks 8 and 9 are determined.

As with the previous spectrum there is an anomaly in the apparent coupling of peaks, in this case nos. 17 and 16. This is difficult to interpret but may be due to the operation of long-range effects through the central planar benzenoid ring.

Oxidation mechanism

Given that at room temperature $C_{60}F_{18}$ appears to be quite stable, and the preparation takes place under vacuum, we presume that the vacuum is imperfect and air enters the high temperature zone causing the oxidation. Oxidation is extensive: as well as the mono-oxides reported here, we have also isolated several dioxides which we hope to describe subsequently. When adequate supplies of $C_{60}F_{18}$ become available, we plan to heat some at high temperature in the presence of air, and examine the reaction products. The absence of significant amounts of light during the current preparation would seem to rule out the role of singlet oxygen.

Calculations

The calculated heats of formation of all mathematically possible epoxides and ethers based on $C_{60}F_{18}$, (Tables 1 and 2, respectively), using two different semi-empirical methods, show that five ethers (in boldface type, Table 2) are predicted to be more stable than any other and more stable than any epoxide. The order of stabilities of the five most stable ethers (bond labels) varies with method. According to MNDO it is:

$$10 \gg 6 > 14 > 7 \approx 4$$

and according to AM1 it is:

$$10 \gg 6 > 7 \approx 4 > 14$$

A rationale for this stability would seem to be the length of the FC–CF bond into which the oxygen inserts. Amongst the ether precursors, this follows the order:

$$10 \gg 6 > 7 \approx 5 > 4$$

It would seem that least strain is introduced when oxygen is inserted into what is already a long bond. The most stable ether (insertion into bond 10, which has C_s symmetry) is the one which we have unambiguously identified by single crystal X-ray diffraction.[7] It is predicted to be significantly more stable than any other, and consistent with this it is obtained in much greater yield. The other C_s symmetry ethers (insertion into either of bonds 5 or 14) are predicted to have lower stability, which is consistent with our failure to isolate thus far a second symmetrical oxide. This leaves only the ethers with oxygen insertion into one of bonds 6, 7, or 4, and 4 has been ruled out by the ^{19}F NMR data. We may be confident therefore that the ethers with oxygen inserted into bonds 6 and 7 are indeed the compounds that we have isolated.

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