Isolation and characterisation of $C_{60}F_4$, $C_{60}F_6$, $C_{60}F_8$, $C_{60}F_7CF_3$ and $C_{60}F_2O$, the smallest oxahomofullerene; the mechanism of fluorine addition to fullerenes

Olga V. Boltalina,[a] Adam D. Darwish,[c] Joan M. Street,[b] Roger Taylor *[c] and Xian-Wen Wei[c]

[a] *Chemistry Department, Moscow State University, Moscow 119899, Russia*
[b] *Chemistry Department, The University, Southampton, UK SO17 1BJ*
[c] *The Chemistry Laboratory, CPES School, Sussex University, Brighton, UK BN1 9QJ*

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From the reaction of [60]fullerene with K_2PtF_6 at 470 °C, we have isolated $C_{60}F_4$, $C_{60}F_6$ (mixed with $C_{60}F_7CF_3$), $C_{60}F_8$ and $C_{60}F_2O$. The ^{19}F NMR spectrum of $C_{60}F_2O$ comprises a single line at −69.3 ppm, consistent with it being the simplest oxahomofullerene. The AA′BB′ spectrum for $C_{60}F_4$ (double doublets at −141.82 and −142.78 ppm) shows it to be isostructural with $C_{60}H_4$, the addends in each case being in a 1,2,3,4-arrangement. The spectrum for $C_{60}F_6$ consists of doublets at −124.39 and −142.41 and a triplet at −139.78 ppm (coupling confirmed by a 2D spectrum), showing the fluorines to be in a previously-conjectured S-shaped motif, giving the molecule overall C_2 symmetry. The $C_{60}F_8$ spectrum comprises five peaks in a 1 : 2 : 2 : 2 : 1 ratio, so that the molecule has C_s symmetry based on a T-shaped motif, also conjectured previously. The peak couplings and symmetry indicate that the structure is created by addition of three pairs of fluorines across contiguous double bonds, followed by 1,8-addition of the final fluorine pair; this unique latter step is attributed to the ability of a pentagon containing three sp^3 carbons to accommodate a double bond, due to the reduction in strain. The $C_{60}F_8$ structure is part of the motif of $C_{60}F_{16}$ and $C_{60}F_{18}$, indicating it to be an intermediate on the pathway to formation of these compounds. The spectrum for $C_{60}F_7CF_3$ shows the presence of one major and one minor isomer, the probable structures of which are deduced.

Introduction

The fundamental reasons that underlie the polyaddition patterns observed with fullerenes are as yet poorly understood, but elucidating them is essential for understanding these fascinating molecules. The patterns tend to fall into three categories: those involving the 1,2-addition of non-bulky groups, and those involving the addition of bulky addends, which can be subdivided into 1,2-cycloadditions and the 1,4-additions. There are numerous published data for each reaction,[1] with cycloadditions being the most studied since analysis of the reaction products and interpretation of the patterns are comparatively easy; most reactions concern [60]fullerene with a few for [70]-, [76]-, [78]-, and [84]fullerenes.

1,2-Additions of sterically undemanding groups are of particular importance since only these can distinguish the electronic effects that operate. They are limited to hydrogenation and fluorination, both radical additions which have been shown to take place hitherto in a series of contiguous 1,2-additions.[2–5] Studies of hydrogenation are however complicated by ready oxidation of the products to fullerenols, and the difficulty of dissecting ^1H NMR spectra having multiply-connected peaks. We have therefore concentrated our efforts in this area on studying fluorination, with analysis of the products by mass and ^{19}F NMR spectroscopy. At this stage of fullerene fluorination development, it is not possible to target the high yield syntheses of a particular *new* derivative, but rather to isolate and characterise the products obtained under specific reaction conditions. These can then be reproduced to produce more of the given derivative if desired subsequently.

We now report the formation of $C_{60}F_4$, $C_{60}F_6$, $C_{60}F_8$, the structure of which throws new insight into the addition mechanism involving an addition step not seen previously, $C_{60}F_7CF_3$, (which comprises one major and one minor isomer), and $C_{60}F_2O$, which is probably the smallest oxahomofullerene that can be isolated.

Experimental

[60]Fullerene was fluorinated with K_2PtF_6 at 470 °C under vacuum (*ca.* 0.1 bar). The product was dissolved in toluene and filtered under conditions which avoided any moisture condensation, since moisture and a co-solvent result in extensive nucleophilic substitution of fluorofullerenes.[6] The toluene solution was then separated by HPLC (High Pressure Liquid Chromatography) using a 10 mm × 250 mm Cosmosil Buckyprep column, with elution by toluene at a flow rate of 4.7 ml min^{-1}. This produced a number of new products together with those described previously, including $C_{60}F_{18}$,[5] $C_{60}F_{18}O$,[7] $C_{60}F_{17}CF_3$,[8] $C_{60}F_{20}$,[9] and $C_{60}F_2$.[10] In order to obtain a pure single product (as indicated by mass spectrometry), each fraction was recycled a number of times to remove tails from earlier fractions.

$C_{60}F_2$

The mass spectrum of this brown compound (HPLC retention time 11.3 min) reported previously was poor due to the presence of volatile impurities; Fig. 1 is an improved spectrum. The ^{19}F NMR spectrum consisted of a single line at δ_F −148.3[10] and this is collated with the other data below.

$C_{60}F_4$

This compound eluted after 16.2 min, and the mass spectrum (Fig. 2) shows the parent ion at 796 amu. In the IR spectrum there are shoulders at 1161, 1153, 1112, 1087, 1023 and 1008 cm^{-1} with sharp bands at 1051 and 1071 (main) cm^{-1}. The ^{19}F NMR spectrum (Fig. 3) comprises two equal-intensity coupled double doublets δ_F −141.82 and −142.78, J = 7.4 Hz.

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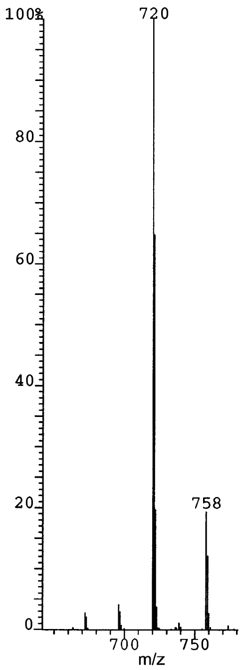


Fig. 1 EI mass spectrum (70 eV) for $C_{60}F_2$.

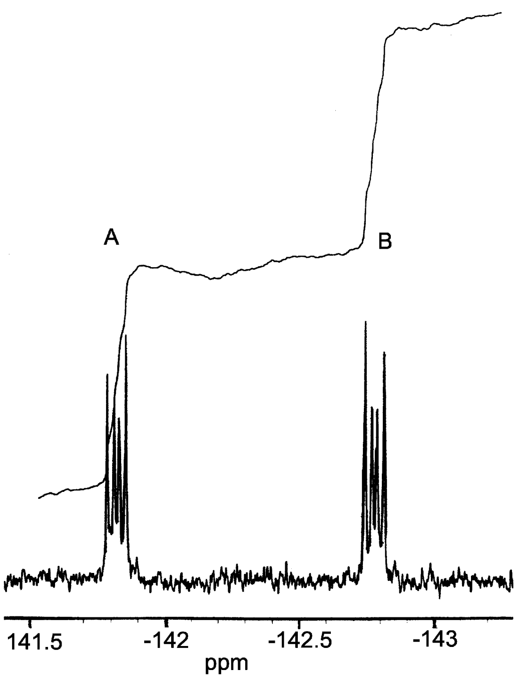


Fig. 3 ^{19}F NMR spectrum for $C_{60}F_4$.

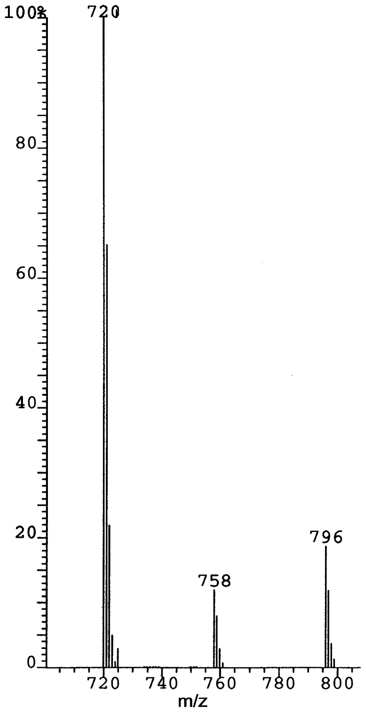


Fig. 2 EI mass spectrum (70 eV) for $C_{60}F_4$.

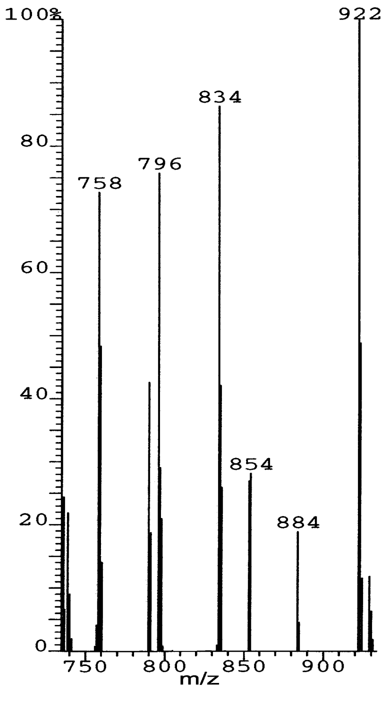


Fig. 4 EI mass spectrum (70 eV) for a mixture of $C_{60}F_6$ and $C_{60}F_7CF_3$.

$C_{60}F_6$

This co-eluted with $C_{60}F_7CF_3$ after 24 min and the mass spectrum (Fig. 4) shows the presence of both components (834 and 922 amu). (An earlier sample of $C_{60}F_4$ co-eluted with a small amount of $C_{60}F_5CF_3$ so it appears that addition of one F and one CF_3 group in each case produces relatively little alteration in the retention time.)

Both components are evident in the ^{19}F NMR spectrum (Fig. 5). The more intense peaks (A, B, C, respectively at δ_F −124.39, d; −139.78 t; −142.41 d, all *J* 30 Hz) are coupled $C \longleftarrow B \longrightarrow A$ and are due to $C_{60}F_6$. The seven equal intensity sp^2C–F peaks of $C_{60}F_7CF_3$ (labelled as 1–7) appear at −123.83, −130.68, −134.11, −136.07, −137.10, −138.78 (some of which are resolvable doublets) and −151.33 (q, *J* 30 Hz). There are two peaks in the CF_3 region, the major doublet at −66.50 ppm (18 Hz) has the correct integration ratio relative to peaks 1–7; the small singlet at −67.08 ppm is attributed to a minor isomer (there are other baseline peaks in the cage C–F region likewise attributable to this isomer).

$C_{60}F_8$

This eluted at 31.4 min, and on further HPLC purification on a 10 mm × 250 mm Cosmosil 5μ Pye column produced two peaks of 14.3 and 22.2 min retention times, each of which on re-injection onto the Buckyprep column gave a peak at *ca.* 31 min. The former is a [60]fullerene derivative, but could not be characterised. The latter was further purified on the Buckyprep column, and the EI mass spectrum (Fig. 6) shows the parent ion

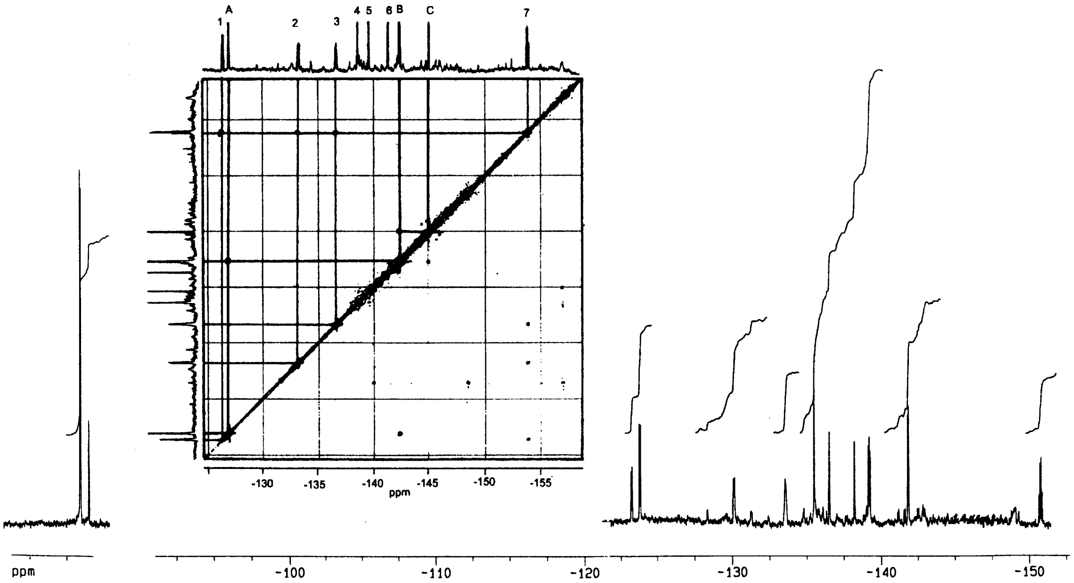


Fig. 5 ^{19}F NMR spectra (1D and 2D) of a mixture of $C_{60}F_6$ and $C_{60}F_7CF_3$ (see text for peak identifications).

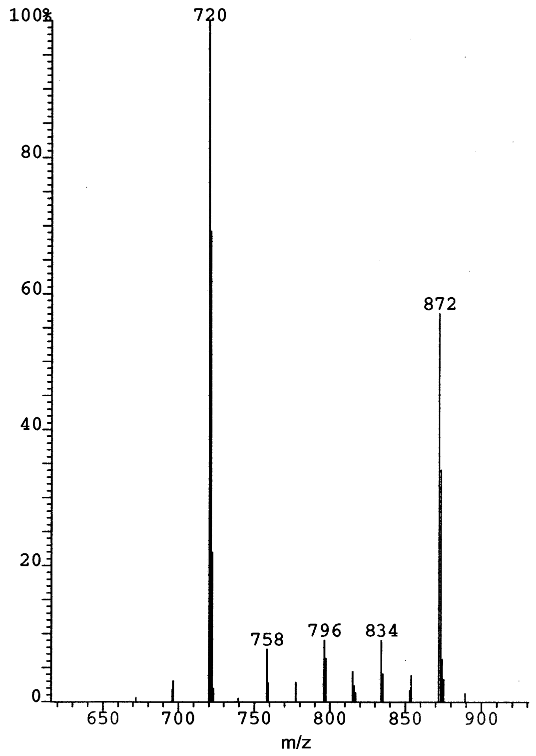


Fig. 6 EI mass spectrum (70 eV) for $C_{60}F_8$.

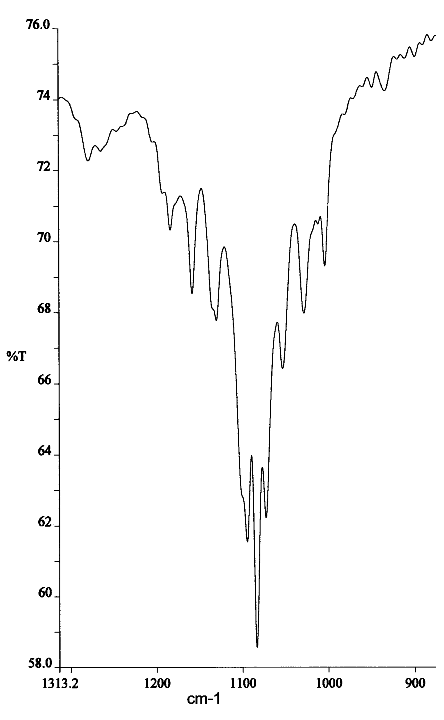


Fig. 7 IR spectrum (KBr) for $C_{60}F_8$.

for $C_{60}F_8$ at 872 amu, together with a fragment arising from stepwise loss of 4 × F_2.

The compound is red–brown (thin films) and gives a deep yellow solution in toluene. It is a characteristic of hydrogenated fullerenes that the colours progress through red, yellow and finally white as the hydrogenation level increases, *e.g.* $C_{60}H_{18}$ is red.[11] The same is evidently true of fluorinated fullerenes (which have similar addition patterns and hence chromophores) so that a progression is $C_{60}F_2$ (brown), $C_{60}F_8$ (red), $C_{60}F_{18}$ (yellow), $C_{60}F_{36}$ (cream–white)[12] and $C_{60}F_{48}$ (white).[13]

Bands in the IR spectrum (Fig. 7) occur at 1158, 1130, 1100 (sh), 1094, 1083, 1073, 1053, 1029 and 1004 cm^{-1}.

The ^{19}F NMR spectrum (376 MHz, Fig. 8) shows five peaks at δ_F −124.5 (1 F, dm, *J* 26 and 4 Hz), −134.9 (2 F, d, *J* 27 Hz), −136.2 (2 F, s), −137.8 (2 F, d, *J* 4 Hz), −153.2 (1 F, dt, *J* 27.3 Hz). The connections A–E, B–E and B–D were deduced from the 2D ^{19}F NMR spectrum (Fig. 9), with very weak A–D, B–C and C–D connections seen only on a spectrum run at higher sensitivity; the observation of weak couplings is a general feature in our ^{19}F NMR work especially of $C_{60}F_{18}$ and derivatives, and may be due to the small size of samples and unquantified structural consequences. The spectrum showed the presence of traces of $C_{60}F_{20}$ at δ_F −132.8, due to carry-over from previous runs in the HPLC separation. Although the concentration is only 0.5%, this compound is detectable here because of its high symmetry.

$C_{60}F_2O$

This eluted after 12.9 min and the mass spectrum (Fig. 10) shows the parent ion at 774 amu with the fragmentation ion at 736 amu due to loss of 2 F. The ^{19}F NMR spectrum (not shown) consists of one single line at −69.27 ppm.

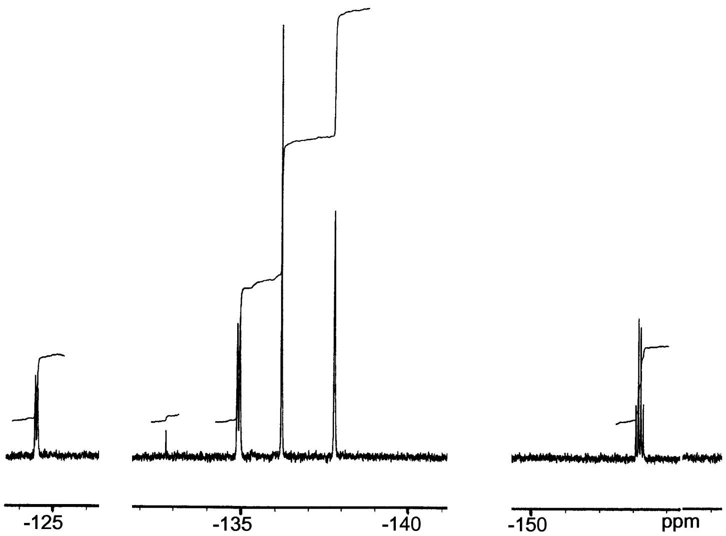


Fig. 8 ^{19}F NMR spectrum for $C_{60}F_8$.

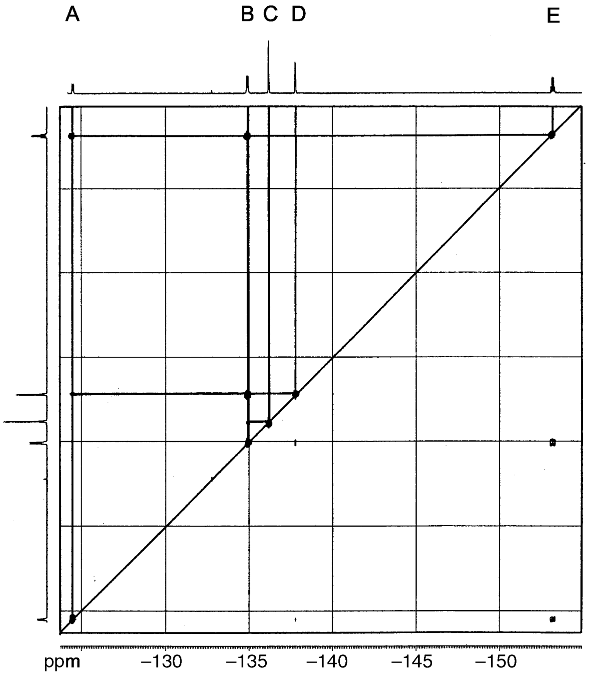


Fig. 9 2D ^{19}F NMR spectrum for $C_{60}F_8$.

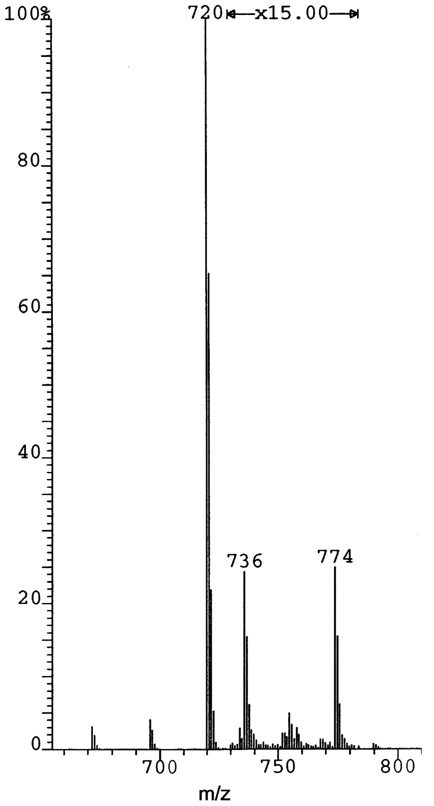


Fig. 10 EI mass spectrum (70 eV) for $C_{60}F_2O$.

Discussion

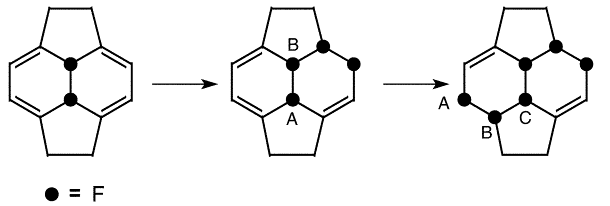
HPLC retention times

The approximate retention times (min) under the standard conditions are: C_{60}, 8.5; $C_{60}F_2$, 11.3; $C_{60}F_4$, 16.2; $C_{60}F_6$, 24; $C_{60}F_8$, 31.6; $C_{60}F_{16}$, 84.0;[4] $C_{60}F_{18}$, 38.0;[5] $C_{60}F_{36}$, 3.5.[12] Thus addition of fluorine causes a regular increase in the retention time to a presumable maximum at $C_{60}F_{16}$ (no information is available for 10–14 F levels) and then decreases as further fluorine is added. There is presently no clear explanation for this behaviour, but it provides some guide as to where in the HPLC separations, other fluorinated derivatives might be found.

Structures of the derivatives

$C_{60}F_2$, $C_{60}F_4$, and $C_{60}F_6$. The ^{19}F NMR data yield not only the structures but show how the contiguous addition of fluorine leads from C_{2v} $C_{60}F_2$, through C_s $C_{60}F_4$ and finally to C_2 $C_{60}F_6$. The AA′BB′ spectrum for $C_{60}F_4$ parallels that found for $C_{60}H_4$,[2] showing these compounds to be isostructural. In each case, and because fullerenes are partially aromatic, addition of the first fluorine pair increases localisation of the electrons in the addended hexagon, so that further addition in this hexagon becomes favourable. The structure of $C_{60}F_6$ is particularly notable as the motif was first conjectured as being an intermediate along the pathway to isostructural $C_{60}H_{18}$,[11] and likewise for $C_{60}F_{18}$,[14] and now we have proof of the reality of this structure. Scheme 1 shows the stepwise contiguous fluorine addition, and the identities of the peaks for C_6F_4 and $C_{60}F_6$ are readily found from the ^{19}F NMR couplings in Figs. 3 and 5.

$C_{60}F_8$. The NMR pattern shows that two fluorines lie on the symmetry plane and three pairs lie symmetrically across it. One of the on-plane fluorines (E) is coupled to the other on-plane fluorine (A) and to two adjacent fluorines (B) either side of the plane. The motif comprised of fluorines A, B and E in the ‘T’ pattern (**1**) resulting from contiguous addition of six F to three adjacent double bonds is the only possible solution. Thus it



Scheme 1 Route to the formation of $C_{60}F_6$ from $C_{60}F_2$; peak labels correspond to those shown in Figs. 3 and 5.

appears that $C_{60}F_{18}$ can be assembled from both of the $C_{60}F_6$ isomers having the conjectured 'S' and 'T' patterns.[11,14] Whereas the 'S' isomer can be isolated as above, the 'T' isomer evidently undergoes further fluorination more rapidly to give $C_{60}F_8$.

Further evidence to support the conjectured structure comes from comparison of the NMR shifts with those for fluorinated fullerenes known to contain this motif:

(i) The multiplet for E appears at δ_F −153.2. For other fluorofullerenes the corresponding upfield multiplets appear at (δ_F) −157.0 ($C_{60}F_{16}$),[4] −158.1 ($C_{60}F_{18}$),[5] −157.6 (average of four positions in symmetrical and unsymmetrical isomers of $C_{60}F_{17}CF_3$) and −157.85 ($C_{60}F_{17}CF_2CF_3$).[8] The upfield locations in each case are due either to the three surrounding (less electron-withdrawing) sp^3 carbons or greater electron donation from the larger number of adjacent F atoms; the slightly more downfield location of E (by *ca.* 4 ppm) is consistent with the presence overall of fewer sp^3 carbons in $C_{60}F_8$. [For three isomers of $C_{60}F_{18}O$,[7] the average value is −161.5 for five positions remote from oxygen, but these values are less diagnostic because all of the peaks in the oxides are shifted upfield by the presence of the additional oxygen addend and hence sp^3 carbons (see also below).]

(ii) The doublet for A (which is directly coupled to E) appears at δ_F −124.5. In each of the fluorofullerenes noted in (i), the most upfield peaks are always coupled to downfield doublets corresponding to A. These appear δ_F −128.5 ($C_{60}F_{16}$),[4] −131.6 ($C_{60}F_{18}$),[5] −131.5 (average for $C_{60}F_{17}CF_3$ isomers as above), and −131.0 ($C_{60}F_{17}CF_2CF_3$).[8] As in the case of peak E, peak A is more downfield than in the related compounds, for the same reason, and by the same amount. (The shifts for corresponding positions in the oxides as above average −133.1)[7]

(iii) The doublet for peak B appears at δ_F −134.9 and is directly coupled to E. In the other fluorofullerenes, the average values for peaks corresponding to B (and likewise coupled to peaks corresponding to E) appear at (δ_F) −135.6, ($C_{60}F_{16}$),[4] −136.0 ($C_{60}F_{18}$),[5] −136.0 (average for $C_{60}F_{17}CF_3$ isomers as above) and −136.4 ($C_{60}F_{17}CF_2CF_3$).[8] The similarities of the positions in the spectrum compared to the related compounds again confirm the structure, and once more the peak position is slightly more downfield in $C_{60}F_8$. (The shifts for corresponding positions in the oxides described above average −140.1 ppm.)

The locations of the remaining four fluorines are deduced as follows:

(iv) The 2D spectrum shows that fluorines D are directly coupled to fluorines B which follows also from the contiguous addition mechanism (see also Scheme 1). The coupling between B and D is < 4 Hz which parallels the behaviour in $C_{60}F_{18}$ where coupling between the fluorine corresponding to B and the adjacent fluorine is only 2 Hz.[5] The peaks corresponding to D appear at (δ_F) −141.5, ($C_{60}F_{16}$, average of two positions),[4] −143.4 ($C_{60}F_{18}$),[5] −143.3 (average for $C_{60}F_{17}CF_3$ isomers as above) and −143.1 ($C_{60}F_{17}CF_2CF_3$, two positions).[8] (The shifts for corresponding positions in the oxides as above average −144.6.)[7]

(v) This leaves the remaining pair to be accounted for. Given that $C_{60}F_8$ is most probably an intermediate on the pathway to $C_{60}F_{18}$, then contiguous addition across an adjacent double bond to give **2** would have been expected, but is ruled out by the observed C_s symmetry. One alternative involves addition to give **3** that has the correct symmetry, but involves addition across a 5,6-bond, does not lead to $C_{60}F_{18}$, and requires three fluorines to have three sp^3 neighbouring carbons. Hence there should be three upfield peaks in the spectrum which are not observed so structure **3** is ruled out. 1,4-Addition *para* to fluorines D would give a structure (not shown), energetically more favourable (by 100 kJ mol^{-1}) than the proposed structure **4** and with the correct symmetry. However, it is not on the pathway to $C_{60}F_{18}$ and would have two isolated fluorines which should appear well downfield in the spectrum, contrary to observation.

The only feasible structure appears to be **4**, formed according to the steps shown in Scheme 2, and consistent with the 2D NMR spectrum. The contiguous addition of three F_2 molecules across 6 : 6-bonds is followed by a unique step, the 1,8-delocalisation of a radical produced by the initial addition of fluorine atom at one end of the double bond contiguous to the fluorines already present. Electron withdrawal by the fluorines will cause this double bond to be polarised to have the highest electron density nearest to the fluorines, hence the fluorine atom (a radical and hence electrophilic) adds at the end of the double bond as shown.

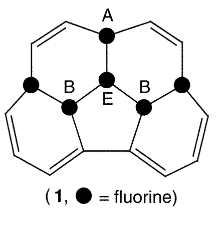
Radicals are poorly delocalised in fullerenes,[15] because such a process involves placing of double bonds in pentagons which is unfavourable.[16] This occurs in the penultimate structure in Scheme 2, but is mitigated here by the presence of three sp^3 carbons in the central pentagon which reduces the strain caused by introduction of the double bond.

In the mass spectrum of one sample of $C_{60}F_8$ a peak of 910 amu ($C_{60}F_{10}$) was seen due presumably to further addition of F_2 *en route* to $C_{60}F_{18}$. However there was not enough material to permit determination of any other spectroscopic details.

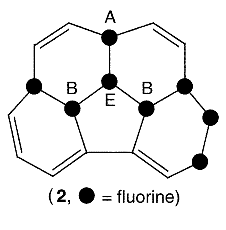
The peaks in the IR spectrum at 1158, 1130, 1100, 1073 and 1053 cm^{-1} are similar to those obtained for both $C_{60}F_{16}$,[4] *viz.* 1154, 1129, 1101, 1062 and 1046 cm^{-1} and $C_{60}F_{18}$ *viz.* 1163, 1133, 1103, 1067 and 1045 cm^{-1}.[5] This further supports the structural analysis.

$C_{60}F_7CF_3$. We assume that this compound is formed (during fluorination) by insertion of a CF_2 fragment into a C–F bond of $C_{60}F_8$. This is confirmed by the presence of the upfield multiplet at −153.37 ppm coupled to a doublet at −126.32, these values being very close to those obtained for peaks E and A respectively, in structure **4**. Since the peak corresponding to E is coupled to three other peaks, then none of these four can be a CF_3 group, and given that previous work showed CF_2 insertion to be more favourable at least hindered sites,[8] the structure of $C_{60}F_7CF_3$ may be deduced as **5**. The CF_2 group is produced through fragmentation of some of the fullerene cages during the fluorination procedure.[17]

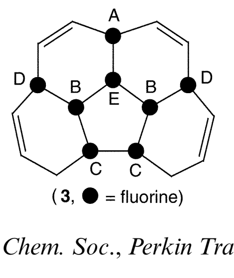
The ^{19}F NMR data of the minor isomer were insufficiently resolved to permit its characterisation.



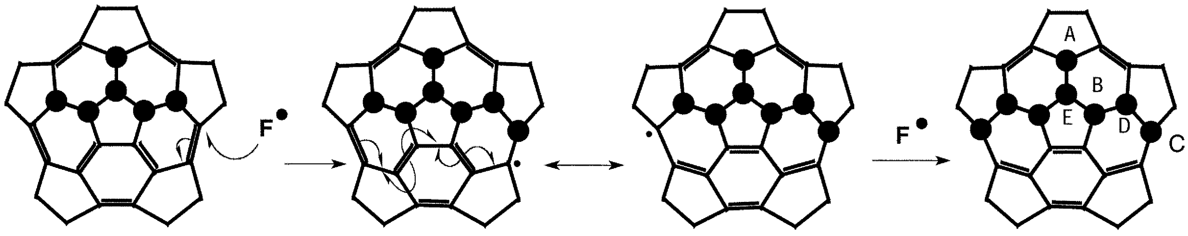
(**1**, ● = fluorine)



(**2**, ● = fluorine)

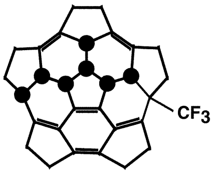


(**3**, ● = fluorine)



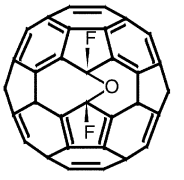
(4)

Scheme 2 Conjectured route to the formation of $C_{60}F_8$.



(5)

$C_{60}F_2O$. The singlet in the ^{19}F NMR spectrum at −69.27 ppm is further downfield than for fluorines adjacent to oxygen in the $C_{60}F_4O$, $C_{60}F_6O$ and $C_{60}F_8O$, where the values range from −74.66 to −82.55. This downfield shift is entirely consistent with the greater electron withdrawal in a less highly addended cage. Earlier the above fluorofullerene oxides were interpreted as epoxides,[18] but the structures were updated later in the light of X-ray data, to be oxahomofullerenes (ethers).[3d] Accordingly the structure of $C_{60}F_2O$ is deduced as **6** and indeed the single NMR line is consistent *only* with an ether. This constitutes the smallest fullerene ether that has been isolated.



(**6**)

Acknowledgements

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