Reaction of $C_{60}F_{18}$ with diethyl bromomalonate: diversion of the Bingel reaction and formation of the first 18π annulenic fullerene†

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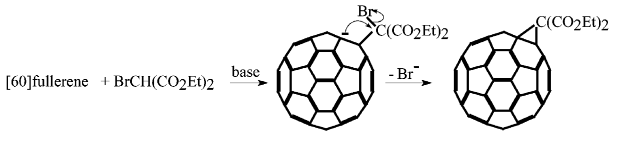
Reaction of $C_{60}F_{18}$ with diethyl bromomalonate in the presence of DBU results in the nucleophilic replacement of either one, two, or three of the most accessible fluorine atoms by $CBr(CO_2Et)_2$ moieties, in preference to formation of a cyclopropanated derivative (the normal Bingel reaction). Substitution that takes place δ to the departing fluorine, is the first proven example of S_N2' substitution in a fullerene, and appears to be sterically driven. The ratio of mono-/poly-substitution products can be controlled by varying the rate of addition of the DBU and the molar ratio between $C_{60}F_{18}$ and the other reagents. The tri-substituted product is an [18]annulene, has an intense emerald-green colour ascribable to the electron delocalisation in the (equatorial) annulene belt (bond length variation 0.018 Å), and has C_{3v} symmetry. This is the first example on an annulenic fullerene (moreover of an all-*trans* annulene or trannulene). The extent of substitution in each compound is identified from the fluorinated fragments ($C_{60}F_{15}$, $C_{60}F_{16}$, and $C_{60}F_{17}$, respectively, for tri-, di-, and mono-substitution) in the EI mass spectra, and by their ^1H and ^{19}F NMR spectra. The structure of the tri-substituted [18]annulene was confirmed by single crystal X-ray diffraction. Normal Bingel cycloaddition also takes place between $C_{60}F_{18}$ and diethyl malonate–DBU in CBr_4, to give $C_{60}F_{18}C(CO_2Et)_2$ and $C_{60}F_{16}C(CO_2Et)_2$ in relatively low yields. Calculations indicate a critical size of substituent required to produce δ-substitution, rather than *ipso*-substitution of the departing fluorine.

The Bingel reaction between diethyl bromomalonate and fullerenes[1] is one of the most extensively studied reactions in fullerene chemistry (Scheme 1).[2] This, and variations using dialkyl malonates in either the presence or absence of iodine, have been employed for attaching to the cage, *via* a cyclopropane moiety, donor groups that might give rise to interesting donor–acceptor properties.[3] The viability of such derivatives depends upon the strong electron-acceptor properties of the fullerene cage and efforts have been directed towards both increasing the electron supply for the addend, and increasing the electron withdrawal by the cage. However, a 'catch-22' situation usually arises with the latter because the sp^3 carbons produced by addition, reduce the electron withdrawal. In polyfluorofullerenes there is a net gain of electron withdrawing power relative to the parent fullerene,[4] and we plan to exploit $C_{60}F_{18}$[5] in this context because it possesses a substantial 'curved fullerene' region[6] where cycloadditions may occur. Supplies of $C_{60}F_{18}$ are presently limited, so initially we are examining some representative reactions to see if the chemistry of the parent fullerenes can be reproduced. In the case of the Bingel reaction we were concerned that the base required for the reaction (DBU) might destroy the fluorofullerene, so that use of this versatile reaction would be precluded.



Scheme 1 Normal course of the Bingel reaction.

In the event, these preliminary studies have shown that the reaction takes a different course. After removal of the proton by the base, the resultant nucleophile displaces fluorine from the cage instead of losing bromine to give the normal three-membered ring. This has produced an entirely new type of fullerene derivative which contains a 18π circuit of delocalised electrons, and which we expect to lead to a large family of fullerene derivatives possessing unique spectroscopic properties.

Experimental

An exploratory reaction, carried out by mixing toluene solutions of $C_{60}F_{18}$ and DBU, was not encouraging. A rapid reaction occurred (colour change), and mass spectrometric analysis of the product showed that all of the fluorine had been lost from the cage. (Ultimately, it may prove possible to use controlled defluorination by DBU to convert polyfluorofullerenes to derivatives of lower and possibly specific addition levels.) Fortunately however, in the presence of diethyl bromomalonate, degradation did not occur and indeed, unreacted $C_{60}F_{18}$ could be recovered from the mixture, showing that reaction of DBU with the ester was substantially faster than with the fluorofullerene. The reaction produced a mixture of the mono-, di- and tri-substitution products, the amounts varying according to the relative proportions of reagents used, and addition procedure.

In a typical experiment, $C_{60}F_{18}$ (5 mg) was dissolved in toluene (20 ml, HPLC grade) together with diethyl bromomalonate (1.4 mg dissolved in 1 cm^3 of toluene), and DBU (0.85 mg dissolved in 0.4 cm^3 of toluene) was added dropwise under argon. The solution turned green immediately, and was stirred

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† Electronic supplementary information (ESI) available: EI mass spectra for fullerenes **1**–**3**. See http://www.rsc.org/suppdata/p2/b1/b105921c/

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at room temperature for a further 1 h. This produced mainly the mono- and tri-substitution product, but a second run using less DBU produced mainly mono- and di-substitution. A third experiment in which the DBU solution was added more slowly to the other reagents produced a greater relative yield of the mono-substitution product. Unreacted $C_{60}F_{18}$ was recovered for re-use.

In each preparation, a black precipitate formed, and this was removed by filtration, the components of the filtrate being then separated by HPLC (high pressure liquid chromatography). For the initial experiment this employed a Cosmosil 5μ-pye column (10 × 250 mm) with elution by toluene at 4.7 ml min^{-1}. For logistical reasons, subsequent separations employed a 10 × 250 mm Cosmosil Buckyprep column (same flow rate).

For the alternative preparative procedure,[7] diethyl malonate (1.14 mg, 1.5 eq.) and CBr_4 (2.34 mg, 1.5 eq.) was added to $C_{60}F_{18}$ (5 mg) in toluene (18 cm^3), and then 1.6 eq. of DBU, dissolved in toluene (0.5 cm^3), was added slowly. The solution, under argon, was stirred for 5 h, during which time the colour changed from yellow ⟶ brown ⟶ yellow ⟶ green ⟶ yellow, and a considerable amount of precipitate was formed. This was removed by filtration and the solution separated by HPLC as before. Identified components eluted at 7.3 and 9.7 min.

Results and discussion

A. Products from the reaction with diethyl bromomalonate

$C_{60}F_{15}[CBr(CO_2Et)_2]_3$ (1). HPLC separation of the crude product gave a fraction eluting at 3.55 min/5μ-pye column (2.6 min/Buckyprep column). Re-purification on the Buckyprep column, (elution with 1 : 1 toluene–heptane at 4.7 ml min^{-1}) gave $C_{60}F_{15}[CBr(CO_2Et)_2]_3$ eluting at 5.0 min. This intense emerald-green compound deposited diamond-shaped crystals from toluene. The spectroscopic properties (^1H and ^{19}F NMR, UV–vis, single crystal X-ray diffraction) have been given in a preliminary report.[8]

The mass spectrum (Fig. 1S, separately available as supplementary information) showed fragmentation ions *m*/*z* at 1639 (M − Br), 1481 [M − $CBr(CO_2Et)_2$] and 1005 ($C_{60}F_{15}$). The latter indicates the number of replaced fluorines (see also the mono- and di-substitution products below). The three-line ^{19}F NMR spectrum indicated C_{3v} symmetry for the product and contrasts markedly with those (below) for the mono- and di-substitution products, and for $C_{60}F_{18}$ and its derivatives, in lacking the upfield peak that occurs at *ca.* −158 ppm when fluorine is attached to carbon surrounded by three fluorinated sp^3 carbons.[5,9] The fluorine in this location now has only two sp^3 neighbours and the signal therefore moves downfield. The ^1H NMR spectrum also confirmed the C_{3v} symmetry.

Two resonance structures for **1** are shown as Schlegel diagrams (Fig. 1) which also includes the equatorial [18]-trannulene belt. The two distinct 6 : 5-bonds and the 6 : 6-bond in this belt have lengths of 1.410, 1.397 (nearer to R), and 1.392 Å, respectively, showing extensive resonance delocalisation, the lengths of the corresponding bonds in $C_{60}F_{18}$ being 1.524, 1.363, and 1.428 Å.[6]

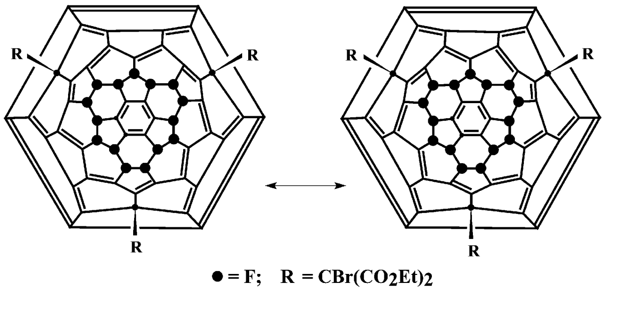


Fig. 1 Schlegel resonance structures for $C_{60}F_{15}[CBr(CO_2Et)_2]_3$ (**1**) showing the delocalised [18]annulene equatorial belt.

Since all the C–C bonds adjacent to the formal double bonds are *trans* to one another, this is an all-*trans* annulene (trannulene),[10] the existence of which was conjectured recently.

$C_{60}F_{16}[CBr(CO_2Et)_2]_2$ (2). This eluted after 2.8 min (Buckyprep column). Fragmentation ions (*m*/*z*) in the mass spectrum (Fig. 2S, separately available as supplementary information) occur at 1479/1481/1483 (M − F), 1261/1263 [M − $CBr(CO_2Et)_2$], 1183 [M − $CBr(CO_2Et)_2$, Br] and 1024 ($C_{60}F_{16}$). In contrast to **1**, this compound is apple-green in colour (nearer to the lemon yellow–green of $C_{60}F_{18}$ derivatives) presumably because it does not have a completely conjugated annulene belt.

^1H NMR spectrum (Fig. 2). This is very complex and shows at least nine overlapping methylene quartets between δ_H 4.58 and 4.37 (2 H, *J* 7.1 Hz, CH_2), due to the eight non-equivalent methylene protons, one of which may be subject to secondary coupling with fluorine at position 1. There are four overlapping equal intensity methyl triplets centred at 1.437, 1.425, 1.414 and 1.411 (3 H, *J* 7.1 Hz, CH_3). The inequivalency in the number of triplets and quartets is attributed to degeneracy in the former. The compound is evidently unsymmetrical and has the structure shown in Fig. 3.

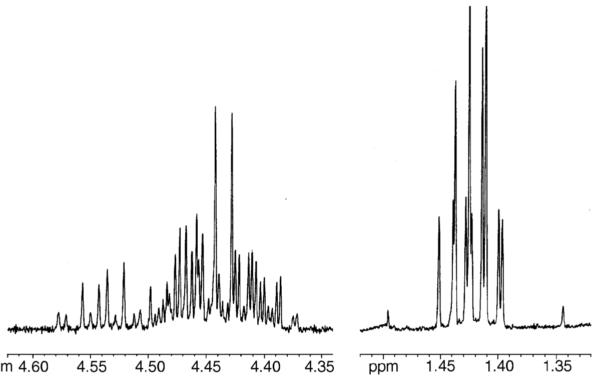


Fig. 2 ^1H NMR spectrum for $C_{60}F_{16}[CBr(CO_2Et)_2]_2$ (**2**).

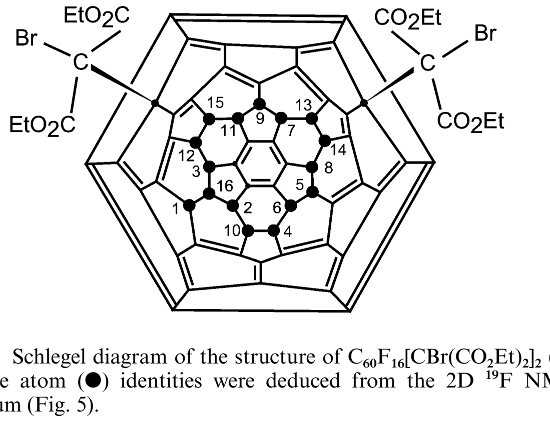


Fig. 3 Schlegel diagram of the structure of $C_{60}F_{16}[CBr(CO_2Et)_2]_2$ (**2**); fluorine atom (●) identities were deduced from the 2D ^{19}F NMR spectrum (Fig. 5).

^{19}F NMR spectrum (Fig. 4). This consists of sixteen lines of equal intensity confirming that two fluorines have been replaced, and that the product is unsymmetrical. From the 2D spectrum (Fig. 5) the fluorine atom locations 1–16 are identified as shown in Fig. 3. Note that in common with other derivatives of $C_{60}F_{18}$,[9] many couplings are evident (*ortho*, *meta*, *para*) across the central benzenoid ring.

$C_{60}F_{17}CBr(CO_2Et)_2$ (3). This mono-substitution product eluted after 6.1 min/5μ pye column or 6.4 min/Buckyprep

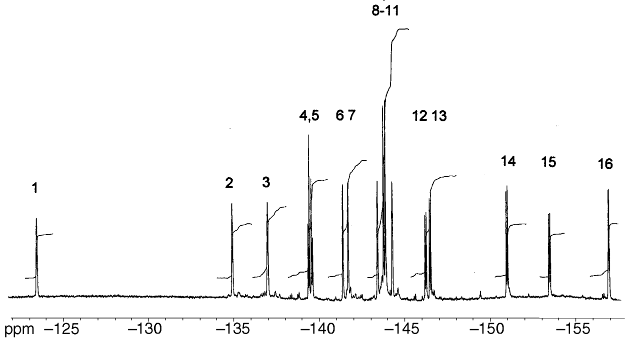


Fig. 4 ^{19}F NMR spectrum (376.4 MHz) for $C_{60}F_{16}[CBr(CO_2Et)_2]_2$ (**2**).

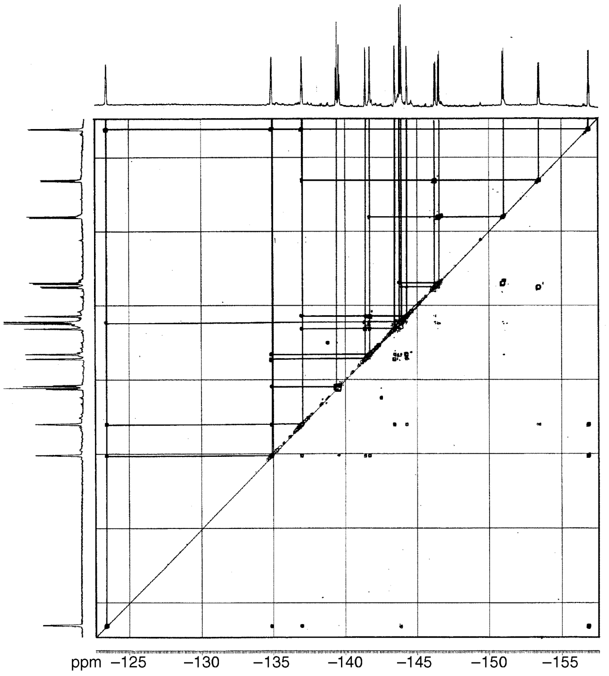


Fig. 5 2 D ^{19}F NMR spectrum for $C_{60}F_{16}[CBr(CO_2Et)_2]_2$ (**2**).

column. The mass spectrum (Fig. 3S, separately available as supplementary information) shows the bromine-containing parent ion at 1280/1282 amu, and fragment ions at 1201 amu (loss of Br) and 1043 amu ($C_{60}F_{17}$). The IR spectrum shows main bands at 1157, 1131, 1090, 1069 and 1059 cm^{-1}, *cf.* 1163, 1133, 1103, 1067 and 1045 cm^{-1} for $C_{60}F_{18}$.[5] Like the di-substituted derivative (**2**), this compound also has an apple-green colour.

^{1}H NMR spectrum (Fig. 6). This shows peaks at δ_H 4.535 (1 H, dq, *J* 7.1 and 10.7 Hz), 4.463 (2 H, q, *J* 7.1 Hz), 4.418, (1 H, dq, *J* 7.1 and 10.7 Hz), 1.434 (3 H, t, *J* 7.1 Hz), 1.427 (3 H, t, *J* 7.1 Hz). As in the case of the di-substituted compound, some triplets are degenerate. The structure is shown in Fig. 7.

^{19}F NMR spectrum (Fig. 8). This consists of fifteen lines of equal intensity and one of double intensity confirming that one fluorine has been replaced, and that the product is unsymmetrical. A notable feature is the downfield peak at −107.2 ppm. Peaks in this region are usually found in fluorofullerene spectra only when the C–F bond is adjacent to oxygen, and a through-space interaction between this fluorine atom and one of the oxygens of the ester substituent may be responsible. Moreover, the 2D spectrum (Fig. 9) is unique in showing substantial coupling of this peak to *seven* others, peaks 5, 6, 10, 13, 14, 15, 16, and presumably the above interaction gives rise to the enhanced coupling. Comparable effects are not seen in the

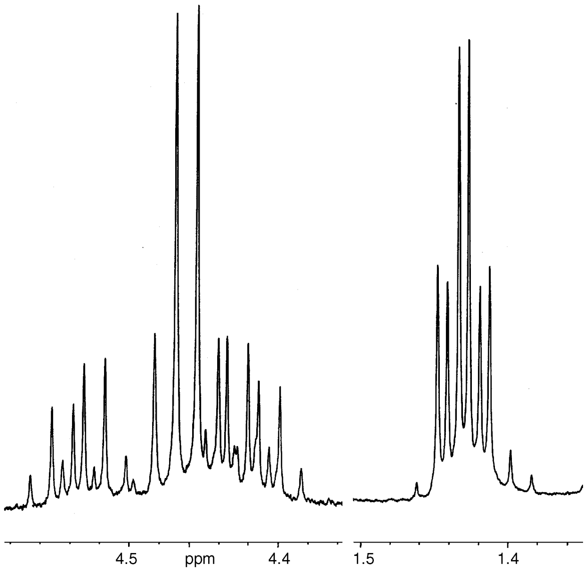


Fig. 6 ^{1}H NMR spectrum for $C_{60}F_{17}CBr(CO_2Et)_2$ (**3**).

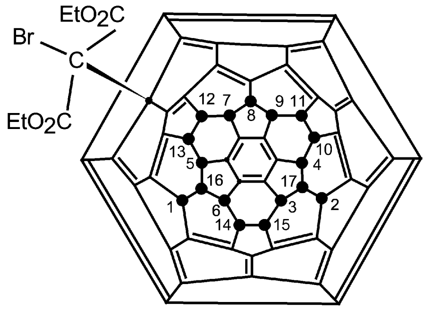


Fig. 7 Schlegel diagram of the structure of $C_{60}F_{17}CBr(CO_2Et)_2$ (**3**); fluorine atom (●) identities were deduced from the 2D ^{19}F NMR spectrum (Fig. 9).

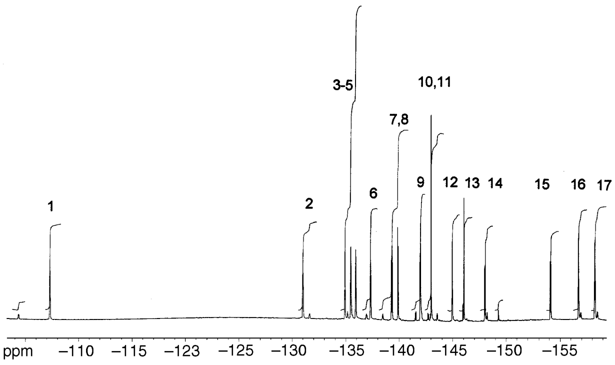


Fig. 8 ^{19}F NMR spectrum (376.4 MHz) for $C_{60}F_{17}CBr(CO_2Et)_2$ (**3**).

di-substituted derivative (above) possibly because interactions between the substituent arms does not allow one of them to approach the cage so closely. As in the case of the di-substituted compound, some long-range couplings occur across the central aromatic ring.

UV-vis spectra. These are shown in Fig. 10 for all three compounds. Because of the small amounts of material currently available and the consequent difficulty of accurate weighing, the extinction coefficients for one compound relative to another are not significant. Above 400 nm, peak maxima occur at *ca.* 441 (sh), *ca.* 501 (sh), 548 and 593 nm for the mono-substituted compound **3**, at 464, 665 and 735 nm for the di-substituted compound **2**, and at 435, 612 and 662 nm for the

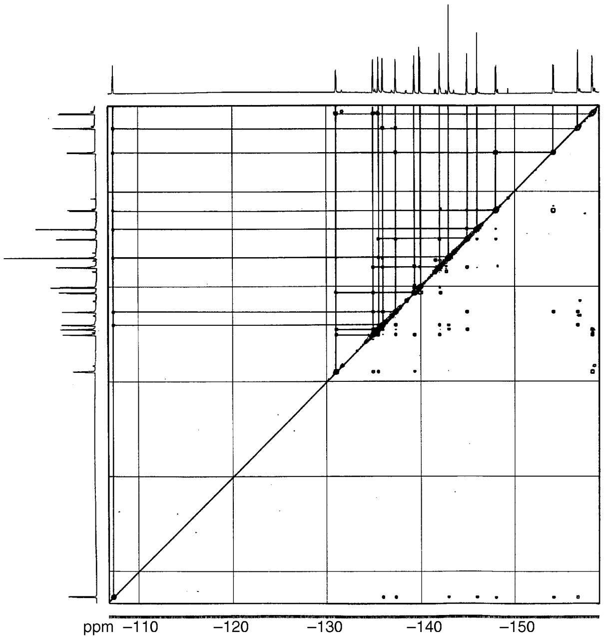


Fig. 9 2D ^{19}F NMR spectrum for $C_{60}F_{17}CBr(CO_2Et)_2$ (**3**).

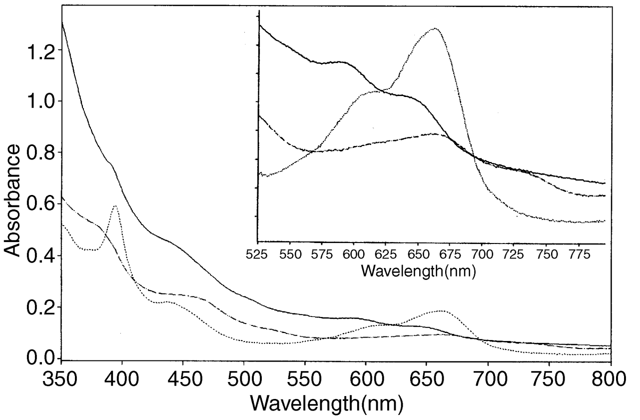


Fig. 10 UV–vis spectra of **1** (··· ··· ·), **2** (------), and **3** (——); inset shows expansion in the 525–775 nm region.

tri-substituted annulenic compound **1**. The intense emerald-green colour of the latter is produced by the band at 662 nm. Both **2** and **3** give shoulder bands in the 380–395 nm region, whereas **1** shows an intense sharp band at 395 nm.

B. Products from the reaction with diethyl malonate

The yields in this reaction were insufficient for full characterisation, but provided enough information to indicate that the expected 'normal' Bingel addition takes place under these conditions.

$C_{60}F_{18}C(CO_2Et)_2$ (4). The mass spectrum (Fig. 11) of the fraction eluting after 9.7 min shows the parent ion at 1220 amu corresponding to $C_{60}F_{18}C(CO_2Et)_2$. The principal fragmentation ion at 878 amu corresponds to $C_{60}C(CO_2Et)_2$ arising from loss of all of the fluorines. There are four possible derivatives that could be obtained by addition of the malonate moiety. In one of these (the most sterically hindered product) the ethyl groups would be equivalent, whereas in the other three they are not. The ^{1}H NMR spectrum shows two quartets centred at δ 4.587 and 4.512 showing that the product is unsymmetrical, which is consistent with addition taking place preferentially across the bond most remote from the fluorines (as happens also in cycloaddition of anthracene).[11]

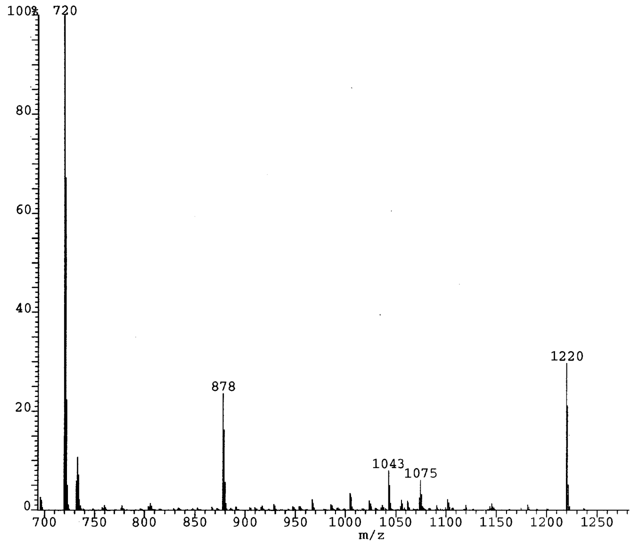


Fig. 11 EI mass spectrum (70 eV) for $C_{60}F_{18}C(CO_2Et)_2$.

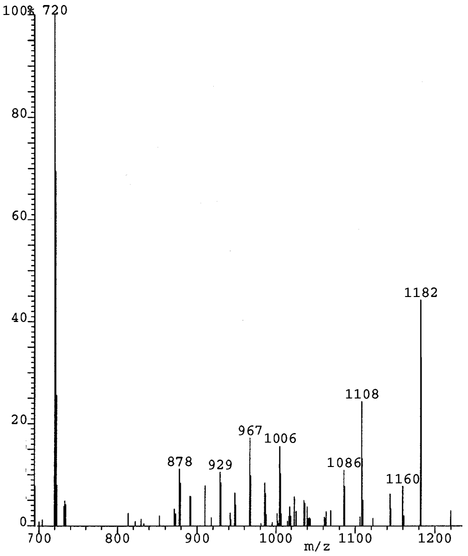


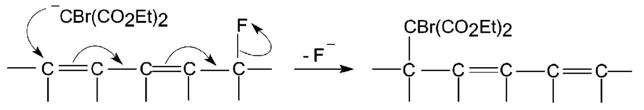
Fig. 12 EI mass spectrum (70 eV) for $C_{60}F_{16}C(CO_2Et)_2$.

$C_{60}F_{16}C(CO_2Et_2)_2$ (5). The mass spectrum (Fig. 12) of the fraction that eluted after 7.3 min shows the parent ion at 1182 amu corresponding to $C_{60}F_{16}C(CO_2Et_2)_2$, with fragmentation down to 878 amu [$C_{60}C(CO_2Et)_2$] due to progressive loss of fluorines. It is unlikely that the structure is produced though the malonate moiety substituting two of the fluorines (the product would be very hindered) but rather that the DBU has caused the fluorine loss (a general process confirmed by analysing mixtures of $C_{60}F_{18}$ and DBU). We have observed loss of two fluorines to give $C_{60}F_{16}$ under other conditions, and the isolation of the derivative here may arise from $C_{60}F_{16}$ being also aromatic.[12]

The substitution process

First we draw attention to our reaction of $C_{60}F_{18}$ with benzene–$FeCl_3$ which gave C_{3v} symmetry $C_{60}F_{15}Ph_3$ ('triumphene'), in which the three outermost fluorines of $C_{60}F_{18}$ were replaced.[13] The location of the phenyl groups was inferred by analogy with the formation of $C_{60}Ph_5Cl$ from benzene–$FeCl_3$–$C_{60}Cl_6$, in which the five most accessible chlorines are *directly* substituted by phenyl.[14] Given the similar reaction conditions/reagents, a common mechanism for phenyldefluorination was indicated.

In the present instance, the same three fluorines are also replaced, but the incoming nucleophiles occupy positions on the cage *different* from the departing fluorines. This appears to be sterically driven, with the incoming nucleophile occupying a position δ to the departing fluorine, so that the mechanism is S_N2' (Scheme 2), typical of nucleophilic substitutions when the α-position is hindered. Substitution at the β-position suffers from the same steric compression as at the *ipso*-position, and is disfavoured with respect to δ-substitution for large incoming groups.



Scheme 2 Mechanism of replacement of fluorine by the bromomalonyl moiety.

The ^{19}F NMR data for $C_{60}F_{15}Ph_3$ gave peaks at δ_F −137.3, −138.4, and −145.0, very similar to the above values obtained for the tri-ester (−136.7, −143.9, and −144.0), which could suggest similar structures. The absence in the trannulene of the upfield peak at −158.1 for $C_{60}F_{18}$ (the one due to fluorine attached to a carbon surrounded by three $sp^3C–F$ groups) arises from removal of a fluorine so converting one $sp^3C–F$ group to sp^2C. In $C_{60}F_{15}Ph_3$ there is likewise no upfield peak in this region, but this corresponds here to the replacement of one fluorine (with its electron-supplying lone pair) by the electron-withdrawing phenyl. Notably, in isostructural $C_{60}H_{18}$[15] the relative positions of the four constituent peaks are also different to those in $C_{60}F_{18}$ due to the absence of the lone-pair electron supply from the addend. Thus phenyldefluorination is unlikely to involve δ-substitution, especially since normal substitution by phenyl of an adjacent chlorine occurs in $C_{60}Cl_6$ give $C_{60}Ph_5Cl$, no marked colour was observed, and results of calculations (below).

Semi-empirical molecular orbital calculations of the substitution pathway

In order to rationalise the experimental observations, a series of molecular orbital calculations at the semi-empirical level have been carried out. As a first step the method was calibrated as far as possible, by calculating the energies (AM1) of all $C_{60}F_{18}$ isomers having the same point group symmetry as that of the isolated and fully characterised isomer (1,2,3,4,8,9,10,16,17,18,22,23,24,36,37,38,39,40-octadecafluoro[60]fullerene).[5,6] (For numbering see Fig. 13). This symmetry restriction reduces the many millions of possible isomers to 112, and consideration of only those that converge as closed-shell systems with retention of symmetry reduces the number to below 40, with calculated energies covering a range of over 900 kJ mol^{-1}; it is encouraging that the lowest energy calculated, by 12.5 kJ mol^{-1}, is that for the isomer isolated in experiment. This 'crown' arrangement of the addends has also been identified[16] as one of the more stable amongst the $C_{60}H_{18}$ isomers, and it is known[17] that fluorine and hydrogen addends to [60]fullerene give a good structure–energy correlation with each other. The energy of the $C_{60}F_{18}$ isomer, where the fluorine atoms are at positions 10, 16 and 40 are instead positioned at 30, 44, and 51 lies at over 150 kJ mol^{-1} above the lowest energy isomer. These are the positions where the new addends are found in **1**, *i.e.* in the δ positions.

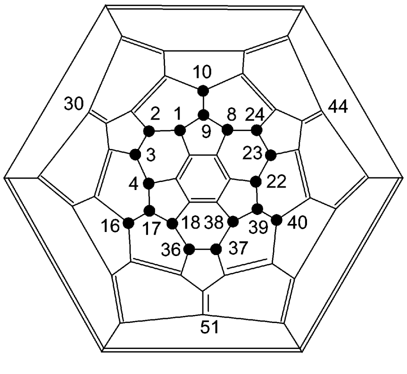


Fig. 13 Numbering for $C_{60}F_{18}$.

Table 1 The energy cost of relocating X from positions 10, 16, and 40, to positions 30, 44 and 51 in $C_{60}F_{15}X_3$[a]

Substituent X	Van der Waals radius/pm	E_{rel}/kJ mol^{-1}
H	120	171
F	135	156
Cl	180	93.3
Ph	185	103
Br	195	66.3
CH_3	200	133
I	215	56
CF_3	253	60
CCl_3	357	23.6
CBr_3	366	−21.5

[a] Defined as the difference in total energy between the two isomers.

Since the crown structure is the most stable of all the C_{3v} point-group arrangements of addends, it is at first sight surprising that nucleophilic attack does not take place by direct displacement of fluoride ion, *i.e.* substitution involving frontside attack. The stability of a particular derivative depends more on the arrangement of the addends than on their nature, as the example of fluorine and hydrogen in the previous paragraph shows. However, if the addend is sufficiently large, a new pattern emerges: a good example is the set of structures of the bromo-adducts of [60]fullerene.[18] Thus, the next question that calculation may rationalise is: which fluorine atom will be displaced from the original crown structure, and further, which position of the fullerene will be occupied by the incoming group?

The first part of this question may be answered by examination of the charges on the various fluorine atoms and the carbon atoms to which they are attached. Both AM1 and PM3 methods agree in assigning a positive charge of 0.21 to the carbon atom from which the fluoride ion is observed to be lost (10, 16, 40): a charge which is 50% higher than at the next most positively charged carbon. Likewise the ejected fluoride ion is the one bearing the largest negative charge in the original structure. Calculation thus rationalises the experimental observation concerning the identity of the displaced fluorine.

Since a steric effect is the most likely explanation of why the incoming group enters at a position δ to that from which the fluorine is lost (Scheme 2), the energies of a series of $C_{60}F_{15}X_3$ (X = substituent) have been calculated first with X in positions 10, 16, and 40, and then with X in positions 30, 44 and 51. Fifteen fluorine atoms are held in their original positions. The groups X were chosen primarily to give a wide range of steric bulk. The differences in energy between the pairs of isomers are given in Table 1 and plotted against Van der Waals radii in Fig. 14. The correlation is reasonable ($r^2 = 0.83$) and shows that substitution is preferred at the original position until the incoming group is larger than CCl_3, when attack at the δ-position becomes favoured. This result suggests that the phenyl groups in $C_{60}F_{15}Ph_3$ occupy the same positions as the departing fluorines, in support of the structural assignment made in ref. 13.

Acknowledgements

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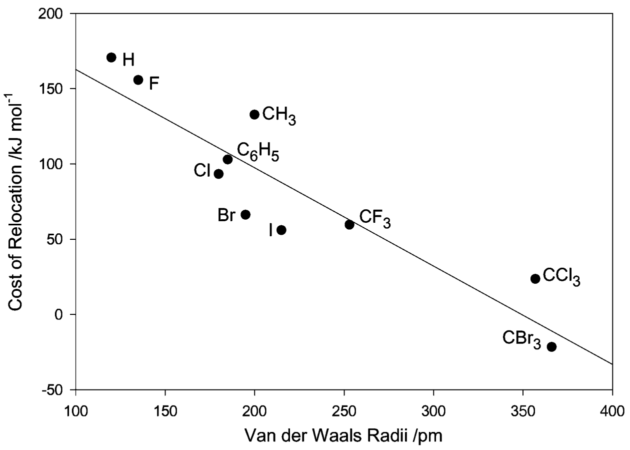

Fig. 14 Correlation between Van der Waals radii and energy cost of relocation of substituent.

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