Some 4-fluorophenyl derivatives of [60]fullerene; spontaneous oxidation and oxide-induced fragmentation to C_{58}

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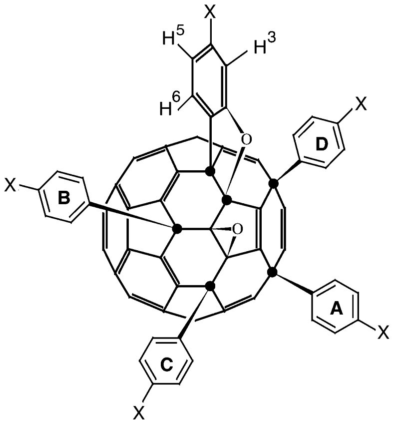
The main products from the reaction of $C_{60}Cl_6$ with fluorobenzene–$FeCl_3$ are $C_{60}(4\text{-}FC_6H_4)_5Cl$, 1,4-$(4\text{-}FC_6H_4)_2C_{60}$ (both of C_s symmetry) and asymmetric $C_{60}(4\text{-}FC_6H_4)_4$, accompanied by a small amount of $C_{60}(4\text{-}FC_6H_4)_4H_2$. Exposure of the product to light and air before processing gives other components, including $C_{60}(4\text{-}FC_6H_4)_4$-$(4\text{-}FC_6H_3)O_2$, $C_{60}(4\text{-}FC_6H_4)_5OH$, and $C_{60}(4\text{-}FC_6H_4)_6$ (each of C_s symmetry), $C_{60}(4\text{-}FC_6H_4)_4O_2$, $C_{60}(4\text{-}FC_6H_4)_6O_2$, $C_{60}(4\text{-}FC_6H_4)_7H$, and $C_{60}(4\text{-}FC_6H_4)_5H(OH)_2/C_{60}(4\text{-}FC_6H_4)_5H$. The formation of the oxides from air-exposed reaction products emphasises the need for atmospheric protection of fullerene derivatives. Fragmentation of the oxides during EI mass spectrometry occurs readily to give C_{58} and derivatives which must contain adjacent pentagons, stabilisation being derived from the presence of a heptagon.

Introduction

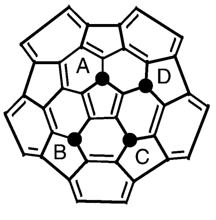
Previously we showed that reaction of $C_{60}Cl_6$ with benzene–$FeCl_3$ produced a mixture of $C_{60}Ph_5Cl$,[1] together with unsymmetrical $C_{60}Ph_4$, and 1,4-$C_{60}Ph_2$ as by-products.[2] Polyaryl- and polyaralkyl-[60]fullerenes have also been made by reaction of [60]fullerene with either Grignard reagents/$CuBr{\cdot}Me_2S$[3] or MR compounds (M = Li, K),[4] respectively. Many other arylated derivatives, including hydrogenated and oxygenated ones, are obtained from the reaction of [60]fullerene with benzene–bromine–$FeCl_3$.[5] The oxygenated species may be produced not only by nucleophilic replacement of halogen followed by Hhal elimination, but also from autoxidation, which fullerenes undergo readily. This combination has been proposed to account for the conversion, on standing in air, of either $C_{60}Ph_5H$ or $C_{60}Ph_5Cl$ into $C_{60}Ph_4C_6H_4O_2$ (**1a**).[6] Allylic oxidation of the (cage)C–H bond in $C_{60}Ph_5H$ to OH, and nucleophilic replacement of Cl in $C_{60}Ph_5Cl$ by OH, would in each case give the fullerenol, which is presumed to undergo oxidative ring closure, followed by (or in concert with) spontaneous epoxide formation across one of the double bonds in the central pentagon. The tendency for this pentagon to participate in epoxide formation has been confirmed in an X-ray study of analogous pentamethyl derivatives.[7]



1a, X = H; **1b**, X = F

The lack of symmetry in the tetraphenyl derivative prevented unambiguous assignment of its structure, which we conjectured to have the motif shown in **2** (● = Ph), with Cl_2 being lost from the starting material *via* a 1,4-elimination. Our conjecture assumed that no rearrangement occurred. However, X-ray characterisation of electrochemically formed asymmetric $C_{60}(benzyl)_4$ has shown it to have the motif in **3** (● = benzyl).[8] This has thrown new light on the addition patterns in [60]fullerene and it is necessary to consider therefore whether the correct structure for $C_{60}Ph_4$ might be **3** (● = Ph). This could be obtained by 1,4-loss of chlorine from $C_{60}Cl_6$ coupled with a 1,3-shift either of one of the remaining chlorines (or of one of the phenyl groups after substitution), or possibly by phenyl addition–chlorine elimination. Structure **3** contains half of the motif found in both $C_{60}Br_8$[9] and $C_{60}Me_8$[10] (**5**), the existence of both of which implies that they derive from a fundamental underlying stability feature; **3** has only two destabilising[11] double bonds in pentagons compared to four in **2**.

We discounted structure **4** (● = Ph) because of the observed free rotation of the phenyl groups, since in $C_{70}Ph_{10}$ the adjacent



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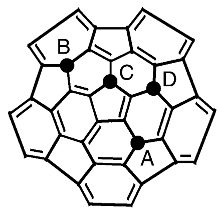

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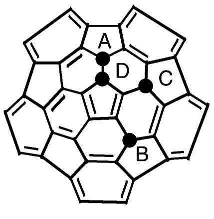

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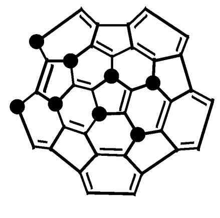

5, ● = Br, Me

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Table 1 HPLC retention times (t_R) and mass spectrometry data for identified products

t_R/min	Batch	Species	m/z[a]
9.1	III	$C_{60}(4\text{-}FC_6H_4)_6$; $C_{60}(4\text{-}FC_6H_4)_6O_2$ (minor species)	1291 (1323)
10.2	III	$C_{60}(4\text{-}FC_6H_4)_7H$	1387
11.5	II	$C_{60}(4\text{-}FC_6H_4)_6O_2$	1323
12.3	I	$C_{60}(4\text{-}FC_6H_4)_6$	1291
12.4	III	$C_{60}(4\text{-}FC_6H_4)_5H$; $C_{60}(4\text{-}FC_6H_4)_5H(OH)_2$ (minor species)	1196 (1230)
13.7	V	$C_{60}(4\text{-}FC_6H_4)_5Cl$[b,c]	
14.2	V	$C_{60}(4\text{-}FC_6H_4)_4$[c]	1100
17.6	V	$C_{60}(4\text{-}FC_6H_4)_2$[c]	910
19.0	I	$C_{60}(4\text{-}FC_6H_4)_4(4\text{-}FC_6H_3)O_2$	1226
19.4	IV	$C_{60}(4\text{-}FC_6H_4)_4O_2$	1132
20.4	II	$C_{60}(4\text{-}FC_6H_4)_5OH$	1213
52.8	V	$C_{60}(4\text{-}FC_6H_4)_4H_2$	1102

[a] Values for minor peaks are in parentheses. [b] Characterised previously.[12] [c] Separated from each batch by silica-gel chromatography, and prior to HPLC.

phenyl groups do not rotate freely. However, we now find that in fully characterised $C_{60}(4\text{-}FC_6H_4)_6$ the adjacent aryl groups *do* rotate freely even at very low temperature (see below). Structure **4** must therefore be reconsidered (and indeed gives the best fit to the NOE data).

In order to obtain further structural information we have examined the reaction of $C_{60}Cl_6$ with fluorobenzene–$FeCl_3$,[12] since this not only provides additional detail through the use of ^{19}F NMR spectroscopy, but the blocking of the *para* position on the aryl rings simplifies analysis of the ^1H NMR spectrum. The major initial product is $C_{60}(4\text{-}FC_6H_4)_5Cl$, and as well as the di- and tetra-aryl by-products, we have identified a number of other arylated derivatives, some of which evidently are produced by spontaneous oxidation. Moreover, different products are obtained from different batches of the same material, depending upon the length of exposure to light and air.

Experimental

Five batches of $C_{60}(4\text{-}FC_6H_4)_5Cl$, designated I-V, were prepared from the reaction of $C_{60}Cl_6$ with fluorobenzene–$FeCl_3$ as described previously.[12] After separation of $C_{60}(4\text{-}FC_6H_4)_4$ and $C_{60}(4\text{-}FC_6H_4)_2$ by silica-gel chromatography, they were processed in different ways as follows: *Batch I* – This sample had been prepared three years earlier[12] and had been stored in air. *Batches II and III* – These were allowed to stand for 3 months after preparation. *Batch IV* – This was exposed to strong sunlight for 10 days. *Batch V* – This was processed immediately after preparation.

Each batch was filtered and separated by HPLC using a 250 × 4.6 mm Cosmosil Buckyprep column, with (1 : 1) toluene–hexane elution at a flow rate of 1 ml min^{-1}. The retention times for the various derivatives are given in Table 1.

EI mass spectra were run at 70 eV; ^1H and ^{13}C NMR were run on a 500 MHz instrument ($CDCl_3$ lock).

Results and discussion

Two general features are evident concerning the HPLC retention times (Table 1). Firstly, these increase the fewer addends that are present (*i.e.*, 12.3, 14.2 and 17.6 min for $C_{60}(4\text{-}FC_6H_4)_n$, where $n = 6$, 4, 2, respectively). Secondly, dihydrogenated and dioxygenated derivatives have longer retention times than their aryl precursors (*i.e.*, 19.4 and 52.8 min for $C_{60}(4\text{-}FC_6H_4)_4O_2$ and $C_{60}(4\text{-}FC_6H_4)_4H_2$, respectively). This parallels previous observations,[5] though the marked difference between the times for the hydrogenated and oxygenated species compared to $C_{60}Ph_4O_2$ *vs.* $C_{60}Ph_4H_2$ (46.8 and 40.5 min, respectively) may reflect polar interactions involving the exposed fluorine atoms. The isolated components are as follows:

$C_{60}(4\text{-}FC_6H_4)_5Cl$

The characterisation of this compound has been described previously.[5]

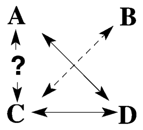
1,4-$(4\text{-}FC_6H_4)_2C_{60}$

This structure was confirmed by ^1H NMR which showed two multiplets, centred at δ 8.13 and 7.27, due to the hydrogens nearest to the cage and fluorine, respectively, showing that the compound has C_s symmetry.

Unsymmetrical $C_{60}(4\text{-}FC_6H_4)_4$

The presence of the *para* fluorine atom in each aryl ring makes interpretation of the ^1H NMR spectrum somewhat easier than that for $C_{60}Ph_4$.[2] It consists of eight pairs of equal intensity multiplets, centred at δ 8.038, 8.028; 7.695, 7.685; 7.534, 7.524; 7.226, 7.216 (aryl-H, *ortho* to the cage) and 7.269, 7.253; 7.038, 7.022; 6.964, 6.948; 6.763, 6.747 (aryl-H, *meta* to the cage); these peak pairs are for aryl groups A–D respectively in each series (ascertained by 2D COSY analysis). The spectrum run at 193 K showed that no restriction of rotation occurs, implying that no aryl groups are adjacent to each other; the same conclusion was reached from the data for the tetraphenyl compound.[2]

The simpler ^1H NMR spectrum (no overlapping peaks) allows a more positive NOE analysis. The phenyl analogue showed coupling between the *ortho* hydrogens of ring A with D, D with C and a weaker coupling between C and B (**6**). Coupling between A and C could not be determined because of peak overlap. The data for the fluoro compound **7** confirm the A→D and D→C couplings and show a substantial A→C coupling, but the B→C coupling is not seen here. Although positive NOE couplings indicate neighbouring groups, negative couplings do not necessarily mean that groups are remote, *e.g.*, the absence of coupling between some *p*-methyl groups in a fully characterised bis epoxide fullerenol.[7]



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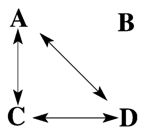

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The ^{19}F NMR spectrum shows four equal-intensity multiplets centred at δ_F −108.05, −108.42, −108.78 and −108.81 (the latter pair overlap), but assignment to a particular aryl ring is not possible.

The tetra-aryl compounds are isostructural. This is shown by the following:

(i) The chemical shifts of the aryl hydrogens *ortho* to the cage for the *p*-fluoro compound are all within an average of 0.05 ppm of the values for the corresponding $C_{60}Ph_4$.

(ii) The ^{13}C NMR chemical shifts for the four sp^3 peaks at δ_C 61.49, 59.62, 59.43 and 58.09 are upfield of those for the phenyl compound (62.26, 60.28, 60.02, 58.69), by an almost constant value of 0.65 ppm.

(iii) The *ipso* sp^2 peaks (adjacent to the cage) at δ_C 138.94, 138.67, 138.65, and 138.36 are downfield of those for the phenyl compound (138.53, 138.27, 138.25 and 138.02) by an almost constant value of 0.4 ppm.

(iv) The fifty-six cage peaks in the sp^2 region are at δ_C 159.01, 155.78, 155.75, 155.05, 154.05, 152.72, 152.40, 152.01, 150.64, 150.27, 149.16, 148.92 (2 C), 148.34, 148.25, 148.17, 148.11, 148.07, 147.97, 147.95, 147.72, 147.56 (2 C), 147.44, 147.24, 147.00, 146.65, 146.55, 146.34, 146.15, 146.08, 146.04, 145.84, 145.76, 145.12, 144.95 (2 C), 144.88, 144.81, 144.55, 144.18 (3 C), 143.89, 143.84, 143.67, 143.66 (2 C), 143.62, 143.50, 142.46 (2 C), 143.28, 143.24, 143.03, 142.87; the eight aryl (C–H) sp^2 peaks are at 129.33, 129.28, 129.19, 129.05, 128.47 and 128.42 (two coincident).

As in the case of $C_{60}Ph_4$, one sp^2-carbon peak lies significantly downfield from the rest; between δ_C 155.8 and 143.3 the peaks for the *p*-fluorophenyl compound are downfield from those of the phenyl compound by an average of 0.58 ppm. This value is exceeded significantly only for the four most upfield peaks, which will be for carbons between the addends and thus most affected by the effects of the fluorine atoms.

The structure of unsymmetrical $C_{60}Ar_4$. Features of the NOE analysis are:

1. The mutual coupling between peaks A, C, and D shows that they *must* be in a triangular relationship. This is consistent with any of structures **2**, **3** or **4**.
2. The lack of coupling between either peaks A and B, or D and B in each series suggests that the corresponding aryl groups are located well apart.
3. For **2** there should be similar NOEs between A, and either B or C since they are equidistant from A. However no enhancement between A and B was observed in either series of compounds; this tends to rule out **2**.

This leaves structures **3** and **4**. A corresponding 1,3-shift of addend (or precursor) required to produce **3** has been identified in the formation of the products of the reaction of $C_{60}Cl_6$ with MeLi,[13] and aryl group migration occurs in the formation of unsymmetrical $C_{60}Ph_6$ from the reaction between $C_{60}Cl_6$ and benzene–$FeCl_3$.[14] However, structure **4** has two double bonds in the central pentagon, which favours it as a precursor for formation of the bis epoxide (see below).

$C_{60}(4\text{-}FC_6H_4)_4H_2$

This structure is confirmed by the −2 amu fragmentation ion at 1100 amu in the mass spectrum (Fig. 1), followed by regular loss of the aryl fragments of 95 amu. Insufficient material was available to allow further characterisation, but the hydrogens probably occupy two of the sites of the original $C_{60}Cl_6$. Given that the loss of chlorine which accompanies the substitution must reasonably involve a radical process, then the capture of hydrogen from the solvent before bond reorganisation can occur is most probably the origin of the hydrogenated species; a similar mechanism would account for formation of other hydrogenated phenylfullerenes that we have detected previously.[5]

$C_{60}(4\text{-}FC_6H_4)_4O_2$

This was the major product (1132 amu, Fig. 2) obtained by stirring $C_{60}(4\text{-}FC_6H_4)_5Cl$, in window sunlight over 10 days. The analogous $C_{60}(C_6H_5)_4O_2$ was one product obtained from heating [60]fullerene with benzene, bromine and $FeCl_3$ followed by exposure to light,[5] and had a retention time of 46.8 min (elution by toluene–hexane at 0.25 ml min^{-1}) ≡ 11.7 min under the present conditions, showing the *para* fluorines to increase the retention time.

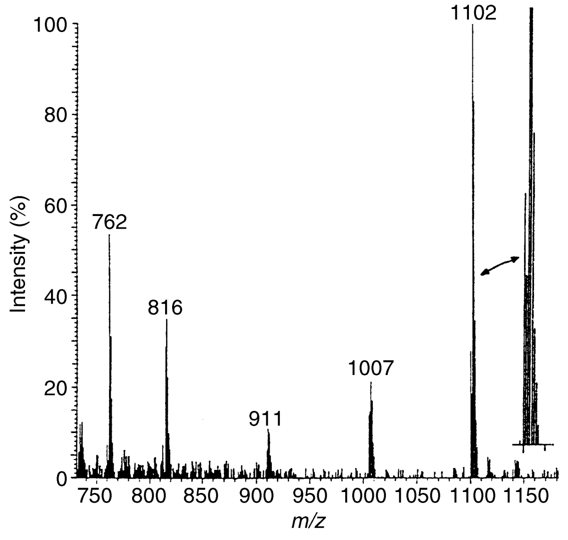


Fig. 1 EI mass spectrum (70 eV) for $C_{60}(4\text{-}FC_6H_4)_4H_2$.

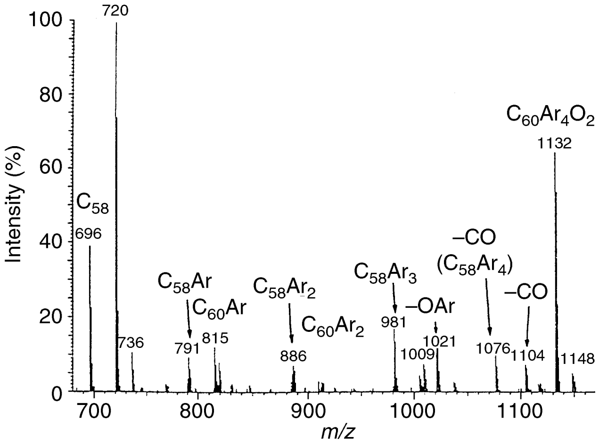


Fig. 2 EI mass spectrum (70 eV) for $C_{60}(4\text{-}FC_6H_4)_4O_2$.

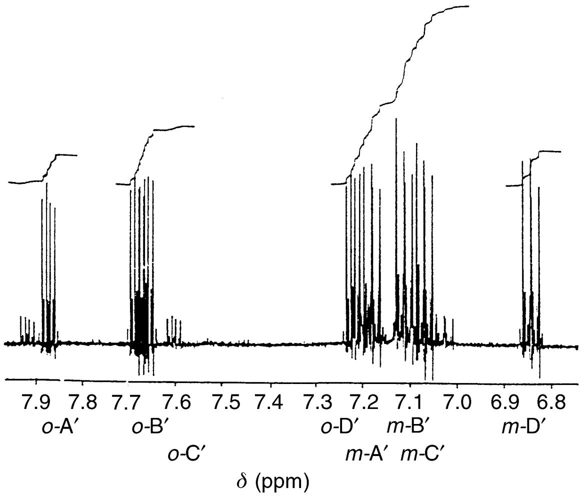


Fig. 3 ^1H NMR spectrum of $C_{60}(4\text{-}FC_6H_4)_4O_2$.

The ^1H NMR spectrum (Fig. 3) consists of eight multiplets centred at δ 7.878, 7.868; 7.685, 7.675; 7.664; 7.654; 7.225, 7.215 (aryl-H, *ortho* to the cage), 7.189, 7.172; 7.120, 7.104; 7.076, 7.060; 6.850, 6.834 (aryl-H, *meta* to the cage) and shows the compound to be asymmetric. The peaks are assigned to aryl rings denoted A′ to D′ respectively (Fig. 3), and relative to the corresponding rings A to D for $C_{60}(4\text{-}FC_6H_4)_4$ (above), the *ortho* (cage) hydrogen resonances are shifted upfield (by 0.16 ppm) for ring A′, and downfield (by 0.13 ppm) for ring C′, those for rings B′ and D′ being unaffected. The peaks for hydrogens *meta* to the cage are also upfield for ring A′, but in this case there is a downfield shift for the hydrogens in each of rings B′, C′ and D′.

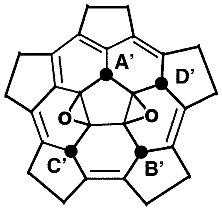
The chemical shifts of the aryl hydrogens *ortho* to the cage in $C_{60}(4\text{-}FC_6H_4)_4O_2$ are all within an average of 0.05 ppm of the values obtained for the corresponding $C_{60}Ph_4O_2$,[3] indicating that these compounds are isostructural. The NOE couplings between the aryl *ortho* hydrogens also show the same pattern observed for $C_{60}Ph_4O_2$,[5] *viz.* A′→D′ and D′→B′. (The B′→C′ coupling for the phenyl compound could not be seen for the fluoro compound because of peak coincidences.) The interactions are significantly different from those for $C_{60}Ar_4$ due either to the electronic effect of the oxygens, or to the aryl groups occupying different positions in the two sets of compounds.

The ^{19}F NMR spectrum shows four multiplets centred at δ_F −114.5, −115.4 and −115.6 (2 F), and the very substantial downfield shift of *ca.* 7 ppm relative to those in $C_{60}Ar_4$ indicates that the oxygen atoms are located on the cage in the vicinity of the aryl groups.

The structure of $C_{60}(4\text{-}FC_6H_4)_4O_2$; formation of C_{58} during EI mass spectrometry. The probable structure of $C_{60}(4\text{-}FC_6H_4)_4O_2$ is deduced from the following arguments:

1. Oxygen can be present either as an epoxide, dioxetane,[15] or ether.[16] Dioxetane formation is rare and requires a diol precursor; ether formation is induced by σ-bond lengthening arising from the presence of adjacent addends, but has been found so far only in fluorofullerenes.[16]

2. The NOE couplings are compatible with the four aryl groups being in the sequence A′-D′-B′-C′ with A′ being remote from B′ and C′. This pattern is consistent with the bis epoxide being either **8** or **9** (derived from **2** or **4**, respectively). The locations of the epoxide functions are consistent with those in an X-ray characterised bis epoxide.[7]



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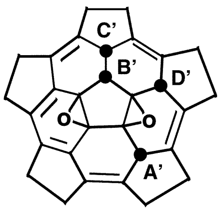

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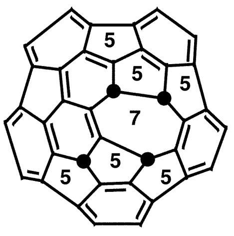
3. The major fragmentation of the parent ion (1132 amu) in the mass spectrum involves two consecutive losses of CO (28 amu) to give $C_{59}(4\text{-}FC_6H_4)_4O$ (1104 amu) and then $C_{58}(4\text{-}FC_6H_4)_4$ (1076 amu). (Loss of CO is typical in EI mass spectra of fluorofullerene epoxides.[17]) Thereafter regular losses of aryl fragments (95 amu) occur (981, 886 and 791 amu) to give finally C_{58}, which shows a remarkable 40% of the C_{60} ion intensity. The fragmentation pathway involving initial loss of aryl groups is trivial by contrast. The fragmentation pattern is very specific since it was observed previously for $C_{60}Ph_4O_2$, where the C_{58} ion intensity was 28% of that of C_{60}.

4. The loss of carbons (as CO) can only occur across a 6 : 5 *double* bond, since all other combinations produce either 4-membered rings, or impossible bonding.[18]

5. The bis epoxide cannot involve the addition of oxygens across a 6 : 6 *double bond* in the fullerene since each CO loss would produce a four-membered ring.[18] Methylfullerene di-epoxides eliminate CO very readily during EI mass spectrometry giving a high concentration of C_{58}; moreover the epoxides each lie across 6 : 5-bonds (double bonds) of a single pentagon.[7] Indeed the enforced presence of the double bonds in structures derived from the $C_{60}X_6$ moiety, seems to be responsible for the facile decarbonylation. (Likewise the enforced presence of a 6 : 5-double bond in $C_{70}X_{10}$ produces related decarbonylation.[19])



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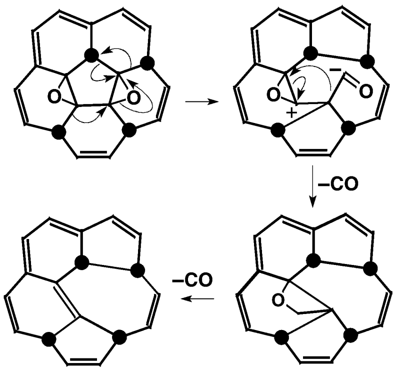
6. Scheme 1 shows how elimination of two CO molecules from epoxides, each located at 6 : 5 double bonds in the central pentagon (here with the aryl group location shown in **8** as in **2**), can lead to the formation of a derivative of C_{58} (**10**). (The sequence of the various steps is not critical, and some involving alternative bond migrations lead to the same overall result; similar decarbonylation can be obtained by using the bis epoxide **9**.) Previously we conjectured (for the corresponding phenyl compound) an alternative elimination of two molecules of CO from a dioxetane, but now consider this less probable.[5] It is not possible to have a similar elimination from a di-epoxide derived from **3** as a precursor, since this does not have two double bonds in the central pentagon. This further suggests that the aryl group location is different in $C_{60}Ar_4O_2$ from that in $C_{60}Ar_4$.



Scheme 1 Proposed mechanism for the formation of C_{58} by CO elimination from a bis epoxide.

7. Although **10** possesses adjacent pentagons, this violation of the 'non-adjacent pentagon' rule,[20] is unimportant here: each pentagon pair is adjacent to a heptagon that substantially removes the strain that would otherwise be present; five pentagons possess an sp^3-hybridised carbon (and one pentagon has two) which also relieves the strain; these sp^3 carbons prevent the anti-aromaticity that arises in a fullerene when two pentagons are adjacent.[11,21] Thus C_{58} formation is here aided by both the location of the oxygens and the presence of the aryl addends.

Two other features of the mass spectrum are: (i) the greater intensity of the $C_{58}Ar_n$ species relative to the corresponding $C_{60}Ar_n$ species; (ii) the loss of ArO (111 amu) to give $C_{60}(4\text{-}FC_6H_4)_3O$ (1021 amu). This latter provides further support for the proposed structure, since ArO loss seems reconcilable only if the epoxide and aryl groups are adjacent. These aspects are considered further with the next compound.

$C_{60}(4\text{-}FC_6H_4)_6$

The EI mass spectrum showed the parent ion at 1291 amu, loss

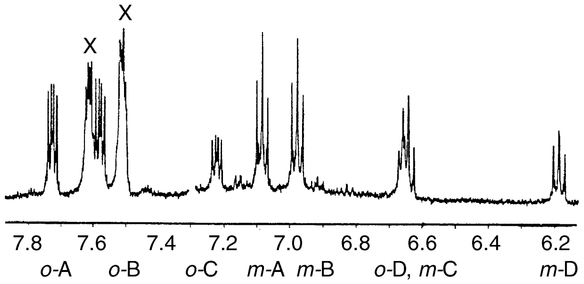


Fig. 4 ^{1}H NMR spectrum of C_s symmetrical $C_{60}(4\text{-}FC_6H_4)_6$.

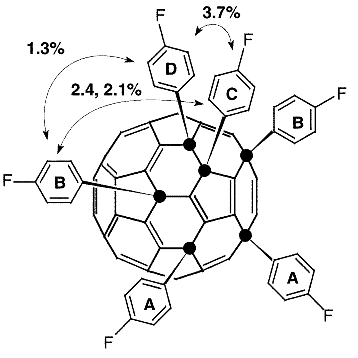


Fig. 5 Structure of C_s $C_{60}(4\text{-}FC_6H_4)_6$, showing *para* (1.3%), *meta* (2.3%), and *ortho* (3.7%) NOE couplings.

of aryl groups with an alternating intensity pattern (*cf.* ref. 22), and a 1226 amu peak due to $C_{60}(4\text{-}FC_6H_4)_4(4\text{-}FC_6H_3)O_2$ (see below) which persisted despite HPLC recycling of the sample.

The amount of compound was just sufficient to provide a ^{1}H NMR spectrum (Fig. 4) (peaks marked × are due to dioctyl phthalate contamination), which showed it to have C_s symmetry. Eight multiplets were obtained at δ 7.727 (4 H, *ortho*-H, rings A), 7.575 (4 H, *ortho*-H, rings B), 7.225 (2 H, *ortho*-H, ring C), 6.655 (2 H, *ortho*-H, ring D); 7.085 (4 H, *meta*-H, rings A), 6.98 (4 H, *meta*-H, rings B), 6.635 (2 H, *meta*-H, rings C), 6.185 (2 H, *meta*-H, ring D) (*ortho*/*meta* are relative to the cage). The structure was deduced from the NOE couplings (Fig. 5); such an arrangement has only been seen in $C_{60}(\text{allyl})_6$,[23] where steric hindrance between the adjacent addends could be expected to be less.

This compound showed no inhibition of aryl ring rotation, even at −83 °C, which is remarkable because in $C_{70}Ph_{10}$ two phenyl groups are also adjacent (and moreover across a longer incipient 5 : 6-bond), yet they *are* sterically hindered from rotating.

$C_{60}(4\text{-}FC_6H_4)_6O_2$

The mass spectrum (Fig. 6) shows both similarities to and differences from that for $C_{60}(4\text{-}FC_6H_4)_4O_2$. Loss of CO is less facile since: (i) the $C_{58}Ar_n$ peak intensities are less than those of the corresponding $C_{60}Ar_n$ peaks; (ii) there is no peak resulting from initial loss of 28 amu; (iii) the 696 amu peak intensity is only 19% of that of the 720 amu peak. The main fragmentation peak arises from loss of ArO, a minor feature of the spectrum for $C_{60}(4\text{-}FC_6H_4)_4O_2$. The overall patterns are otherwise comparable, indicating structural similarities, and it is probable that both epoxides are in the central pentagon. Since the hexa-aryl compound is probably more sterically crowded, relief of strain (most easily accomplished by ArO loss), dominates here.

The ^{1}H NMR spectrum (Fig. 7) consists of twelve sets of multiplets at δ 7.788, 7.669, 7.406, 7.229, 7.211 and 6.931 (aryl hydrogens adjacent to the cage, designated *ortho*), 7.131, 7.061, 6.938, 6.876, 6.831 and 6.733 (aryl hydrogens *meta* to the cage and adjacent to fluorine, designated *meta*), showing that the compound is asymmetric. The pattern observed previously for phenylated fullerenes[22] is found here also, *viz.* the shift for the hydrogens in a particular ring parallels the separation between the *ortho* and *meta* resonances for that ring. The IR spectrum shows bands at 1508, 1238 and 1163 cm^{-1}.

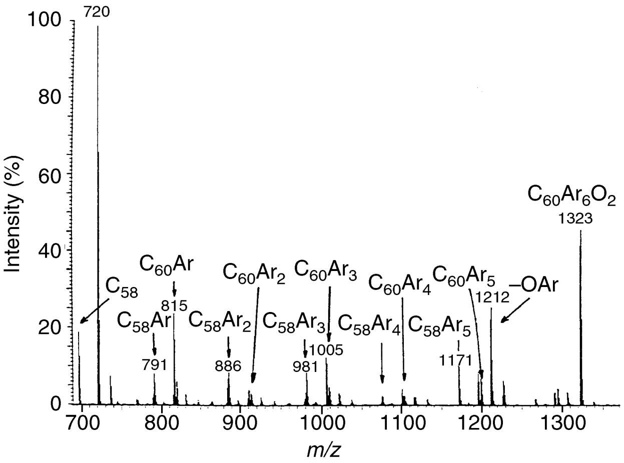


Fig. 6 EI mass spectrum (70 eV) for $C_{60}(4\text{-}FC_6H_4)_6O_2$.

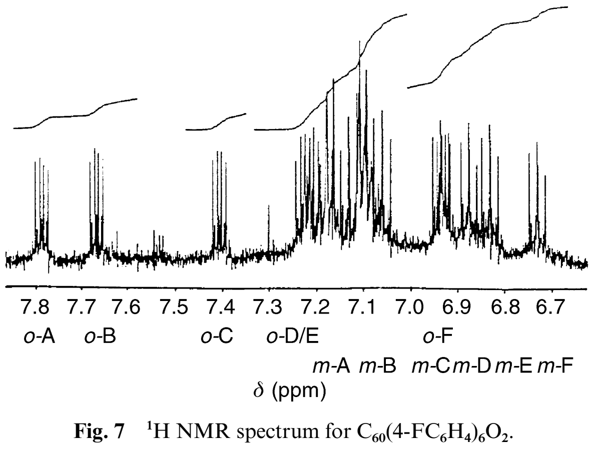


Fig. 7 ^{1}H NMR spectrum for $C_{60}(4\text{-}FC_6H_4)_6O_2$.

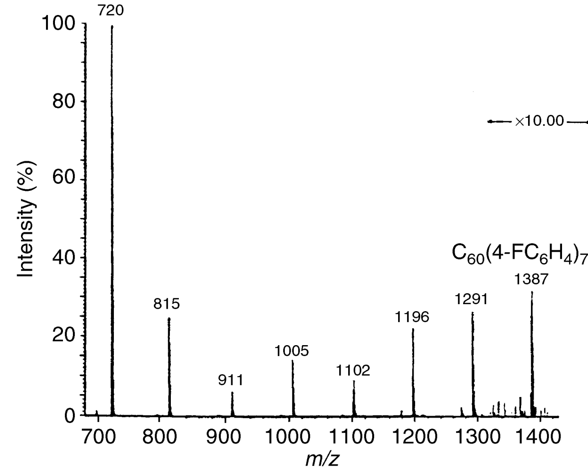


Fig. 8 EI mass spectrum (70 eV) of $C_{60}(4\text{-}FC_6H_4)_7H$.

A single peak fraction that eluted at 9.1 min gave similar mass spectra (1291 and 1323 amu) to $C_{60}(4\text{-}FC_6H_4)_6$ and $C_{60}(4\text{-}FC_6H_4)_6O_2$, which eluted at 12.3 and 11.5 min, respectively. This derivative is probably an isomeric di-epoxide which fragments readily, but there was insufficient material for further analysis.

$C_{60}(4\text{-}FC_6H_4)_7H$

This gave a parent ion at 1387 amu in the mass spectrum (Fig. 8). It may be formed either by disproportionation, or

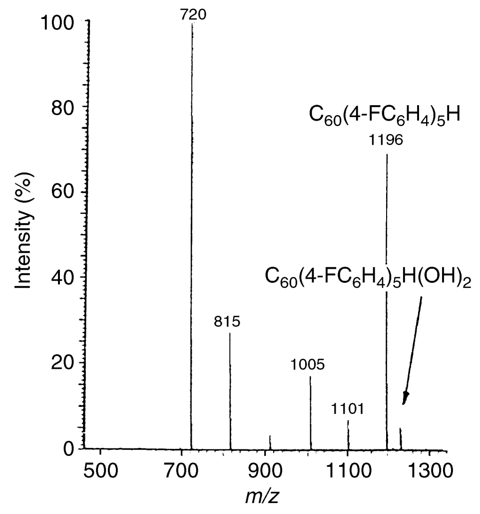


Fig. 9 EI mass spectrum (70 eV) of the fraction eluting at 12.4 min.

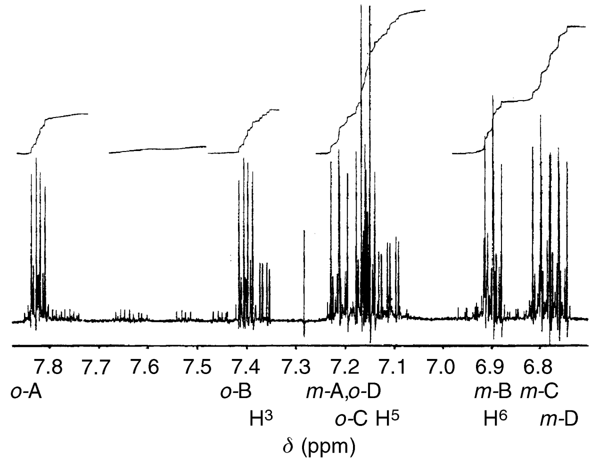


Fig. 10 ^{1}H NMR spectrum of $C_{60}(4\text{-}FC_6H_4)_4(4\text{-}FC_6H_3)O_2$.

from some $C_{60}Cl_8$ (an as yet unknown compound) present in the $C_{60}Cl_6$ precursor. It is only the third example of eight-fold addition in C_{60}, seen previously only in $C_{60}Br_8$[24] and $C_{60}Me_8$.[10] The amount available precluded further analysis.

$C_{60}(4\text{-}FC_6H_4)_5H/C_{60}(4\text{-}FC_6H_4)_5H(OH)_2$

The mass spectrum (Fig. 9) shows a main peak at 1196 amu [$C_{60}(4\text{-}FC_6H_4)_5H$] and a smaller one at 1230 amu corresponding to the di-hydroxy derivative. After reprocessing the material using a Cosmosil 5 μ PYE column, the mass spectrum was unchanged, suggesting that the di-hydroxy compound is the parent ion (which fragments readily), rather than a component of a mixture. The former possibility is indicated by the presence in the mass spectrum of a doubly-charged ion for $C_{60}(4\text{-}FC_6H_4)_5H$, but not for the dihydroxy compound.

$C_{60}(4\text{-}FC_6H_4)_4(4\text{-}FC_6H_3)O_2$

This eluted at 19.0 min (25.4 min on recycling with 30 : 70 toluene–hexane at 2 ml min^{-1}). The mass spectrum showed the parent ion at 1226 amu, and all of the features of the spectrum obtained for the non-fluorinated analogue (see Fig. 2 in ref. 6), confirming the derivative to be **1b**. The IR bands were at 1508, 1237 and 1162 cm^{-1}.

The structure was confirmed by ^{19}F NMR [multiplets centred at δ_F −117.0, −118.43, −118.45, −118.62, −124.86 (all 1 F, *J* all *ca.* 4 Hz)] and ^{1}H NMR [multiplets at δ 7.822 (2 H), 7.40 (2 H), 7.363 (1 H, H^3), 7.21 (2 H), 7.163 (2 H), 7.154 (2 H), 7.113 (1 H, H^5), 6.90 (1 H, H^6), 6.897 (2 H), 6.799 (2 H), 6.763 (2 H)]. In the latter (Fig. 10) the aryl hydrogen labels correspond to the ring notation in **1b**, hydrogens adjacent to the cage and to fluorine being designated *ortho* and *meta*, respectively. The aryl ring assignments are based on the NOE couplings between their *ortho* hydrogens; NOE couplings confirmed the adjacency of H^5 and H^6.

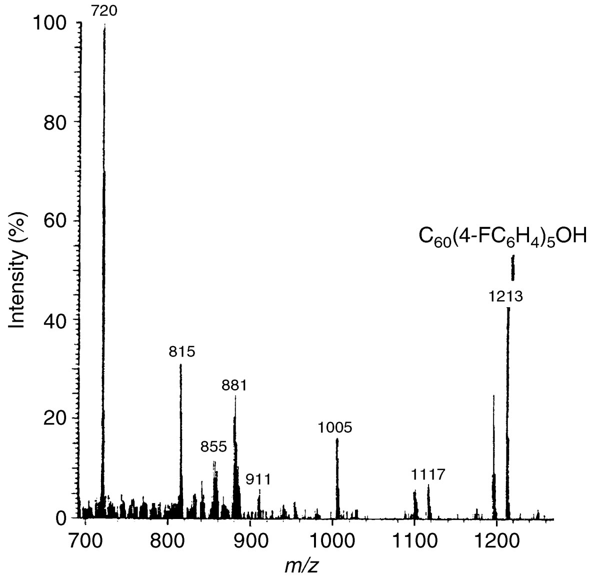


Fig. 11 EI mass spectrum (70 eV) of $C_{60}(4\text{-}FC_6H_4)_5OH$.

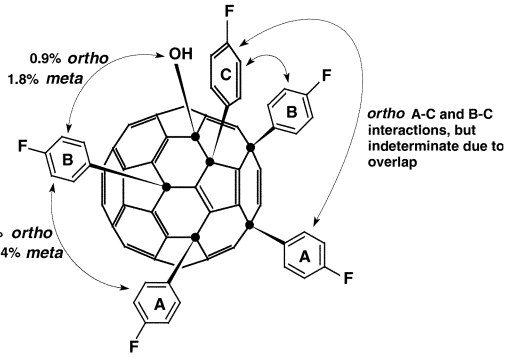


Fig. 12 Structure of C_s $C_{60}(4\text{-}FC_6H_4)_5OH$ showing NOE values.

$C_{60}(4\text{-}FC_6H_4)_5OH$

The mass spectrum of this component (Fig. 11) shows the parent ion at 1213 amu with fragmentation involving either loss of 17 amu (OH) followed by regular loss of aryl groups, or loss of one aryl group, then OH and finally the remaining aryl groups. The bands in the IR spectrum are at 1507, 1236, 1160, 836 and 812 cm^{-1}.

The compound has C_s symmetry, the ^{1}H NMR spectrum showing six sets of multiplets in a 2 : 2 : 2 : 2 : 1 : 1 ratio. The hydrogens *ortho* to the cage appear at δ 7.622 (4 H, ring A), 7.436 (4 H, ring B), 6.887 (2 H, ring C), hydrogens *meta* to the cage at 7.035 (4 H, ring A), 6.909 (4 H, ring B), 6.437 (2 H, ring C), 6.23 (1 H, OH). The relationship between the groups was established by NOE (Fig. 12), and the structure parallels that for the non-fluorinated compound.[14] During nucleophilic substitution, an aryl group undergoes a 1,2-migration in order to combat the anti-aromaticity of the 4π cyclopentadienyl cationic ring created by loss of the chlorine. Here, anchimeric assistance results in rearrangement.[25]

The ^{13}C NMR spectrum showed the required 26 × 2C + 2 × 1 C in the sp^2 region (161.2–143.0 ppm) for the cage, and the five *ipso* aryl-cage sp^2 peaks (130.7–129.2 ppm) but was unresolved in the sp^3 region due to insufficient material being available.

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