Products from the reaction of $C_{60}F_{18}$ with sarcosine and aldehydes: the Prato reaction

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Various pyrrolidinofullerenes (both mono- and bis-addition products) have been isolated from the reaction between toluene solutions of $C_{60}F_{18}$, *N*-methyl-2-aminoethanoic acid (sarcosine) and either formaldehyde or benzaldehyde. Both mono- and bis-addition products were obtained and either partially of fully characterised. The main mono-addition product from the reaction with formaldehyde was also obtained from reactions with the other aldehydes, indicating that formaldehyde may be present in sarcosine, or generated from it through *in situ* oxidation by the fullerene. The main mono-addition product from reaction of $C_{60}F_{18}$ with toluene solutions of sarcosine and benzaldehyde was obtained also in the *absence* of benzaldehyde. This anomaly was traced to the presence of benzaldehyde (0.05%) in HPLC grade toluene, which may be increased by oxidation of toluene during the reaction conditions.

As part of a programme to investigate the utility of $C_{60}F_{18}$ for the preparation of donor–acceptor diads, we are carrying out preliminary studies of archetypal reactions that have been employed for this purpose with [60]fullerene. The [3 + 2] dipolar cycloaddition reaction between aldehydes, amino acids and [60]fullerene (Prato reaction)[1–13] has been used very extensively in particular in this connection. We have therefore embarked on a programme of investigating such reactions with $C_{60}F_{18}$ (a better electron acceptor than [60]fullerene). In the first instance we have used formaldehyde and benzaldehyde as the aldehydes in the reaction with *N*-methyl-2-aminoethanoic acid (sarcosine), and have isolated a number of mono- and bis-addition products. These cycloadditions also take place in the *absence* of added aldehyde due possibly to the presence of formaldehyde in the sarcosine, or generated from the latter by fullerene-catalysed oxidation. Similar anomalous cycloaddition takes place (to give the main product formed normally in the presence of benzaldehyde) just on heating sarcosine, toluene and [60]fullerene.

Experimental

N-Methyl-2-aminoethanoic acid (1 mg) and paraformaldehyde (1 mg), added to a solution of $C_{60}F_{18}$ (5 mg in 20 cm^3 of HPLC grade toluene) under argon, were heated under reflux for 2 h. The crude product was filtered and separated by HPLC (high pressure liquid chromatography) using a 10 × 250 mm Cosmosil Buckyprep column, eluted with toluene at a flow rate of 4.7 ml min^{-1}. Fractions were collected with retention times of 43, 29, 27, 21, 18.4, 12.9, 12.4, 10.9 and 10.2 min. The EI mass spectra of all of these fractions showed only the presence of $C_{60}F_{18}$ due to the retro reaction.

A second reaction was carried out using benzaldehyde instead of paraformaldehyde. Products were separated having retention times of 44.6, 38, 26.5, 22.0, 18.8, 16.0, 13.1, 11.7, 8.7, 6.9, and 6.5 min; the 38 min fraction was recovered $C_{60}F_{18}$, and the 22 min fraction proved to be identical to the 21 min fraction obtained with formaldehyde.

Further reactions were carried out as above but using: (i) $C_{60}F_{18}$, sarcosine and toluene; (ii) C_{60}, sarcosine and benzene; (iii) C_{60}, sarcosine, benzaldehyde and toluene; (iv) C_{60}, sarcosine, and toluene.

^{1}H NMR spectra recorded at 500 MHz, and ^{19}F NMR at 376.5 MHz.

Results and discussion

Before interpreting the individual results we consider the various bonds across which addition can occur. These are a–d on the Schlegel diagram (Fig. 1). Thus there are four mono-addition sites, and for reaction with sarcosine and formaldehyde, two products will be symmetrical (a and c addition), and two will be unsymmetrical (b and d addition). It is reasonable to assume, that reaction across bond d will be sterically unfavourable.

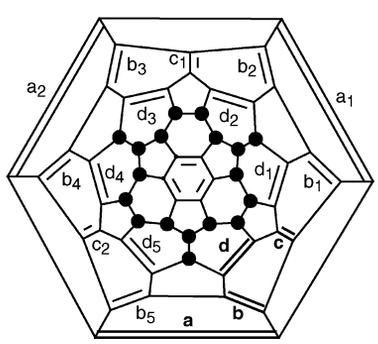

Fig. 1 Schlegel diagram for $C_{60}F_{18}$ (● = F), showing the four different bonds (a–d) across which cycloaddition can occur; equivalent bonds are a_1 etc.

Bis-addition of these reagents to [60]fullerene occurs readily and has been studied in detail.[14] For bis-addition to $C_{60}F_{18}$, symmetrical products can arise from addition across bonds (a + a_1), (a + c_1), (b + b_1), (b + b_3), (b + b_5), (c + c_1), (d + d_1), (d + d_3), and (d + d_5), whilst the unsymmetrical products arise from addition across bonds (a + b), (a + b_1), (a + b_2), (a + c), (a + d), (a + d_1), (a + d_2), (b + b_2) [≡(b + b_4)], (b + c), (b + c_1),

(b + c_2), (*b* + *d*), (*b* + d_1), (*b* + d_2), (*b* + d_3), (*b* + d_4), (*b* + d_5), (*c* + d_1), (*c* + d_2), (*c* + d_3), (*d* + d_2), (*d* + d_4). Since those involving *d* additions (italicised) can be disregarded for steric reasons, we can expect in principle up to six symmetrical and eight unsymmetrical bis-addition products.

The reaction involving formaldehyde

The products obtained and their characterisation (where possible) are as follows.

The 43 min component (1). This was a major component, and the ^{1}H NMR spectrum (Fig. 2) comprises δ 2.88 (3 H, s,) and

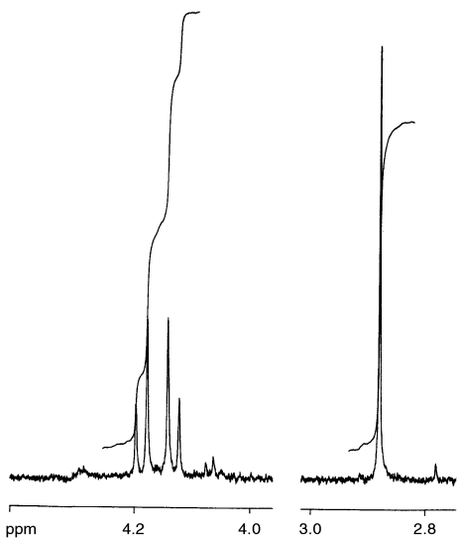

Fig. 2 ^{1}H NMR spectrum for **1**.

4.187, 4.132 (4 H, dd, *J* 9.75 Hz). The latter show that the compound has C_s symmetry but that the methylene hydrogens are non-equivalent, consistent only with a mono-adduct arising from addition across bond a. This derivative also has the longest retention time (it is characteristic of the column used that the long retention times correlate with lower addition levels), consistent with it being a monoadduct.

The ^{19}F NMR spectrum (Fig. 3) consists of ten lines at δ_F

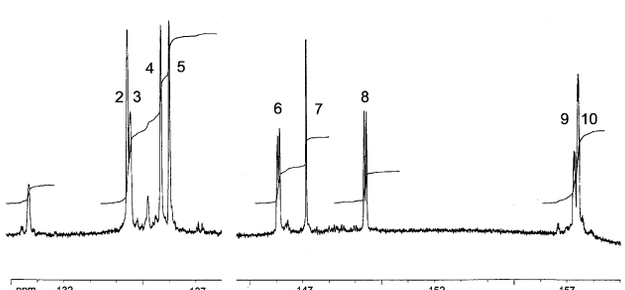

Fig. 3 ^{19}F NMR spectrum for **1**.

−130.62 (1 F, br s), −134.38 (2 F, br s), −134.50, (2 F, br s), −135.65 (2 F, br s), −135.98 (2 F, br s), −146.05 (2 F, d, *J* 30 Hz), −147.09 (2 F, s), −149.33 (2 F, d, 30 Hz), −157.23 (1 F, m, *J* 10 Hz), −157.38 (2 F, m, *J* 9 Hz), confirming the C_s symmetry. From the 2D spectrum (not shown) the connectivities were established and all of the peaks identified as shown in the Schlegel diagram (Fig. 4). The spectrum shows the usual characteristics of $C_{60}F_{18}$ derivatives,[15] so that peaks 1 and 3 (which have only one neighbouring sp^3-CF group) are downfield, whereas peaks 9 and 10 (which have three such neighbours) are the most upfield and are multiplets.

The 29 min component (2). The ^{1}H NMR spectrum comprised

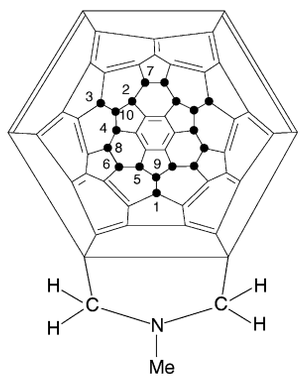

Fig. 4 Schlegel diagram for **1** (● = F) identifying the fluorine peaks.

eight doublets, all *J ca.* 9.2 Hz, centred at *δ* 4.067, 3.512; 3.853, 3.765; 3.690, 2.792; 3.675, 3.237 (the coupling of the pairs was ascertained by NOE), and two methyl singlets at *δ* 2.765 and 2.558. There was insufficient sample to permit acquisition of a ^{19}F NMR spectrum.

This compound is evidently an asymmetrical bis-adduct. The separations in chemical shifts for coupled methylene peaks (0.555, 0.088, 0.898, 0.438 ppm, respectively), together with the far upfield location of one of the doublets, suggests considerable asymmetry; this could result from a methylene hydrogen being close to a fluorine atom, or adjacency of the addends. The most likely combination seems to be addition across both bonds a and b.

The 27 min component (3). The ^{1}H NMR spectrum consists of eight doublets, all *ca. J* 9.4 Hz, centred at *δ* 3.872, 3.484; 3.770, 3.464; 3.735, 3.546; 3.555, 3.484, (the coupling of the pairs was ascertained from a 2D spectrum), and two methyl singlets at *δ* 2.671 and 2.613. There was insufficient material for a ^{19}F NMR spectrum.

This compound is a second unsymmetrical bis-adduct, but the differences in chemical shifts for coupled methylene hydrogens (0.388, 0.306, 0.189, 0.071 ppm) is much smaller than for compound **2**. This implies involvement of one of the following combinations (a + b_1), (a + b_2), (b + b_2).

The 21 min component (4). The ^{1}H NMR spectrum (Fig. 5)

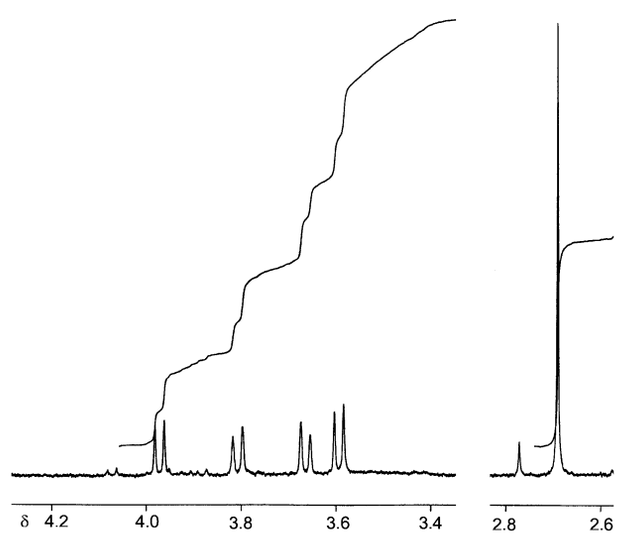

Fig. 5 ^{1}H NMR spectrum for **4**.

comprised four doublets, centred at *δ* 3.97 (1 H, *J* 9.58 Hz), 3.59 (1 H, *J* 9.64 Hz), 3.80 (1 H, *J* 9.89 Hz), 3.66 (1 H, *J* 9.90 Hz) and a singlet at 2.691 (3 H); other peaks in the methyl region were shown by T_1 inversion recovery not to be attached to a fullerene

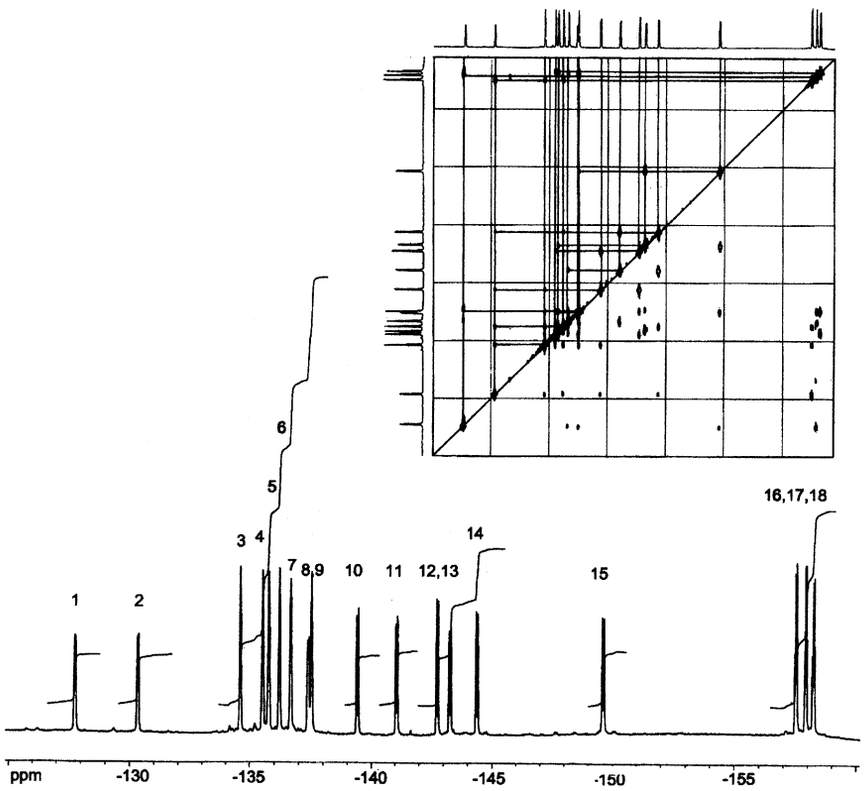

Fig. 6 ^{19}F NMR spectrum for **4**; inset shows the 2D spectrum with connectivities.

molecule. The compound is an unsymmetrical mono-adduct and the unequal chemical shifts of the coupled methylene hydrogens (0.38 and 0.14 ppm) show that one methylene must be nearer to fluorines than the other. Compound **4** therefore involves addition across bond b.

The asymmetry is confirmed by the ^{19}F NMR spectrum (Fig. 6) which comprises eighteen lines (all 1 F intensity) at δ_F −127.8, −130.35, −134.6, −135.55, −135.8, −136.1, −136.5, −137.45, −137.5, −139.4, −141.05, −142.7, −143.25, −144.35, −149.6, −157.2, −157.95, −138.25. The connectivities were established from the 2D spectrum (inset to Fig. 6) and all of the peaks identified as shown in the Schlegel diagram (Fig. 7). The three upfield peaks are those attached to carbon having three sp^3-CF neighbours.

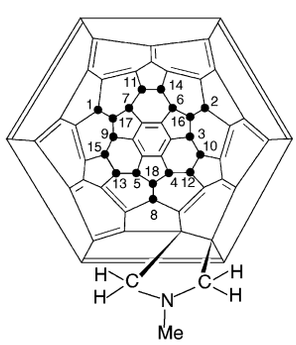

Fig. 7 Schlegel diagram for 4 (● = F) identifying the fluorine peaks.

The 18.4 min component (5,6). There was sufficient material of this component to obtain a ^{1}H NMR spectrum only. This showed it to be a mixture (*ca.* 1 : 1) of two bis-adducts, one of C_s symmetry, the other unsymmetrical, confirmed by four methyl resonances (each 3 H) at δ 2.864, 2.739, 2.601, 2.579.

Resonances for the methylene groups of the symmetrical component **5** consist of two overlapping doublets at δ 4.129 and 4.149 (each 2 H, *J* 15.6 Hz) and two singlets at δ 3.599 and 3.530 (each 2 H). This can only be obtained from addition across bond a and bond c_1 on the opposite side of the fluorinated crown. For the bond c_1 addend the hydrogens in each methylene pair are equivalent, so producing singlets. However, one methylene group is much nearer to the fluorinated crown than the other, giving rise to the significant chemical shift of 0.069 ppm. The hydrogens for a given methylene group of the bond a addend are non-equivalent, and so give rise to doublets. Since the addend is further from the fluorines, here there is only a small chemical shift difference of 0.02 ppm. Overall, this result shows that steric hindrance is insufficient to preclude addition across bond c.

The methylene peaks for the unsymmetrical component **6** appear as eight doublets (all 1 H, and *ca.* 9 Hz), centred at δ 4.04, 3.57; 3.935, 3.57 (two doublets coincide at 3.57 ppm); 3.75, 3.375; 3.55, 3.12. The couplings were determined by NOE. The structure cannot be deduced since there are eight possibilities, but given the identical retention time to that of the symmetrical component, an a + c combination may be involved.

The 12.9 min component (7). This is a symmetrical bis-adduct, and almost certainly arises from an a + a′ combination. In the ^{1}H NMR spectrum (Fig. 8), there are four methylene doublets at δ 3.825 (2 H, d, *J* 10.1 Hz), 3.815 (2 H, d, *J* 9.4 Hz), 3.70 (2 H, d, *J* 10.0 Hz), 3.475 (2 H, d *J* 9.5 Hz), and a methyl singlet at 2.66 (6 H, s). These peaks are all slightly upfield compared to those for the corresponding monoadduct (**1**), as is usual for a higher addition level to a fullerene, because of the reduction in the number of sp^2 carbons.

More compelling evidence for the similarities in structures of **1** and **7** is provided by the ^{19} F NMR spectrum for **7** (Fig. 9), which shows a strong resemblance to that obtained for **1**, and consists of ten lines at δ_F −129.72 (2 F), −135.66 (2 F), −136.78 (2 F), −136.98 (2 F), −141.30 (1 F), −143.11 (2 F, d, *J* 28 Hz), −148.45 (2 F, d, *J* 28 Hz), −158.35 (2 F, m), −158.73 (1 F, m). The 2D spectrum was too weak to determine all of the connectivities but they can be deduced (Fig. 10) from intensities, multiplicities, and positions in the 1D spectrum.

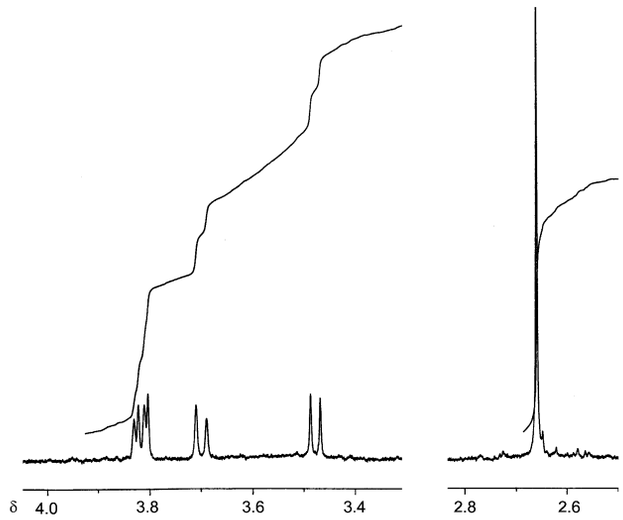

Fig. 8 ^{1}H NMR spectrum for **7**.

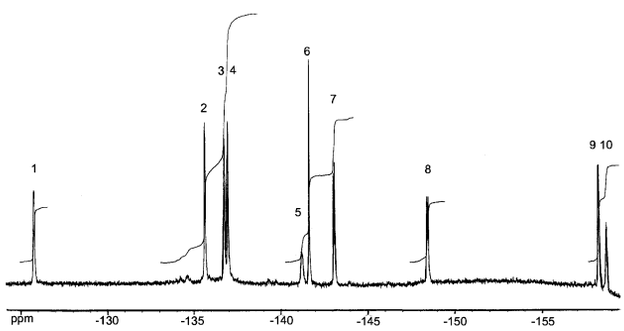

Fig. 9 ^{19}F NMR spectrum for **7**.

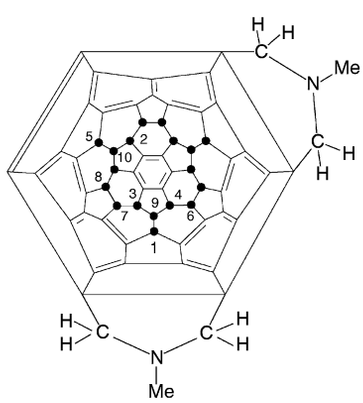

Fig. 10 Schlegel diagram for 7 (● = F) identifying the fluorine peaks.

The 12.4 min component (8). There was insufficient of this fraction to purify completely so that there were additional minor peaks in the ^{1}H NMR spectrum. It comprises four doublets at δ 3.90, 3.87, 3.42 and 3.30 (all 1 H), together with a singlet (3 H) at 2.65. This must therefore be a symmetrical bis-adduct and in the light of the other components may be assigned as arising from either the (b + b_1), (b + b_3), or (b + b_5) combinations.

The 10.9 min component (9). This is an unsymmetrical bis-adduct. The ^{1}H NMR spectrum (Fig. 11) consists of eight doublets. One set (all *J* 9.4 Hz) centred at δ 3.925, 3.572; 3.854, 3.733 is coupled to a methyl singlet at 2.69, the other set (all *J* 10.1 Hz) centred at 3.773, 3.482; 3.647, 3.579 is coupled to a methyl singlet at 2.62; the pair couplings were ascertained from a 2D spectrum. The difference spread in chemical shifts of the methylene hydrogens (0.353, 0.121 compared to 0.291, 0.068) suggests different locations with respect to the fluorinated crown. This makes it unlikely that this compound is comprised

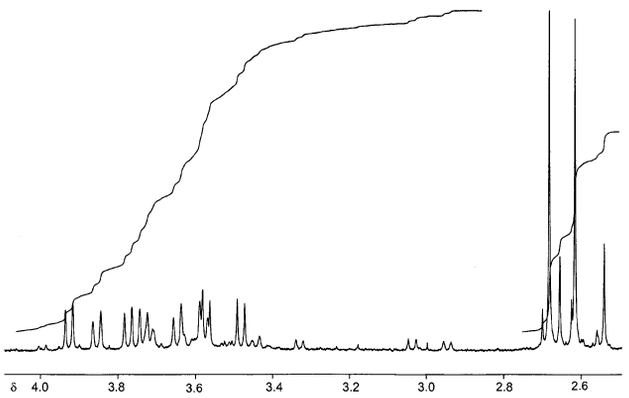

Fig. 11 ^{1}H NMR spectrum for **9**.

of two *b* motifs. Moreover the spectrum is very similar (location and pattern of the chemical shifts) to that of the 27 min component, and arguments presented below indicate that both arise from combinations of *a,b* motifs.

The asymmetry is confirmed by the 18-line ^{19}F NMR spectrum (Fig. 12, all 1 F intensity lines and singlets except where indicated) at δ_F −127.02, −133.88, −134.29, −135.05, −135.77, −136.51 (2 F), −136.71, −137.40 (2 F), −141.64 (d, *J* 22.5 Hz), −141.21, −143.50 (d, *J* 22.5 Hz), −148.93 (d, *J* 26.3 Hz), −151.55 (d, *J* 26.3 Hz), −157.73 (2 F, m), −158.53 (m). There was insufficient material for a 2D spectrum, so the peaks cannot be assigned. However, the three upfield fluorines are those attached to carbons surrounded by three sp^3 CF groups, and one will be adjacent to the most downfield peak. The two pairs of doublets, being relatively upfield will be due to four of the six fluorines that are more remote from the central benzenoid ring.

Both spectra showed the presence of a minor component, which was not identified.

The 10.2 min component (10). This is an unsymmetrical bis-adduct. It shows four coupled pairs of methylene doublets (all *J* 10 Hz) at δ 4.358, 2.648; 4.080, 3.182; 3.904, 2.455; 3.527, 3.144, and two methyl peaks at 2.609, 2.583. The methylene resonances show the widest chemical shifts between adjacent hydrogens than for any other derivative (1.71, 0.898, 1.449, 0.383 ppm), indicating considerable asymmetry consistent with this component being comprised of a b,c motif combination.

The ^{19}F NMR spectrum was less good than for the other components because of the small sample size, but showed 17 lines (one being of 2 F intensity due to coincidence), at δ_F −124.04, −133.67, −134.10, −135.06, −135.52 (2 F), −136.08, −136.41, −138.67, −138.99, −139.57, −141.36 (br s), −143.23 (br s), −149.71 (2 F, d, *J* 24 Hz), −154.20 (2 F, d, *J* 24 Hz), −156.63, −157.67, −158.54. Again there are three upfield peaks due to fluorines attached to carbons with three sp^3 neighbours, one of the three 'outer' fluorines gives the peak at −124 ppm (the others cannot be assigned without a 2D spectrum). The four broad singlet and doublet peaks can be assigned to four of the six fluorines that are most remote from the central aromatic ring (see Fig. 1).

Summary of the reaction with formaldehyde

Of the three mono-adducts that can be formed reasonably free of steric hindrance, we have characterised the products arising from addition across bonds a and b, the former being in the largest yield since it is most remote from the fluorines. Given the preponderance of addition across the a bond, the most probable bis-adducts should involve the combinations (a + a_1), (a + b), (a + b_1), (a + b_2), (a + c), (a + c_1). Compounds **7** and **5** involve the (a + a_1) and (a + c_1) combinations, respectively. Compounds **2**, **3**, and **9** are believed to involve the (a + b),

(a + b_1), and (a + b_2) combinations, with **2** being most probably the former because of the unusual spread of the chemical shifts for the methylene group. Unsymmetrical compound **10** probably involves a combination of (b + c) motifs the adjacency of addition being indicated by the very wide spread of methylene chemical shifts, as for **2** and symmetrical compound **8** must be one of the three possibilities that can result from b,b motif combinations.

Compared with reaction on [60]fullerene itself, the presence of the fluorines results in a substantially greater number of possible isomeric products, most of which we have isolated and characterised. In principle it could be possible, by working with larger quantities, to isolate and characterise further components. However, our main objective was to show that the reaction proceeds normally and without loss of fluorine, and further work will now be directed towards minimising bis-addition in reactions with better donor groups. The size of these is likely also to limit the reaction largely to mono-addition across the a bond.

The reaction involving benzaldehyde

This can in principle give many more products than the reaction with formaldehyde. For example, mono-addition across either of bonds a or c can give two products in each case, whilst mono-addition across either of bonds b or d can give four. Steric hindrance in the case of c and d addition would probably reduce these to two and one, respectively, so that the total mono-addition products could number eight. Of the ten fractions obtained (apart from recovered $C_{60}F_{18}$) those with retention times of 44.6, 26.5, 18.8, and 16.0 min were very minor and were not analysed further.

22.0 min component. The HPLC retention time for this derivative was similar to that obtained for compound **4** and *gave an identical NMR spectrum*. Thus formaldehyde must be present in the reaction mixture and can in principle have come from either the toluene or sarcosine. This is discussed further below.

13.1 min component (11,12). This consists of a mixture of two mono-adducts in *ca.* 4 : 1 ratio. The ^{1}H NMR spectrum for the major isomer gave δ 4.49 (1 H, d, *J* 9.5 Hz, CH_2), 4.09 (1 H, s, CHPh), 3.42 (1 H, d, *J* 9.6 Hz, CH_2), 2.34 (3 H, s, N-Me), and for the minor isomer, 4.76 (1 H, d, *J* 9.6 Hz, CH_2), 4.73 (1 H, s, CHPh), 4.05(1 H, d, *J* 9.6 Hz, CH_2), 2.695 (3 H, s, N–Me); the combined multiplets for the phenyl groups lie between δ 7.06 and 7.61.

11.7 min component (12,13). This consists of a mixture of two mono-adducts in a 65 : 35 ratio. The ^{1}H NMR spectrum for the major isomer gave δ 4.87 (1 H, d, *J* 9.5 Hz, CH_2), 4.49 (1 H, s, CHPh), 3.84 (1 H, d, *J* 9.6 Hz, CH_2), 2.72 (3 H, s, N–Me), and for the minor isomer, 4.76 (1 H, d, *J* 9.6 Hz, CH_2), 4.73 (1 H, s, CHPh), 4.05(1 H, d, *J* 9.6 Hz, CH_2), 2.695 (3 H, s, N–Me); the combined multiplets for the phenyl groups lie between δ 7.06 and 7.61.

The data show that the minor isomer in each of the 13 and 11.7 min components was the same compound. This could in principle be separated by further HPLC using solvent mixtures but this was unnecessary for our purposes. No CH_2 group in any of the three isomers showed any secondary coupling to fluorine in contrast to the other derivatives described below. This shows that the addends in them are remote from fluorine indicating addition across bond a and bond b.

8.7 min component (14,15). This comprised a mixture of the 6.9 min component (see below) and an unidentified compound. This latter gave two overlapping 'quartets' at δ 4.23 and 4.22 (*J* 10.5 Hz) but which must be four overlapping doublets since there are no associated triplets, and two methyl groups at δ 2.49 and 2.45.

6.9 min component (16). The ^{1}H NMR spectrum for this consists of two sets of coupled peaks: (i) at δ 4.57 (dd, 1 H, *J* 9.8 and 2 Hz, CH_2), 4.32 (s, CHPh), 3.45 (d, 1 H, *J* 9.9 and 1.1 Hz, CH_2), and 2.54 (s, N–Me); (ii) δ 4.42 (dd, 1 H, *J* 9.8 and 2 Hz, CH_2), 4.03 (s, CHPh), 3.41 (d, 1 H, *J* 10.3 Hz, CH_2), and 2.51 (s, N–Me). The product is then either a 1 : 1 mixture of two mono-adducts (statistically improbable) or a bis adduct, the shorter retention time being consistent with the latter. Note that *three* of the methylene hydrogens are coupled with fluorines which confirms (as does the number of NMR lines) that the product is asymmetric. A combination of two b motifs or a b and c motif seems probable.

6.2 min component (17). The ^{1}H NMR spectrum is very simple and consists of four sets of lines at δ 4.24 (d, 1 H, *J* 10 Hz, CH_2), 4.18 (s, CHPh), 3.06 (dd, 1 H, *J* 10.2 and 1.3 Hz), 2.49 (s, 3 H, N–Me). The simplicity of the spectrum made it possible to identify the phenyl resonances at δ 7.56 (d, 2 H, *J* 7.4 Hz, *ortho*), 7.50 (t, 2 H, *J* 7.4 Hz, *meta*), 7.44 (d, 1 H, *J* 7.3 Hz, *para*).

This compound can be either: (i) a mono-addition product involving addition across bond c (the methylene hydrogen adjacent to phenyl being forced towards the fluorines resulting in the observed coupling); (ii) a bis-addition product involving

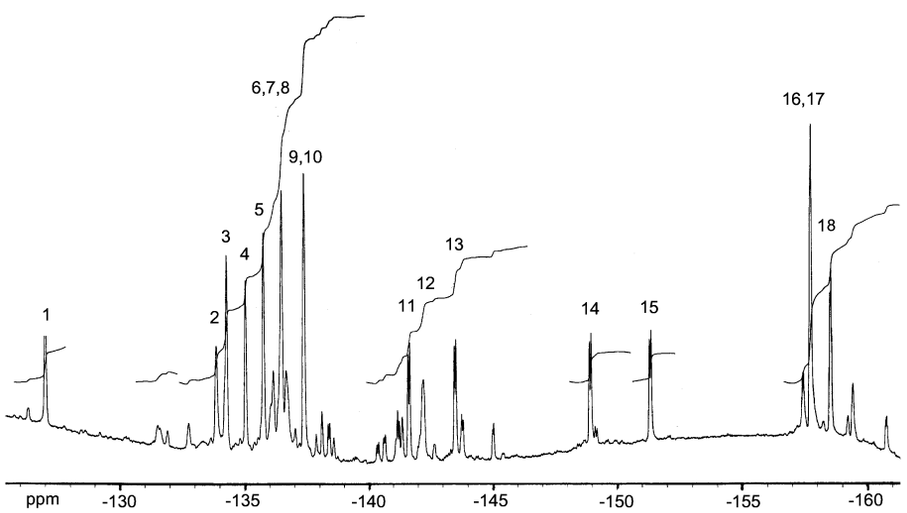

Fig. 12 ^{19}F NMR spectrum for **9**.

addition across two bonds b. One hydrogen will be nearer to fluorine and so will show the observed secondary coupling. Bis-addition across two bonds a can probably be discounted because neither of the methylene hydrogens should be very near to fluorines. The short retention time would be consistent with a bis-addition product.

Summary of the reaction with benzaldehyde

Six 'major' and four minor reaction products were obtained. The former consisted of seven components, one of which is a derivative that was obtained with formaldehyde, three were monoadducts, one could not be resolved, and the remaining two were very probably bis adducts. The amounts of each were insufficient for obtaining ^{19}F NMR spectra, which would facilitate analysis, but this work could be undertaken when larger amounts of $C_{60}F_{18}$ become available. However, the main purpose of the work at this stage was to verify that the reaction proceeds normally as a preliminary to using more complex addends.

The reaction *without* added aldehyde

The product from formaldehyde. The reaction of sarcosine and $C_{60}F_{18}$ in toluene gave products having retention times of 6.5, 7.0, 13.2, 22.5 and 45 min together with recovered $C_{60}F_{18}$. The presence of the readily identified 22.6 min component and the production of this from reaction with both aldehydes above (and also from ferrocenealdehyde in preliminary experiments), suggested that either toluene or sarcosine is oxidised to formaldehyde by the fullerene or that formaldehyde is present in the sarcosine. The oxidising property of fullerenes is best known from their ability to be readily hydrogenated under a variety of conditions;[16] [60]fullerene also readily oxidises carbon disulfide to sulfur.[17]

To investigate this aspect further, a reaction was carried out with [60]fullerene itself and sarcosine. The normal addition product was obtained having an HPLC retention time of 6 min and giving a parent ion at 777 amu in the mass spectrum. The ^1H NMR spectrum showed two singlets at δ 4.35 (CH_2) and 2.95 (CH_3) identical to the literature value for the normal product obtained from reaction in the presence of formaldehyde.[1a] A minor component was also present giving δ 4.75 (d, 2 H, *J* 9.4 Hz, CH_2), 4.20 (d, 1 H, *J* 9.4 Hz), 2.30 (s, 3 H, N–Me), and presumed to be due to bis-addititon. Thus formaldehyde is present in the reaction mixture, and to check if the toluene is responsible a further reaction was carried out using sarcosine, benzene and $C_{60}F_{18}$. Compound **4** was again obtained showing that the formaldehyde is not produced from toluene, so must be present in sarcosine originally, or produced by *in situ* oxidation by the fullerene.

The product from benzaldehyde. [60]Fullerene was reacted with sarcosine and benzaldehyde to give a product of 4.4 min retention time showing δ 5.01 (d, 1 H, *J* 9.2 Hz, CH_2), 4.95 (s, CHPh), 4.28 (d, 1 H, *J* 9.5 Hz), 2.83 (s, 3 H, N–Me), due to the normal monoadduct. The reaction was repeated without benzaldehyde and an identical product (NMR, HPLC) was obtained. This implied that benzaldehyde is also produced from toluene by fullerene-catalysed oxidation, and indeed analysis of a solution of HPLC grade toluene after heating with [60]fullerene under reflux for 3 h revealed that 0.05% of benzaldehyde was present (^1H NMR peak at δ 10.05). However, similar analysis of stock toluene showed it to contain a similar quantity of benzaldehyde, whereas a redistilled sample contained less than 0.01%. Thus whilst these experiments prove clearly the presence of benzaldehyde in toluene, it is not possible to rule out additional formation through oxidation during the reaction.

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