

The [4 + 2] cycloaddition of anthracene with C₆₀F₁₈; anthracene goes ring walking

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From the [4 + 2] cycloaddition of anthracene at the curved face of C₆₀F₁₈ we have isolated two main isomers of C_s and C₁ symmetry (isomers **1** and **2**, respectively) in *ca.* 3 : 2 relative yields; isomer **2** contained traces of a third isomer, also of C_s symmetry. Of the four mono adducts that can, in principle, be formed by this cycloaddition, the yields of the three obtained reflect differences in steric hindrance between the fluorine and aromatic addends. The major C_s isomer (**1**) is reasonably stable, but the more crowded C₁ isomer (**2**) reverts readily to C₆₀F₁₈ and anthracene on standing, and also undergoes rearrangement to isomer (**1**). This is the first example of spontaneous migration of a cycloaddend from one 6 : 6-bond to another on the same fullerene cage surface. The UV/VIS spectrum of **1** is significantly different from that for C₆₀F₁₈, suggesting that some electronic interaction may exist between the addend and the cage. Anthraquinone is produced as a by-product of the reaction (and also from that between either C₆₀ or C₆₀Cl₆ and anthracene) showing the fullerene cage acts here as an oxidant.

Introduction

The fluorofullerene C₆₀F₁₈ is unique in possessing a flat aromatic face, strong electron-withdrawal due to the presence of the fluorines, and a substantial 'curved fullerene' region where cycloadditions can occur.^{1,2} If suitable donor addends can be attached, the molecule promises to be exceptionally useful in applications involving electron-transfer properties, and we plan to investigate the chemistry of C₆₀F₁₈ in this context. The compound is available currently only in *ca.* tens of milligrams, and so our initial experiments will be focused on determining the kinds of reactions that are possible. Subsequently, as we are able to produce larger quantities, promising derivatives will be produced in amounts suitable for electrochemical and related experiments, in order to determine the donor-acceptor electronic interactions.

The use of C₆₀Cl₆ and C₆₀Br_{6,8} in the formation of charge-transfer complexes with organic donors (*i.e.* with no covalent bonding between them) has been reported recently, it being anticipated that the increased electron withdrawal by the halogenated cage would increase the electron transfer.³ However, these halogenofullerenes proved to be unsuitable for this purpose because strong donors caused dehalogenation (the stability following the order C₆₀Cl₆ > C₆₀Br₈ > C₆₀Br₆) whilst weak donors showed no charge transfer. The greater strength of the C-F bond causes fluorofullerenes to be much more resistant to halogen loss than these other halogenofullerenes; it is possible to obtain their EI mass spectra, something which is impossible with chloro- or bromofullerenes. Fluorofullerenes can be expected therefore to be more stable towards the formation of donor-acceptor derivatives.

The only derivative of C₆₀F₁₈ made so far, C₆₀F₁₅Ph₃ ('triumphene'), was produced by electrophilic substitution of the C₆₀F₁₈ electrophile into benzene, catalysed by FeCl₃ (this can be described also as nucleophilic substitution of fluorine by phenyl).⁴ Since no cycloadditions are known, we decided in the first instance to carry out the reaction with anthracene.

The reaction of [60]fullerene with anthracene to give a 1 : 1-addition product has been reported a number of times,⁵⁻⁸ and gives also a brown insoluble precipitate,⁷ which we confirm (but it appears only upon removal of the reaction solvent). The 1 : 1-addition product is unstable, especially on heating, and readily undergoes the retro Diels-Alder reaction to give the original components. A bis adduct of D_{2h} symmetry was also isolated⁸ and this is produced quantitatively from the mono-adduct on heating in the solid state;⁹ by contrast, five bis-adducts are obtained by heating the mono-adduct in solution.⁹ The 1 : 1-adduct between [60]fullerene and 9,10-dimethylantracene is also unstable at room temperature (apparently more so than the anthracene adduct, due probably to steric interactions between the methyls and the cage), consequently this addend has been used as a removable blocking and directing group.¹⁰ Lastly, the 1 : 1 adduct between anthracene and C₇₀Ph₈ has been described.¹¹

Reaction of anthracene with C₆₀F₁₈ can, in principle, give four products from addition at the curved surface. The bonds across which addition can occur are labelled *a-d* in Fig. 1. Addition across either of bonds *a* and *c* will give a product of C_s symmetry, whilst addition across bond *b* and *d* will give a product of C₁ symmetry. Steric hindrance between the anthracene addend and fluorines will increase from *a*→*d*, with the latter being very improbable because of the extent of this hindrance. Force field calculations give the heats of formation as 698.8, 710.1, 716.3 and 766.6 kcal mol⁻¹, respectively, and whereas the differences *a*→*b* and *b*→*c* are 11.3 and 6.2 kcal mol⁻¹, respectively, the difference *c*→*d* is 50.3 kcal mol⁻¹. The number of ¹H NMR signals obtained for each isomer will be: *a*, 4 × 2 (sp² region), 1 × 2 (sp³); *b*, 8 × 1 (sp²), 2 × 1 (sp³); *c*, 4 × 2 (sp²), 2 × 1 (sp³); *d*, 8 × 1 (sp²), 2 × 1 (sp³). The number of ¹⁹F NMR signals will be 10, 18, 10, 18, respectively, with the readily distinguished upfield multiplets (due to the fluorines attached to sp³ carbons themselves attached to sp³ carbons) comprising resonance combinations: 1 × 2 F + 1 × 1 F; 3 × 1 F; 1 × 2 F + 1 × 1 F; 3 × 1 F.

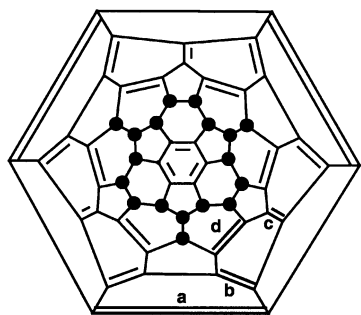


Fig. 1 Schlegel diagram for $C_{60}F_{18}$ (● = F), showing the four different bonds (*a-d*) across which cycloaddition can occur.

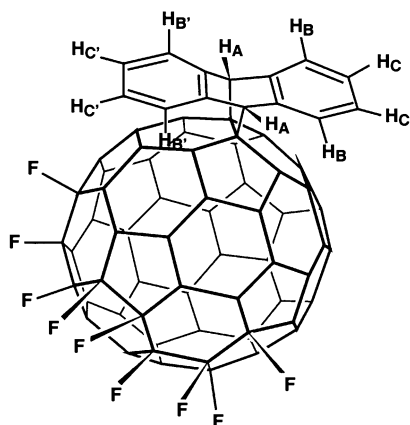


Fig. 2 The structure of isomer **1** (addition across bond *a*); 'visible' fluorines only are shown.

Experimental

An excess of anthracene (20 mg, 0.112 mmol) was added to $C_{60}F_{18}$ (6 mg, 0.006 mmol) dissolved in toluene (20 cm³, HPLC grade), and the bright yellow mixture was heated under reflux for 24 h under argon, during which time the colour changed to orange. The crude product was filtered with exclusion of atmospheric moisture (to avoid any nucleophilic replacement of fluorine) from a small amount of fine red crystals which were produced, and separated by HPLC (high pressure liquid chromatography) using a 10 mm × 250 mm Cosmosil Buckyprep column, with toluene elution at a flow rate of 4.7 ml min⁻¹. Fractions were obtained with retention times of 41 min (recovered $C_{60}F_{18}$ *ca.* 1 mg), 13 min (isomer **1**), 9 min (isomer **2**), combined yields of these two isomers *ca.* 3 mg, 2.4 min (recovered anthracene) and 3 min (anthraquinone); the **1** : **2** isomer ratio was approximately 3 : 2. EI mass spectra were obtained at 70 eV, ¹H NMR were run at 500 MHz, and ¹⁹F NMR spectra were run at 376.5 MHz.

We were unable to identify the red crystals (which were very insoluble in toluene, chloroform *etc.*), but they appeared to be a derivative of $C_{60}F_{18}$ because this was regenerated after a toluene suspension was allowed to stand for 2–3 weeks.

Results and discussion

Isomer 1

The EI mass spectrum (70 eV) showed peaks only for $C_{60}F_{18}$ (1062 amu with some normal fragmentation of C_{60} at 720 amu) and anthracene (178 amu). Since both of these components were absent from the HPLC-purified sample, it is clearly an adduct (which can only be a 1 : 1 adduct because of steric considerations).

The structure was confirmed by the ¹H NMR (500 MHz CDCl₃), which gave peaks at δ_H 7.74 (2 H, dd, *J* 5.4 and 3.2 Hz, H_{B'}), 7.60 (2 H, dd, *J* 5.4 and 3.2 Hz, H_B), 7.47 (2 H, dd, *J* 5.4

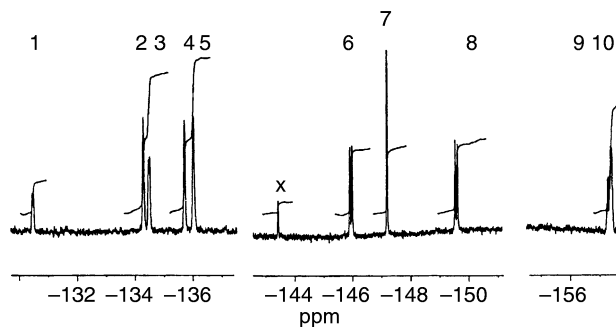


Fig. 3 ¹⁹F NMR spectrum of isomer **1**.

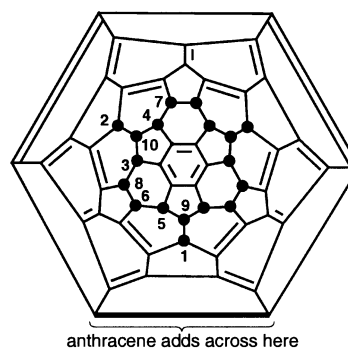


Fig. 4 Location of the fluorines identified from the 2 D ¹⁹F NMR spectrum of **1**.

and 3.2 Hz, H_{C'}), 7.45 (2 H, dd, *J* 5.4 and 3.2 Hz, H_C), 5.74 (2 H, s, H_A). The 5.74 ppm peak showed 3.8% NOE couplings to each of the 7.74 and 7.60 ppm peaks, confirming these latter to be the B' and B hydrogens (Fig. 2) The pattern is consistent only with the product from addition across the *a* bond (Fig. 1) as shown in Fig. 2. Moreover, formation of this isomer in the highest yield is compatible with it being the least hindered one. During the acquisition of the spectrum, traces of the peaks for anthracene appeared, showing that the adduct slowly reverts to products (see also below).

The ¹⁹F NMR spectrum (Fig. 3) showed ten lines at δ_F -130.48 (1 F, d, *J* 20 Hz, **1**), -134.49 (2 F, dd, *J* 4 and 16 Hz, **3**), -135.72 (2 F, s, **4**), -136.03 (2 F, s, **5**), -145.95 (2 F, d, *J* 30 Hz, **6**), -147.20 (2 F, s, **7**), -149.58 (2 F, dt, *J* 5 and 30 Hz, **8**), -157.31 (1 F, dt, *J* 10 and 20 Hz, **9**), -157.42 (2 F, dt, *J* 10 and 18 Hz, **10**); some of the singlets were broad and unresolved. The spectrum showed similarities to that of C_s C₆₀F₁₇CF₃¹² in having two almost superimposed upfield peaks (in a 2 : 1 intensity ratio) due to the unique fluorines attached to carbons themselves surrounded by three sp³ carbons.

The bold numbers above identify the fluorines in Fig. 4, and were deduced from a 2 D spectrum. As in the case of $C_{60}F_{18}$ the fluorines nearest to the central aromatic ring (nos. **3**, **4** and **5**) are more downfield than those further away (nos. **6**, **7** and **8**). Relative to the corresponding fluorines in $C_{60}F_{18}$, peaks **2** and **6–8** are more upfield, the rest are more downfield. Analyses such as these will be valuable in analysing the structures of other derivatives of $C_{60}F_{18}$, which we hope to produce in due course.

Traces of $C_{60}F_{18}$ arising from the retro cycloaddition are evident, the two main peaks for this occurring at -143.43 and -136.03 ppm [coincident with peak no. **5**, but evident on the 2 D spectrum (not shown)]. The integrated intensities show the amount to be 5.5%, which represents the extent of the retro reaction after *ca.* 2 weeks at room temperature. This derivative therefore appears to have similar stability to that of the C₆₀:anthracene complex.

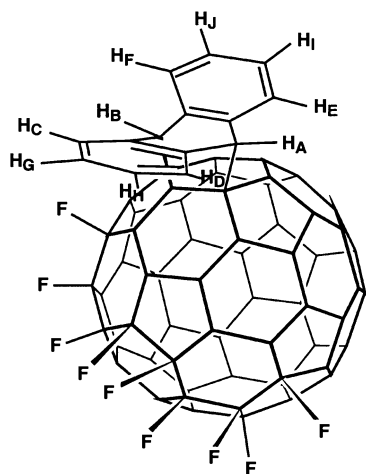


Fig. 5 The structure of isomer 2 (addition across bond *b*); 'visible' fluorines only are shown.

Isomer 2

As for isomer 1 the EI mass spectrum consisted only of the anthracene and C₆₀F₁₈ fragmentation ions. The ¹H NMR spectrum (500 MHz, CDCl₃) showed 2 to be unsymmetrical, giving ten lines overall at δ_H 7.65 (1 H, d, *J* 7.4 Hz, H_C), 7.60 (1 H, d, *J* 7.5 Hz, H_D), 7.57 (1 H, d, *J* 7.4 Hz, H_E), 7.47 (1 H, d, *J* 7.1 Hz, H_F), 7.442 (1 H, dd, *J* 7.4 and 1.3 Hz, H_G), 7.405 (1 H, dd, *J* 7.6 and 1.3 Hz, H_H), 7.392 (1 H, dd, *J* 7.5 and 1.3 Hz, H_I), 7.365 (1 H, dd, *J* 7.4 and 1.3 Hz, H_J), 5.623 (1 H, s, H_A), 5.495 (1 H, s, H_B). The relationships between H_{C-F} and H_{G-J}, Fig. 5) were determined by a 2D-COSY experiment. Couplings (NOE) between H_A-H_D, H_A-H_E, H_B-H_C, and H_B-H_F were determined as 8.0, 7.3, 9.3 and 7.5%, respectively. Some other double doublets, of about half the above intensities were evident in the 7.34-7.45 ppm region, and these are attributed to a trace of a third isomer of C_s symmetry (produced by addition across bond *c*) as shown also by the ¹⁹F NMR spectrum, Fig. 6.

Isomer 2 is less stable than isomer 1, significant amounts of anthracene being evident from the ¹H NMR spectrum, showing that decomposition was occurring fairly rapidly. In principle, isomer 2 could involve addition across bond *d*. However, given the extreme steric hindrance that models indicate for the latter, this possibility can be ruled out.

The ¹⁹F NMR spectrum, run *ca.* 2 weeks after formation of the adduct, is shown in Fig. 6, all of the associations between peaks from the same component being determined from a 2D spectrum. There are four main peaks arising from C₆₀F₁₈ produced by the retro Diels-Alder reaction, eighteen peaks due to isomer 2, and (marked ×) nine of the ten peaks due to the presence of the alternative C_s isomer produced by addition across bond *c* (Fig. 1); their intensities relative to those for isomer 2 appear greater because of the higher symmetry.

Most significant, however, are the peaks marked ● due to isomer 1 produced from isomerisation of isomer 2 (and possibly also some of the second symmetrical isomer). We are confident that isomer 1 was not present originally in isomer 2 because the former eluted *after* the latter in the HPLC separation and so would not be present due to 'tailing' and, moreover, there was no trace of it in the ¹H NMR spectrum that was run *ca.* 10 days before the ¹⁹F NMR spectrum. This appears to be the first example of spontaneous migration of a cycloaddend across the same cage surface. Such a migration can only be detected in the presence of a second addend (in our case the fluorine atoms), and has been observed previously only during electrochemistry of bis malonates (shown to be intramolecular through the use of a standard cross-over procedure).¹³ In view of the lability of the anthracene it is possible that separation-recombination occurs in our case, but this mechanistic aspect cannot be readily

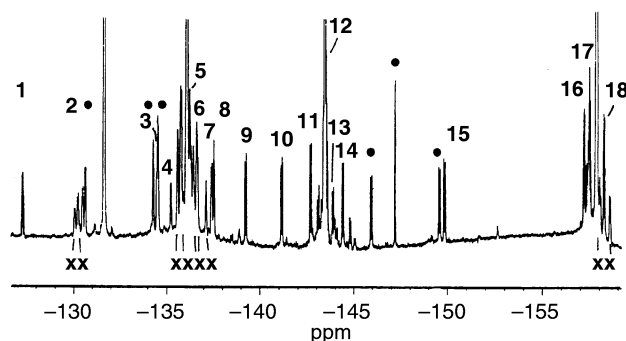


Fig. 6 ¹⁹F NMR spectrum of isomer 2. Peaks marked ● are due to isomer 1 produced by isomerisation, and peaks marked × are due to the second C_s isomer arising from addition across bond *c*.

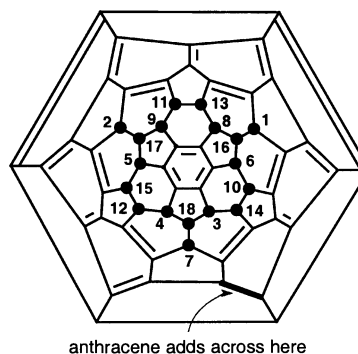


Fig. 7 Location of the fluorines identified from the 2D ¹⁹F NMR spectrum of 2.

solved at this time; separation of anthracene from a 1 : 1 adduct with [60]fullerene and recombination with a *second* cage takes place in the solid state.⁹ Interconversions from a 6,6-closed- to a 6,5-open structure (methanofullerene to homofullerene) have been reported previously,¹⁴ but these are mechanistically different since they involve simultaneous 1,3-shifts of two C-C bonds.

The eighteen lines for isomer 2 appeared at δ_F -127.25 (1 F, d, *J* 20 Hz, 1), -130.46 (1 F, d, *J* 20 Hz, 2), -134.48 (1 F, sh 3), -135.20 (1 F, s, 4), -136.25 (1 F, s, 5), -136.65 (1 F, sh 6), -137.43 (1 F, d, *J* 20 Hz, 7), -137.57 (1 F, s, 8), -139.24 (1 F, ddd, *J* 6, 6 and 33 Hz, 9), -141.14 (1 F, dd, *J* 9 and 26 Hz, 10), -142.68 (1 F, ddd, *J* 6, 6 and 26 Hz, 11), -143.53 (1 F, d, *J* 28 Hz, 12), -143.87 (1 F, d, *J* 28 Hz, 13), -144.40 (1 F, ddd, *J* 5, 5 and 26 Hz, 14), -149.85 (1 F, ddd, *J* 7, 7 and 28 Hz, 15), -157.19 (1 F, dt, *J* 11 and 21 Hz, 16), -157.49 (1 F, dt, *J* 10 and 19 Hz, 17), -158.25 (1 F, dt, *J* 10 and 20 Hz, 18). The bold numbers identify the fluorines in Fig. 7 as deduced from a 2D spectrum. The small amount of compound prevented identification of some of the couplings, hence some assignments may be interchanged; the couplings 17→2, 18→7, 13→11→9, 4→12→15, 16→1→6→10→14, and 16→8 were clearly identified. As for isomer 1 (and C₆₀F₁₈ derivatives in general) the fluorines nearest to the central benzenoid ring (nos. 3, 4, 5, 6, 8, 9) are more downfield than those further out (nos. 10, 11, 12, 13, 14, 15). The peak 7 (and hence peak 18) was assigned on the basis of its marked upfield shift assumed to arise from the proximity of the anthracene addend.

The presence of the components in the ¹⁹F NMR spectrum of 2 is readily seen in the region where the resonances appear for the fluorines attached to sp³-hybridised carbons, themselves attached to sp³-hybridised carbons (Fig. 8). This shows the intense off-scale peak due to regenerated C₆₀F₁₈, the three equal intensity double triplets for peaks 16-18 of isomer 2 (marked A), the two double triplets for peaks 9 and 10 of isomer 1 (marked B - one of these is partially superimposed on one of

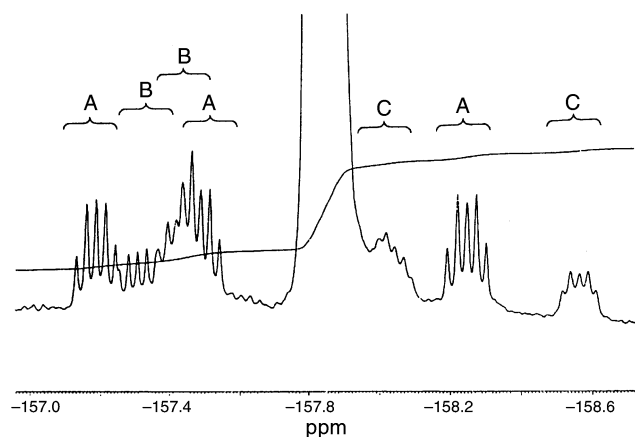


Fig. 8 Expanded $-(157-159)$ ppm region of the ^{19}F NMR spectrum of **2**.

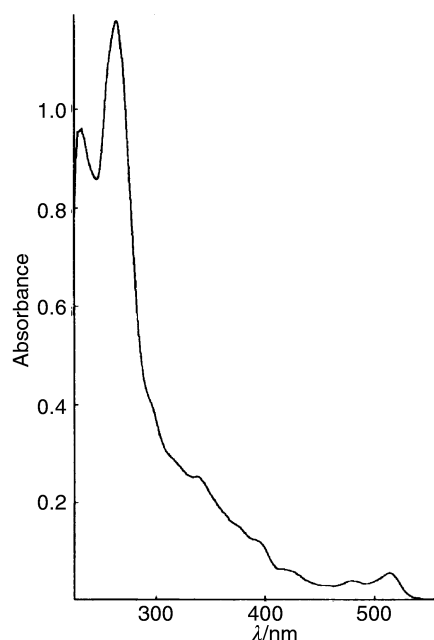


Fig. 9 UV/VIS spectrum (dichloromethane) for **1**.

the bands for isomer **2**) and two other double triplets for the other symmetrical isomer (marked C).

UV spectra (dichloromethane)

The spectrum of $\text{C}_{60}\text{F}_{18}$ shows two bands at 253.3 nm (main) and 342.4 nm (this latter has a small shoulder at ca. 362 nm). The spectrum for isomer **2** is fairly similar, the main band appearing at 255.2 nm, the minor band at 341.7 nm with a second shoulder at ca. 378 nm. [This similarity could in principle be attributed to the rapid reversion to $\text{C}_{60}\text{F}_{18}$ and anthracene, though none of the sharp anthracene bands (326.2, 341.9, 359.3, 378.7 nm) could be seen.] By contrast, the spectrum for **1** (Fig. 9) shows substantial differences, with two major bands at 232.9 and 265.1 (main) nm, and many minor bands at 342.7, 399.6, 428.7, 484.0 and 518.4 nm. This suggests significant electronic interaction between the addend and the cage, though the effect of interruption of the cage surface

conjugation needs to be considered. Although there is a major difference between the spectra for the two derivatives there is a precedent for this.¹⁵

Oxidation to anthraquinone

As noted in the experimental, anthraquinone was isolated from the reaction mixture. This was identified by two equal intensity multiplets at δ_{H} 8.30 and 7.83 (lit.¹⁶ 8.21–8.38 and 7.67–7.83). This same product was also obtained from the reaction between both [60]fullerene and anthracene, and C_{60}Cl_6 and anthracene. The fullerene cage is evidently acting as an oxidant. This seems not to have been reported before in the reaction with anthracene, but previously we reported that [60]-fullerene will readily oxidise H_2S to sulfur.¹⁷

Further reactions of $\text{C}_{60}\text{F}_{18}$ are planned.

Acknowledgements

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