Isolation and characterisation of fluorinated derivatives of [76]- and [78]fullerenes

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Received (in Cambridge, UK) 20th September 1999, Accepted 18th October 1999

From the fluorination of [76]fullerene with MnF_3 at 450–500 °C, followed by HPLC separation of 2–3 mg of the products, we have isolated and characterised the following derivatives: $C_{76}F_{36}$, $C_{76}F_{38}$ (the main component, of C_1 symmetry), $C_{76}F_{40}$ (five isomers, one of which has C_2 symmetry), $C_{76}F_{42}$, $C_{76}F_{44}$, $C_{76}F_{40}O$, and $C_{76}F_{39}OH$ (containing also some $C_{76}F_{37}OH$, and $C_{76}F_{41}OH$) and $C_{78}F_{42}$ (arising from traces of [78]fullerene present in the original [76]fullerene). Two unresolved mixtures were also obtained, one consisting of $C_{76}F_{32}$ and $C_{78}F_{38}$, the other consisting of other isomers of $C_{76}F_{36}$, $C_{76}F_{38}$, $C_{76}F_{40}$ and $C_{76}F_{42}$. The compounds are essentially colourless, but give lemon-coloured solutions in toluene due to formation of charge-transfer complexes.

Introduction

In previous papers describing the metal fluoride fluorination of fullerenes[1] we reported the formation and characterisation of $C_{60}F_{18}$,[2] $C_{60}F_{18}O$,[3] $C_{60}F_{36}$,[4] some oxides and hydroxides derived from the latter,[5] and of $C_{59}NF_{33}$.[6] Additional spectroscopic characterisation of some of these materials has been described,[7] as has a preliminary account of the isolation and characterisation of more than forty fluorinated derivatives of [70]fullerene.[8]

Halogenofullerenes have importance because of the derivatives that may be made by subsequent nucleophilic replacement of halogen by *e.g.* aryl groups. This is exemplified by the formation of $C_{60}Ar_5Cl$, $C_{60}Ph_2$ and $C_{60}Ph_4$ from $C_{60}Cl_6$,[9] and of $C_{70}Ph_8$ and $C_{70}Ph_{10}$ from $C_{70}Cl_{10}$.[10] Use of fluoro precursors confers the advantage of greater solubility and higher reactivity, coupled with lower steric hindrance towards fluorination which results in a completely different halogenation pattern. This opens the way to a range of derivatives having entirely different regiochemistries from those obtained with the chloro precursors, as exemplified recently by the formation of $C_{60}Ph_3F_{15}$.[11]

While the chemistry of [60]- and [70]fullerenes has now been studied in considerable detail,[12] comparatively little is yet known regarding the higher fullerenes. For [76]fullerene the few reactions reported to date concern osmylation,[13] hydrogenation,[14] the formation of methylene derivatives,[15] and cycloaddition,[16] the derivatives having been characterised in the latter reaction only. Likewise [78]fullerene has been subjected only to hydrogenation,[14] methylenation[15] and cycloaddition,[16] with product characterisation in the latter reaction only; these higher fullerene reactions have been reviewed recently.[17] In a preliminary report of the metal fluoride fluorination of a mixture of [76-, 78-, and 84]fullerenes, we found a fraction that had a retention volume of 7.9 ml on a 4.6 mm diameter Cosmosil Buckyprep column to be $C_{76}F_{38}$, though the amount was too small to characterise further.[18] A trace of $C_{78}F_{54}$ was detected in high temperature fluorination of [60]fullerene conditions under forcing conditions that produced $C_{60}F_{48}$.[19] We now report the results of a more complete investigation of the fluorination of [76]fullerene (containing a trace of [78]fullerene).

Experimental

All EI mass spectra were run at 70 eV and the ^{19}F NMR spectra at 338.8 MHz. The IR spectra (KBr) are reported here in detail because we have found fluorofullerene spectra to differ markedly between compounds and even isomers. Thus when replicating work, IR is very useful for identifying fluorofullerene samples, and avoids the need to recourse to either mass spectrometry (which requires the use of a DCI probe for satisfactory results), or high field ^{19}F NMR spectroscopy, neither of which may be readily available. All solvents used during HPLC were recovered using a rotary evaporator coupled to a refrigerated trap, and re-made up to the required composition, this being ascertained from the refractive index. Solvent recovery not only reduces costs and is environmentally sound, but has the added advantage that the ubiquitous dioctyl phthalate becomes removed at an early stage. Degassing also becomes unnecessary and moisture is removed by the rotary evaporation process. Solvents were stored over molecular sieve.

A mixture of crude higher fullerenes, mixed with mineral oil, was supplied by Hoechst. This was soxhlet extracted with acetone to remove most of the mineral lattice-trapped oil, and a sample of the residue was purified by HPLC using a 4.6 mm × 25 cm Cosmosil Buckyprep column with toluene elution. This produced a fore-run of the residual oil and then the usual elution of fullerenes, the fraction of 17.0 ml retention volume being collected. The solvent was removed and 5 mg was then transferred to Moscow University where it was ground with a 10-fold excess of MnF_3, the mixture being then heated to 450–500 °C in a Knudsen cell incorporated within a MI-1201 mass spectrometer. EI mass spectra (70 eV) recorded during the reaction showed the formation of $C_{76}F_{38}$ as major product, with no significant change in the ion distribution with either time or temperature. The products were condensed within the mass spectrometer onto a nickel plate which was then returned to Sussex University, where the condensed material (*ca.* 2–3 mg) was removed with toluene and separated by HPLC, after filtration through a Pasteur pipette which had been very firmly packed with a 10 mm length of tissue; this latter technique was used to minimise solvent evaporation and hence exposure to moisture through condensation. The EI mass spectrum of the crude product indicated that $C_{76}F_{38}$ was the main component.

Initial HPLC separation was carried out using toluene as eluent, at a flow rate of 1 ml min^{-1}, followed by additional work first with a flow rate of 0.5 ml min^{-1}, and then using mixtures of toluene–heptane (50 : 50 followed by 20 : 80). As the following data show, the usual tendency for addended fullerenes of the Cosmosil Buckyprep column was observed, *i.e.*, elution is faster the greater the number of addends. This is not followed precisely because minor differences in structure of fluorofullerenes can produce substantial differences in polarity. All fractions had to be recycled because fluorofullerenes 'tail' on the column, but further recycling of any fractions which still retained secondary components was not undertaken because of the very small amounts of material available. A total of 130 manual runs were carried out, but only the main details are described here. Fractions (which were not weighed but were of the order of 0.2 mg or less) were collected at the following retention times:

(**A**) *Toluene, 1 ml min^{-1}*

(1) 3–6 min. This was saved for reprocessing with toluene–heptane mixtures.

(2) 7.9 min. This was saved for reprocessing with toluene–heptane mixtures.

(3) 9.2 min, 1634 amu, $\mathbf{C_{76}F_{38}}$. This is a fairly stable species as shown by the presence in the mass spectrum of the doubly-charged ion species at 817 amu (Fig. 1), though [76]fullerene was produced through degradation, in contrast to the behaviour of some other derivatives (see below). The IR spectrum (Fig. 2) shows main bands at 1163, 1149, 1127 and 1107 amu. The ^{19}F NMR spectrum (Fig. 3) shows 38 lines of equal integrated intensity, and shows the symmetry to be C_1.

(4) 11.5 min, 1596 amu, (mainly) $\mathbf{C_{76}F_{36}}$. In order to try to remove most of the other components present it was recycled with toluene–heptane (20 : 80), the retention time under these conditions being 54 min. The mass spectrum (Fig. 4) shows that some $C_{76}F_{38}$ remained in the sample. The amount was too small to permit measurement of the IR spectrum.

(5) 13.3 min, 1672 amu, (mainly) $\mathbf{C_{76}F_{40}}$ (isomer **1**). The EI mass spectrum (Fig. 5) shows this fraction to contain also minor amounts of $C_{76}F_{36}$ and $C_{76}F_{38}$. It indicates also that this isomer is less stable than isomers **2**–**5** (described below) since it fragments to [76]fullerene, and gives no doubly-charged ion. The IR spectrum (Fig. 6) showed a main band at 1144 cm^{-1}

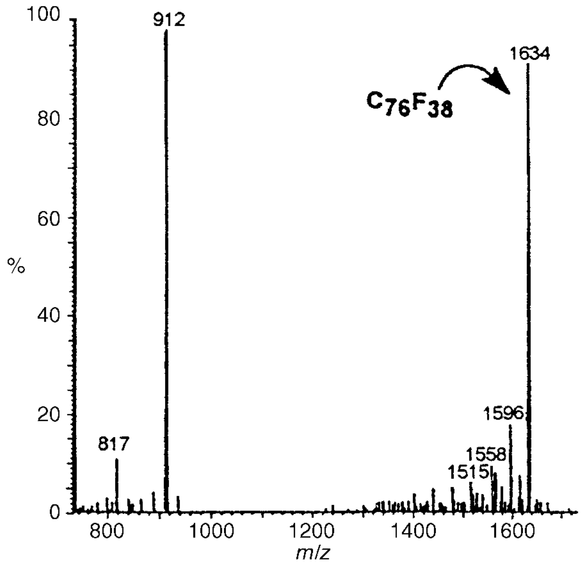

Fig. 1 EI mass spectrum (70 eV) for $C_{76}F_{38}$; also showing the presence of the doubly-charged ion (*m*/*z* 817).

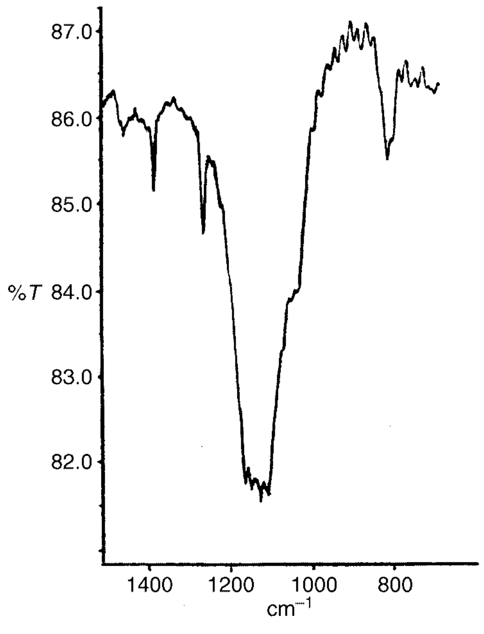

Fig. 2 IR spectrum (KBr) for $C_{76}F_{38}$.

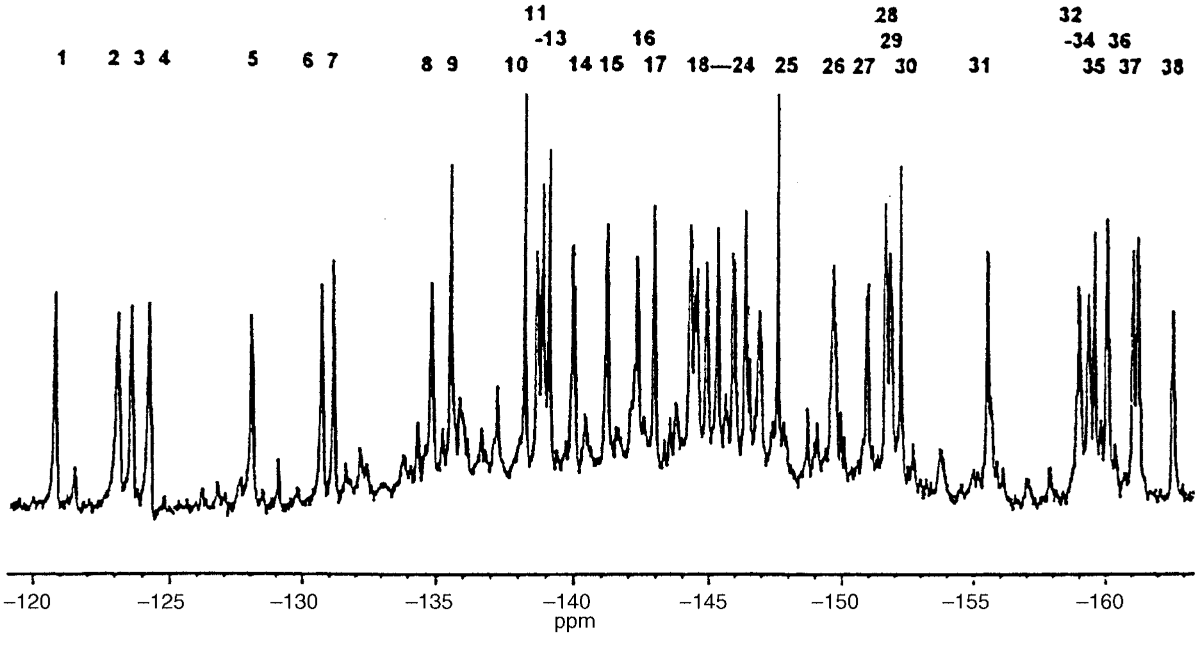

Fig. 3 ^{19}F NMR spectrum for $C_{76}F_{38}$ showing 38 peaks which integrate (not shown in Figure) to equal intensity.

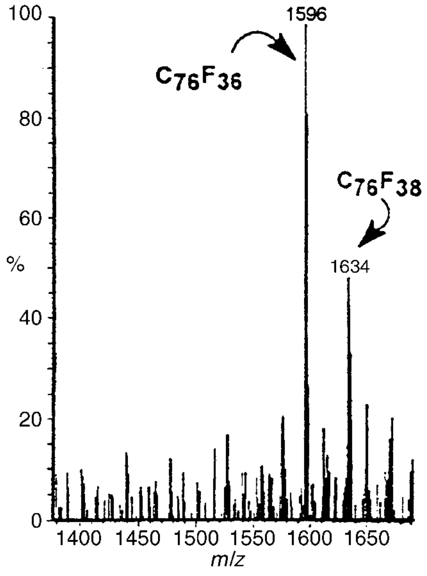

Fig. 4 EI mass spectrum (70 eV) of $C_{76}F_{36}$ also showing the presence of some $C_{76}F_{38}$.

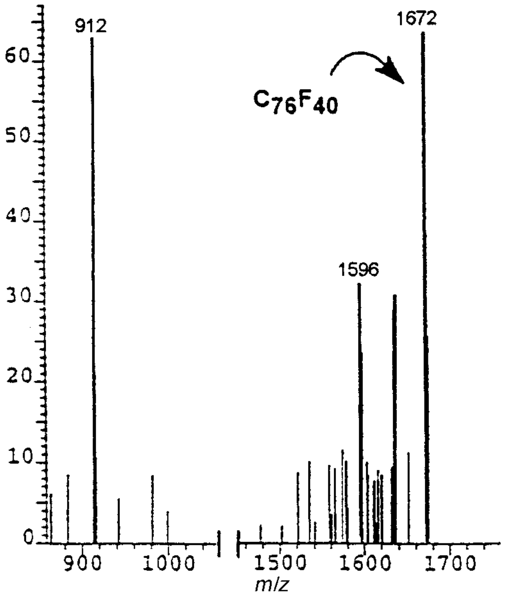

Fig. 5 EI mass spectrum of $C_{76}F_{40}$ (isomer **1**) showing the presence of some $C_{76}F_{38}$ and $C_{76}F_{36}$.

with shoulders at 1179, 1164, 1134, 1110 and 1078 cm^{-1}. Although this spectrum is obviously not a definitive one, the main bands differ from those found with the other isomers of $C_{76}F_{40}$ further confirming that it is a separate isomer.

(6) 26.5 min. A mixture of $\mathbf{C_{76}F_{30}}$ (1482 amu), $\mathbf{C_{76}F_{32}}$ (1520 amu) and $\mathbf{C_{78}F_{38}}$ (main component, 1658 amu), which was not resolved due to quantity limitations. These components are evident in the mass spectrum (Fig. 7) which also exhibited doubly-charged ions (not shown) for each of them, together with some fragmentation to the parent fullerenes.

(**B**) *Toluene, 0.5 ml min^{-1}*

No individual species were obtained from processing the above 7.9 min fraction under these conditions, but a fraction eluting at 7.1 min was collected and the mass spectrum showed it to contain various fluorinated derivatives with fluorine contents up to that of $C_{76}F_{44}$.

(**C**) *Toluene–heptane (50 : 50), 1 ml min^{-1}*

The above 7.1 min fraction was reprocessed with this solvent to give the following:

(7) Peaks at 2.8/3.9, 4.9 and 5.9 min which could not be separated further. The material was collected for reprocessing with solvent system D.

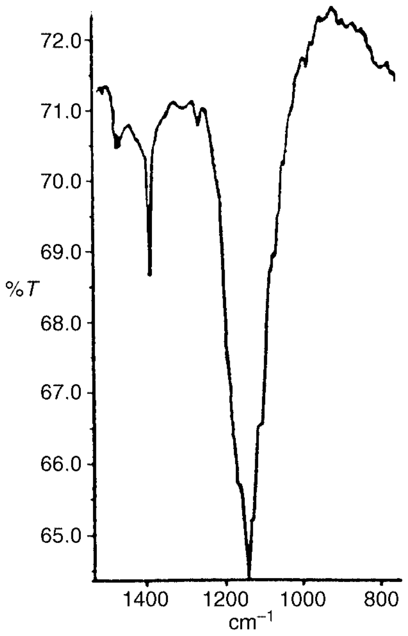

Fig. 6 IR spectrum (KBr) of $C_{76}F_{40}$ (isomer **1**).

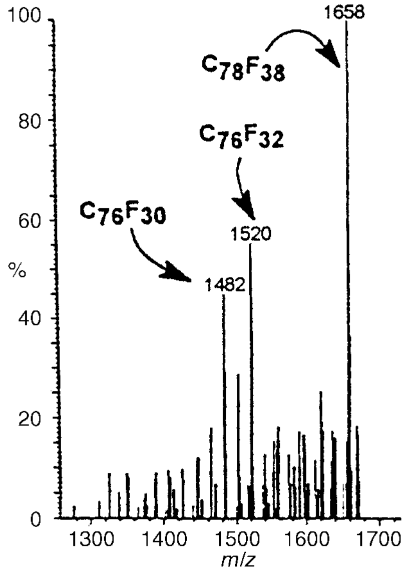

Fig. 7 EI mass spectrum (70 eV) of a mixture of $C_{76}F_{30}$, $C_{76}F_{32}$ and $C_{78}F_{38}$.

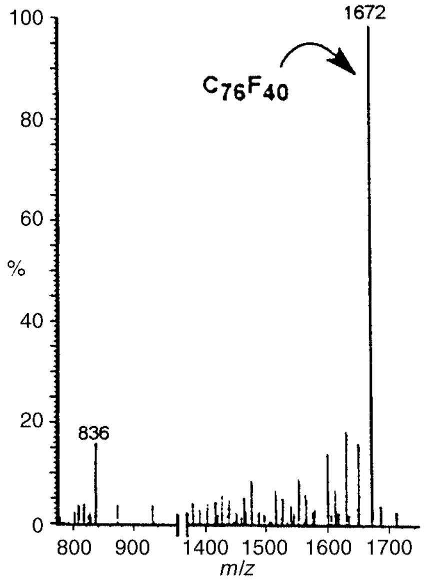

Fig. 8 EI mass spectrum (70 eV) of $C_{76}F_{40}$ (isomer **2**).

(8) 7.9 min, 1672 amu, $\mathbf{C_{76}F_{40}}$ isomer (**2**). This compound appears to be very stable since the EI mass spectrum (Fig. 8) shows both the doubly-charged ion at 836 amu, *and* the complete absence of a [76]fullerene degradation peak. The peak at 1603 amu is due to loss of CF_3, a common feature of fluorofullerene EI mass spectra, and is evident in many other spectra (below). The IR spectrum (Fig. 9) shows a main band at 1111 cm^{-1} with shoulders at 1197, 1148, 1098, 1061 and 1034 cm^{-1}. The ^{19}F NMR spectrum (Fig. 10) is exceptionally interesting because it shows nineteen out of the required twenty lines. Two lines must be coincident, but the very small sample size (which necessitated 74,000 scans) rendered accurate peak integration difficult, so we are unable to state categorically at this stage where the coincidence occurs. The surprising feature however, is that this compound has C_2 symmetry, given that the parent fullerene has D_2 symmetry (see Discussion section). We hope eventually to obtain a larger sample so that a full 2D analysis can be performed.

(**D**) *Toluene–heptane (20 : 80), 1 ml min⁻¹*

All of the above eluent (7), together with eluent (1) from **A** was reprocessed with this solvent, to give the following fractions:

(9) 4.2 min, 1748 amu, $\mathbf{C_{76}F_{44}}$. The EI mass spectrum (Fig. 11) shows this also to be very stable since there is a doubly-charged ion and no [76]fullerene degradation peak; the peak at 1679 amu due to loss of CF_3 is evident here. The IR spectrum (Fig. 12) shows a main band at 1178 cm^{-1} and shoulders at 1221,

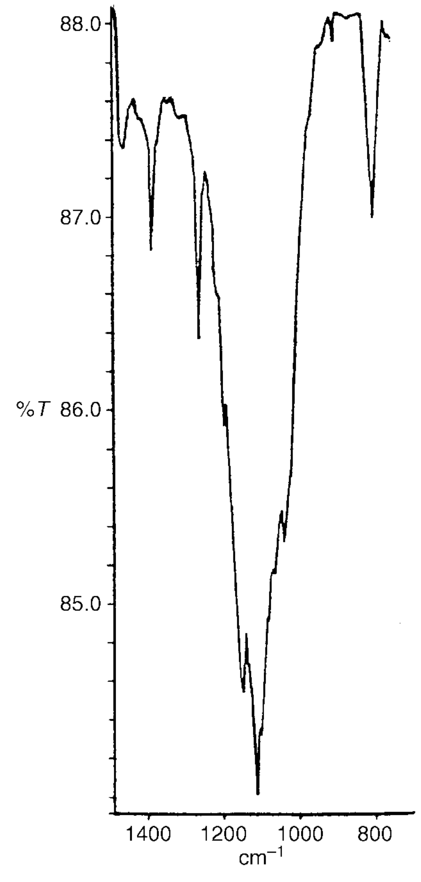

Fig. 9 IR spectrum (KBr) of $C_{76}F_{40}$ (isomer **2**).

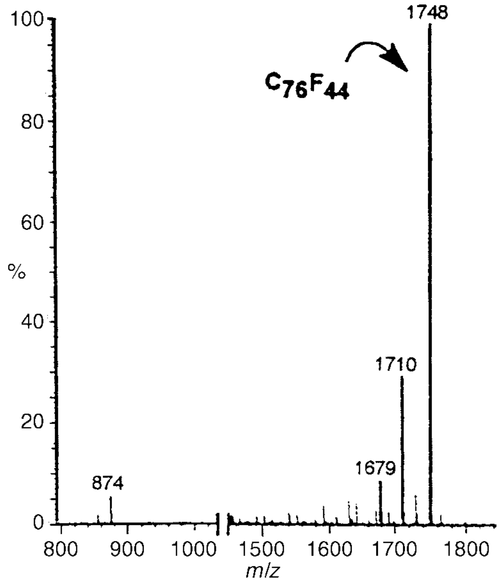

Fig. 11 EI mass spectrum (70 eV) of $C_{76}F_{44}$.

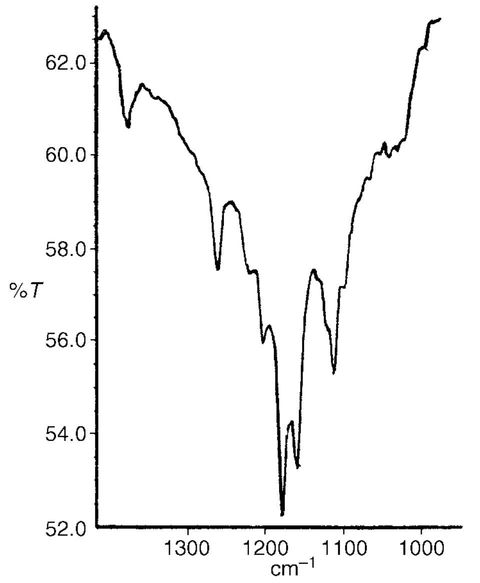

Fig. 12 IR spectrum (KBr) of $C_{76}F_{44}$.

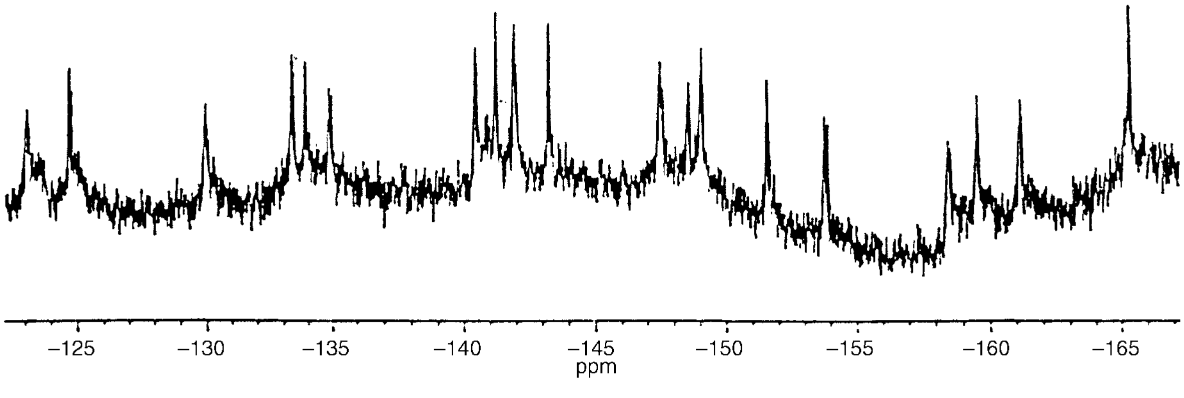

Fig. 10 ^{19}F NMR spectrum of $C_{76}F_{40}$ (isomer **2**).

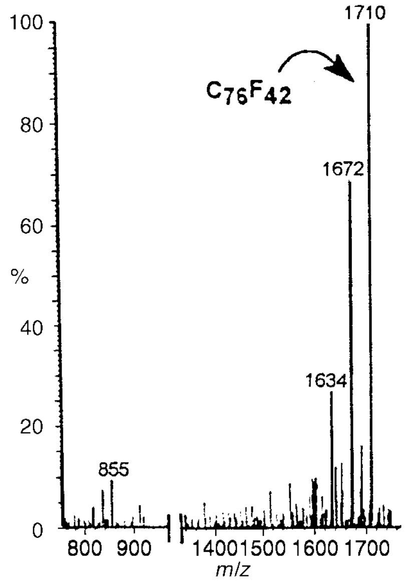

Fig. 13 EI mass spectrum (70 eV) of $C_{76}F_{42}$.

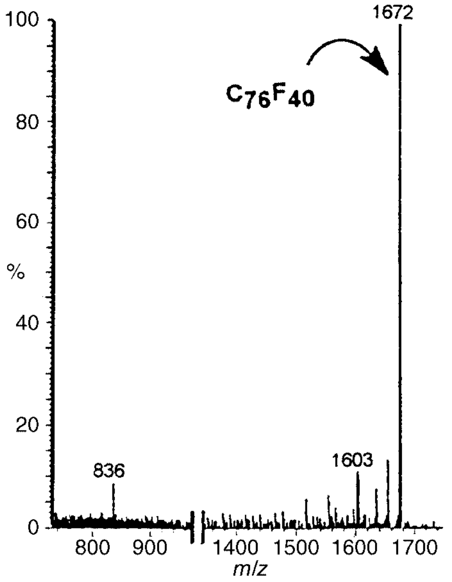

Fig. 14 EI mass spectrum (70 eV) of $C_{76}F_{40}$ (isomer **3**).

1201, and 1158 cm^{-1}. There is a secondary peak at 1111 cm^{-1} but we do not attribute this to the presence of any of $C_{76}F_{40}$ (isomer **2**) because the peak shape of this secondary band is different, the latter isomer elutes later, and because of the quality of the EI mass spectrum.

(10) 6.1 min, 1670 amu, $\mathbf{C_{76}F_{40}O}$. This was not a pure component and the mass spectrum (not shown) had peaks present also for $C_{76}F_{38}O$, $C_{76}F_{38}$, $C_{76}F_{40}$, $C_{76}F_{42}$, and $C_{76}F_{44}$ as well as $C_{76}F_{38}(OH)_2$ (1668 amu) and $C_{76}F_{42}(OH)_2$ (1744 amu). No further purification of this component was possible at this stage.

(11) 9.8 min, 1710 amu, $\mathbf{C_{76}F_{42}}$. The intensities of the 1672 and 1634 amu peaks in the spectrum (Fig. 13) suggest that they may be due to impurities rather than to fragmentation. This view is reinforced by the presence of a doubly-charged ion at 855 amu and very little [76]fullerene showing that the main species is very stable. There was insufficient of this component for an IR spectrum to be obtained.

(12) 11 min, 1672 amu, $\mathbf{C_{76}F_{40}}$ (isomer **3**). The EI mass spectrum (Fig. 14) also shows a doubly-charged ion at 836 amu, no [76]fullerene peak, and a peak at 1603 amu due to CF_3 loss. The IR spectrum (Fig. 15) shows a main band at 1110 cm^{-1}, a major shoulder at 1174 cm^{-1}, and minor ones at 1227, 1053 and 1038 cm^{-1}.

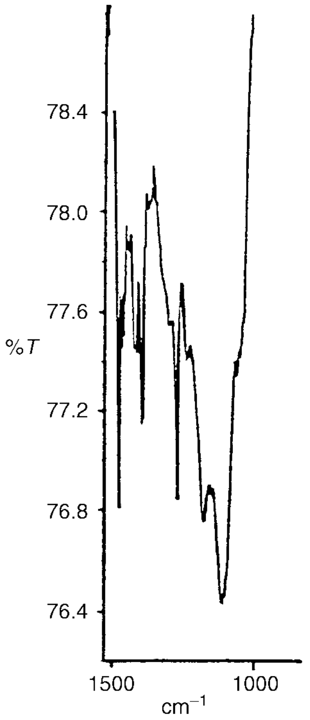

Fig. 15 IR spectrum (KBr) of $C_{76}F_{40}$ (isomer **3**).

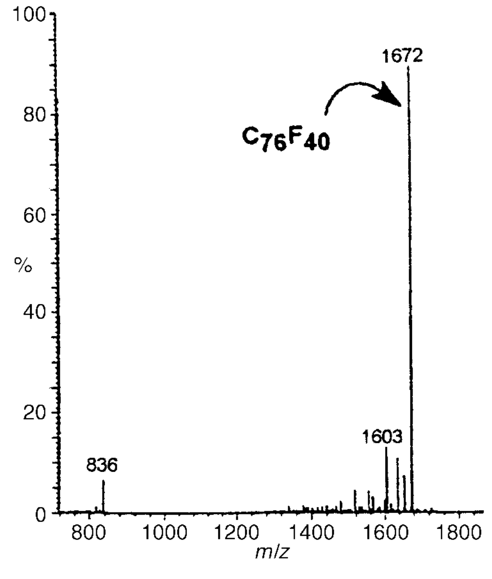

Fig. 16 EI mass spectrum (70 eV) of $C_{76}F_{40}$ (isomer **4**).

(13) 13.3 min, 1672 amu, $\mathbf{C_{76}F_{40}}$ (isomer **4**). The EI mass spectrum (Fig. 16) is virtually identical to that for isomer **3**, but the compound is different as shown by the IR spectrum (Fig. 17) which exhibits four similar-intensity bands at 1168, 1156, 1141 and 1114 cm^{-1}, with shoulders at 1208, 1074, 1040, and 1022 cm^{-1}.

(14) 18.5 min, 1672 amu, $\mathbf{C_{76}F_{40}}$ (isomer **5**). The EI mass spectrum (not shown) is indistinguishable from those shown in Figs. 13 and 15, but the IR spectrum (Fig. 18) is again different from that of the other isomers and shows a main band at 1102 cm^{-1} and shoulders at 1118, 1090, 1072, 1052, 1035 and 1020 cm^{-1}.

(15) 28 min, 1734 amu, $\mathbf{C_{78}F_{42}}$. This is also a stable compound since the EI mass spectrum (Fig. 19) shows only the double-charged ion at 867 amu, and no [78]fullerene. The sample was not entirely free from $C_{76}F_{40}$, but no further processing was possible on the available quantity. The IR spectrum (Fig. 20)

Table 1 HPLC elution times (min) for $C_{76}F_n$ and $C_{78}F_n$ compounds

Solvent	$C_{76}F_{36}$	$C_{76}F_{38}$	$C_{76}F_{40}$	$C_{76}F_{42}$	$C_{76}F_{44}$	$C_{76}F_{40}O$	$C_{78}F_{38}$	$C_{78}F_{42}$	$C_{78}F_{39}OH$
Toluene	11.5	9.2	13.3 (**1**)				26.5[a]		
Toluene–heptane (50:50)			7.9 (**2**)						
Toluene–heptane (20:80)			11.0 (**3**) 13.3 (**4**) 18.5 (**5**)	9.8	4.2	6.1[b]		28.0	30–36[c]

[a] This contained some $C_{76}F_{30}$ and $C_{76}F_{32}$. [b] This contained (i) some $C_{76}F_{38}O$; (ii) $C_{76}F_{38}(OH)_2$ and $C_{76}F_{42}(OH)_2$; (iii) traces of $C_{76}F_{38}$, $C_{76}F_{40}$, $C_{76}F_{42}$ and $C_{76}F_{44}$. [c] This contained some $C_{76}F_{37}OH$, $C_{76}F_{41}OH$, $C_{76}F_{36}O$, $C_{76}F_{38}O$, and $C_{76}F_{40}O$.

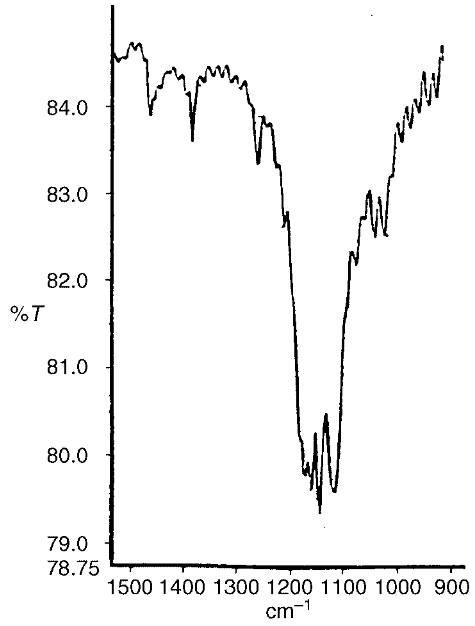

Fig. 17 IR spectrum (KBr) of $C_{76}F_{40}$ (isomer **4**).

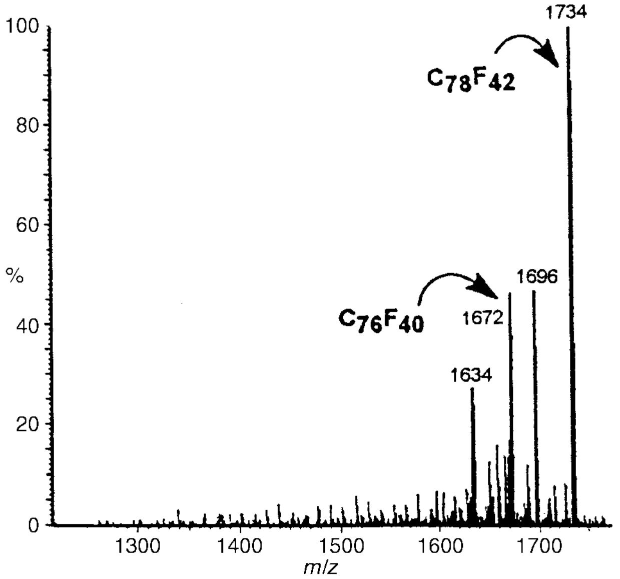

Fig. 19 EI mass spectrum (70 eV) of $C_{78}F_{42}$.

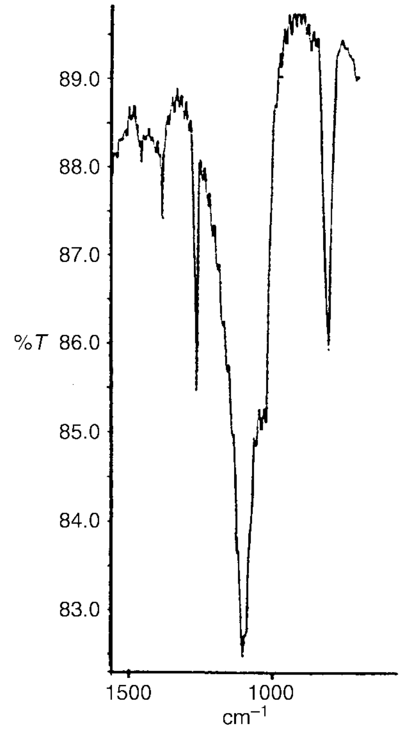

Fig. 18 IR spectrum (KBr) of $C_{76}F_{40}$ (isomer **5**).

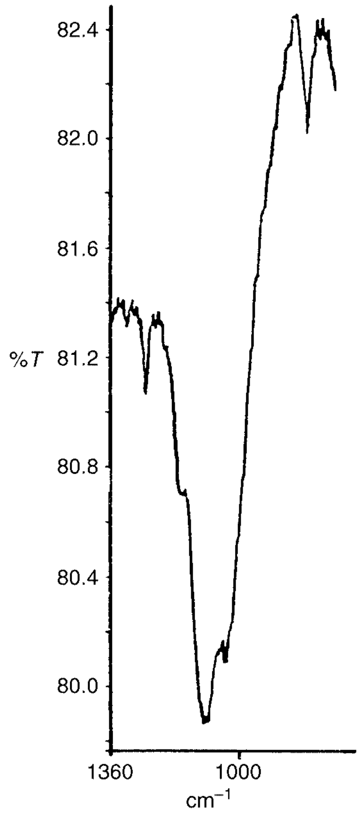

Fig. 20 IR spectrum (KBr) of $C_{78}F_{42}$.

shows main bands at 1094 and 1083 cm^{-1} and a prominent shoulder at 1031 cm^{-1}.

(16) 30–36 min (broad peak), 1670 amu, **$C_{76}F_{39}OH$**, but the mass spectrum showed also the presence of $C_{76}F_{41}OH$ (1708 amu), $C_{76}F_{37}OH$ (1632 amu), $C_{76}F_{40}O$ (1688 amu), $C_{76}F_{38}O$ (1650 amu), and $C_{76}F_{36}O$ (1612 amu), the oxides arising from HF loss from the hydroxide precursors.

The main details of the HPLC separation are summarised in Table 1.

Results and discussion

Derivatives isolated

We have isolated in either pure or semi-pure form the following components:

(i) Fluoro derivatives of [76]fullerene *viz.* $C_{76}F_{36}$, $C_{76}F_{38}$, $C_{76}F_{40}$ (five isomers), $C_{76}F_{42}$ and $C_{76}F_{44}$. Furthermore we detected $C_{76}F_{30}$ and $C_{76}F_{32}$, mixed with other components and a mixture of $C_{76}F_{36}$, $C_{76}F_{38}$, $C_{76}F_{40}$ and $C_{76}F_{42}$, which, from the HPLC retention times, are isomers different from those listed above.

(ii) Fluoro derivatives of [78]fullerene, *viz.* $C_{78}F_{38}$ and $C_{78}F_{42}$.

(iii) Hydroxides, *viz.* $C_{76}F_{39}OH$ together with lesser amounts of $C_{76}F_{37}OH$ and $C_{76}F_{41}OH$.

(iv) Oxides, *viz.* $C_{76}F_{40}O$ together with lesser amounts of $C_{76}F_{38}O$ and $C_{76}F_{36}O$.

Polyaddition level

An ultimate goal of this work is to determine the regiochemistries involved in high polyaddition levels in fullerenes and to ascertain their origins, an aspect that will be crucial in any understanding of the fundamental fullerene properties. This is a formidable task requiring first the determination of the levels and secondly the actual structures of the derivatives. Thus far, progress has been made only with [60]fullerene for which it is now firmly established that in both hydrogenation and fluorination, only two isomers for $C_{60}X_{36}$ are obtained, *viz.* T and a C_3.[4] This has demonstrated an important feature which is that these additions appear to proceed in a sequential manner, resulting from contiguous activation of double bonds adjacent to addition sites. This gives products which are not necessarily the most stable thermodynamically. Thus the D_{3d} isomer, predicted to be very stable,[20] is not obtained because it consists of two addition regions separated by a continuous band of (unreacted) double bonds. It could only be formed by two initial additions (one of which would be disfavoured by the above reasoning) at the 'correct' sites for further stepwise addition, a scenario of very low probability.

Under the conditions used, the fluorination level for [76]-fullerene spans a narrow band just as is found with [60]fullerene (which gives almost exclusively $C_{60}F_{36}$)[4] and [70]fullerene (which gives $C_{70}F_{34}$ to $C_{76}F_{44}$).[8] This would appear to be true also of [78]fullerene, the data being somewhat restricted here because traces of this fullerene only were present initially, making it probable that other derivatives were produced but which escaped isolation.

Structures of the derivatives

Determination of the actual structures of the derivatives is not possible at this stage, nor did we set out with this objective in mind. Rather, this study lays the groundwork for future work and identifies the main components that are present and the conditions under which they can be produced and isolated. Full characterisation will require solution of 2D spectra (itself a very difficult task), obtained with larger amounts of materials. Nevertheless, one unexpected result has emerged, namely the presence of a C_2 isomer of $C_{76}F_{40}$. (The symmetry cannot be C_s because of the D_2 symmetry of the parent fullerene.) The C_2 isomer can be produced in either of two ways:

(i) Addition at or near each pole and proceeding from each in the same direction (which may be either a left- or right-handed spiral). This gives rise to a problem however, because it requires addition to start at two different points, which is unfavourable given the activation of the bonds adjacent to the initial addition site. On the other hand, the highest π-bond orders calculated for [76]fullerene are greater than for any bond in [60]- or [70]fullerene,[21] so this could compensate here for the above activation and allow commencement of the addition in two localities. Of course the addition does not have to either proceed or commence in a symmetrical way, which would account for the formation of the other isomers (assuming that they are all C_1).

(ii) Addition commencing from one pole at or near the symmetry axis and proceeding equally in both left- and right-handed directions. This seems a more attractive option but has the defect that if say addition commences across the 1,6-bond, which is the one that straddles the symmetry axis, then symmetrical addition *via* equal and opposite pathways requires the product to have $4n + 2$ fluorine atoms, and (discounting formation of an unstable diradical) does not permit formation of $C_{76}F_{38}$. If addition occurs initially at some point offset from the axis, then addition at the equal and opposite offset point becomes rather unlikely unless the π-bond order effect noted above is particularly compensating.

Both [70]- and [76]fullerenes have structural similarities, namely carbon atoms located at the junctions of three hexagons. For [70]fullerene, these are the 'E' carbons (see ref. 22 for definition) where no addition occurs because of the higher energy required to change to sp^3 hybridisation at these more planar sites. In [76]fullerene there are eight carbons at similar junctions *viz.* C18, C27, C33, C34, C34, C43, C44, C50 and C59 (for numbering see ref. 12), and it is reasonable to assume that no addition will occur at these. In the eventual solution of the structures of these fluorinated derivatives, it will be reasonable to assume that no addition will occur at these eight carbons. Moreover, just as 1,4-addition occurs across the D,D carbons of [70]fullerene,[23,24] so similar addition may occur across the corresponding carbons of [76]fullerene *e.g.* across either of the C16–C36 or C17–C35 pairs in the ring containing C18 and C34, so providing a 'bridge' between addition at the two poles of the molecule.

Oxide and hydroxide formation

Fewer oxides and hydroxides were obtained in this work compared to earlier HPLC separations of fluorinated [60]fullerenes.[5] This may reflect the greater experience gained in handling these materials, better exclusion of water *etc.*, but it may also mean that fluoro[76]fullerenes are less susceptible towards nucleophilic substitution. This latter is probably a contributory factor since fullerenes tend to decrease in reactivity with increasing size.[12]

Further work

We hope that eventually we may be able to secure larger quantities of these higher fullerenes, so permitting a more comprehensive investigation involving the use of ^{19}F NMR spectroscopy of higher sensitivity which will facilitate 2D NMR characterisation of the products.

Acknowledgements

We thank the Royal Society for a Joint Project Award (O. V. B. and R. T.), and the Royal Society of Chemistry for an Author's Grant (O. V. B.).

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Paper 9/07606I