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Unusual addition patterns in trifluoromethylation of [60]fullerene

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From pyrolytic trifluoromethylation of [60]fullerene with CF_3CO_2Ag at 300 °C we have isolated *ca.* sixty $C_{60}(CF_3)_n$ isomers (numbers in parentheses) as follows: $n = 2$ (1), 4 (8), 6 (13), 8 (21) 10 (11), 12 (5), 14 (4), twenty-one of which have been characterised by ^{19}F NMR. Compounds with addition levels up to $n = 20$ have also been identified. With increasing value of *n*, yields decrease and the separation of compounds of similar HPLC retention time but different addend levels becomes more difficult. Many of the ^{19}F NMR spectra show combinations of quartets and septets (the latter tending to be more downfield) due to 'linear' addend arrays. The spectra are consistent with addition across both 6:6- *and* 5:6-ring junctions [double (1,2) and *single* (1,6) bonds, respectively], giving corresponding coupling constants for adjacent addends of *ca.* 14.5 and 12.0 Hz respectively, the differences being attributable to the different 1,2- and 1,6-bond lengths. The ^{13}C NMR spectrum of $C_{60}(CF_3)_2$ shows the CF_3 groups are in either a 1,4- or 1,6-relationship; the UV-vis band appears at 442 nm. Other unsymmetrical tetra-adducts are comprised of isolated pairs of CF_3 groups. The exceptionally large number of derivatives and isomers, (much greater than in any other fullerene reaction), no dominant product, and unusual addition pattern indicates that thermodynamic stability is not of primary importance in governing product formation. EI mass spectrometry of trifluoromethylfullerenes is characterised by loss of CF_3 groups, the more highly addended compounds also showing fragmentation by CF_2 loss, attributable to steric compression. The CF_3 group shows strong IR bands at *ca.* 1260 and 1190 cm^{-1}. The compounds are stable to aq. acetone, which contrasts to the behaviour of fluorofullerenes. Trifluoromethylation by the Scherer radical ($C_9F_{19}^{\bullet}$) gave addition of up to eight CF_3 groups, together with hydrogen in some products. During EI mass spectrometry of some of these, loss of HF attributable to CF_3 and H adjacency can occur, giving CF_2-containing derivatives.

Introduction

At the inception of fullerene research it was hoped that fluorofullerenes might be super-lubricants like Teflon.[1] This expectation was unfulfilled because the cages cannot distort to render reaction sites inaccessible to nucleophiles (*cf.* Teflon), and the intrinsic electron-withdrawing property of the cages increases their nucleophilic reactivity compared to that of aliphatic chains. Thus fluorofullerenes are rapidly degraded by hydroxylic solvents,[2] especially if a specific motif is present in their structures.[3]

In an attempt to circumvent the nucleophilic substitution problem, the DuPont group created fluorine-surrounded fullerenes (in which access to the cage surface was restricted) by perfluoroalkylation (reaction with perfluoropropionyl peroxide, or perfluoroalkyl iodide).[4] Per-trifluoromethylation of both [60]- and [70]fullerenes was also achieved using either CF_3I/copper,[5] or the $C_9F_{19}^{\bullet}$ radical,[6] whilst reaction with bis(trifluoromethyl) nitroxide radicals attached $ON(CF_3)_2$ groups.[7] In these studies the maximum number of [60]fullerene addends was *ca.* 18, which could indicate either the maximum occupancy feasible without cage rupture, or imply a particularly stable addition level, akin to $C_{60}X_{18}$ (X = H, F).[8,9] Trifluoromethylated fullerenes can also be produced by reacting fluorofullerenes with methanol,[10] a method not yet fully explored. In none of these reactions were specific compounds obtained, and in most, H addition (from solvent abstraction) also occurs.

In these reactions, the CF_3 groups were added to the preformed fullerene, but an alternative method due to Fritz and Hiemeyer[11] involving arc-discharge formation of the [60]fullerene in the presence of sodium trifluoroacetate (which pyrolytically decarboxylates to '$NaCF_3$' and thence the CF_3 radical, *cf.* carboxylic acids and derivatives),[12] resulted in the addition of up to 8 CF_3 groups. A variation involving pyrolytic decarboxylation of silver trifluoroacetate in the presence of [60]fullerene gave addition of up to 22 CF_3 groups.[13]

Four perfluoroalkyl fullerenes have been isolated as by-products of fluorination of [60]fullerene, and characterised *viz.* $C_{60}(CF_3)_2$,[14] $C_{60}F_{17}CF_3$ (three isomers),[15] $C_{60}F_{17}C_2F_5$,[15] and $C_{60}F_7CF_3$,[16] whilst $C_{60}F_{35}CF_3$,[17] $C_{60}F_{23}CF_3$,[17] $C_{60}F_{15}(CF_3)_3$,[17] $C_{60}(CF_3)_5F$,[17] semi-pure $C_{60}F_5CF_3$,[14] and $C_{60}(CF_3)_4O$,[14] have been identified by EI mass spectrometry. Both $C_{60}(CF_3)_4$ and $C_{60}(CF_3)_6$ were detected in mixtures with their dihydro derivatives;[14] we have also separated, and characterised by ^{19}F NMR, trifluoromethyl derivatives of aza[60]fullerene.[18] These compounds are thought to arise mainly from insertion of **:**CF_2 carbenes (from fluorofullerene fragmentation)[19] into C–F bonds of the cage.[15]

Current emphasis on fluorofullerenes is focused on their electron-withdrawing properties in connection with use in light-harvesting compounds *e.g.* ref. 20. Trifluoromethylfullerenes, which show reduced susceptibility to nucleophilic substitution,[17] are potentially more useful in consequence, and moreover the CF_3 group is more electron-withdrawing than F due to C–CF negative hyperconjugation.[21] We have therefore undertaken a thorough investigation of trifluoromethylation, to determine the extent to which derivatives of specific addition levels can be obtained, and to learn more about the parameters that may direct the positions of addition to fullerenes. We have obtained extensive data for trifluoromethylation of [60]-, [70]-, [76]-, [78]-, [84]-, and aza[60]-fullerenes and report here results for [60]fullerene under both protic and aprotic conditions.

Being a radical reaction, trifluoromethylation in a protic solvent produces derivatives such as $C_{60}(CF_3H)_n$. Thus trifluoromethylation using suspensions of the Scherer radical $C_9F_{19}^{\bullet}$ (which degrades to CF_3 radicals on heating),[22] produced mainly

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Table 1 Retention times (min) and components from processing of $C_{60}(CF_3)_n$ material

	Toluene:heptane		Values of n in $C_{60}(CF_3)_n$							
No	1:1	3:7	2	4	6	8	10	12	14	Other
1	19.5									$C_{60}(CF_3)_5H$[a]
2	17.8				√					
3	17.4		√							
4	16.5	50		√						
5	14.1			√						
6	13.0			√	√					
7	12.3				√					
8	11.1			√	√	Trace				
9	10.6				√	√				
10	8.1			Trace	√	Trace				
11	7.35				√	√				
12	7.0					√	√			
13	6.7					√ × 2				
14		35.6			√ × 2					
15		34.9			√	√ × 2				
16		32.7			√	√				
17		31.5		√		√				
18		30.6		√						
19		29.3		√						
20		28.6			√	√				
21		27.0			√	Trace				
22		24.5				√				
23		21.3				√				
24		20.6				√				
25		18.1				√				
26		17.5				√	√			
27		16.3				√	√			
28		15.3					√			
29		14.7				√	√			
30		12.8				√	√			
31		11.6					√			
32		9.9					√			
33		9.3					√			
34		6.4					√	√		
35		5.8					√	√	√	
36		5.1						√	√	16–18
37		4.5						√	√	16–20
38		3.95/3.75						√	√	16–18
39		3.55								[b]

[a] Together with some $C_{60}(CF_3)_4H_2$ [b] The most prominent peaks in the mass spectrum were all for odd values of n.

compounds containing both CF_3 and H addends, accompanied in some instances by a facile elimination reaction. This made analysis of structures very complex. We therefore also investigated a variation of the Hiemeyer method,[11] but our initial use of sodium trifluoroacetate caused difficulties in product work-up, so silver trifluoroacetate (available from other work) was used instead (*cf.* ref. 13). The silver is readily recovered and for large scale work can be reconverted to the oxide and thence back to the salt by reaction with TFA.

Results and discussion

Toluene solutions of trifluoromethyl[60]fullerenes all have a chestnut-brown colour. They are highly soluble in toluene. Some general aspects of this work are:

1. The greater the number of addends the more rapid the HPLC elution; this parallels behaviour of other addended fullerenes on a Cosmosil column.

2. HPLC separation (toluene eluent) is more difficult than is the case for fluorofullerenes, with many components of differing addition level having identical retention times. Use of mixed solvents *e.g.* toluene/heptane aids separation but some trifluoromethylfullerene becomes retained on the column; this may be recovered by subsequent elution with toluene.

3. Compounds $C_{60}(CF_3)_mH_n$ have a longer retention time than the corresponding $C_{60}(CF_3)_m(CF_3)_n$ compounds *cf.* HPLC of polyphenylated compounds and their hydro derivatives.[23]

4. The CF_3 group gives IR bands at *ca.* 1260 and 1190 cm^{-1}. In highly polytrifluoromethylated derivatives the presence of double bonds in localised aryl rings gives broad bands centred around 1660 cm^{-1}.

5. The CF_3 groups give ^{19}F NMR resonances in the δ_F −(57–70) region.

6. The ^1H NMR spectra of compounds containing CF_3 and H groups show a sharp peak in the δ 10.2 ± 0.1 region presumed to be due to protons adjacent to CF_3 groups; it was shown not to be due to HF (δ 5.1, $CDCl_3$).

7. Some compounds containing CF_3 and H show a mass loss of 20 amu (HF) in their EI mass spectra, whereas other components of same molecular formula do not. We attribute the HF elimination to adjacency of CF_3 and H in the former, giving a CF_2-containing derivative.

(a) Using silver trifluoroacetate

HPLC processing. HPLC processing (1:1 toluene:heptane) produced many fractions that consisted of a single symmetrical peak, yet the mass spectra indicated the presence of a product mixture. Reprocessing of each fraction (3:7 toluene:heptane) then produced further peaks, but the mass spectra of some indicated that these *also* comprised mixtures. Further processing with less polar solvent mixtures was not undertaken as the law of diminishing returns became manifest, with recovered material being insufficient for spectroscopic analysis. Moreover separation of compounds with different numbers of addends becomes harder, the higher the addition level. Our object at this stage was to determine the main features of the components. The results are summarised in Table 1, which shows that the more highly addended derivatives tend to have the shortest retention times. However, there is no precise correlation and this caused initial difficulties in interpretation of the data. For example, one isomer of $C_{60}(CF_3)_6$ eluted after $C_{60}(CF_3)_2$, whilst a number of isomers of $C_{60}(CF_3)_4$ eluted before isomers of both $C_{60}(CF_3)_6$ and $C_{60}(CF_3)_8$. Overall more than sixty components have been isolated; ^{19}F NMR spectra confirmed that the components of each fraction were different.

EI mass spectra (70 eV). The mass spectrum of the crude trifluoromethylated fullerene showed the addition of up to twenty CF_3 groups (*cf.* ref. 13). Representative spectra of one or more isomers of compounds $C_{60}(CF_3)_n$, for n = 2, 4, 6, 8, 10, (12,14,16,18) and 12–20, are given in Figs. 1–7, respectively. Some significant features are (i) the presence of doubly-charged ions showing the high stabilities of the trifluoromethylfullerenes; (ii) fragmentation by CF_2 loss for compounds with ten or more addends (Figs. 5–7), attributable to steric acceleration arising from the increased crowding; (iii) the predominance of even n fragmentation ions at low n values, and odd n ions at high n values, the changeover point being around n = 5.

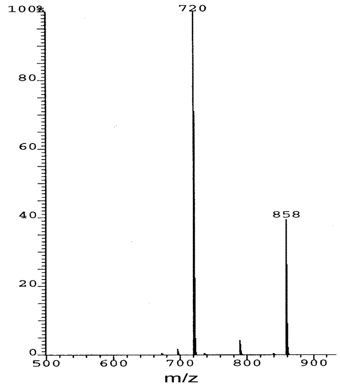


Fig. 1 Mass spectrum (70 eV) for $C_{60}(CF_3)_2$.

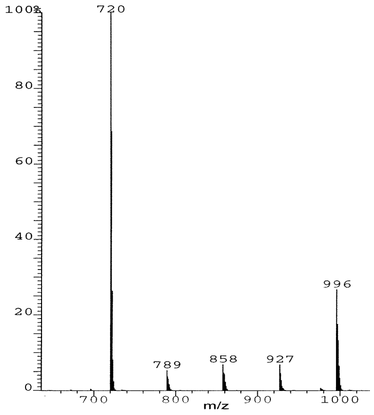


Fig. 2 Mass spectrum (70 eV) for $C_{60}(CF_3)_4$.

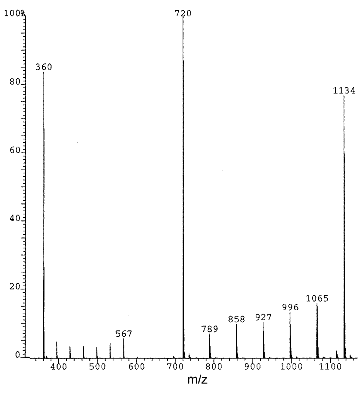


Fig. 3 Mass spectrum (70 eV) for $C_{60}(CF_3)_6$.

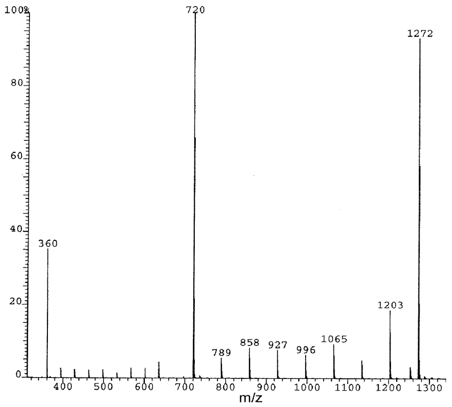


Fig. 4 Mass spectrum (70 eV) for $C_{60}(CF_3)_8$.

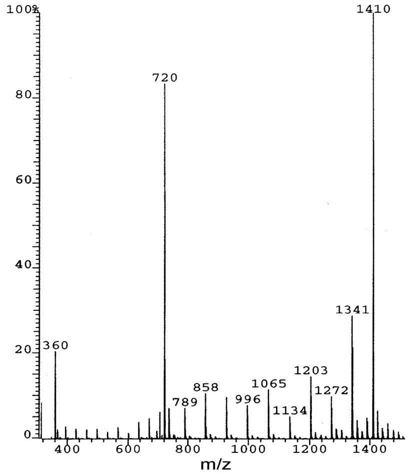


Fig. 5 Mass spectrum (70 eV) for $C_{60}(CF_3)_{10}$.

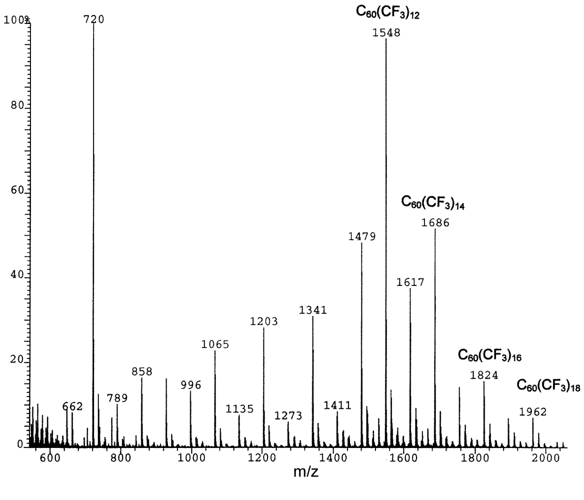


Fig. 6 Mass spectrum (70 eV) for $C_{60}(CF_3)_{12/14/16/18}$.

^{19}F NMR spectra and structural interpretation. All spectra with clearly resolved resonances comprise either all quartets, or septets and quartets, the septets being always more downfield. The quartets in compounds exhibiting quartet/septet combinations, *consistently* have significantly different coupling constants (*ca.* 12 and 15 Hz). Our interpretations of the data are based on the following:

A priori we anticipated that addition would follow the pattern seen in bromination,[24] which recently we have discussed with regard to a general mechanism of bulky group addition.[25] Thus

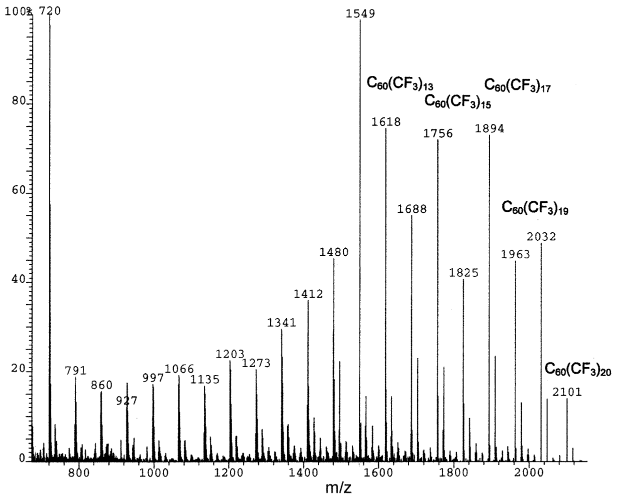


Fig. 7 Mass spectrum (70 eV) for fraction **37**, showing dominance of odd *n* in the $C_{60}(CF_3)_{13–20}$ range and fragmentation loss of CF_2 moieties.

for example we had expected to find two-fold symmetry $C_{60}(CF_3)_8$ as a major product, whereas there was no evidence for it. Other problems with interpretation of the present data in these terms (see below) led us to suggest a unique alternative pattern.[26] The problems are endemic in all addition levels, but fraction **4** of $C_{60}(CF_3)_4$ (see Fig. 8) illustrates the general difficulties:

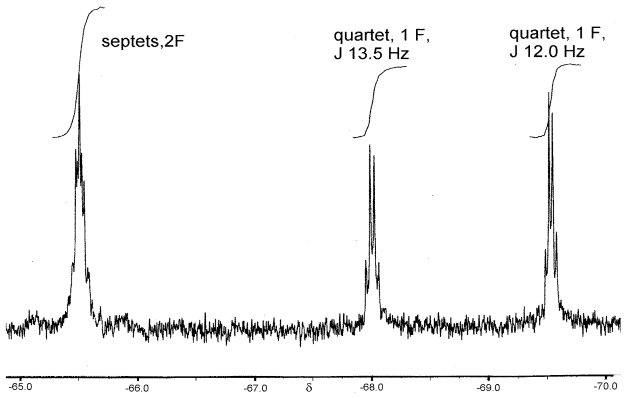
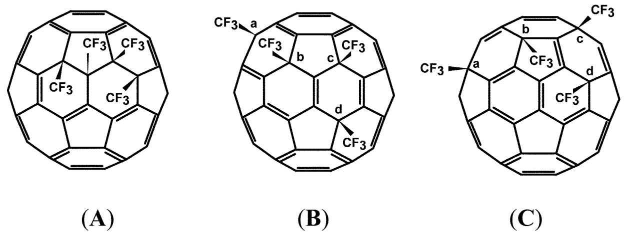


Fig. 8 ^{19}F NMR spectrum of $C_{60}(CF_3)_4$ fraction **4**.

This isomer gives four equal-intensity peaks (two overlapping septets resolved at 50 °C into δ_F −65.60 and −65.74) and two quartets at δ_F −68.17 and −69.71, *J* 13.5 and 12 Hz respectively (Fig. 8). The compound is therefore unsymmetrical and possesses a 'linear' array of CF_3 groups, giving $q_a \longrightarrow sept_b \longrightarrow sept_c \longrightarrow q_d$. Particularly significant are the $q_a \longrightarrow sept_b$ and $sept_c \longrightarrow q_d$ coupling constant differences. Three structures (**A**–**C**, each of which has two pentagons possessing a double bond) are the feasible possibilities. Structure **A**, which we have proposed,[26] involves contiguous addition across a 5:6- and a 6:6-ring junction, *i.e.* 1,6-(single) and 1,2-(double) bonds, respectively; the different coupling constants are then consistent with the disposition of the CF_3 groups across bonds of slightly different lengths.

Structures **B** and **C**, involving 1,4-addition are superficially attractive (**C** is isostructural with tetrabenzyl[60]fullerene),[27] but problems with both are the following:

(i) The *ca.* 13 Hz 1,4-coupling constants would need to arise from through-space interactions of the CF_3 groups, (*cf.* ref. 28). Previous work for numerous fluorofullerenes (which have two *fewer* intervening carbons), shows 1,2-, 1,3-, and 1,4-fluorine couplings of *ca.* 27, 5–8, and 0–4 Hz respectively. There are no comparable trifluoromethyl structures in the standard reference work on ^{19}F NMR spectra.[29]



(ii) The coupling differences of the terminal quartets *a* and *d* vary between 1.5–2.5 Hz for all the compounds examined, *i.e.* 13–20% of the total coupling value. But in **C** for example, the distances between the carbon (and hence fluorine) centres of the *ab* and *cd* CF_3 groups differ (Universal Force Field) by only 0.04 Å (4.36 ± 0.02 Å). These small values seem insufficient to account for the coupling differences; in $C_{70}(CF_3)_n$ compounds the differences are a factor of almost two.

(iii) In terms of intervening atoms, both *b* and *c* are equidistant from *d*, so that secondary coupling of *b* with *d* could be expected; none is seen.

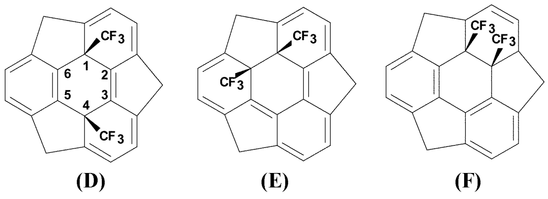
(iv) If the 13 Hz coupling is due to through-space 1,4-coupling of the *ab* and *cd* CF_3 groups, then significantly larger 1,3-coupling between the groups on positions *b* and *c* should be observed (calculated distance 3.81Å); this is also not seen.

(v) Particularly compelling are the data for fraction **2** of $C_{60}(CF_3)_6$, which has C_s symmetry with two *adjacent* trifluoromethyl groups, and a coupling constant for the these (on symmetry plane groups) of 11.7 Hz. This argues against assignment of the *ca.* 13 Hz couplings to 1,4-interactions.

Any further distinction will require single crystal X-ray analysis, though none of the derivatives appear to crystallise.

Key features of the results are:

$C_{60}(CF_3)_2$ (*fraction 3*). A single peak at δ_F −69.3, agrees with a previous report on a small sample obtained by a different route,[14] conjectured to be a 1,2-isomer, but this is disproved by the ^{13}C NMR spectrum[26] which showed (sp^2 region) 25 × 2 C + 4 × 1 C, *cf.* 27 × 2 C + 4 × 1 C required for either 1,4-, or 1,6-addition, and 13 × 4 C + 3 × 2 C for 1,2-addition (motifs **D**, **E**, and **F**, respectively). (The spectrum is not fluorine decoupled, hence resonances for the four carbons adjacent to the CF_3 groups are not seen.)



The location of bis addends may in principle be deduced through their UV/vis spectra, since 434 and 448 nm bands are said to indicate 1,2- and 1,4-addition, respectively.[30] The spectrum (hexane) of $C_{60}(CF_3)_2$ shows two broad bands centred at 407 and 442 nm. Whilst the latter is consistent with the ^{13}C NMR in disproving 1,2-addition it is insufficiently specific concerning the two alternatives.

After standing in $CDCl_3$/Cr(acac)$_3$ for 4 weeks, some disproportionation occurred giving derivatives containing from one to eight CF_3 groups with, in some case the addition of hydrogen (presumed to have come from moisture traces in the solvent). Such rearrangement could be expected from a compound possessing inherent steric hindrance.

$C_{60}(CF_3)_4$

Eight isomers were obtained, (some associated with other derivatives that could not be separated). Satisfactory ^{19}F NMR spectra were obtained with fractions: **4**, **5**, **6** and **17**.

(i) Fraction 4. This is described above.

(ii) Fractions 5 and 6. (Figs. 9,10). Each consist of four equal-intensity quartets at δ_F −67.93, −68.37, −69.40, and

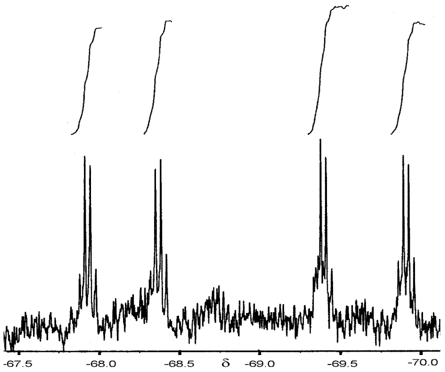


Fig. 9 ^{19}F NMR spectrum for $C_{60}(CF_3)_4$, fraction **5**.

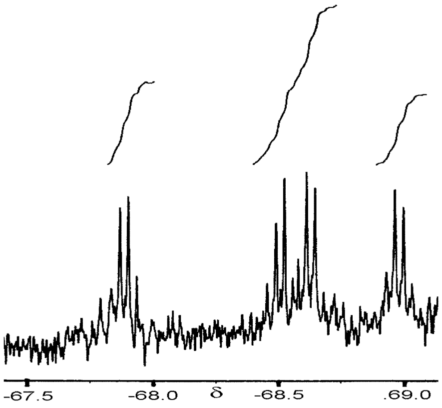
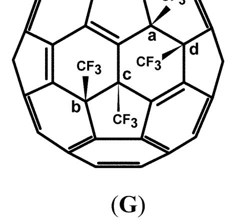


Fig. 10 ^{19}F NMR spectrum for $C_{60}(CF_3)_4$, fraction **6**.

−69.91 (*J* all 12.4 Hz); −67.88, −68.51, −68.63, −68.98, (*J* 12.5, 12.9, 12.6, 13.0 Hz, respectively). Each of these compounds is therefore unsymmetrical and comprises two isolated pairs of neighbouring CF_3 groups. They cannot involve addition across 6:6 ring junctions, since for tetra-addended derivatives only one (*trans*-2) is unsymmetrical. The magnitude of the coupling constants indicates these compounds each to have *bis* 5:6-addition patterns. Since many more isomers of this type are possible, all of the uncharacterised isomers in fractions **8**, **1**, **18** and **19** may be of this type.

(iii) Fraction 17. Four equal intensity multiplets at δ_F −57.3 (*a*), −64.2 (*b*), −66.8 (*c*), −69.2 (*d*), showed this to be an unsymmetrical isomer, with coupling of $d \rightarrow a$, and $c \rightarrow b$ and *a* (this latter is very weak), deduced from a 2 D COSY spectrum. Thus there are two coupled CF_3 addends with weak coupling between them, indicating a motif such as in **G**. This fraction also contained eight minor peaks described under $C_{60}(CF_3)_8$, below.



(G)

$C_{60}(CF_3)_6$

Thirteen isomers were separated, and ^{19}F NMR spectra obtained for fractions **2**, **6**, **7**, **9–11**, **14–16**; those for the first four fractions were clearly resolvable.

(i) Fraction 2. The four-line spectrum, δ_F −58.4 (1 F, sept, *J*, 11.3 Hz), −59.85 (1 F, m), −63.9 (2 F, m), −65.8 (2 F, q, *J*, 12.7 Hz) (Fig. 11 labelled *a–d*, respectively) shows the compound to have C_s symmetry. A 2 D COSY spectrum showed the connections $c \rightarrow d$, $c \rightarrow a$ and $a \rightarrow b$. The two fluorines (*a,b*) that lie on the symmetry plane can *only* straddle a 6:6-ring junction, this being consistent with **H** (X = CF_3) having a 'T' pattern conjectured for fullerene additions.[31] Alternative interpretation in terms of isostructurality with $C_{60}Br_6$ or $C_{60}Cl_6$[24,32] is problematical as noted above with the $b \rightarrow a$ coupling constant of 11.7 Hz and the *ca.* 13 Hz values, if these are due to 1,4-long-range coupling. The broadness of the peaks evident in Fig. 11, indicates secondary coupling consistent with close proximity of the addends.

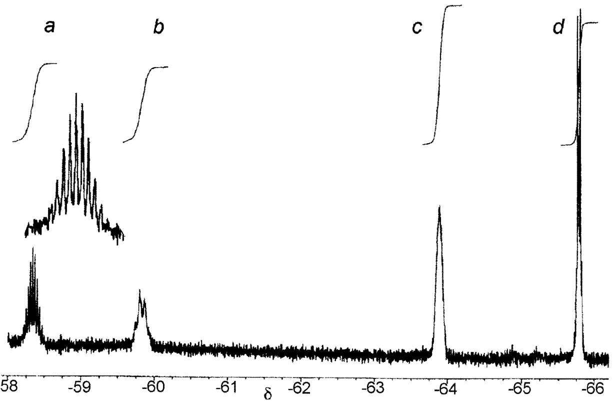
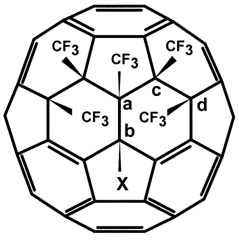


Fig. 11 ^{19}F NMR spectrum for $C_{60}(CF_3)_6$, fraction **2**; inset is δ_F −58.4 expansion.



H, (X = CF_3 or H, see text)

(ii) Fractions 7 and *9*. The ^{19}F NMR spectra each show six equal intensity resonances at δ_F:

(a) −64.37 (1 F, sept, *J* 11.7 Hz), −65.45 (1 F, sept, *J* 11.7 Hz), −65.51 (1 F, sept, *J* 12.3 Hz), −66.52 (1 F, sept, *J* 14.2 Hz), −67.38 (1 F, q, *J* 14.1 Hz) and −69.64 (1 F, q, 11.6 Hz) (Fig. 12).

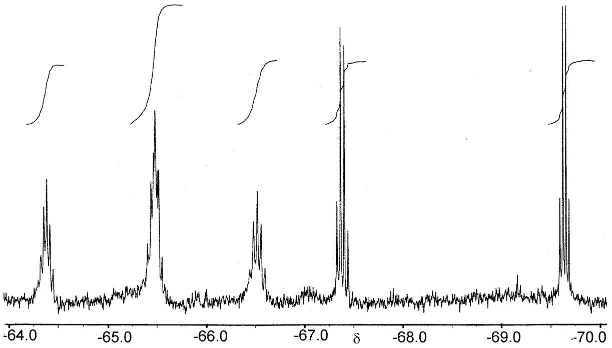


Fig. 12 ^{19}F NMR spectrum for $C_{60}(CF_3)_6$, fraction **7**.

(b) −63.31 (1 F, sept, *J* 12.4 Hz) −65.17 (1 F, sept, *J* 12.7 Hz), −65.61 (1 F, sept, *J* 12.3 Hz), −65.65 (1 F, sept, *J* 14.3 Hz), −67.70 (1 F, q, *J* 14.5 Hz), −68.38 (1 F, q, *J* 12.3 Hz), (Fig. 13; minor peaks marked x are due to the presence of a small amount of a $C_{60}(CF_3)_8$ isomer).

The data show each compound to have 'linear' arrays of CF_3 groups, in unsymmetrical q_a-$sept_a$-$sept_b$-$sept_c$-$sept_d$-q_d patterns.

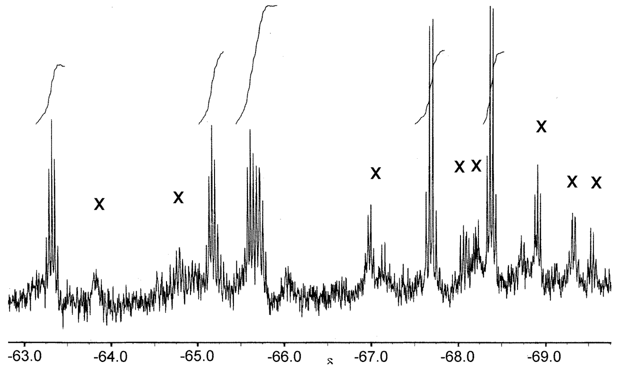
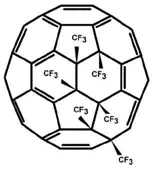
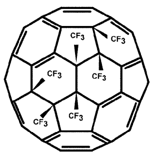


Fig. 13 ^{19}F NMR spectrum for $C_{60}(CF_3)_6$, fraction **9**.

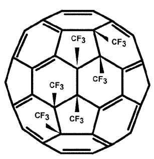
Here again the $q_a \rightarrow sept_a$ and $sept_d \rightarrow q_d$ coupling constants for each fraction differ [as in fraction **4** of $C_{60}(CF_3)_4$]. The data are consistent with one each of structures **I** and **J** (having respectively one and two double bonds in pentagons) in which the terminal pairs of CF_3 groups lie across 5:6- and 6:6-ring junctions.



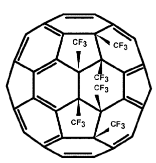
(I)



(J)



(K)



(L)

(iii) Fraction ***6***. The spectrum (Fig. 14) comprises three equal intensity peaks at δ −64.26 (sept, 2 F), −64.66 (sept, 2 F), −69.38 (q, 2 F, 11.7 Hz), showing that this compound has either C_s or C_2 symmetry, with the trifluoromethyl groups arranged in an q_a-$sept_a$-$sept_b$-$sept_b$-$sept_a$-q_a pattern. The coupling constant indicates that *aa* is a 5:6 ring junction, the data being compatible with either C_2 K or C_s L. (Note that if a 1,4-addition regime was involved the product would have to have a C_2 symmetry.)

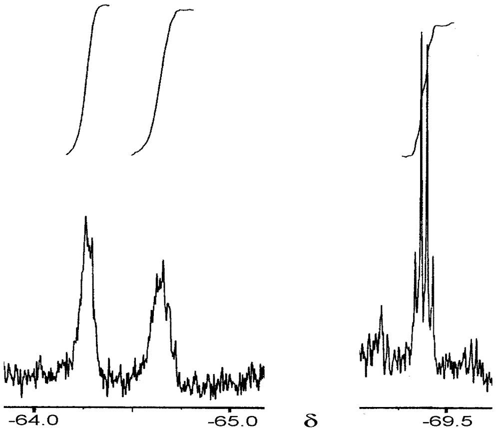


Fig. 14 ^{19}F NMR spectrum for $C_{60}(CF_3)_6$, fraction **6**.

(iv) Fraction ***14***. This consists of two unsymmetrical isomers in *ca.* 1:1 ratio giving twelve resonances at δ_F: −64.0 (1 F, sept, *J* 12.2 Hz), −64.59, (1 F, sept, *J* 12.2 Hz), −64.7 (1 F, sept, *J* 12.2 Hz), −64.81 (1 F, sept, *J*, 13.5 Hz), −66.95 (1 F, q, *J*, 14.1 Hz), −67.22 (1 F, q, *J*, 13.4 Hz) −67.7 (2 F, superimposed multiplet), −67.9 (1 F, sept, *J*, 11.6 Hz), −68.21 (1 F, q, *J*, 12.1 Hz) −69.51 (2 F, overlapping q, *J*, 11.4 and 11.9 Hz). Further work on larger samples would be needed to resolve these structures. Notably, the general pattern is again evident here, with coupling constants for pairs of quartets of *ca.* 12 and 14 Hz, indicating terminal addition in each case across 5:6- and 6:6 ring junctions.

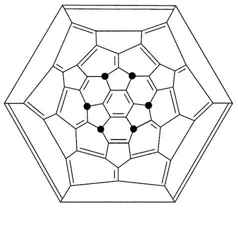
(v) Fractions ***15*** *and* ***16***. The mass spectra showed these both to be $C_{60}(CF_3)_6/C_{60}(CF_3)_8$ mixtures. The respective ^{19}F NMR spectra showed:

(a) Twenty-two resonances, many overlapping or multiplets, centred at δ_F −58.0 (1 F), −58.35 (2 F), −58.9 (1 F), −59.5 (1 F), −60.7 (1 F) −63.0 (1 F), −63.75 (1 F), −64.2 (1 F), −64.4 (2 F), −64.9 (1 F) −65.4 (1 F), −65.55 (2 F), −66.25 (2 F), −66.72 (1 F), −67.1 (2 F) −68.8 (2 F), interpreted in terms of two isomers of $C_{60}(CF_3)_8$ and one of $C_{60}(CF_3)_6$.

(b) Fourteen near equal-intensity resonances at −58.21 (m), −60.13 (m), −63.04 (m), −63.57 (m), −64.91 (sept, *J* 13.1 Hz), −65.90 (sept, *J* 12.7 Hz), −66.10 (q, *J*, 12.3 Hz), −66.42 (sept, *J* 12.0 Hz), −66.97 (q, *J* 12.0 Hz), −67.42 (q, *J* 14.4 Hz), −68.78 (q, *J* 12.0 Hz) −69.10 (sept, *J* 12.7 Hz), −69.28 (two overlapping multiplets). The similarity of the peak intensities indicated this fraction to consist of an approximately 50:50 mixture. Yet again the 12.0/14.5 Hz coupling pattern is evident.

Insufficient material was available to distinguish these sets by means of a 2 D COSY spectrum, but they probably could be separated using larger amounts and different HPLC column/conditions.

If 1,4-addition were involved, one might expect to see also the formation of structure **M** since this has central fully aromatic hexagon in the manner of $C_{60}F_{18}$.[9] However, there is no evidence for a single line in the ^{19}F NMR spectrum for any $C_{60}(CF_3)_6$ fraction; no equivalent structure is seen either for *e.g.* $C_{60}Br_6$. This could indicate that mechanistic aspects as we have suggested,[25] play a significant role in determining the addition patterns rather than thermodynamic ones.



(M)

$C_{60}(CF_3)_8$

Twenty-one isomers were separated, (some in association with other derivatives, Table 1), and the ^{19}F NMR spectra were obtained for eight of them (fractions **10–13**, **15–17**, **25**). Fractions **15** and **16** were unresolved mixtures with $C_{60}(CF_3)_6$ (described above), and fraction **10** was poorly resolved due to low concentration. Fraction **11**, a mixture with $C_{60}(CF_3)_8$ showed a number of downfield septets and (between *δ* −66.5 and −69.6) at least ten quartets (mostly 11–12.5 Hz, but with one at 14.1 Hz), so the pattern observed with the less addended derivatives is evident here also.

(i) Fraction ***12***. The ^{19}F NMR spectrum was not well resolved giving δ_F −62.64 (1 F), −63.26 (1 F), −64.10 (2 F), −64.88 (2 F), −68.34 (1 F), −69.12 (1 F). The two upfield resonances (well separated from the rest) are probably quartets with the other six being septets (*cf.* other spectra above), so indicating a 'linear' sequence of CF_3 groups (see also the shifts for fraction **13** below).

(ii) Fraction ***13***. Two isomers are present. Resonances for the minor one were not fully resolved, but those for the main one appear at δ −63.10 (1 F, sept, *J* 11.8 Hz), −64.66 (1 F, sept, *J* 14.9 Hz), −64.87 (1 F, sept, *J* 12.8 Hz), −65.48 (1 F, sept, *J*14.8 Hz), −67.45 (1 F, q, *J* 14.6 Hz), −67.65 (1 F, q, *J* 12.0 Hz), −68.48 (1 F, q, *J*12.2 Hz), −69.51 (1 F, q, *J* 11.3 Hz). The presence of four quartets and four septets show this compound to have a 'linear' sequence of six CF_3 groups (note again the coupling constants of *ca.* 12 and 15 Hz) together with

two coupled to each other but remote from the others, most probably the pair at δ_F −67.65 and −68.48 since they have similar coupling constants.

(iii) Fraction ***17***. This is a mixture with an isomer of $C_{60}(CF_3)_4$ described above. Resonances (1–8, respectively) were at δ_F −65.87 (1 F, m), −67.58 (1 F, q, *J* 12.0 Hz), −68.52 (1 F, q, *J* 13.2 Hz), −69.10 (1 F, q, *J*, 12.4 Hz), −69. 27 (1 F, q, 11.5 Hz), −69.57, (1 F, s), −69.70 (1 F, q, *J* 12.0 Hz), −69.96 (1 F, q, *J* 12.6 Hz). There are thus six quartets, coupled (2 D spectrum) as follows: 2–7, 3–5, 4–8, indicating the compound to contain three isolated pairs of CF_3 groups. The singlet (peak 6) shows that a CF_3 group lies remote from the rest; the NMR spectra of some trifluoromethyl derivatives of [70]fullerene show a similar feature, indicative of a 1,3-shift of one addend. However, there are anomalies because the multiplet should preclude the possibility of the three coupled doublets. Further consideration of this structure is deferred pending availability of a better separation technique and sample.

(iv) Fraction ***25***. The spectrum comprises six peaks with two coincident pairs so that multiplicity cannot be fully assigned. Resonances are at δ −62.89 (1 F, sept, *J* 11.2 Hz), −65.22 (2 F, m), −65.48 (2 F, m), −65.70 (1 F, sept, *J* 12.9 Hz), −67.26 (1 F, q, *J* 14.2 Hz), −67.81 (1 F, q, *J* 12.0 Hz). This indicates a 'linear' array, with the ubiquitous differential coupling constants for the doublets indicating that the terminal CF_3 pairs lie across 6:6- and 5:6-ring junctions. Addition of a pair of CF_3 groups to either of **I**, **J**, or **K** would give a structure consistent with these data.

$C_{60}(CF_3)_{10,12,14}$

Eleven isomers of $C_{60}(CF_3)_{10}$ are present in fractions **12** and **26–35**, five isomers of $C_{60}(CF_3)_{12}$ are present in fractions **34–38**, and four isomers of $C_{60}(CF_3)_{14}$ are present in fractions **35–38**, but in each case the ^{19}F NMR spectra were either too weak or complex to be analysed. Although in principle it may be possible to obtain more definitive information using much larger samples, the information gained may not be of sufficient value to justify the very extensive work required.

$C_{60}(CF_3)_{16-20}$

These components were present in fractions **36–38**.

$C_{60}(CF_3)_5H$, *fraction 1*

The mass spectrum shows two main peaks at 1066 and 998 amu, assigned to $C_{60}(CF_3)_5H$ and $C_{60}(CF_3)_4H_2$, respectively, but the ^{19}F NMR spectrum could not be resolved satisfactorily. The ^1H NMR spectrum showed a sharp peak at δ 3.425 in contrast to other H-containing compounds (see Results, item 6). A possible structure for $C_{60}(CF_3)_5H$ could be **H** (X = H).

(b) Using the Scherer radical C_9F_{19}

Many components were obtained having similar mass spectra but different HPLC retention times. With but one exception, extensive reprocessing failed to yield a pure single component. In order to illustrate the general trends and observations found with this material, we describe some representative examples under the HPLC retention times:

(i) 2–4 min. The mass spectrum (Fig. 15) indicates this to be a mixture of components, containing up to eight CF_3 groups, the peak at 1275 amu being due to $C_{60}(CF_3H)_3(CF_3)_5$, but some of the lower mass species may be fragmentation ions. The high intensity peak at 1274 amu may be due to $C_{60}(CF_3H)_2(CF_3)_6$. Characteristic of hydrogenated fullerenes is the loss of hydrogen through fragmentation, and for $C_{60}(CF_3H)_3(CF_3)_5$, the loss of the three hydrogens is readily seen. The main component is $C_{60}(CF_3H)_2(CF_3)_2$ (998 amu).

This spectrum shows the ready loss of HF (20 amu), evident at each addition level $C_{60}(CF_3)_n$, $n = 2$–8, the following being an illustrative example. Consider the peak at 1068 amu (the ^{13}C isotope pattern of which shows that a species of 1070 amu is also present). There are also three associated peaks due to hydrogen loss so that overall the peak cluster in this region is due to: $C_{60}(CF_3H)_5$ (1070 amu), $C_{60}(CF_3H)_3(CF_3)_2$ (1068 amu), $C_{60}(CF_3H)_2(CF_3)_3$ (1067 amu), $C_{60}CF_3H(CF_3)_4$ (1066 amu) and $C_{60}(CF_3)_5$ (1065 amu). Loss of HF from the 1070, 1068, and 1066 amu peaks then gives the cluster at 1046, 1048 and 1050 amu. Similar arguments apply throughout the spectrum. For three species (the clusters around 1204, 1136 and 998 amu), *two* HF molecules are lost.

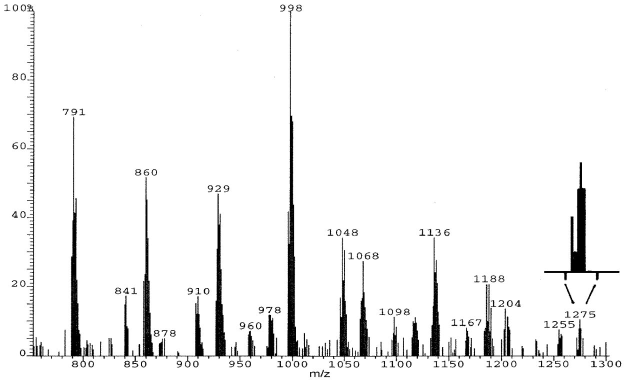


Fig. 15 EI mass spectrum (70 eV) of the 2–4 min fraction from reaction of [60]fullerene with the Scherer radical.

(ii) 3.7 min. The mass spectrum (not shown) indicates the presence of $C_{60}(CF_3H)_4(CF_3)_2$ at 1138 amu with associated fragment ions.

(iii) 5.9 min. This fraction contains up to five addend groups (Fig. 16). The highest addend level comprises three components of 1070 [$C_{60}(CF_3H)_5$], 1068 [$C_{60}(CF_3H)_3(CF_3)_2$] and 1066 [$C_{60}CF_3H(CF_3)_4$] amu, the stepwise loss of hydrogen pairs being evident in the spectrum. The spectrum also shows $C_{60}(CF_3H)_3$ (930 amu) with prominent HF loss giving $C_{60}(CF_3H)_2CF_2$ (910 amu) followed by loss of H_2 (908 amu). The $C_{60}(CF_3H)_2$ peak at 860 amu also shows prominent H_2 loss.

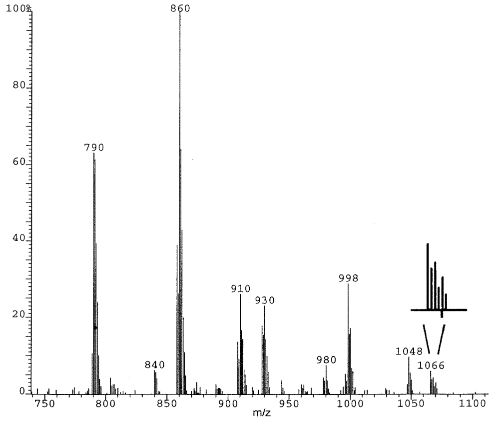


Fig. 16 EI mass spectrum (70 eV) of the 5.9 min fraction from reaction of [60]fullerene with the Scherer radical.

(iv) 6.6 min. The mass spectrum (Fig. 17) shows mainly $C_{60}(CF_3H)_2$ at 860 amu together with the dehydro fragmentation ion at 858 amu. Here there is *no* significant HF loss from the main ion indicating that there are no adjacent CF_3 and H groups.

(v) 9.7 min. The mass spectrum (Fig. 18) shows a number of similarities to Fig. 16, a significant difference being the insignificant loss of HF except from the 860 amu species, indicating the presence of a compound having few adjacent CF_3 and H groups.

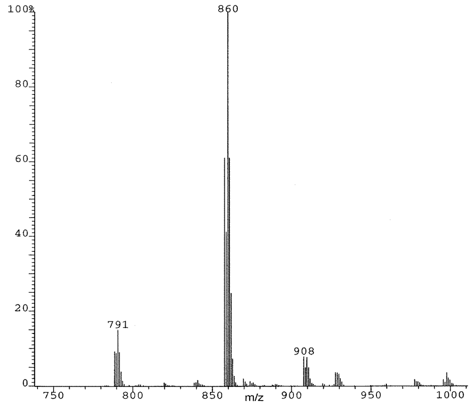


Fig. 17 EI mass spectrum (70 eV) of the 6.6 min fraction from reaction of [60]fullerene with the Scherer radical.

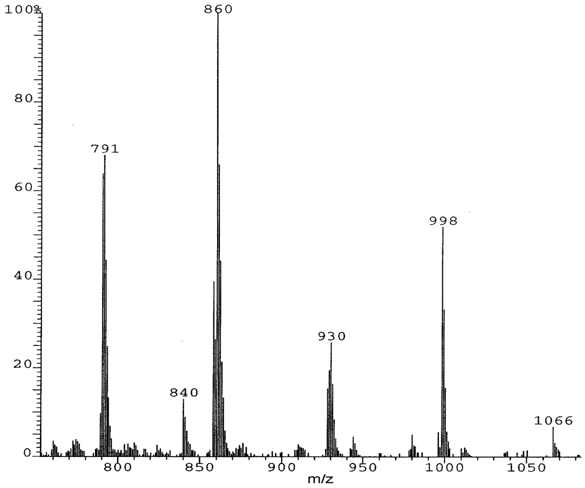


Fig. 18 EI mass spectrum (70 eV) of the 6.6 min fraction from reaction of [60]fullerene with the Scherer radical.

(vi) 28.4 min. This is pure $C_{60}CF_3H$, 790 amu which showed no fragmentation except to C_{60}.

Overall the most significant features of these results are that addition of up to eight CF_3H moieties occurs, isomers are evidently present. Most notably, HF loss occurs readily from some fractions and components under EI conditions.

Summary

We have separated a large number of trifluoromethylated derivatives, and obtained detailed ^{19}F NMR spectra on twenty-one of them, thereby allowing many provisional structural assignments, that we have based on a combination of addition across 5:6- and 6:6-ring junctions. We have defined the HPLC conditions that will enable isolation and full identification of components that were not resolved in this study. Trifluoromethylation yields a greater variety of derivatives than any other fullerene reaction, and this may make it pre-eminent for further development of theories of fullerene addition. A problem that needs to be overcome is the predominance of C_1 derivatives, which makes structural characterisation difficult, especially of isomers. This could possibly be solved in future by matching the observed patterns with theoretical predictions of ^{19}F NMR spectra.

In contrast to fluorination, high yields of specific addition levels are not obtained, and this is evidently related to the derivatives either not having exceptional stability, or, more probably, to the reaction being kinetically rather than thermodynamically controlled. This latter would also account for the unusual addition patterns, and the very large number of derivatives.

Our data should aid the separation of substantial amounts of isomers of a limited addition range for investigation with regard to light-harvesting applications. The use of the more stable trifluoromethylated fullerenes as opposed to fluorofullerenes for formation of photovoltaic devices may be environmentally advantageous in view of their greater stability.

Because sufficient space needs to remain on the cage for the attachment of electron-donor addends, derivatives with not more than eight CF_3 groups should be targeted for this purpose, (possibly by limiting the acetate:fullerene ratio). In terms of large-scale practical applications, separation of individual components is unrealistic, as is the use of HPLC separation. Substantial separation can probably be achieved by differential sublimation since the compounds are very volatile;[11] moreover, unreacted fullerene (a consequence of the above limited reagent ratio) should concentrate in the residue that could then be recycled.

Experimental

(a) Using silver trifluoroacetate

[60]Fullerene (30 mg) was ground intimately with CF_3CO_2Ag (198 mg) (a dry box is unnecessary), and placed in a tube connected to a vacuum pump (0.01 mBar), inside a furnace. The tube was heated stepwise to 80 °C, 160 °C, and 240 °C, (each for 30 min) to thoroughly remove any moisture. The temperature was then raised to 285 °C for 1 h, and raised further to 300 °C for 1 h. Above 285 °C, a slight brown toluene-insoluble deposit formed on a cold zone of the tube, but this is not a trifluoromethyl derivative. Surprisingly, in view of the high volatility of trifluoromethylfullerenes, the product was retained in the reagent matrix; perhaps some co-ordination with silver occurs, (aromatics are known to co-ordinate with Ag^+ ions).[33] The product (which contained very little unreacted fullerene) was dissolved in toluene, filtered to remove traces of silver (most is deposited on the tube walls), and separated by HPLC (high pressure liquid chromatography).

(b) Using the Scherer radical $C_9F_{19}^{\bullet}$

[60]Fullerene (50 mg, 0.069 mmol) was heated in a Schlenk tube equipped with a stirrer bar *in vacuo* at 165 °C during 6 h. The tube was filled with dry deoxygenated argon and cooled down to room temperature. 1,2,4-Trichlorobenzene (1.9 ml) and 201 l, 0.7 mmol of the Scherer radical (C_9F_{19}) were added, and the mixture stirred for 10 min. A 1 µl sample was removed, dissolved in perfluorodecalin (0.2 mL) and analysed by EPR after degassing by a double freeze-thaw procedure. The tube contents were degassed by triple freeze-thawing, the tube was filled with argon and heated with stirring in the dark at *ca.* 100 °C during 3 h. After cooling a sample for EPR-analysis was taken, and the tube was kept overnight in the dark under argon. This heating procedure was then repeated, after which EPR analysis showed only *ca.* 1% of unreacted Scherer radical to remain in the mixture. The EI mass spectrum of the crude product (94 mg) displayed ion peaks of fullerene derivatives containing up to ten CF_3 groups, with some products containing hydrogen. This corresponds to an average addition of *ca.* nine CF_3 groups per fullerene molecules. The crude mixture was separated by HPLC as described below.

Reaction with acetone. A sample of trifluoromethylated {60]fullerene was added to acetone and the solution allowed to stand for a few hours. The mass spectrum was then taken and found to be identical to the material before the addition of acetone. By contrast, fluorofullerenes are decomposed immediately by this procedure.

Spectroscopy. EI mass spectra were run at 70 eV, ^{19}F NMR and ^{1}H NMR at 376.5 and 500 MHz, respectively (all in $CDCl_3$).

IR spectra (KBr). Fraction **5** provided a representative spectrum (Fig. 19) showing the typical CF_3 bands at 1261 and 1188 cm^{-1}.

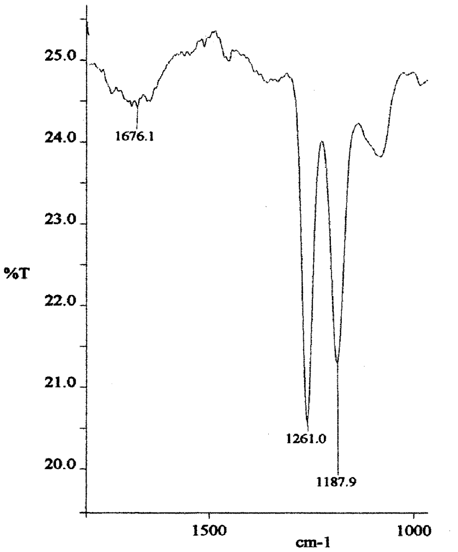


Fig. 19 IR spectrum (KBr) for $C_{60}(CF_3)_4$ fraction **5**.

HPLC. This employed a 10 × 250 mm Cosmosil Buckyprep column (elution either by toluene or 1:1 toluene:heptane, 4.7 ml min^{-1}) or a Cosmosil 5 PYE column (elution by 3:7 toluene : heptane, 4 ml min^{-1}) (see under individual compounds, Table 1).

Acknowledgements

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