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# In the first proven $S_N2'$ fullerene reaction, both $C_3$ and $C_1$ $C_{60}F_{36}$ hydrolyse to $C_1$ isomers of $C_{60}F_{35}OH$ that eliminate HF to give epoxides $C_{60}F_{34}O$; $C_{60}F_{36}O$ oxides are shown to be ethers, and a fourth isomer of $C_{60}F_{36}$ exists†

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On standing in organic solvents containing traces of water, $C_3$ and $C_1$ isomers of $C_{60}F_{36}$ slowly convert to $C_1$ isomers of $C_{60}F_{35}OH$. Both fluorofullerenols eliminate HF during EI mass spectrometry to give $C_{60}F_{34}O$ epoxides, one fullerenol being much less stable than the other to the extent that the mass spectrum shows only the epoxide. Both $C_{60}F_{35}OH$ isomers have $C_1$ symmetry, one being identified by the remarkable linear relationship between chemical shifts in its $^{19}F$ NMR spectrum and those in the spectrum of $C_1$ $C_{60}F_{36}$; the spectrum of the other shows the pattern of $C_3$ $C_{60}F_{36}$ rendered asymmetrical by the replacement of one F by OH. The reactions are facilitated by the presence of isolated double bonds, and provide the first proven examples of an $S_N2'$ reaction of a fullerene derivative. Our observation explains why only a limited number of fluorines are readily replaced in $C_{60}F_{36}$ and why $C_{60}F_{18}$ is by contrast much more resistant to hydrolysis. We have isolated also a pure isomer of $C_{60}F_{36}O$, which is shown to be an oxahomofullerene (ether) apparently derived from $C_1$ $C_{60}F_{36}$, and an impure fraction comprising a fourth isomer of $C_{60}F_{36}$, a trifluoromethyl derivative of $C_{60}F_{36}$, a second isomer of $C_{60}F_{36}O$, and an unknown species of 1392 u.

## Introduction

In previous work, HPLC (high pressure liquid chromatography) processing of $C_{60}F_{36}$ (with toluene/hexane mixtures) was found to be accompanied by isolation of fractions which appeared to contain $C_{60}F_{35}OH$ (1402 u) and $C_{60}F_{34}O$ (1382 u) as well as some other dihydroxy and epoxyhydroxy derivatives.[1] This was attributed to hydrolysis arising from traces of moisture in the solvent, exacerbated by the volatility of hexane which facilitated moisture uptake. To reduce this problem, all subsequent HPLC work was carried out with mixtures of toluene and less volatile heptane (stored over molecular sieve), although these give less separation than comparable toluene : hexane mixtures. Due to the small quantities of material available, pure components could not be isolated.

Recently we have scaled up production of $C_{60}F_{36}$ in connection with other studies, during which we isolated a new $C_1$ isomer of $C_{60}F_{36}$,[2,3] further details of the $^{19}F$ NMR spectrum of which are given here; the $C_1$ isomer is interrelated to the $C_3$ isomer by means of a 1,3-F shift. During processing of the products we have isolated substantial quantities of two isomers of $C_{60}F_{35}OH$, deduced the structure of both and determined their formation mechanisms, which involve the first proven examples of $S_N2'$ substitution in a fullerene. We prove that they are formed by reaction with the solvent, show why few further fluorines appears to be replaced readily, and why a comparable sensitivity to moisture does not beset processing of $C_{60}F_{18}$. We have isolated also: (i) a pure isomer of $C_{60}F_{36}O$, shown that this is an ether, and deduced its probable structure, (ii) a mixture comprising a second isomer of $C_{60}F_{36}O$ (shown also to be an ether) a fourth isomer of $C_{60}F_{36}$, $C_{60}F_{35}CF_3$ and an unidentified component of 1392 u.

## Experimental

The crude product from fluorinating [60]fullerene with $MnF_3$/$K_2NiF_6$ at 480 °C (ref. 4) was purified by HPLC using a 10 × 250 mm Cosmosil Buckyprep column operated at a flow rate of 4.7 ml $min^{-1}$, and eluting successively with toluene, 1 : 1 toluene : heptane, and finally 1 : 9 toluene : heptane. Toluene elution produced early fractions of *ca.* 3 min retention time, which contained substantial quantities of $C_{60}F_{36}$ isomers (these being set aside for further processing) and then fractions with retention times that are temperature dependent, being 4.0 and 4.55 min at *ca.* 15 °C and 3.5 and 3.8 min at 21 °C. These appeared to be $C_{60}F_{35}OH$ and an epoxide $C_{60}F_{34}O$ derived from it by HF elimination (see the EI mass spectra, Figs. 1 and 2, respectively). However, both proved (see Discussion) to be $C_{60}F_{35}OH$ isomers (**1** and **2**, respectively), the later eluting isomer being particularly susceptible to HF elimination under EI conditions, this elimination being partly evident in the spectrum (Fig. 1) of the other isomer.

After removing these components (and later eluting products *e.g.* $C_{60}F_{18}$, *etc.*), the early fraction was reprocessed with 1 : 1 toluene : heptane; after a large amount of early eluting (<4 min) $C_{60}F_{36}$ isomers was collected, the two fullerenols were again obtained, with retention times of 5.75 and 7.45 min respectively. The procedure was repeated, the early-eluting fraction being eluted with 1 : 9 toluene : heptane (which allowed separation of the $C_{60}F_{36}$ isomers), but once more the fullerenols were obtained with retention times of 7.5 and 9.6 mins respectively (all at *ca.* 15 °C). The component pairs from each separation were shown to be identical by their $^{19}F$ NMR spectra. The quantities of each of these isomers overall was *ca.* 15 mg of

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† Electronic supplementary information (ESI) available: IR spectra of **1**, **2**, and $C_{60}F_{36}O$; EI and $^{19}F$ NMR spectra of mixture eluting at 15 min (heptane). See http://www.rsc.org/suppdata/ob/b2/b209760p/

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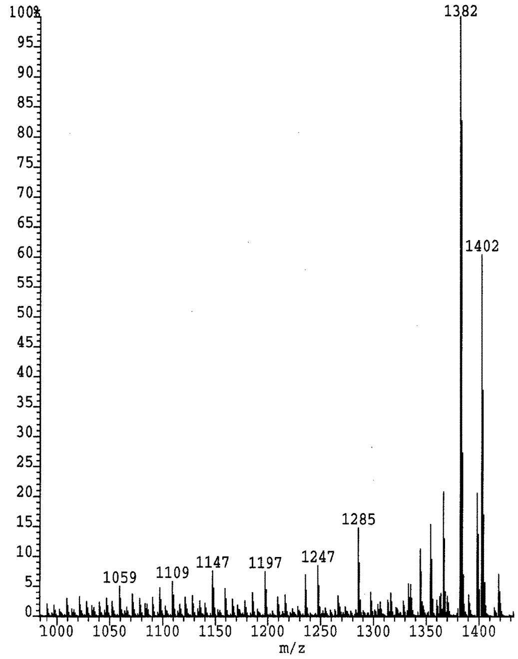


**Fig. 1** EI mass spectra (70 eV) for $C_{60}F_{35}OH$ (isomer **1**).

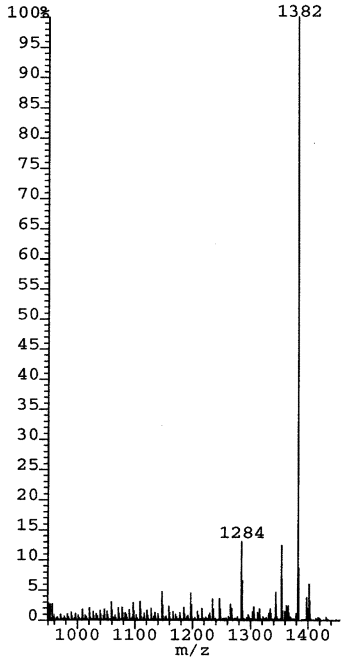


**Fig. 2** EI mass spectra (70 eV) for $C_{60}F_{35}OH$ (isomer **2**).

each, from fluorination of 800 mg of [60]fullerene as described recently.[2]

Further processing of the early fraction obtained from the 1 : 9 toluene : heptane mixture, with heptane alone yielded a fraction of retention time 13.0 min, and which proved to be a $C_{60}F_{36}O$ isomer. This was characterised as described in the Discussion. Further fractions were obtained of 3, 10.8 and 15 min retention time, the mass spectra (not shown) indicating the first two to be isomers of $C_{60}F_{38}$, and the latter to be a mixture of $C_{60}F_{36}$/$C_{60}F_{36}O$/$C_{60}F_{35}CF_3$/a component of 1392 u. These mixtures could possibly be separated using a different column, or by peak cutting, but we were unable to undertake this.

### EI mass spectra (70 eV)

Figs. 1 and 2 are the mass spectra for the $C_{60}F_{35}OH$ isomers (**1** and **2**), respectively, showing partial and total HF elimination under EI conditions. Fig. 3 is the mass spectrum for $C_{60}F_{36}O$.

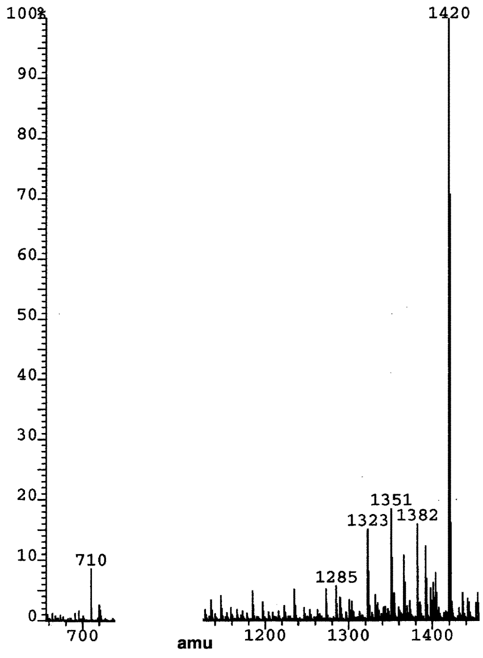


**Fig. 3** EI mass spectrum (70 eV) for $C_{60}F_{36}O$.

### IR spectra (KBr)

The IR spectra (KBr) of **1**, **2**, and $C_{60}F_{36}O$ (C–F stretching region) (Fig. S1, see electronic supplementary information (ESI) †) are closely similar, the main bands ($cm^{-1}$) appearing at 1221, 1167, 1130, and 1066 for **1**, 1215, 1164, 1132, 1070, and 1008 for **2** and 1163, 1131, 1069 and 1019 for $C_{60}F_{36}O$. Both **1** and **2** showed a sharp band at 3570 $cm^{-1}$ attributable to the OH groups.

### $^{19}F$ NMR spectra (376 MHz, $CDCl_3$)

These are described in the discussion section below.

## Results and discussion

### Formation of 1 and 2 through reaction with solvent

Both $C_{60}F_{35}OH$ isomers were isolated from three consecutive processing regimes, each of which removed these components from the main product ($C_{60}F_{36}$ isomers) prior to reprocessing of the latter. These two hydrolysis products from each processing regime were shown by $^{19}F$ NMR to be identical. They can only have been formed therefore by reaction of the recycled $C_{60}F_{36}$ with fresh (recycled) solvent. The latter was stored over molecular sieve, but very large quantities are used in processing. Typically, an initial run with toluene lasting 85 min in order to remove $C_{60}F_{18}$, $C_{60}F_{18}O$ and $C_{60}F_{20}$ will involve the use of 375 ml of solvent for processing *ca.* 5 mg of mixed fluorofullerenes. A mere trace of water in the solvent will inevitably provide sufficient for a significant amount of reaction to occur.

### The structure of $C_1$ $C_{60}F_{36}$

In order to interpret correctly the structure of isomer **1** it is necessary first to interpret and understand the $^{19}F$ NMR spectrum of $C_1$ $C_{60}F_{36}$ (Fig. 4), the structure of which was recently defined by single-crystal X-ray analysis.[2] The corresponding 2D $^{19}F$ NMR spectrum is shown in Fig. 5. The structure is shown as a Schlegel diagram (Fig. 6), in which the filled circles denote the positions of the fluorine addends, and the numbers refer to the peaks in the spectrum; fluorines attached to carbons having three $sp^3$–C neighbours are shown enlarged.

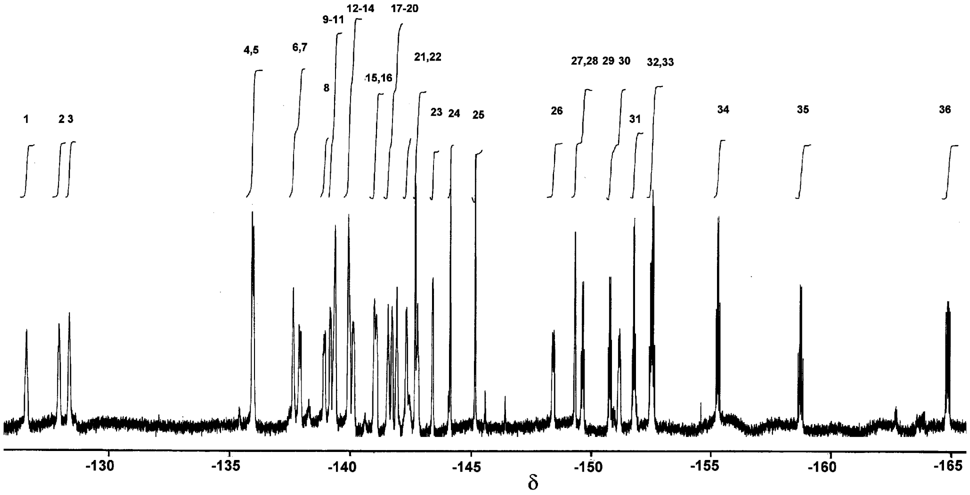


**Fig. 4** 1D $^{19}F$ NMR spectrum for $C_1$ $C_{60}F_{36}$.

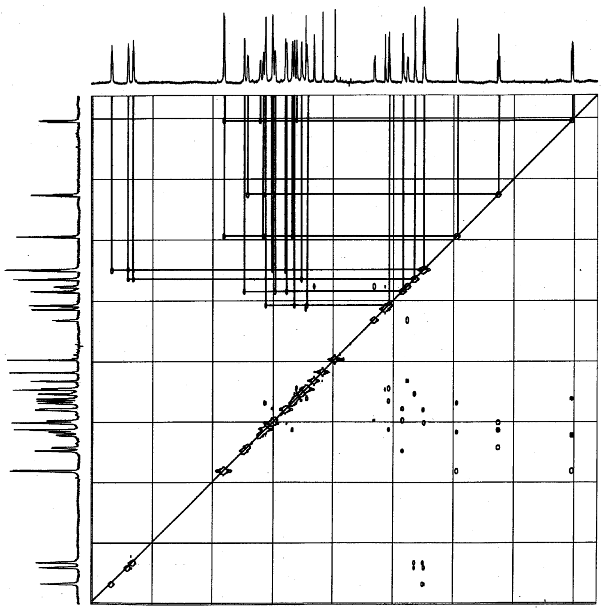


**Fig. 5** 2D $^{19}F$ NMR spectrum for $C_1$ $C_{60}F_{36}$.

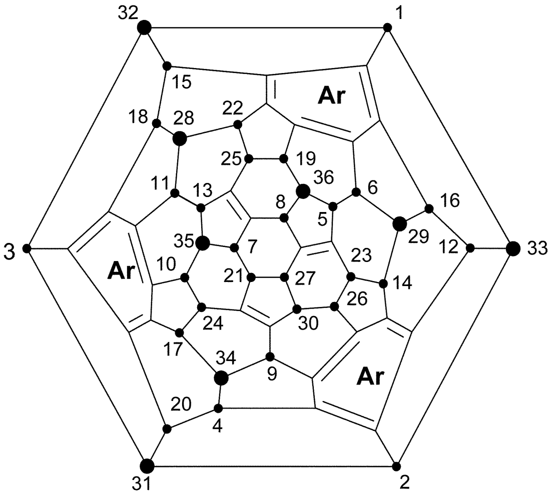


**Fig. 6** Schlegel diagram of the structure of $C_1$ $C_{60}F_{36}$ with NMR peak assignments (● = F, see text); pairs (2 and 3), (32/15 and 33/12) may be reversed.

Points to note are:

(i) Fluorines that are attached to carbon having three $sp^3$ carbons always appear as upfield multiplets in $^{19}F$ NMR spectra of fluorofullerenes. Fig. 6 reveals that there should be eight such multiplets, five of which should each be coupled to three different fluorines. From the 2D spectrum we can assign these five peaks as nos. 36, 35, 34, 28, and 27, and these can be distinguished (see below) as the five fluorines of this type nearer the centre of the Schlegel diagram.Their couplings are: 36–19,8,5; 35–13,10,7; 34–17,9,4; 29–16,14,6; 28–22,18,11.

Superimposed multiplets nos. 32 and 33 couple to a total of five other peaks 1, 2, 3, 12, 15. Peaks 2 and 3 also couple to multiplet 31 which in turn couples to peak 20. This allows assignment of these peaks to the positions shown. Note that the similar structural locations of the fluorines, nos. 32 and 33 result in them having similar locations in the spectrum, and indeed virtually coinciding since their structural positions are near symmetry-equivalent. (Peaks 32,15 may be interchanged with peaks 33,12 and likewise peaks 2 and 3 may be interchanged, but this does not affect the general assignments, which are required for our analysis of the structure of **1**.)

(ii) There are seven peaks thus far unaccounted for, and these are nos. 21, 23, 24, 25, 26, 27 and 30; no. 30 couples to both 23 and 26 and weakly to no. 27, which couples to no. 21. Peak 21 is absent in the spectrum for **1** (described below), in which the peak corresponding to no. 27 is perturbed. This allows assignments of these peaks as shown in Fig. 6. Moreover, the similar locations of fluorines 23, 24 and 25 are consistent with their appearance in the same region of the NMR spectrum. Couplings that are either 1,2-, 1,3-, 1,4- and/or conjugated are: 33/32–13/12, 33–16, 32–15, 30–23, 29–16,6, 28–18,11, 27–21,5, 26–14, 25–22,8,7, 24–10,9, 21–8, 17–10,9, 16–12, 14–6,5, 13–11,8,7, and 8–7,5. Longer-range couplings (some very weak) are 25–5, 21–19,14, 20–18, 15–4, 12–6, and 7–6. (Note that some of these appear to be of longer range on the 1D Schlegel diagram than is actually the case.)

### The structure of $C_{60}F_{35}OH$, isomer 1

Figs. 7 and 8 are the (1D and 2D) $^{19}F$ NMR spectra, respectively for **1**, and Fig. 9 is the Schlegel diagram with peaks assignments deduced from these spectra (as in Fig. 6, fluorines attached to carbons having three $sp^3$ neighbours are shown enlarged). A second 2D spectrum was run to identify long-range couplings and these have been transferred to the upper half of the Fig. 8 only, to distinguish them from the main couplings which appear in both halves of the spectrum. The similarity of the spectra in Figs. 4 and 7 is evident and thus for example there are eight upfield multiplets as in the case of $C_{60}F_{36}$. The couplings for these are: 35–18,13,6; 34–17,8,4; 33–16,9,5; 32/31–15/11/3/2/1; 30–20,3,2; 28–14,12,7; 27–21,19,10. For this compound there are only six peaks (nos. 22, 23, 24, 25, 26, and 29) that are not part of these 'quartets'; 29 is coupled to 26, 25 and 23, whilst 25

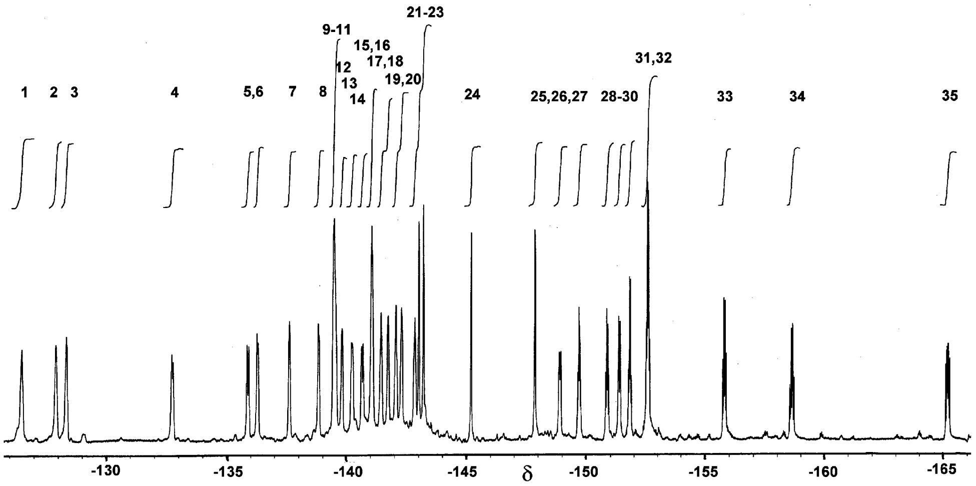


**Fig. 7** 1D $^{19}$F NMR spectrum for $C_{60}F_{35}OH$ (isomer **1**).

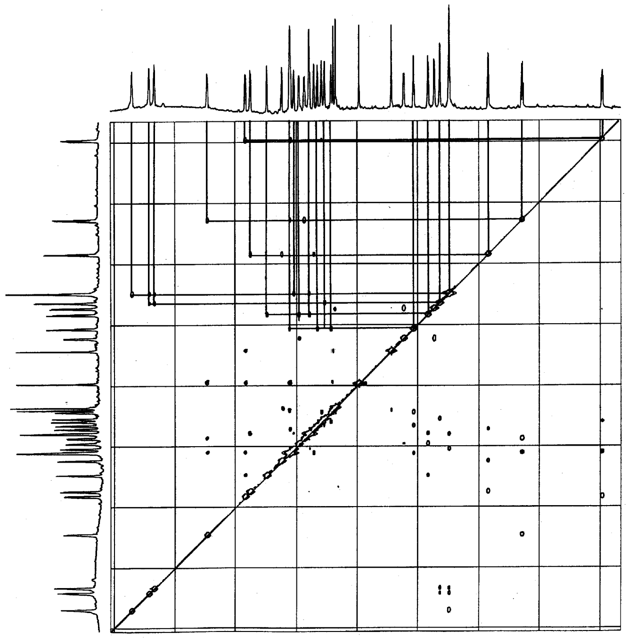


**Fig. 8** 2D $^{19}$F NMR spectrum for $C_{60}F_{35}OH$ (isomer **1**).

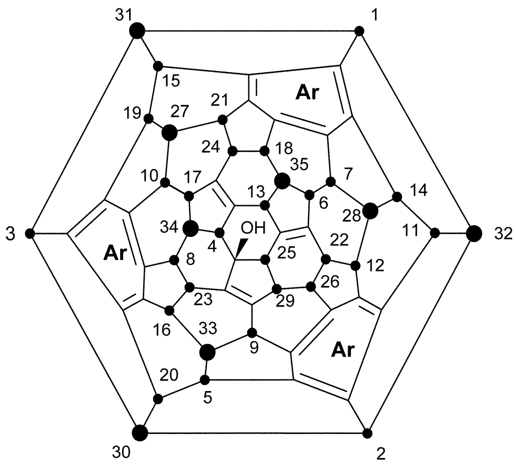


**Fig. 9** Schlegel diagram of the structure of $C_1$ $C_{60}F_{35}OH$, isomer **1**, (● = F, see text); assignment pairs (2 and 3), (31/15 and 32/12) may be reversed.

is coupled to 22 and 6, and 26 is coupled to 25 and 12. These couplings (some involve favourable conjugative interactions) also locate the no. 28 and 35 'quartet centres'. The peak that corresponds to no. 21 in $C_1$ $C_{60}F_{36}$ is absent showing where the OH group must be located. Further evidence for this is deduced below. Other couplings that are either 1,2-, 1,3-, 1,4- and/or conjugated are: 30–20, 24–13,4, 23–9, 21–19,18,17,15,10, 20–2, 19–10,3, 18–14,13,2, 17–10,4, 16–9,8,5, 15–3, 14–11,7, 13–6,4, 12–7, 11–1, 8–4,3 and 1–2,3. Weak long-range couplings are: 18–14,2, 14–2, and 12–5.

## Correlation of the $^{19}$F NMR spectra for $C_1$ $C_{60}F_{36}$ and isomer 1

Fig. 10 shows the remarkable correlation between the chemical shifts for fluorines in like-positions in the $^{19}$F NMR spectra of (**1**) and $C_1$ $C_{60}F_{36}$. Notably, two points lie above the correlation line: **A** corresponds to peaks 4($C_{60}F_{35}OH$) and 7($C_{60}F_{36}$), and **B** corresponds to peaks 25($C_{60}F_{35}OH$) and 27($C_{60}F_{36}$). Each is offset because of the replacement of the adjacent F by OH; point **A** is the more deviant since it involves electronic transmission across a shorter 6:6 bond.

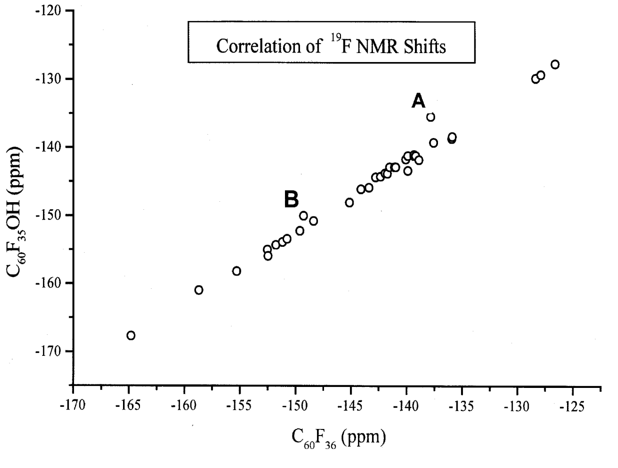
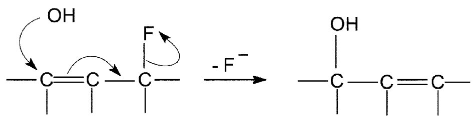


**Fig. 10** Correlation of the $^{19}$F NMR chemical shifts for $C_1$ $C_{60}F_{36}$ and $C_{60}F_{35}OH$ (isomer **1**).

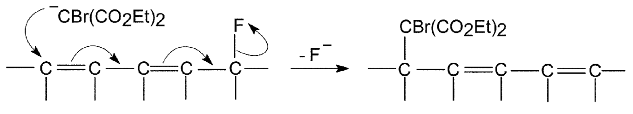
## The $S_N2'$ elimination mechanism

The mechanism of replacement of one group by another on the fullerene surface has long been perplexing. An $S_N2$ reaction is ruled out by the inability to have backside attack, whilst an $S_N1$ mechanism seemed improbable because of the strong electron-withdrawing nature of the cage.[4] More recent work involving ferric chloride-catalysed aryldehalogenation,[5] almost certainly does involve an $S_N1$ reaction, since the formation of a carbocation has been conclusively demonstrated.[6] Such a mechanism is not possible in the absence of a Friedel–Crafts catalyst, and for hydroxydefluorination, we conjectured that an $S_N2'$ mechanism (Scheme 1) must apply,[7] but no evidence has been



**Scheme 1** The $S_N2'$ mechanism for hydroxydefluorination.

available hitherto. Recently we obtained conclusive evidence that an 'extended $S_N2'$ mechanism' (which we have defined as $S_N2''$, Scheme 2) applies in the formation of *trans* annulenes (trannulenes) from $C_{60}F_{18}$.[8]



**Scheme 2** The $S_N2''$ mechanism involved in the formation of trannulenes.[8]

The present work now provides the first conclusive evidence for the $S_N2'$ mechanism, depicted as shown in Scheme 3. Thus $C_3$ $C_{60}F_{36}$[9,10] becomes converted into $C_1$ $C_{60}F_{35}OH$ (isomer **1**), and the driving force for the substitution can be seen to be the presence of two electron-withdrawing fluorines adjacent to one end of a double bond. The reason for the specific attack at one end of the double bond rather than the other (which would give instead the product shown in Fig. 11) follows from density functional calculations which show that the $C_{60}F_{36}$ isomer isostructural with the alternative $C_{60}F_{35}OH$ is (13.3 kcal mol $^{-1}$) higher in energy then the $C_1$ $C_{60}F_{36}$isomer[2] that is isostructural with the isolated $C_{60}F_{35}OH$. The alternative product would also require only seven upfield multiplets in the $^{19}F$ NMR, which is not seen.

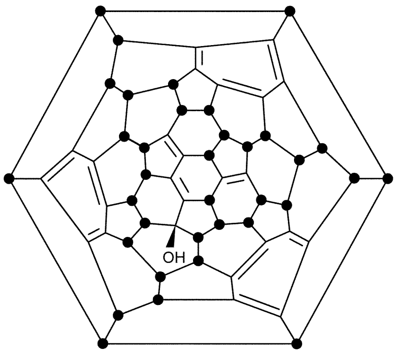


**Fig. 11** Higher energy hydroxydefluorination product (F = ●), which is not obtained.

The mechanism now explains why only a limited number of fluorines appear to be replaced in $C_{60}F_{36}$,[1] giving the restricted substitution/elimination sequence:

$$C_{60}F_{36} \longrightarrow C_{60}F_{35}OH \longrightarrow C_{60}F_{34}O \longrightarrow C_{60}F_{33}O.OH \longrightarrow C_{60}F_{32}O_2.^{1}$$

Replacement of further fluorines by OH groups, causes relocation of the double bonds and increasingly less stable structures. It also explains why the corresponding substitution does not take place with either the *T* isomer, or in $C_{60}F_{18}$ since neither has activated double bonds present. In general, only fluorofullerenes that have the required motif will readily undergo hydrolysis, and indeed its occurrence may help structural characterisation of polyfluorinated fullerenes.

### The structure of $C_{60}F_{35}OH$, isomer 2

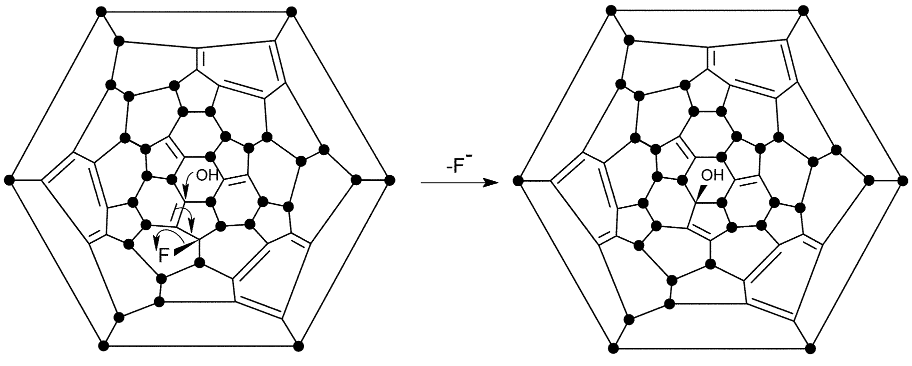
The structural identification of **2** is based on both the 1D (Fig. 12) and 2D $^{19}F$ NMR spectra. But first we consider the origin of this compound. Clearly it cannot come from the $C_3$ isomer of $C_{60}F_{36}$, because on standing with moist solvent this produces only isomer **1**. This leaves only the $C_1$ isomer from which there can be twelve possibilities, arising from addition of OH to either end of the three double bonds, with elimination of fluorine (two ways) at the other end. However, the number for consideration is reduced by inspection of the NMR spectrum which shows that there are eight upfield multiplets [due to fluorines in a **F**–C(CF)$_3$ arrangement], comprising one coincident pair (34,34 at $\delta$ −166.3) and two coincident triplets (27–29 and 30–32 at $\delta$ −154.5 and −153.6, respectively). In addition there is one upfield double doublet (at $\delta$ −165.1) which is due to the HOC.C**F**(CF)$_2$ motif.

Only structures I–V (Scheme 4) are consistent with these details. The 2D spectrum (not shown) reveals that none of the fluorines in the HOCCF(CF)$_2$ group are coupled with any of the eight multiplets. This reduces the possibilities to I and III only, the former being very strongly favoured by heats of formation (DFT) for their isostructural $C_{60}F_{36}$ isomers which are: I, 2.75; II, 19.0; III, 14.8; IV, 18.5; V, 29.4 kcal mol$^{-1}$.

Further analysis of the spectrum narrows the structure to I (see also Fig. 13). The analysis is complicated by coincidences, and the couplings (with options shown) are: 35–6,9,13; 34–5,11,12/13; 33–10,14; 30/31/32–1/2/3, 20/21/22/23; 25–5, 9,11; 26–10,11; 27/28/29–4,8,15/16, 17/18/19, 23; 19–14; 15–12/13; 11–9,5; 9–6. (Three long-range couplings seen *viz*. 26–11, 25–9 and 24–10, are all equivalent.) However, it proved possible to solve the structure and peak assignments (Fig. 13), the key to success being the unique fluorine no. 33, and again we see that this product can only have been formed by an $S_N2'$ reaction. Proof that the assignments are correct comes from comparison of the chemical shifts with those for $C_3$ $C_{60}F_{36}$,[10] from which it is seen that peaks occupying analogous positions in the Schlegel diagram occupy similar positions in the spectrum.

### The structure of $C_{60}F_{36}O$

The EI mass spectrum (1420 u, Fig. 3) of the fraction eluting at 13.0 min in 1 : 9 toluene : heptane) shows the double-charged



**Scheme 3** Conversion of $C_3$ $C_{60}F_{36}$ into $C_1$ $C_{60}F_{35}OH$ (isomer **1**) *via* an $S_N2'$ mechanism; F = ● except where otherwise indicated.

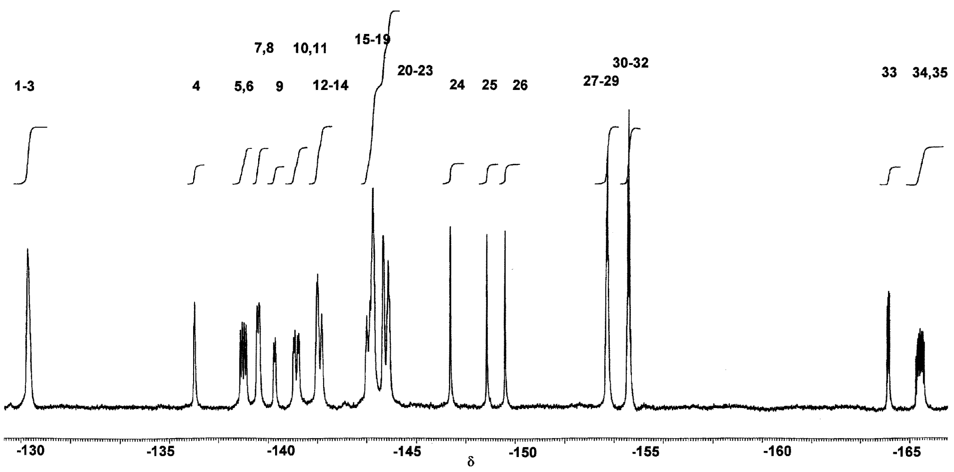
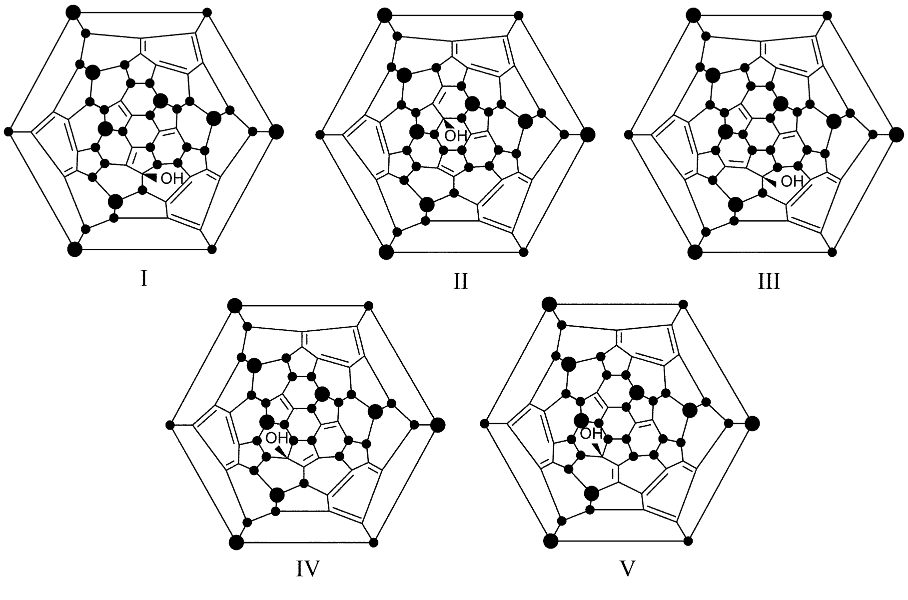


**Fig. 12** 1 D $^{19}$F NMR spectrum for $C_{60}F_{35}OH$ (isomer **2**).



**Scheme 4** Possible structures (see text) obtained from $S_N2'$ hydrolysis of $C_1$ $C_{60}F_{36}$.

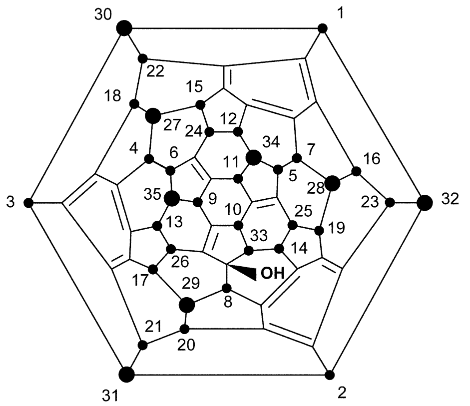


**Fig. 13** Schlegel diagram of the structure of $C_1$ $C_{60}F_{35}OH$, isomer **2**, with NMR peak assignments (● = F, see text).

ion at 710 u and almost no $C_{60}$ present, which indicates the high stability of this compound, typical of an ether.

The $^{19}$F NMR spectrum (Fig. 14) shows 36 lines confirming the presence of 36 fluorine atoms, and the compound has $C_1$ symmetry. We have not been able to assign a precise structure based on the 2D spectrum (not shown) but two features are evident:

(i) There two peaks at −96.1 and −119.05 ppm (difference 23.05), downfield from the range normally obtained with fluorofullerenes and due to adjacent oxygen. They are typical of an ether, their location is very similar to those for isomer **5** of $C_{60}F_{18}O$,[11] ($\delta$ −91.6 and −115.8, difference 24.2) showing the oxygen to be interspersed between fluorines in a –CFC**F**–O–C**F**(CF)$_2$– motif.

(ii) Previous work on ethers derived from $C_{60}F_{18}$ showed that the oxygen inserts into the longest FC–CF bonds and indeed the relative yields parallel the bond lengths. The $C_1$ isomer of $C_{60}F_{36}$ has a number of very long bonds (> 1.65 Å) as follows (using the NMR locations of Fig. 6): 32–15, 33–12, 31–20, 16–29, 18–28, 4–34.[2] Each of these positions conforms to the prediction above, and of these the first bond is the longest (1.683 Å) in any fluorofullerene so far measured.[2]

(iii) Insertion into the longest bond of the $T$ isomer[12] would give the downfield NMR pattern described above, but would require twelve upfield multiplets. Insertion into a bond of the required type of the $C_3$ isomer (the bond lengths are not known) would require eight upfield multiplets, whilst insertion into the $C_1$ isomer requires seven upfield multiplets. Seven multiplets (at $\delta$ −170.0, −169.1, −166.5, −165.5, −156.9, −155.7, −155.05) can be clearly identified. Coupling of the two most downfield peaks (nos. 1 and 2) in the 2D spectrum (not shown) reveals the peak at $\delta$ −162.7 (no. 32) to be due to

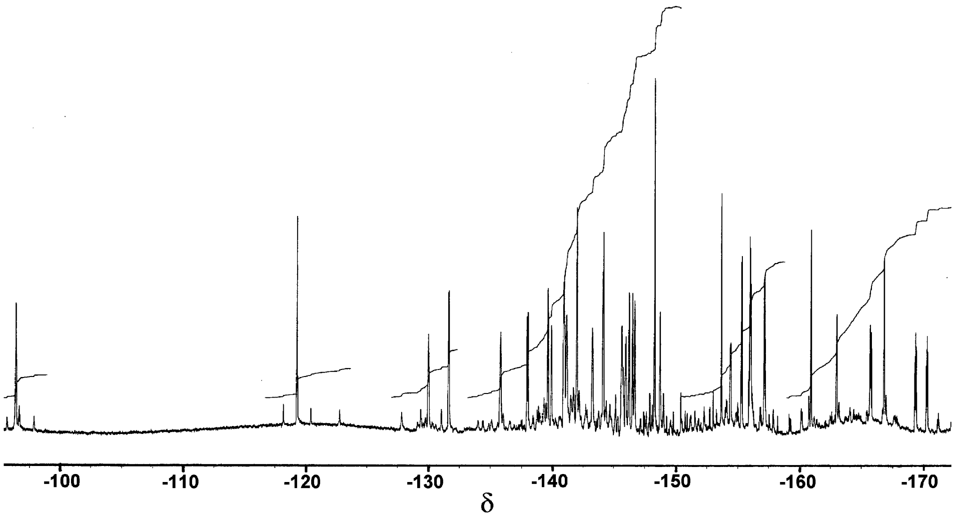


**Fig. 14** The $^{19}$F NMR spectrum of $C_{60}F_{36}O$.

the O–(FC)CF fluorine whilst the multiplet at −154.15 ppm (no. 27) is due to the O–FC–(CF)$_2$ fluorine; these in turn are coupled to nos. 34 and 28, respectively.

The evidence points therefore in favour of an ether derived from the $C_1$ isomer, and in the conjectured structure (Fig. 15), oxygen is inserted into the longest bond that corresponds to 6–7 (nomenclature numbering)[2] or 32–15 (numbering of $^{19}$F NMR peaks, Fig. 7). The $^{19}$F NMR spectrum show consistency with this conjecture, in the coupling of peak no. 32 with the multiplet no. 34 at $\delta$ −165.5), and the coupling of peak no 27 with no. 28, $\delta$ −155.05 (there are two options for this, see Fig. 15). There are one or more other isomers of $C_{60}F_{36}O$ (one of which we have isolated semi-pure, see below), and it seems significant that one isomer appears to dominate. Calculations of the energies of all of the possible ethers of all three main isomers of $C_{60}F_{36}$ (insertion into the long bonds that are now evidently favoured) could be instructive.

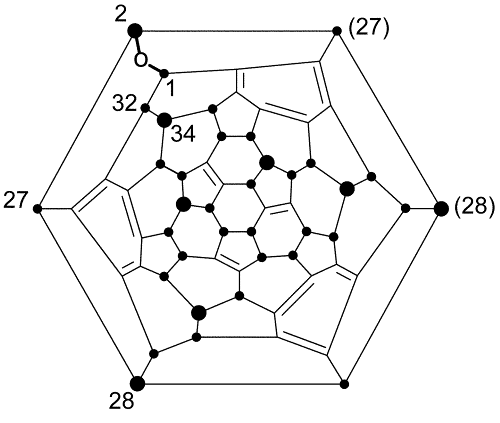


**Fig. 15** Conjectured structure of $C_{60}F_{36}O$, derived from oxygen insertion into the longest bond of $C_1C_{60}F_{36}$.

### Other components

From elution with 1 : 9 toluene : heptane produced a fraction of 4.75 min retention time and 15 min retention time after reprocessing with heptane; this fraction therefore eluted later than either of the three characterised isomers of $C_{60}F_{36}$. The mass spectrum (Fig. S2, see ESI †) indicated that it consisted of a mixture of $C_{60}F_{36}$ (1404 u), $C_{60}F_{36}O$ (1420 u), $C_{60}F_{35}CF_3$ (1454 u), and a component of 1392 u; the $^{19}$F NMR spectrum (Fig. S3, see ESI †) confirmed that it is a mixture.

The peak of 1392 u has been seen in mixtures before,[13] but has not been identified. It may derive from CO loss from the associated $C_{60}F_{36}O$ isomer if this is of lower stability.

The $^{19}$F NMR spectrum shows no peaks for the $C_1$ isomer of $C_{60}F_{36}$ (the one most likely to be present due to HPLC tailing) so that a new isomer must be present. It also shows that the isomer of $C_{60}F_{36}O$ present differs from the above characterised one, since the two downfield signature peaks occur at different resonances ($\delta$ −96.0 and −122.5), but again in the same region. Thus there is a second isomer of $C_{60}F_{36}O$ as expected from the reasoning given above, and it seems probable that others could eventually be isolated.

### Future directions

The ease of making $C_{60}F_{36}$ and the ready conversion of the highest yield isomers into the corresponding hydroxy derivatives, offers the possibility of derivatising the latter for various applications *e.g.* light-harvesting. This is to be investigated.

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