PERKIN 2

Isolation and characterisation of forty-nine fluorinated derivatives of [70]fullerene †

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Received (in Cambridge, UK) 1st December 1999, Accepted 8th March 2000

From 100 mg of the product of fluorination of [70]fullerene with MnF_3 at 450 °C at *ca.* 0.1 bar, we have isolated forty-nine components by HPLC and characterised them by mass spectrometry, together with IR and both 1D and 2D ^{19}F NMR spectroscopy (where quantities permitted). The separation was carried out using a 4.6 mm diameter Cosmosil 'Buckyprep' column with elution by either toluene, various toluene–heptane mixtures, or heptane, and entailed some 950 manual runs. The products comprise numerous isomers of $C_{70}F_{44}$, $C_{70}F_{42}$, $C_{70}F_{40}$, $C_{70}F_{38}$, $C_{70}F_{36}$, $C_{70}F_{34}$, $C_{70}F_{40}O$, $C_{70}F_{38}O$, $C_{70}F_{36}O$, $C_{70}F_{36}O_2$, $C_{70}F_{35}O{\cdot}OH$, $C_{70}F_{37}{\cdot}O{\cdot}OH$, and $C_{70}F_{34}O_3$. A component that eluted just before one of the $C_{70}F_{38}$ isomers, was indicated by mass spectrometry to be $C_{70}F_{37}$ but is probably an exceptionally stable fragment produced by degradation of an oxide precursor, a view supported by temperature-degradation studies. One each of $C_{70}F_{42}$, $C_{70}F_{38}$, $C_{70}F_{36}$ isomers, at least two $C_{70}F_{40}$ isomers, and $C_{70}F_{34}O_3$ have either C_s or C_2 symmetry, all the other compounds have C_1 symmetry. The main components are two $C_{70}F_{38}$ isomers (nos. **8** and **14**). Other components detected in trace amounts were $C_{70}F_{39}O{\cdot}OH$, the poly-epoxides $C_{70}F_{36}O$, $C_{70}F_{36}O_2$ and $C_{70}F_{36}O_3$ and the poly-epoxy dihydroxides, $C_{70}F_{30}O_2(OH)_2$, $C_{70}F_{30}O_3(OH)_2$, and $C_{70}F_{30}O_4(OH)_2$.

Introduction

In a preliminary report of the fluorination of [70]fullerene with MnF_3 we showed (EI mass spectrum) that the product consisted mainly of $C_{70}F_{36-40}$, with $C_{70}F_{38}$ being the predominant species present.[1] (Likewise, in preliminary work, Selig and co-workers found fluorination of [70]fullerene to produce $C_{70}F_{36-44}$.[2]) The ^{19}F NMR spectrum of our product consisted of well over one hundred major lines (and numerous minor ones).[1] More recently we were successful in separating the two isomers of $C_{60}F_{36}$,[3] together with various hydroxy/epoxy derivatives of these.[4] Such separation becomes possible because the fluorofullerenes are soluble in solvents suitable for processing, and very minor changes in the structure of the fluorofullerene produce large changes in retention time due to the high polarity of the C–F bond. This encouraged us to attempt the daunting separation of the very complex mixture of products that is obtained on fluorinating [70]fullerene, and we now describe the results of analysis that involved carrying out 950 manual HPLC runs. The very small amounts of the stock solution, the slight variations in retention times with each run that is characteristic of fluorofullerene separations, and the need to cut peaks having shoulders, ruled out the use of automatic procedures.

A reason for undertaking this work was to try to ascertain the polyaddition pattern in [70]fullerene. A strong parallel exists between hydrogenation and fluorination of both [60]-, [70]-, and [84]-fullerenes,[1,3,5–7] and this has been further demonstrated by ^3He NMR spectroscopy of $C_{60}H_{36}$ and $C_{60}F_{36}$.[8] The parallel exists for these reactions of [70]fullerene as indicated by the formation in each of mainly $C_{70}X_{36}$, $C_{70}X_{40}$, the major component being $C_{70}X_{38}$ (X = F, H). Whilst the structure of $C_{60}X_{36}$ has finally been solved[8] the structure of $C_{70}X_{36}$ is still unknown but (in the case of the hydrogenated species) has been the subject of various predictions.[9]

Experimental

[70]Fullerene was fluorinated with MnF_3 as described previously.[1] Fluorinated fullerenes react rapidly with atmospheric moisture, especially when in solution. Procedures adopted to overcome this included the following: (i) the crude fluorofullerene solution (in toluene) was filtered through a Kleenex tissue plug of 1.5 cm length, which was rammed hard into a Pasteur pipette. This provided very effective filtration without the risk of toluene evaporation and hence moisture condensation; (ii) heptane rather than hexane was used in processing, to reduce moisture condensation through evaporation that occurs upon fraction collection; and (iii) removal of solvent (rotary evaporator) was carried out at 30 °C using a vacuum pump protected by a refrigerated trap. The low bath temperature ensured a relatively low water vapour pressure in the vicinity of the sample flasks as they were either attached to, or detached from, the evaporator. All solvent collected in the evaporator and the trap was recycled for economic, and environmental considerations, and had the further benefit of being freed from the ubiquitous dioctyl phthalate plasticiser, present in as-supplied commercial solvents (including those of so-called 'HPLC grade'). All connection lines in the solvent recovery system were flexible stainless steel with Cajon couplings, *i.e.* no plastic or rubber tubing was used.

The results described here encompass the processing of four batches of product totalling approximately 100 mg (from *ca.* 250 mg of [70]fullerene). HPLC analysis was carried out using a 4.6 mm × 25 cm analytical Cosmosil 'Buckyprep' column, operated at a flow rate of 1 ml min^{-1}. The general procedure was to elute with toluene initially; less polar components eluted together and very rapidly, and were collected for reprocessing. The more polar materials eluted as separable peaks and were reprocessed to remove tailing material, and then analysed by mass spectrometry, IR, and ^{19}F NMR. The less polar material was then reprocessed with a less polar solvent *e.g.*, toluene–heptane (50 : 50), the least polar peaks being again set aside for reprocessing with an even less polar solvent, the more polar

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† Further IR and ^{19}F NMR spectra (Figs. S1–S26) are available as supplementary data. For direct electronic access see http://www.rsc.org/suppdata/p2/a9/a909490c/

DOI: 10.1039/a909490c

materials being repurified by recycling, and analysed as described above. This general procedure was repeated using a succession of toluene–heptane mixtures (30:70, 20:80, 15:85, 10:90, 5:95) and lastly heptane, a series of decreasing polarity. The refractive indices of recovered solvents were determined and one or other component then added to produce the required composition levels, this being confirmed by the refractive index.

Numerous injections (volumes ranged from 50 to 1000 µl) were necessary with each solvent composition because of the limited capacity of the column. It was also occasionally necessary to flush the column with methanol because it became blocked with fluorofullerene decomposition products (high back pressure), and this sometimes eluted an alarming amount of black material (after which the pressure was restored to normal) but fortunately the subsequent column performance was unaffected. However, it was necessary to elute with non-protic solvent for 2–3 hours afterwards to ensure removal of all methanol traces which destroy fluorofullerenes. Four other problems were encountered:

(i) A feature of fluorofullerene HPLC is that the column retention time for a given derivative is not exactly reproducible, and can also diminish with time as sites on the column become blocked. Thus the retention times given below are 'accurate' to only ±5%, with variations also due to minor differences between solvent batches. This necessitated manual separation entirely.

(ii) Secondly, due to reaction with traces of moisture, the composition of some eluents changed somewhat during reprocessing. This difficulty became less of a problem during later work once it was recognised and combated.

(iii) During some runs, the column pressure started to decrease dramatically (not due to failure of the non-return valves), and eventually returned to normal if the column was pumped with solvent only. This may be due to degradation involving release of either F_2 or HF (gas) in the column, but did not affect subsequent performance of the column. This observation may be related to a recent report of fluorine loss, believed to have occurred on HPLC of $C_{60}F_{44}$.[10]

(iv) There was initial confusion when different fractions gave the same mass spectrum, but this was later realised to be due to the presence of many isomers.

We also obtained a deep yellow product from column flushing with toluene, mass spectrometry of which indicated the absence of high mass species. However it possessed a strong band in the IR C–F stretching region, suggesting that this material is a fluoro-containing polymer derived from toluene and/or the fullerene. Such a high mass species could be insufficiently volatile for mass spectrometric detection. We hope to investigate this material subsequently.

The overall HPLC procedure necessitated some 950 runs. This number would be reduced very substantially in repetition of this work, since exploratory runs would be unnecessary. We are also able now to achieve a four-fold reduction in processing time following the acquisition of a 10 mm diameter Cosmosil 'Buckyprep' column.

Four sets of material were processed. Because of the extreme difficulties encountered in the HPLC work, two sets (which were obtained at fluorination temperatures of *ca.* 350 and 450 °C), were processed together with a small amount of material obtained by fluorinating with CeF_4. The fourth and largest batch (*ca.* 70 mg) was processed separately, but no appreciable difference in the components from the two batches was observed.

Overall the improvements in separation procedure are evident from comparison of the mass spectra of the derivatives isolated in this work, with those which we obtained earlier on HPLC separation of fluorinated derivatives of [60]fullerene.[4]

We describe only the main components and those for which the mass spectra (and in some cases the IR and ^{19}F NMR spectra) were obtained. Some others were obtained in quantities sufficient for spectroscopic examination, but this was not carried out because the mass spectra indicated the presence of minor components which could not be readily separated. Numerous other minor peaks were obtained which either gave poor EI mass spectra, or spectra that misleadingly indicated the presence of [70]fullerene only. This is due probably to the presence of oxides that degrade during EI mass spectrometry, but it was impractical to follow up these many minor leads with the amounts of material available. It was also necessary to avoid being misled by the nature of mass spectrometry which can over-estimate the amount of the more volatile components in a mixture; in general fluorofullerene volatility increases with the fluorine content.

Results and discussion

A description of the isolation of the various components from each processing batch is not given because of the very large number of variations in procedure. Moreover, not all of the minor components were isolated each time, due possibly to differences in the temperature of formation, and to reaction with moisture traces.

The isolated species. Results for separation and isolation of derivatives $C_{70}F_n$ are given in Table 1 which shows the solvent used, the retention time and the assigned number for the derivative. Overall we have isolated one isomer of $C_{70}F_{34}$, six isomers of $C_{70}F_{36}$, eight isomers of $C_{70}F_{38}$, at least (see below) five isomers of $C_{70}F_{40}$ and one each of $C_{70}F_{42}$ and $C_{70}F_{44}$. The two components isolated in the largest amounts were the $C_{70}F_{38}$ isomers **8** and **14**. The data in Table 1 show that the derivatives with fewest fluorines elute more slowly. (A few exceptions arise from different polarities of isomers.) This parallel between addend number and retention time is a general feature of the Cosmosil 'Buckyprep' column, evident for example with arylated fullerenes.[11]

Table 2 shows the data for various oxide and hydroxide derivatives. [Compound $C_{70}F_{34}O_3$ (**40**) was obtained after the column had become blocked after using various mixed solvent mixtures, and was stripped with toluene. It was not present in the unprocessed material and may have been formed on the column by hydrolysis/elimination during processing.] We have isolated nine isomers of $C_{70}F_{36}O$, seven isomers of $C_{70}F_{38}O$, four isomers of $C_{70}F_{40}O$, three isomers of $C_{70}F_{35}\cdot O\cdot OH$, two isomers of $C_{70}F_{37}\cdot O\cdot OH$ and one each of $C_{70}F_{36}O_2$ and $C_{70}F_{34}O_3$; $C_{70}F_{37}O\cdot OH$ and $C_{70}F_{39}O\cdot OH$ were detected as minor components of some $C_{70}F_{35}\cdot O\cdot OH$ samples (see Table 2).

Overall, the amounts of each isolated component (fluorofullerene and epoxide derivatives) ranged from *ca.* 0.1–3 mg, but we did not record the actual amounts for each compound in order to minimise handling, and to concentrate on the essential tasks of obtaining the spectra.

The oxides have longer retention times than the unfluorinated precursors, (the same is true of the unfluorinated fullerenes)[12] and show a decreased retention time with increased fluorine content, though the retention times seem to *decrease* with increasing number of oxygens, after the addition of the first. This is to some extent understandable if the oxides are considered in terms of the precursor fluorofullerene. Thus $C_{70}F_{36}O_2$ (derived from $C_{70}F_{40}$) elutes faster than $C_{70}F_{36}O$ (derived from $C_{70}F_{38}$), though there is some ambiguity due to the existence of different isomers.

The mechanism for the formation of the epoxides (Scheme 1)[13] requires the presence of water, and this may account for the general lack of higher oxides; no further reaction occurs once residual traces of water in the solvents have been used up. Given that oxygen occupies two sites (as an epoxide) and

Table 1 Elution times (min) for $C_{70}F_n$ compounds (assigned no. in parentheses) in the solvents indicated

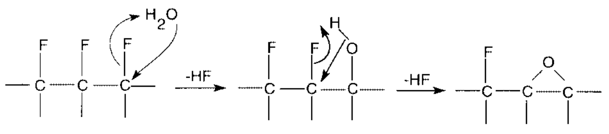
Solvent	$C_{70}F_{34}$	$C_{70}F_{36}$	$C_{70}F_{38}$	$C_{70}F_{40}$	$C_{70}F_{42}$	$C_{70}F_{44}$
Toluene	18.0 (**1**)	17.2 (**2**)				
Toluene–heptane (30:70)		41.0 (**3**)				
		31.5 (**4**)				
		27.4 (**5**)				
		16.7 (**6**)				
Toluene–heptane (20:80)		55.5 (**6**)	17.8 (**8**)	8.1 (**15**)		
		51.5 (**7**)				
Toluene–heptane (15:85)			49.5 (**9**)			
			34.8 (**10**)			
Toluene–heptane (10:90)			63 (**11**)	32.0 (**16**)		
			40.2 (**12**)	25.2 (**15**)		
			16.4 (**13**,**13a**)	11.7 (**17**)		
			6.7 (**14**)			
Toluene–heptane (5:95)			12.0 (**14**)	67.2 (**16**)		
				21.5 (**17**)		
Heptane				9.5 (**18**)	5.0 (**19**)	3.5 (**20**)

Table 2 Elution times (min) for $C_{70}F_nO_m$ compounds (no. in parentheses) in the solvents indicated

Solvent	$C_{70}C_{36}O$	$C_{70}F_{38}O$	$C_{70}F_{40}O$	$C_{70}F_{36}O_2$	$C_{70}F_{34}O_3$	$C_{70}F_{35}O{\cdot}OH$
Toluene	30.9 (**21a**,**b**)			20.2 (**39**)	8.5 (**40**)	
	18 (**22**)					
Toluene–heptane (30:70)						48.0 (**41**)
						22.0 (**42**)^a
						16.0 (**43**)^b
Toluene–heptane (20:80)	19.8 (**23**)	9.5 (**29**,**29a**)				
Toluene–heptane (15:85)	65–74 (**24**)	37.6 (**30**)				*$C_{70}F_{37}O{\cdot}OH$*
	55–65 (**25**)					42 (**44**)
	51 (**26**)					48 (**45**)
	47 (**27**)					
Toluene–heptane (10:90)	59 (**28**)	56 (**31**)				
		36.8 (**32**)				
		29.9 (**29**,**29a**)				
Toluene–heptane (5:95)		74 (**33**)	19.1 (**35**)			
		15.2 (**34**)	17.6 (**37**,**38**)			
			13.9 (**36**)			
Heptane			72.6 (**37**)			
			67.9 (**38**)			

^{a} This contained some $C_{70}F_{37}O{\cdot}OH$. ^{b} This contained some $C_{70}F_{39}O{\cdot}OH$ and $C_{70}F_{37}O{\cdot}OH$.

OH occupies one, the oxygen-containing species can be seen to be derived from the $C_{70}F_{38–42}$ precursors that we have identified. This provides support for the formation mechanism given in Scheme 1.



Scheme 1 Mechanism for epoxide formation from fluorofullerenes.

The species formed in fluorination

It is most remarkable that it has been possible to separate so many components of similar fluorine contents. Moreover, given that the retention times of these are now established, it may now be possible to isolate these components from the product of fluorination using fluorine gas, a much cheaper route that would need to be employed in any large scale fullerene fluorination. A second feature of note is that at the 'extremes' of the fluorination range, only a single isomer is detected and isolated ($C_{70}F_{34}$, $C_{70}F_{42}$, $C_{70}F_{44}$) whereas for in-between fluorination levels, the number of isomers is as many as eight. The implication is that addition of pairs of fluorines to $C_{70}F_{34}$ is possible at a variety of sites resulting in the formation of a range of isomers. Then, as fluorination progresses, the unoccupied sites for each of the different isomers gradually fill up causing convergence to a single isomer for $C_{70}F_{42}$. Such reasoning combined with theoretical calculations may help to establish the structures of all of the derivatives.

Mass spectra

Because so many components were obtained, only the mass spectrum for one example of each isomer is shown. Fig. 1 shows a montage of the spectra for $C_{70}F_{34}$, $C_{70}F_{36}$, and $C_{70}F_{38}$, and Fig. 2 is likewise a montage for $C_{70}F_{40}$, $C_{70}F_{42}$ and the most rapidly eluting material (see Table 1), showing the presence of $C_{70}F_{44}$. Fig. 3 is an anomalous spectrum of what appears to be $C_{70}F_{37}$ (this material was obtained from two separate batches), but we believe that it may be a very stable radical cation that is produced by fragmentation of an oxide-containing species, as described below. Fig. 4 is the montage of the spectra for $C_{70}F_{36}O$, $C_{70}F_{38}O$, and $C_{70}F_{40}O$, whilst Fig. 5 shows the mass spectra for $C_{70}F_{36}O_2$, $C_{70}F_{34}O_3$, and $C_{70}F_{35}O{\cdot}OH$.

IR spectra (KBr discs)

It was not possible to isolate sufficient quantities of all of the components to obtain IR spectra; in a few cases, complete separation of components from those of closely similar retention times could not be achieved given the amount of material available, and so the spectra were not run.

Spectra were obtained of $C_{70}F_{34}$ (**1**) [1176, 1152, 1145 (main), 1092 cm^{-1}], $C_{70}F_{36}$ (**2**) [1158, 1129 (main), 1079 (sh) cm^{-1}],

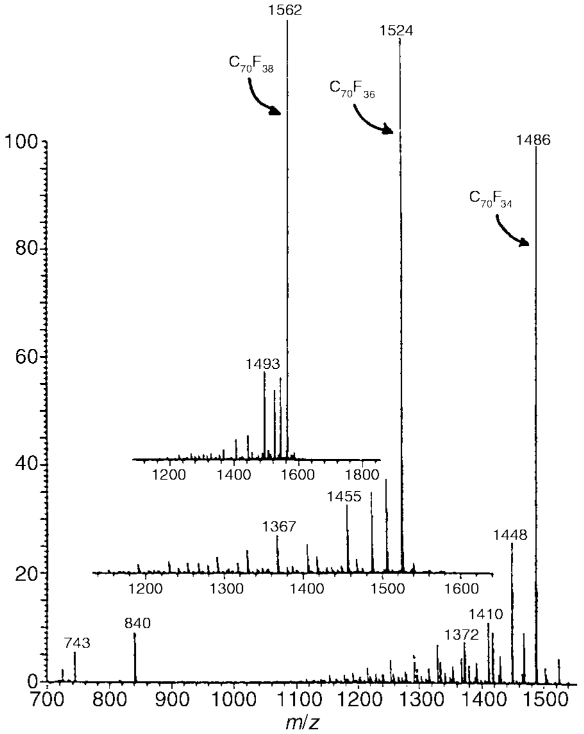


Fig. 1 EI mass spectra (70 eV) for $C_{70}F_{38}$, $C_{70}F_{36}$, and $C_{70}F_{34}$.

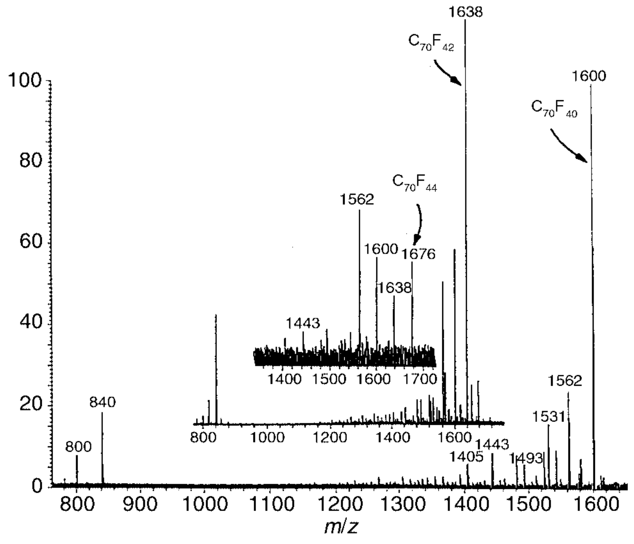


Fig. 2 EI mass spectra (70 eV) for $C_{70}F_{44}$, $C_{70}F_{42}$, and $C_{70}F_{40}$.

$C_{70}F_{38}$ (**8**), [1213, 1162 (main), 1154 (sh), 1144 (sh), 1114, 1092, 1067 cm^{-1}], $C_{70}F_{38}$ (**11**) [1160 (main), 1144 cm^{-1}], $C_{70}F_{38}$ (**13/13a**) [1206, 1164 (main), 1135 cm^{-1}], $C_{70}F_{38}$ (**14**) [1215, 1212, 1167 (main), 1149, 1135, 1110, 1105, 1087, 1082, 616, 594, 580, 564, 548, 531, 485 cm^{-1}], $C_{70}F_{40}$ (**15**) [1212, 1170, 1138 (main), 1100, 1073, 604 cm^{-1}], $C_{70}F_{40}$ (**16**) [1262, 1205, 1161, 1149, 1127 and 1120 (=main) cm^{-1}], $C_{70}F_{40}$ (**17**) [1205, 1171, 1162, 1140 (main), 1075 cm^{-1}], $C_{70}F_{40}$ (**18**) [1211, 1162 (main), 1145, 1112 (sh), 1080 (sh) cm^{-1}], $C_{70}F_{42}$ (**19**) [1242, 1210, 1168, 1148 (main), 1120, 1100, 1079, 614, 597, 583, 574, 562, 475 cm^{-1}], $C_{70}F_{36}O$ (**28**) [1258, 1161, 1127 (main) cm^{-1}], $C_{70}F_{38}O$ (**29**) [1211, 1164 (main), 1152, 1131 cm^{-1}], $C_{70}F_{38}O$ (**31**) [1163, 1141, 1135 (*ca.* all equal intensity)]. These are shown in Figs. S1–S4, Figs. 6–8, Figs. S5–S7, Fig. 9, Figs. S8–S10, respectively.

Where duplicate spectra were taken of samples obtained from a second batch of crude material, the spectra were accurately reproduced. This provides an important means of referencing the derivatives without recourse to ^{19}F NMR spectroscopy which requires high field instrumentation and a large amount of acquisition time. With the exception of $C_{70}F_{34}$ (**1**), the spectra all show a C–F stretching band at 1164 ± 6 cm^{-1} and most show one at 1145 ± 7 cm^{-1}. However, they have very different fine structure in this region, even for isomers (*e.g.* Figs. 10 and 11 for $C_{60}F_{38}$). Ultimately, it may be possible to compare the IR spectra with those predicted for certain structures, and limit the assignment of possible structures. The spectrum for

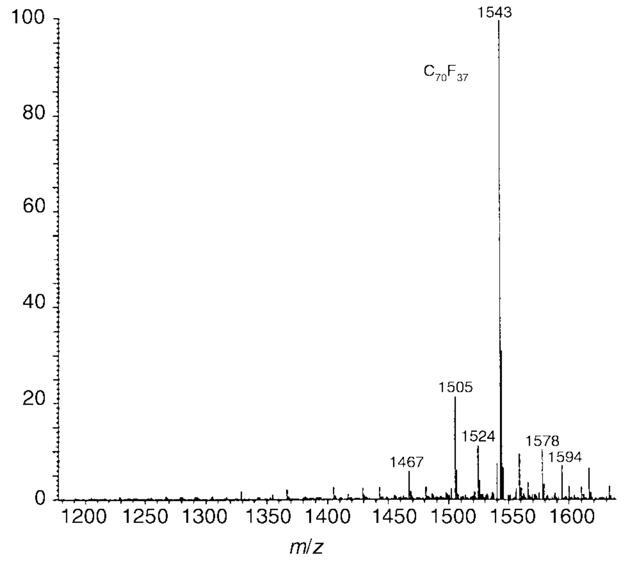


Fig. 3 EI mass spectrum (70 eV) indicating the presence of $C_{70}F_{37}$ (**44**) at 1543 amu.

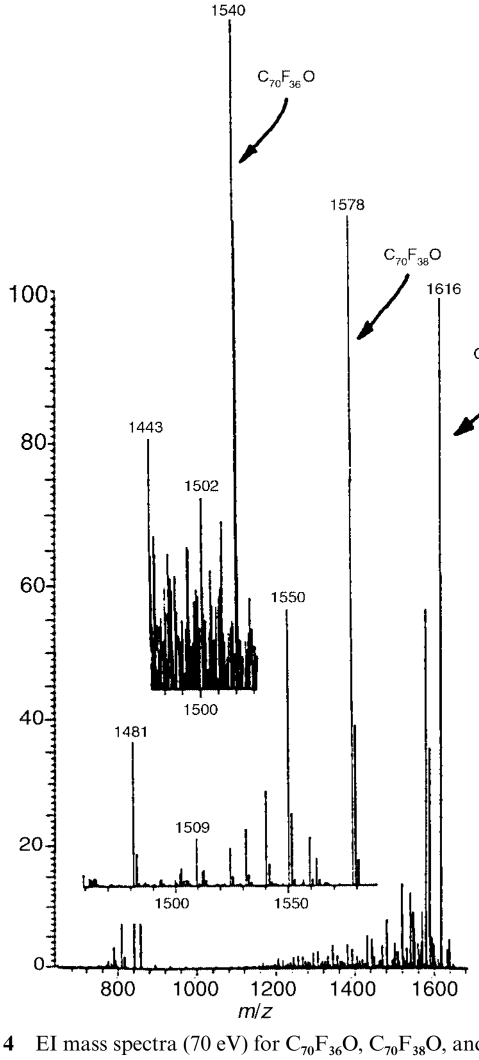


Fig. 4 EI mass spectra (70 eV) for $C_{70}F_{36}O$, $C_{70}F_{38}O$, and $C_{70}F_{40}O$.

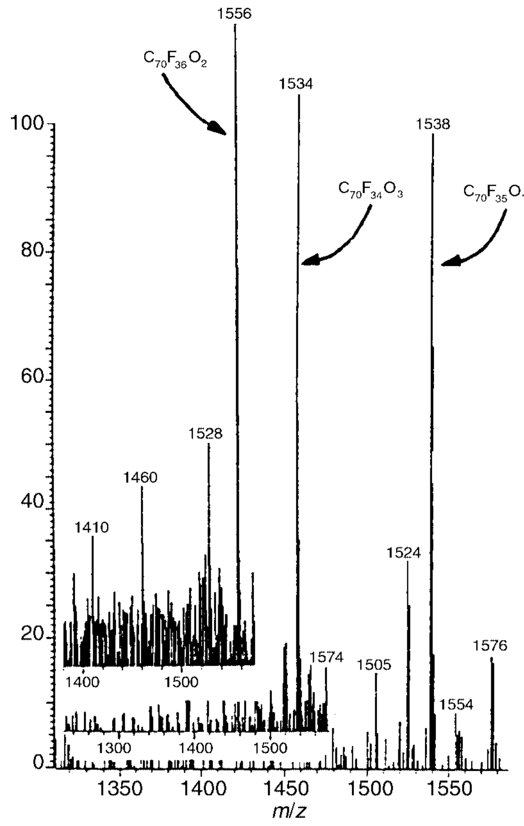


Fig. 5 EI mass spectra (70 eV) for $C_{70}F_{36}O_2$, $C_{70}F_{34}O_3$, and $C_{70}F_{35}O{\cdot}OH$.

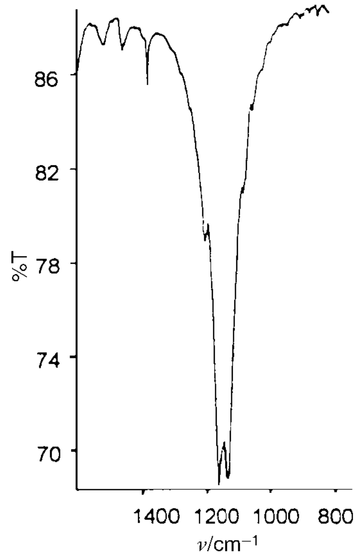


Fig. 6 IR spectrum (KBr) for $C_{70}F_{38}$ (**13**).

(**13**/**13a**), Fig. 10, shown to be a mixture by the NMR data (below), is surprisingly sharp and suggests a similarity of structure of the components (as indicated also by the common retention times).

^{19}F NMR spectra (339 MHz)

Satisfactory spectra have thus far been obtained of compounds **1**–**3**, **5**–**8**, **13**–**19**, **21**, **26**, **29**, **33**, **36**, **40**, **41** and **44**. Attempts to obtain spectra for some of the other derivatives were unsuccessful due to the small amounts of material available, the spectra being either very noisy, or showing no distinguishable peaks. Integration showed coincident peaks in each spectrum.

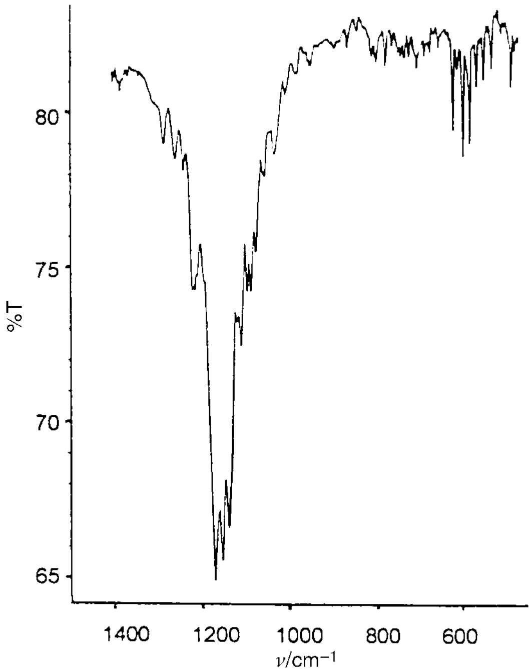


Fig. 7 IR spectrum (KBr) for $C_{70}F_{38}$ (**14**).

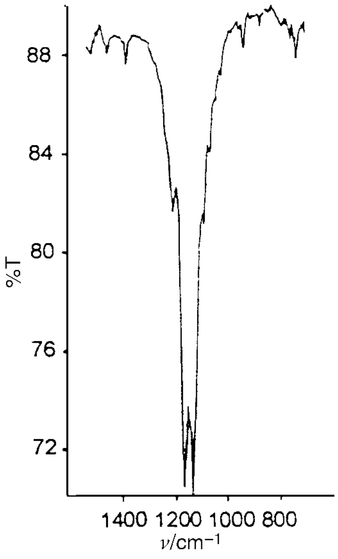


Fig. 8 IR spectrum (KBr) for $C_{70}F_{40}$ (**15**).

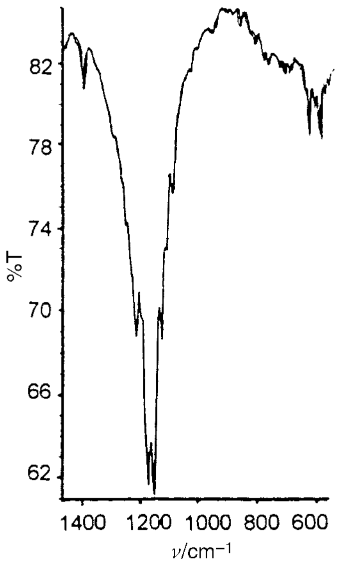


Fig. 9 IR spectrum (KBr) for $C_{70}F_{42}$ (**19**).

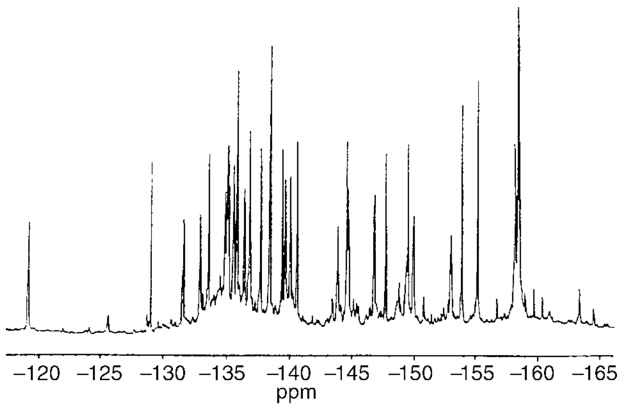


Fig. 10 ^{19}F NMR spectrum for $C_{70}F_{34}$ (**1**).

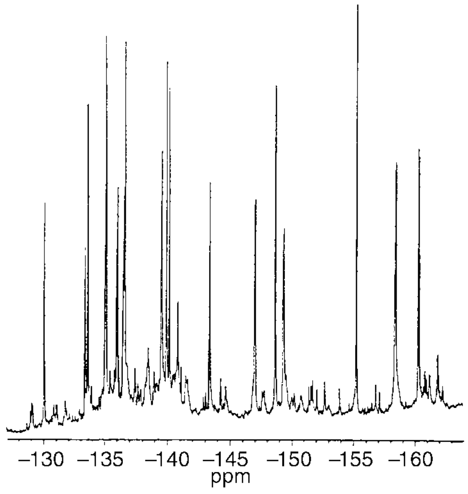


Fig. 11 ^{19}F NMR spectrum for $C_{70}F_{36}$ (**6**).

$C_{70}F_{34}$ (1). The spectrum for this compound (Fig. 10) shows 34 lines, confirming the mass spectrum and showing that the compound has C_1 symmetry.

$C_{70}F_{36}$ (2, 3, 5, 6, 7). Spectra for these isomers are given in Figs. S11–S13, Fig. 11, and Fig. S14. The spectrum for compound **4** was very poor and is not shown. The spectrum for compound **3**, Fig. S12, is also unsatisfactory but serves to confirm that it is clearly different from the other isomers. From the integrated spectrum (not shown), 35 lines can be distinguished proving that the structure has C_1 symmetry; by processing larger quantities of material it might be possible subsequently to obtain a satisfactory spectrum.

The spectra for isomers **2**, **5** and **7** each exhibit 36 lines showing that each has C_1 symmetry. By contrast the spectrum for isomer **6**, Fig. 11, consists of 18 lines, and thus this has either C_2 or C_s symmetry. This aspect is addressed further below.

$C_{70}F_{38}$ (8, 13/13a, 14). Spectra for these isomers are given in Figs. S15, S16 and 12, respectively. The spectrum for isomer **8** consists of 38 lines, shown by the integrated spectrum (not shown) to be of equal height. This isomer thus has C_1 symmetry. The spectrum for **13/13a** consists of *ca.* 72 lines of approximately equal intensity, together with a number of less intense lines. It must therefore consist of a mixture of two C_1-symmetry isomers, present in approximately equal amounts (which is surprising), together with a small amount of either an impurity or a third isomer.

Isomer **14** was obtained in greater quantity than any other, and this is reflected in the quality of the spectrum, Fig. 12, which consists of 19 peaks, three of which are coincident. This isomer therefore has either C_s or C_2 symmetry.

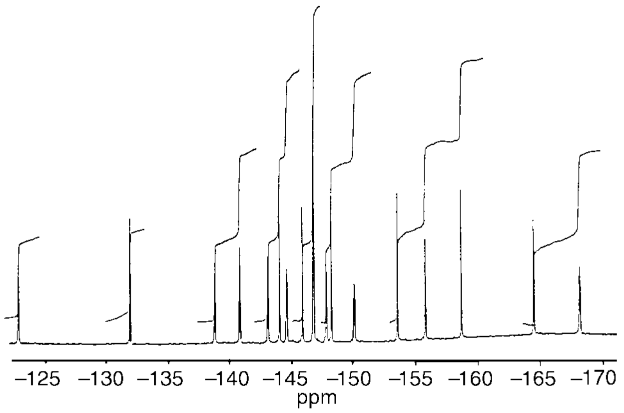


Fig. 12 ^{19}F NMR spectrum for $C_{70}F_{38}$ (**14**).

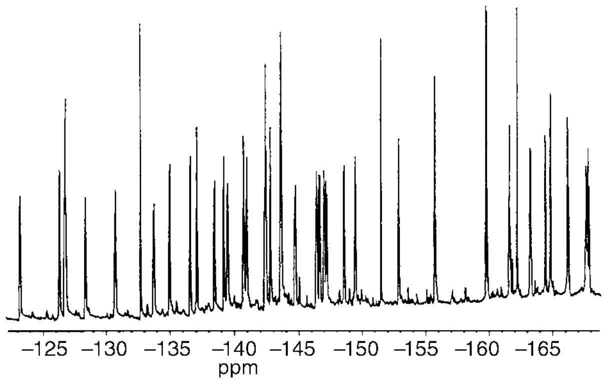


Fig. 13 ^{19}F NMR spectrum for $C_{70}F_{40}$ (**15**).

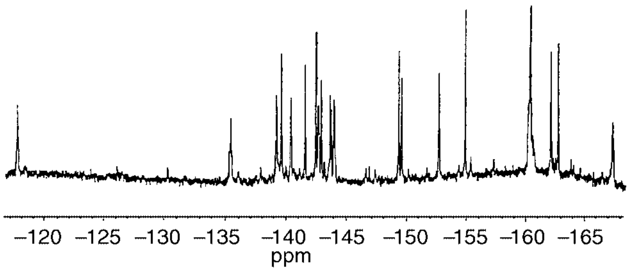


Fig. 14 ^{19}F NMR spectrum for $C_{70}F_{42}$ (**19**).

$C_{70}F_{40}$ (15, 16, 17/17a, 18). Spectra for these isomers, Figs. 13, S17–S19, are comprised of 40, 39, 60 and 39 clear peaks respectively, deduced by integration (which revealed also a number of coincident peaks in each spectrum). The 'missing' peaks are likely to be present as shoulders. Isomers **15**, **16**, and **18** evidently have C_1 symmetry, but the 60 line spectrum for **17/17a**, Fig. S18, is consistent only with either three components of C_s/C_2 symmetry (3×20 F) or one each of C_s/C_2 and C_1 symmetry (20 F + 40 F). A surprising feature therefore is the apparent approximate equivalence in concentration of the components that either of these solutions requires.

$C_{70}F_{42}$ (19). The spectrum for this compound, Fig. 14, consists of 21 peaks (three of which are coincident) and the compound therefore has either C_s or C_2 symmetry.

$C_{70}F_{36}O$ (21/21a). Approximately 69 peaks can be identified from integration of the spectrum, Fig. S20 which has a number of coincidences, hence the uncertainty. Nevertheless it is clear that two components are present. No downfield peaks were seen suggesting that the oxygen function is remote from any C–F bond (see below).

$C_{70}F_{36}O$ (26). The spectrum for this compound, Fig. S21, has 36 peaks showing it to be a single component. The absence of

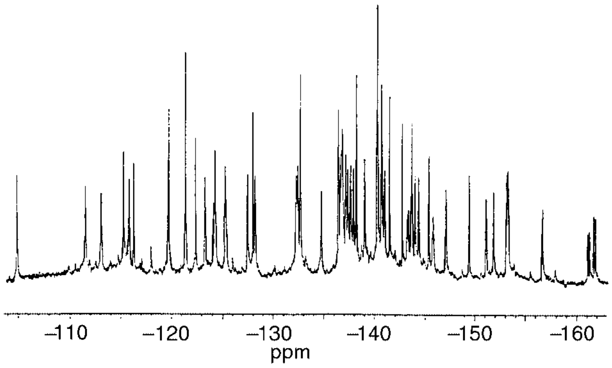


Fig. 15 ^{19}F NMR spectrum for '$C_{70}F_{37}$' (**44**).

downfield peaks again indicates that the oxygen is more than one carbon removed from any C–F bond.

$C_{70}F_{38}O$ (29/29a). The spectrum for this compound, Fig. S22, consists of *ca.* 60 peaks (at least four of which are coincident) showing that two components are present, and the peak intensities appear to fall into two groups of *ca.* 2:1 intensity ratio. The number of peaks is consistent with the components comprising one of C_1 symmetry (38 lines), the other of C_s or C_2 symmetry (19 lines). Three peaks (not shown in Fig. S22) occur well downfield, at −78.9, −91.2, and −93.5 ppm (2:2:1 ratio) and are due to C–F bonds being in the vicinity of oxygen.[14] Thus the value of −78.9 is typical of a C–F bond being immediately next to the oxygen, whilst the other two values correspond to a C–F bond being one carbon removed from the oxygen.

$C_{70}F_{38}O$ (33). The amount of this material was very small and consequently the spectrum, Fig. S23 is poor, but *ca.* 36 peaks (four groups are coincident) can be distinguished in the spectrum.

$C_{70}F_{40}O$ (36). The amount of this material was also small but *ca.* 41 peaks, one of which is downfield at −100.2 ppm, can be distinguished in the spectrum, Fig. S24.

$C_{70}F_{34}O_3$ (40). The spectrum for this compound, Fig. S25, consists of 17 × 2 F lines (with one pair coincident) and proves that the compound cannot be the equivalent mass $C_{70}F_{35}O(OH)_3$ because this would have to comprise either 18 lines (17 × 2 F) + (1 × 1 F) or 35 lines (35 × 1 F). Despite the presence of three oxygens, none of the peaks are significantly downfield, indicating that the oxygens are somewhat remote from the C–F bonds.

$C_{70}F_{35}O{\cdot}OH$ (41). The spectrum for this compound, Fig. S26, consists of *ca.* 36 lines.

'$C_{70}F_{37}$' (44). The spectrum for this compound, Fig. 15, is especially interesting because it consists of *ca.* 63 peaks one of which is downfield at −105 ppm, and five other peaks between −111 and −117 ppm. The compound appears thus to be a particularly unstable oxide, and this is discussed further below.

In summary the NMR spectra are overall in excellent agreement with the mass spectra, with regard to the number of peaks expected on the basis of the latter.

2D COSY ^{19}F NMR spectra

In order to deduce the structural pattern in these additions, we obtained 2D NMR spectra for those compounds (**1**, **6**, **8**, **14**, **15**, **16**, **17/17a**, **18**, **19**, and **40**) for which sufficient material was available. As yet, these spectra have not been solved, because in each there are coincident lines which complicate resolution. Fig. 16 shows an example of a connectivity diagram [deduced from the 2D COSY ^{19}F NMR spectrum of $C_{70}F_{38}$ (**14**)] which has a triple coincidence for peaks 9–11. Full and dashed horizontal lines indicate strong couplings (probably 1,2) and weaker couplings (1,3 or conjugated 1,4), respectively; distinguishing some with absolute certainty will require higher resolution instrumentation, not yet available.

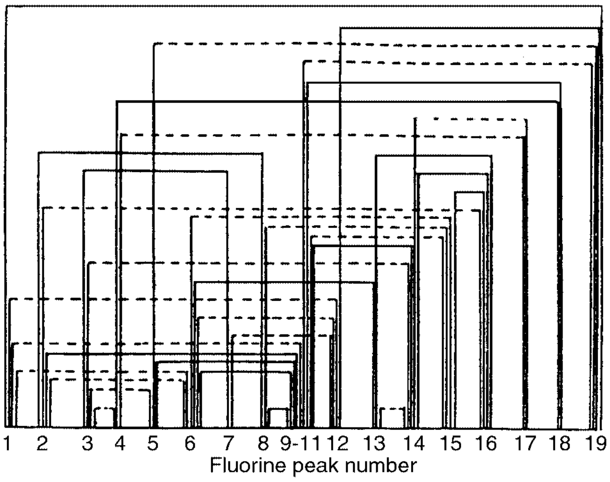


Fig. 16 Connectivity diagram from the 2D COSY ^{19}F NMR spectrum of $C_{70}F_{38}$ (**14**); full and dashed horizontal lines indicate strong and weaker couplings, respectively.

Overall the spectra show what is a common trend for fluorofullerenes, *viz.* peaks which have multiple large couplings (*i.e.* for adjacent fluorines) appear more upfield. This arises because the electronic environment of a fullerene cage carbon depends considerably upon the hybridisation state of the adjacent carbons. Since the electronegativities of sp^3 carbons are less than those of sp^2 carbons, a fluorine that is attached to a carbon which has more sp^3 neighbours will appear more upfield compared to one which has less. It follows that upfield fluorines will tend to be coupled to more fluorines than those which are more downfield.

However, the situation is complicated in [70]fullerene by the differing electronegativities of the A–E carbons.[15] Thus fluorines attached to 'D' carbons may be expected to appear more upfield than some others. Moreover, it is most unlikely that fluorines will be attached to equatorial 'E' carbons (none has been observed in any other reaction), because to do so introduces an sp^3 carbon at the junction of three six-membered rings, which creates excessive strain.[16] This may help to identify the fluorines attached to 'D' carbons because not only will they appear relatively upfield in the spectrum, but they are likely to have only one direct neighbour. Peak no. 17 in Fig. 16 fulfils this requirement, and corresponding peaks are evident in the connectivity diagrams for some of the other compounds (not shown).

If $C_{70}F_{38}$ (**14**) has C_s symmetry then the following restrictions apply: (i) no fluorine can lie on the symmetry plane (otherwise 1 F intensity peaks would result); (ii) fluorines cannot be symmetrically distributed across the pole-to-pole plane of symmetry and that which is orthogonal to it since this would result in C_{2v} symmetry (unless symmetry-breaking occurs elsewhere). They can however be distributed symmetrically across *one* of these planes.

If $C_{70}F_{38}$ (**14**) has C_2 symmetry then: (i) pairs of fluorines may lie on the pole-to-pole symmetry plane; (ii) they cannot be symmetrically disposed either side of this plane, otherwise C_{2v} symmetry would again result (provided here too that symmetry-breaking did not occur elsewhere).

Although the contiguous nature of the addition might seem to favour C_s rather than C_2 symmetry, a key factor may be the need for fluorine addition to cross the equatorial 'barrier' in a

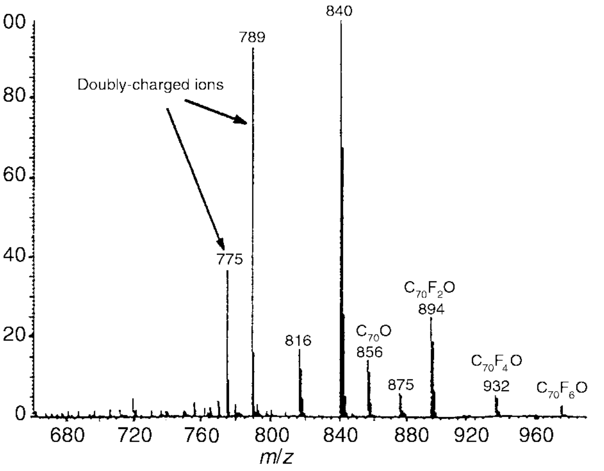
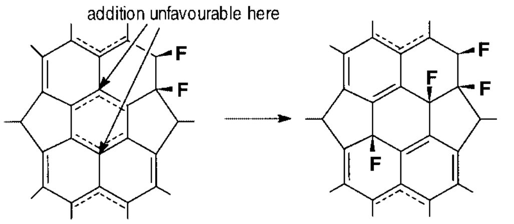


Fig. 17 Doubly-charged region of the EI mass spectrum of $C_{70}F_{38}O$ (**29**), showing the high intensity of the 775 amu peak due to CO loss (*cf.* Fig. 4).



Scheme 2 Unfavourable bond disposition in [70]fullerene equatorial region due to double bonds being exocyclic to pentagons; 1,4 addition overcomes this (reaction at 'E' carbons is also avoided).

diagonal 1,4-manner (Scheme 2). Unless this occurs at *two* points symmetrically disposed across pole-to-pole symmetry planes, a product $C_{70}F_n$ which shows $n/2$ peaks in the ^{19}F NMR will have C_2 rather than C_s symmetry.

Thermal degradation of epoxides

The mass spectrum of $C_{70}F_{38}O$ (**29**) (Fig. 4) is notable in showing a substantial fragmentation peak (1550 amu) due to the loss of CO. The stability of this species ($C_{69}F_{38}$) is evident from the intensity of the doubly-charged ion at 775 amu (Fig. 17); in some spectra (not shown) the intensity of this doubly-charged ion relative to that of the doubly-charged ion of the precursor is actually *greater* compared to the relative intensities of the singly-charged ions. It is not yet possible to suggest a definite structure for $C_{69}F_{38}$, but if all the valencies are satisfied it must be an intramolecular spirane. We have shown previously that $C_{70}F_{38}O$ readily produces a very stable matrix-isolated CO on heating,[16] and the loss of CO is now also clearly evident in the mass spectrum. The IR spectrum obtained on heating KBr discs of both this (and many fluorofullerenes) is also significant in that a strong band is produced at 1524 cm^{-1}. This very unusual band could possibly be due to a fluorine-substituted alkene, though its high intensity suggests that a carbonyl band is more probable. It could for example be due to a matrix-trapped $COCF_3$ radical, since the mass spectrum shows this to be eliminated on fragmentation, giving a peak for $C_{68}F_{35}$ at 1481 amu (Fig. 4).

Is '$C_{70}F_{37}$' derived from a fluorinated dimeric oxide?

Compound '$C_{70}F_{37}$' (**44**) eluted with a retention time of 14.8 min in 10:90 toluene–heptane, *i.e.* just before $C_{70}F_{38}$ isomer (**13**,**13a**). Both this retention time, and the mass spectrum (Fig. 3) were duplicated in two batches of material, suggesting that it must be a very stable radical cation, $C_{70}F_{37}^{+\bullet}$. (The lack of satisfactory isotope peaks is due to the very small sample size.)

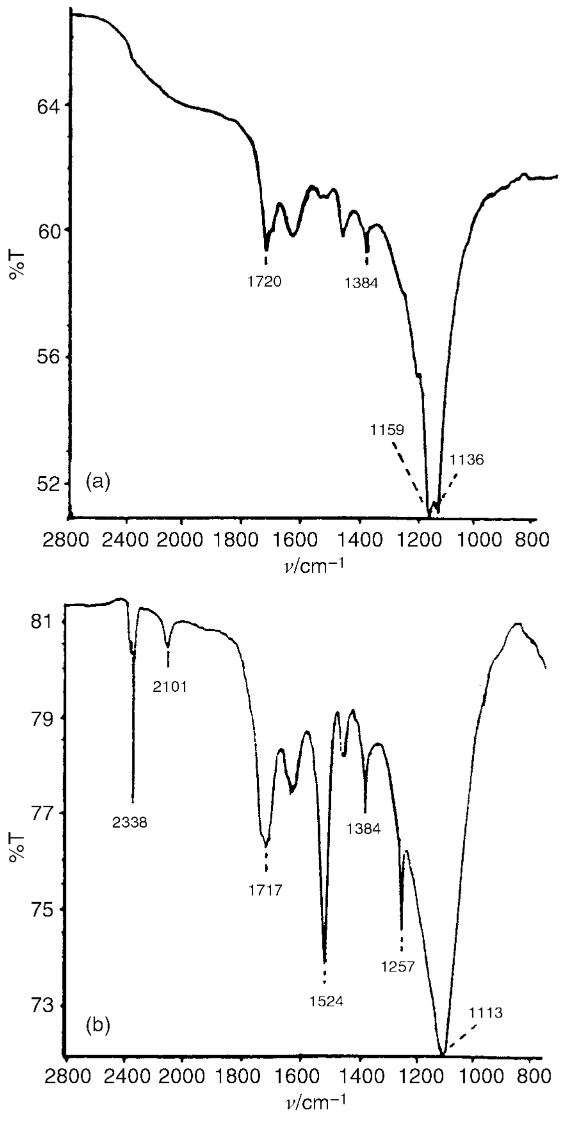


Fig. 18 (a) IR spectrum (KBr) of '$C_{70}F_{37}$'. (b) IR spectrum (KBr) of '$C_{70}F_{37}$' after heating for 6 h at 100 °C followed by a further 3 h at 125 °C. The peaks at 2338 and 2101 cm^{-1} are due to matrix-isolated CO_2 and CO, respectively (see text). Note the appearance of the strong band at 1524 cm^{-1} (see text).

A possibility that $C_{70}F_{37}$ is produced by loss of FO_2 from a particular isomer of $C_{70}F_{38}O_2$, is supported by the appearance of a 1543 amu peak (but at much lower intensity) in the mass spectra of other $C_{70}F_{38}O_2$ species. Though FO_2 is a very uncommon leaving group, the ^{19}F NMR spectrum (which is well-resolved) shows a peak at −105 ppm, due evidently to a C–F bond in the vicinity of an oxygen. Other fluorines are also not far away from the oxygen since there are five other downfield peaks. However, the spectrum integrates for 59 or 60 fluorine atoms, and the peak intensities are equal (within the limits of the integration) suggesting that only one component is present. Since it is most unlikely that we have fluorinated a single cage to this level, two cages may have combined during the fluorination/subsequent oxidation process, giving a derivative of $C_{140}O$. Dimeric fullerene oxides are likely to be less stable towards EI mass spectrometry than monomeric species, hence the ready fragmentation observed. This, however, is inconsistent with the formation of $C_{70}F_{37}$ since the other half of the dimer would be *ca.* $C_{70}F_{22}$ which is unlikely. Of course a dimer would be deficient in fluorine where the two fullerene cages face each other, but that also itself fails to account for $C_{70}F_{37}$ on fragmentation. Further work will be necessary involving a 2D COSY analysis on a larger sample, before a satisfactory conclusion as to the structure can be reached.

Proof that the precursor is an oxide was obtained by heating samples in a KBr matrix (Fig. 18). The appearance of the matrix-isolated peaks for CO_2 and CO at 2338 and 2101 cm^{-1}, respectively, prove the presence of oxygen in the material (*cf.* ref. 17).

Acknowledgements

O. V. B. and R. T. thank the Royal Society for financial support through a Joint Project grant, and O. V. B. thanks the Royal Society of Chemistry for a Foreign Author's grant.

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