Electrophilic Aromatic Substitution by the Fluorofullerene $C_{60}F_{18}$

Adam D. Darwish,[a] Anthony G. Avent,[a] Ala'a K. Abdul-Sada,[a] Ilya V. Gol'dt,[b] Peter B. Hitchcock,[a] Igor V. Kuvytchko,[b] and Roger Taylor*[a]

Abstract: The $FeCl_3$-catalysed arylation of $C_{60}F_{18}$ gives tri-substituted compounds $C_{60}F_{15}Ar_3$, where Ar = phenyl, 4-tolyl, 4-methoxyphenyl, 4-phenoxyphenyl, 4-chlorophenyl, 3,4-dichlorophenyl, 2-biphylenyl and 2-fluorenyl, together with some bis- and mono-substituted product. Bis-substitution was achieved with biphenylene and fluoranthene, and mono-substitution with biphenylene (2-position), pyrene (1-position), and naphthalene (1- and 2-positions); the tris-phenyl and tris-biphenylene derivatives are fluorescent. The 2-naphthyl substituent freely rotates at 328 K, whereas rotation of the 1-naphthyl substituent is prevented by interaction of the *peri*-hydrogen atom with fluorine. The 1-naphthyl derivative eliminates a molecule of HF during EI mass spectrometry, whilst the 2-naphthyl derivative eliminates HF and all fluorenes to give a naphthaleno[60]fullerene. The reaction rate is relatively unaffected by electron supply in the aryl rings, but no product was obtained with benzotrifluoride which defines the lower reactivity limit. The low discrimination between aromatics makes it possible to isolate derivatives having different aryl groups attached to the cage. Reactions occur mainly when the reagent solutions (or solutions in 1,2-dichlorobenzene) are evaporated to dryness. In most $FeCl_3$-catalysed reactions, unreacted $C_{60}F_{18}$ was recovered, more if the less effective $SnCl_4$ was used as a catalyst; use of $AlCl_3$ resulted in polyarylation and degradation of the $C_{60}F_{18}$. The structure of $C_{60}F_{17}$(1-biphenylyl) was confirmed by single-crystal X-ray analysis. Reaction of $C_{60}F_{18}$ with perylene/$FeCl_3$/*o*-dichlorobenzene gave red fluorescent "tagliatelli"-like threads (up to 1 cm long) of self-assembled π-stacked tetrachloroperylene arising from chlorination by $FeCl_3$.

Keywords: arenes · electrophilic substitution · fullerenes · NMR spectroscopy · steric effects

Introduction

One of the first investigations of the chemistry of fullerenes was their use as electrophiles for aromatic substitution, initial reactions being carried out using unhalogenated [60]fullerene in a Friedel–Crafts reaction. In a qualitative study with [60]fullerene, aromatic compounds PhR (R = H, Me, 1,3-Me_2, F, Cl, OMe, and NMe_2) were used,[1] and the effectiveness of catalysts followed the normal Friedel–Crafts order, namely, $AlBr_3 > AlCl_3 > FeCl_3 > FeBr_3 > GaCl_3 > SbCl_5$;[1,2] $TiCl_4$, $SnCl_4$, $GeCl_4$, BF_3 and BCl_3 were ineffective.[3] [60]Fullerene was more reactive than with [70]fullerene[4] because its electron withdrawal is greater, that is, it is the better electrophile.

Other studies involved the use of the more electrophilic halogenofullerenes. These can be generated in situ, for example, using a mixture of aromatic compounds, bromine, ferric chloride and [60]fullerene,[1,4,5] but like the foregoing reactions, gave products that were difficult to separate and/or characterise.

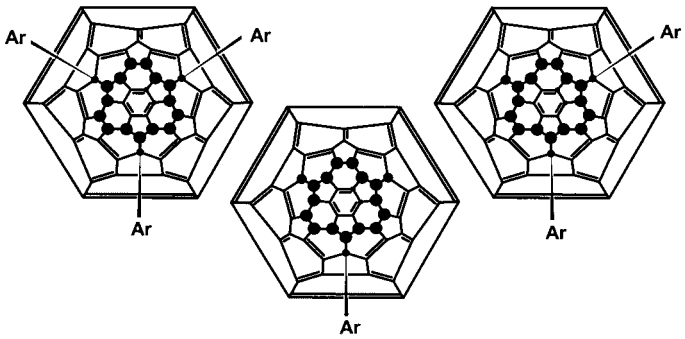
The most successful studies have used reactions of preformed chlorofullerenes with aromatic compounds (mostly benzene), which proceed via intermediate formation of fullerene carbocations.[6] This led to isolation and characterisation of compounds such as, $C_{60}Ar_5Cl$ and $C_{60}Ph_5H$,[7,8] $C_{60}Ph_4$ and $C_{60}Ph_2$,[9] a phenylated *iso*quinolino[3,4:1,2][60]fullerene,[10] benzo[*b*]furano[60]- and [70]fullerenes,[11] $C_{70}Ph_{10}$ and $C_{70}Ph_8$,[12] $C_{70}Ph_9OH$,[13] and two [70]fullerendiol isomers, $C_{70}Ph_8(OH)_2$.[14]

The use of a fluorofullerene as an electrophile has been reported in one study only, involving the $FeCl_3$-catalysed reaction of $C_{60}F_{18}$ with benzene, which produced the triphenyl derivative ("triumphene") (**1**, Ar = Ph).[15] We now report the formation of a range of compounds derived from the reaction of a variety of aromatic compounds with $C_{60}F_{18}$/$FeCl_3$

[a] Dr. A. D. Darwish, Dr. A. G. Avent, Dr. A. K. Abdul-Sada, Dr. P. B. Hitchcock, Prof. R. Taylor
Chemistry Department
University of Sussex
Brighton BN1 9QJ (UK)
Fax: (44) 1273-677-196
E-mail: R.Taylor@sussex.ac.uk

[b] I. V. Gol'dt, I. V. Kuvytchko
Chemistry Department
Moscow State University
Moscow 119899 (Russia)

 DOI: 10.1002/chem.200400036



(**1**, • = F) (**3**, • = F) (**2**, • = F)

and which give rise variously to tris-, bis- or mono-aryl derivatives (**1**–**3**); some aromatic compounds did not give derivatives due either to competing side reactions (self-condensation) or steric hindrance.

Results and Discussion

The overall results are summarised in Table 1.

The effect of using the toluene solvate: In some initial experiments, the toluene solvate of $C_{60}F_{18}$ (see Experimental Section) was used, which resulted in substitution of both the desired aromatic and toluene from the solvate. Thus in the reaction with benzene, the product with a retention time of 6.1 min was shown by both ^{1}H NMR and ^{19}F NMR spectra to contain both phenyl and tolyl groups. This was accompanied by a fraction with a retention time of 7.85 min, which was attributed to $C_{60}F_{15}Ph_3$ (giving identical mass, ^{1}H NMR and ^{19}F NMR spectra to those described previously).[15]

The lack of aromatic selectivity reflects the high reactivity of the $C_{60}F_{18}$ electrophile.

Table 1. Products, HPLC retention times (min) and mass spectra details for products obtained from $FeCl_3$-catalysed reaction of $C_{60}F_{18}$ with aromatic compounds.

Aromatic compound	Retention time	Type	ms [amu]
benzene	7.85	tris	1236
	6.1	see text	see text
toluene	6.0, 6.4	tris	1278
	8.9	bis	1206
	15.5	mono	1134
anisole	6.85	tris	1326
	9.75	bis	1238
	17.7	mono	1150
diphenyl ether	4.8	tris[a]	1512
	7.85	bis[b]	1362
	15.1	mono	1212
chlorobenzene	9.5	tris	1340
1,2-dichlorobenzene	19.1	tris	1442
biphenyl	6.1, 7.8	tris[c]	1465
	16.6	mono	1196
fluorene	7.1	tris	
	18.0	mono	1208
biphenylene	19.2[d,e]	mono	1194
	12.3[d]	bis	1326
	9.1[d]	tris	1458
naphthalene	6.85, 7.25, 7.95	tris	1386[f]
	10.8	tris/bis	1386, 1278
	16.4, 19.0	mono	1170
pyrene	18.5	mono	1244
fluoranthene	12.0	bis	1426
	18.1	mono	1244

[a] A peak at 1851 amu shows addition of two further diphenyl ether molecules to the cage. [b] Shows the presence of *o* and *p* groups. [c] Also a trace of $C_{60}F_{15}$ (biphenylyl)$_3$O (1481 amu) at 7.3 min. [d] These compounds have an orange fluorescence. [e] Orange crystals. [f] Together with other components (see text).

The extent of substitution: The extent of substitution varies somewhat according to the nature of the aromatic. Thus tris-substitution is obtained for reactions with benzene, toluene, anisole, diphenyl ether, chlorobenzene, 1,2-dichlorobenzene, biphenylene, and fluorine, bis-substitution in reaction with toluene, biphenylene and fluoranthene, and mono-substitution in reaction with biphenylene, pyrene, naphthalene and fluoranthene. The reason for the failure to obtain poly-substitution with naphthalene, fluorene and pyrene is unclear but may have a steric origin. Likewise the failure to obtain some mono-substitution products would seem to reflect the high reactivity of the electrophile. It is probable that if required, the mono-substitution products for example could be produced by using a deficiency of aromatic.

Unreactive aromatic compounds: Perylene, coronene, thiophene, azulene and benzotrifluoride did not give the desired products. Reaction with perylene gave 1 cm long bright red "tagliatelli"-like threads of a highly fluorescent derivative, shown by analysis to be 3,4,9,10-tetrachloroperylene,which evidently undergoes self-assembly π-stacking, and formed through chlorination by the $FeCl_3$ catalyst. A number of other related derivatives (similar HPLC retention times) were also obtained, due we believe to substitution at other positions of the perylene.

No substitution into thiophene could be obtained, due possibly to self-substitution. Use of a toluene solution of thiophene resulted in normal substitution into toluene, as described above.

Azulene also failed to be substituted, despite the 1-position of azulene being extraordinarily electron supplying ($\sigma^+ = -1.6$).[16] Instead only polyazulenyl compounds were obtained, attributed to a reactive electrophile being formed between azulene and $FeCl_3$, which then self-substitutes. In an attempt to overcome this $SnCl_4$ was used as a catalyst, but again only polyazulenyl compounds were obtained. It is significant that other electrophilic substitutions of azulene in the presence of Lewis acids are largely unsuccessful.

The lack of reaction with benzotrifluoride indicates the lower limit of aromatic reactivity when using $FeCl_3$ as catalyst.

***ortho* substitution**: The fullerene size (exacerbated by the presence on the cage of neighbouring halogens) can restrict substitution at hindered sites. For example, previously no reaction was observed between mesitylene and $C_{60}Cl_6$.[8] However, the smaller size of fluorine reduces this problem and *ortho* substitution occurs here in reaction with toluene, biphenyl, diphenyl ether, and surprisingly, at the 1-position of naphthalene.

Interactions between aryl groups and fluorine atoms on the cage: The mono-substitution product obtained from reaction at the 1-position of naphthalene showed in the ^{1}H NMR spectrum, a 2.8 Hz coupling of the H-8 *peri*-hydrogen atom to the adjacent fluorine atom on the cage. Likewise the mono-substitution product obtained from reaction at the 1-position of pyrene showed a 2 Hz coupling between the H-10 *peri*-hydrogen atom and the neighbouring fluorine atom. The proximity of an aryl hydrogen atom and a cage fluorine atom in the case of $C_{60}F_{17}$2-naphthyl resulted in loss of HF and ring closure during EI mass spectrometry.

Free rotation of the aryl groups: The distance between the aryl groups is too large to hinder free rotation at room temperature (but may in the case of large aromatics hinder substitution of the other labile fluorines, see **2** above). In the mono-substituted derivatives, the 2-naphthyl substituent is able to rotate freely, but rotation of the 1-naphthyl- and 1-pyrenyl derivatives is restricted due to hindrance by the fullerene cage.

Substitutions of the individual aromatic compounds:

Benzene: This has been described under **1** above.

Toluene: Four fractions were obtained with retention times of 6.0, 6.4, 8.9 and 15.5 min. The spectroscopic data (see Experimental Section) showed that these were due to $C_{60}F_{15}(tol)_3$, (all-*para* substituted), $C_{60}F_{15}(tol)_3$, (two *para* and either a *meta* or an *ortho* group), $C_{60}F_{16}(tol)_2$, and $C_{60}F_{17}$tol, respectively. The monosubstitution derivative was isolated as the main one, but in low yield, in the reaction using $SnCl_4$ as catalyst, confirming that this is less effective than $FeCl_3$.

Anisole and diphenyl ether: Anisole gave fractions with retention times of 6.85, 9.75 and 17.7 min due to $C_{60}F_{15}$(anisyl)$_3$, $C_{60}F_{16}$(anisyl)$_2$, and $C_{60}F_{17}$(anisyl), respectively, whilst diphenyl ether gave fractions of 4.8, 7.85 and 15.1 min, due to $C_{60}F_{15}(C_6H_4OPh)_3$, $C_{60}F_{16}(C_6H_4OPh)_2$, and $C_{60}F_{17}(C_6H_4OPh)$, respectively (see Experimental Section).

Another sample of $C_{60}F_{15}(C_6H_4OPh)_3$ showed a mass spectrum peak at 1851 amu, which was attributed to the addition of two further diphenyl ether molecules to the unfluorinated part of the cage.

The lack of symmetry in the ^{1}H NMR spectrum (not shown) for $C_{60}F_{16}(C_6H_4OPh)_2$, revealed that it did not consist of a single isomer having two 4-C_6H_4OPh substituents. Thus, *ortho* substitution had occurred giving isomers having either a 4- and a 2-C_6H_4OPh substituent or two 2-C_6H_4OPh substituents present, which was confirmed by the ^{19}F NMR spectrum (Figure 1). For $C_{60}F_{18}$ and derivatives, the fluorine resonances fall generally within the following four main areas of δ_F values: 128–134 (the three outermost fluorine atoms), 136–138 (the six fluorine atoms attached to the central aryl ring), 141–151 (the six fluorine atoms further out from this ring), 157–170 ppm (the three fluorine atoms surrounded by three sp^3-hybridised carbon atoms. These latter

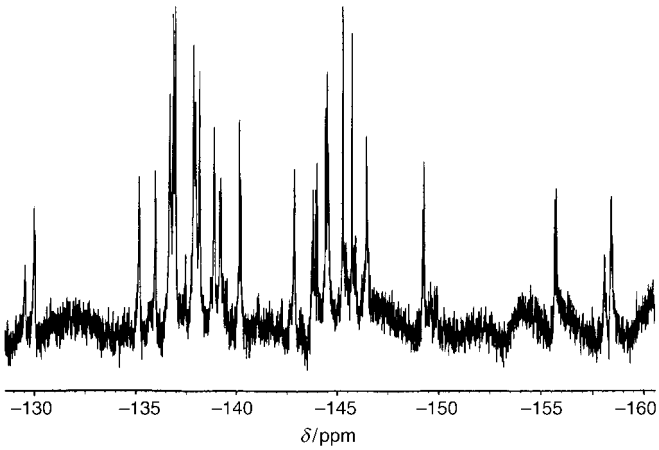


Figure 1. ^{19}F NMR spectrum of $C_{60}F_{16}(C_6H_4OPh)_2$.

peaks are moved downfield to around $\delta = -137$ ppm when fluorine is replaced by aryl. For a symmetrical bis-*para*-substituted derivative there should therefore be a total of nine lines, with just one upfield peak, and similarly a bis-*ortho*-substituted derivative (assuming free rotation of the aryl groups) would also give nine lines, whilst an *o*/*p* combination would give 15 lines, and again just one upfield peak. The 25-line spectrum (some overlap) indicates a combination of all three, which was confirmed by the presence of three upfield lines in a ratio of approximately 2:2:1, due to *p*/*p*, *o*/*p* and *o*/*o* combinations, respectively.

Chlorobenzene: This formed the tri-substituted derivative showing the parent ions at 1338/1340 amu and fragmentation ions at 1227, 1116 and 1005 amu due to stepwise loss of the aryl groups. The halogen atoms in the aryl group provide a pathway for further derivatisation.

1,2-Dichlorobenzene: Despite the electron-withdrawing effect of two chlorine atoms, this gave a tris-adduct, 1442 amu, eluting at 19.1 min. Figure 2 shows the single-crystal X-ray structure (the first for a member of the "triumphene" family) and crystal packing. It confirms the symmetry and substitution at the 4-position of 1,2-dichlorobenzene, but since the R factor is 20% (*m*-chloro substituent occupies either of the 3- and 5-positions), crystallographic data are not given.

Biphenyl: This gave fractions with HPLC retention times of 6.1, 7.8, and 16.6 min due to the two tris-substituted [$C_{60}F_{15}$(biphenyl)$_3$] and one mono-substitution product [$C_{60}F_{17}$(biphenyl)], respectively; the different tris-product retention times are due to *para* and, remarkably, *ortho* substitution. An (uncharacterised) oxide derivative of the tris compound eluted at 7.3 min (see Experimental Section).

Fluorene: Using toluene as solvent gave an early eluting component (4 min), which according to MS was assigned to a mixture of fluorene dimers and trimers resulting from self substitution, together with the main yellow-orange mono-

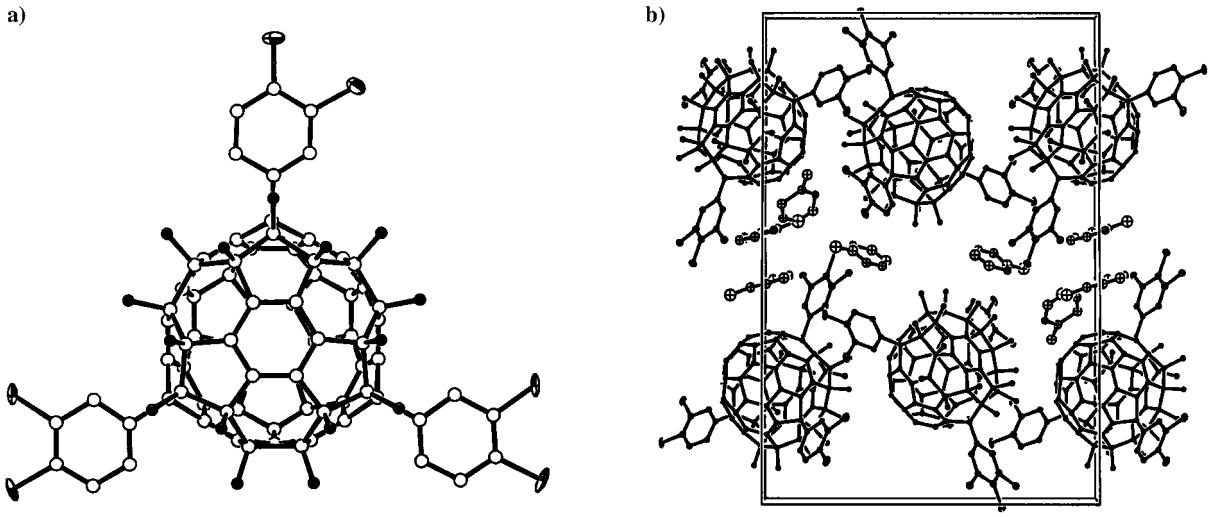


Figure 2. Single-crystal X-ray structure (a) and packing diagram (b; projection view down the *a* axis) of $C_{60}F_{17}(1,2\text{-}Cl_2C_6H_5)_3$.

substitution product **3**, Ar = 2-fluorenyl, 1208 amu, eluting at 18.0 min.

The tris-substituted product was obtained by carrying out the reaction in 1,2-dichlorobenzene. The structure was confirmed by the ^{19}F NMR spectrum which at low temperature became more complicated due to restricted rotation of the 2-fluorene substituents which may lie in either "A" or "B" conformations, giving three possibilities: AAA, ABB, AAB.

Biphenylene: This gave the mono-, bis- and tris-substituted derivatives (1194, 1326 and 1428 amu, respectively) with corresponding HPLC retention times of 19.2, 12.3 and 9.3 min. We anticipated reaction at the 2-position of biphenylene since it is the most reactive towards electrophilic substitution,[17] and this was confirmed by the single-crystal X-ray structure of the orange crystals of the mono-substitution product, two views of which are shown in Figure 3.

Naphthalene: Four fractions were obtained at 7.25, 7.95 min [both $C_{60}F_{15}(naphthyl)_3$ isomers, with combinations of 1- and 2-naphthyl substituents], 16.4 min ($C_{60}F_{17}$(2-naphthyl)) and 19.0 min ($C_{60}F_{17}$(1-naphthyl)). The 2-naphthyl mono-substitution product gave a parent ion in the EI mass spectrum at 1170 amu, with fragmentation ions for $C_{60}F_{17}$ (1043 amu). The peak assignments (Figure 4) are deduced from the respective ^1H and ^{19}F NMR spectra (see Experimental Section).

The structure of $C_{60}F_{17}$(1-naphthyl) (Figure 5) was confirmed by EI mass, ^1H, and ^{19}F NMR spectra (see Experimental Section). The mass spectrum (see Figure 10) differs from that of the 2-naphthyl isomer, in the presence of the 1150 amu peak due to HF elimination of H^8 and an F atom, which are in close proximity, giving a naphthaleno[60]fullerene. The ^{19}F NMR spectrum shows that free rotation of the 1-naphthyl substituent is prevented (giving C_1 symmetry) and that H^8 shows 2.4 Hz coupling to the adjacent F atom, a

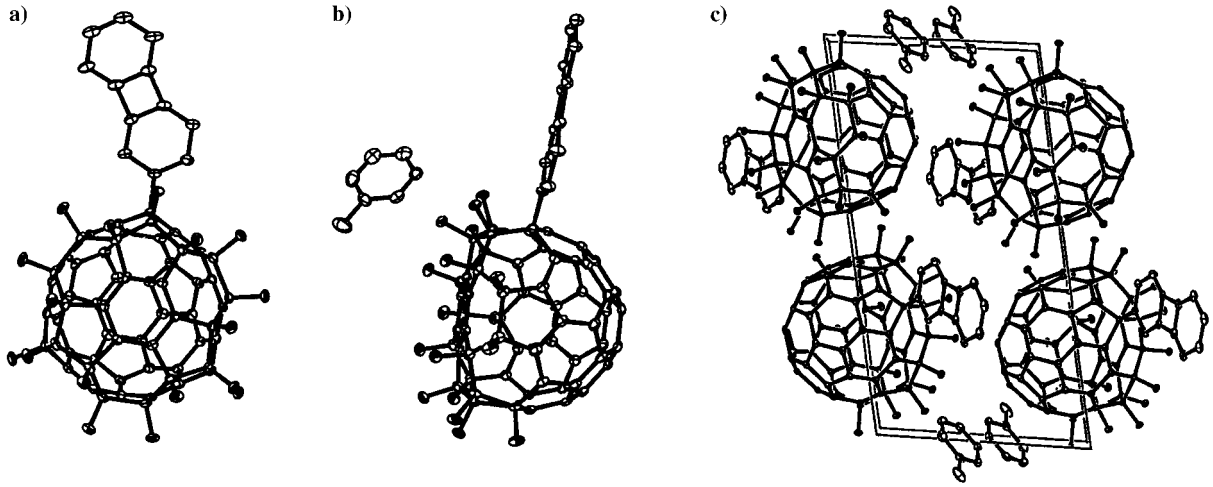


Figure 3. a) The single-crystal X-ray structure of $C_{60}F_{17}$(2-biphenylenyl); b) view showing the location of the toluene solvate; c) lattice structure with projection down the *b* axis.[18]

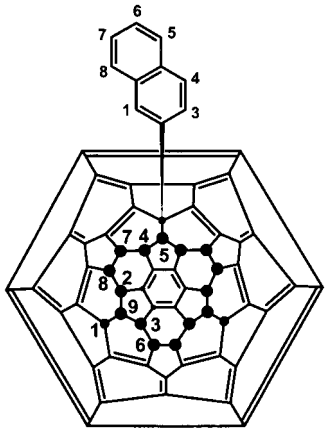


Figure 4. Schlegel diagram for $C_{60}F_{17}$(2-naphthyl); numbers in the aryl ring and fullerene cage refer to the ^{1}H and ^{19}F NMR spectra, respectively.

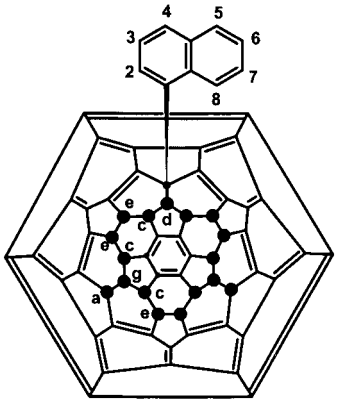


Figure 5. Schlegel diagram for $C_{60}F_{17}$(1-naphthyl); numbers in the aryl ring refer to the ^{1}H NMR spectrum; letters on the fullerene cage refer to the ^{19}F NMR data (see text for resonances).

similar coupling being observed with the *peri*-hydrogen atom of pyrene (see below).

Fluoranthene: This gave both mono- (1244 amu) and bis- (1426 amu) substitution products. The NMR spectra were in each case very complicated as expected since there are two sites each more reactive than the 1-position of naphthalene, and two each more reactive than the 2-position of naphthalene.[19] Consequently a mixture of derivatives results.

Pyrene: Using 1,2-dichlorobenzene as solvent gave the mono-substitution product, 1244 amu, with a retention time of 18.1 min. Substitution occurs at the most reactive 1-position ($\sigma^+ = -0.705$, cf. -0.36 for the 5-position).[20] As in the case of the 1-naphthalene derivative, free rotation is prevented, but the ^{19}F NMR spectrum (Figure 6 assignments deduced from 2-D COSY), shows near symmetry with peaks 6 and 11, 7 and 10, 5 and 12, 2 and 15, 8 and 9, 16 and 17, showing close coincidence. The near symmetry indicates that the plane through pyrene is almost at right angles to the plane that passes through the centeral benzenoid ring of the fluorofullerene.

Substitution in the 1-position was confirmed by the ^{1}H NMR spectrum; the peaks were assigned (Figure 7) by decoupling and 2D COSY. There is a 2 Hz coupling between *peri*-hydrogen H^{10} and the nearest fluorine atom on the fullerene cage, as found similarly for the 1-naphthyl derivative.

Derivative fluorescence: Fullerenes strongly quench the fluorescence of species that normally fluoresce in the visible, due evidently to transfer of energy from the excited singlet state of the arene to the fullerene, see for example reference [21]. The biphenylene derivatives nevertheless appeared to show orange fluorescence when irradiated at 365 nm. We therefore carried out a preliminary investigation of fluorescence of three of the tris-substituted compounds containing phenyl, fluorenyl and biphenylenyl substituents.

Irradiation of the phenyl compound at 344 nm produced an emission with a maximum at 530 nm (curve b, Figure 8), irradiation of the biphenylenyl compound at 344 and 375 nm produced emissions at 525 and 515 nm (curves c and a, respectively, Figure 8), whereas irradiation of the fluorenyl compound at either 344 or 375 nm produced no emission (curve d, Figure 8).

We hope subsequently to be able to carry out a more detailed study of the fluoresence of a greater range of arylated fullerenes.

Conclusion

Through reaction of $C_{60}F_{18}$ with a variety of aromatic compounds we have shown that electrophilic substitution of the fullerene into many aromatic compounds can be accomplished, which paves the way for the formation of a wide

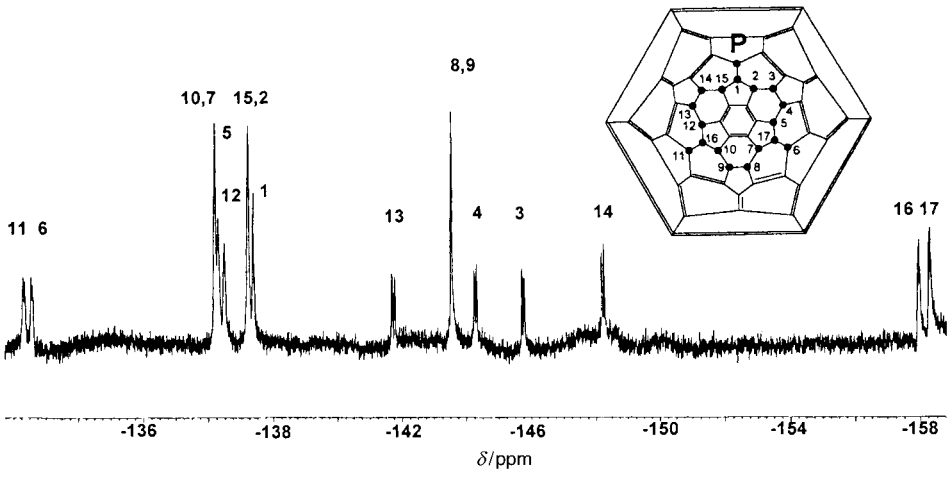


Figure 6. ^{19}F NMR spectrum for $C_{60}F_{17}$(1-pyrene).

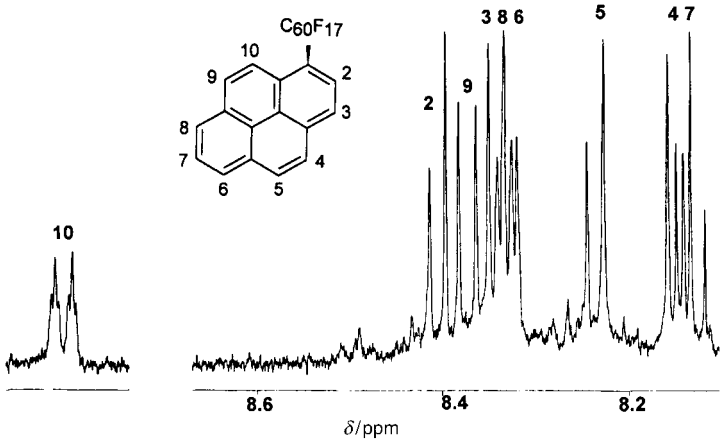


Figure 7. ^{1}H NMR spectrum for $C_{60}F_{17}$(1-pyrene).

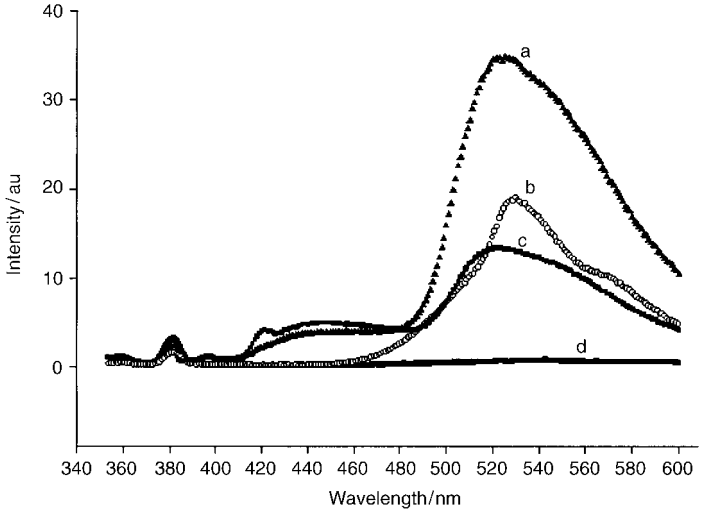


Figure 8. Emission spectra of some tris-substituted aryl fluorofullerenes (for details see text).

range of more complex arylfullerenes, all of which retain the unique shape of $C_{60}F_{18}$. These compounds are potentially important donor–acceptor dyads, combining as they do the enhanced electron withdrawal by the fluorofullerene core, and the presence of three electron-donating addends. Some of the compounds are rare examples of fluorescent fullerenes.

Experimental Section

Reagents: All aromatic compounds were commercial samples used without further purification.

Preparation of $C_{60}F_{18}$: A small-scale preparation of $C_{60}F_{18}$ has been described before[22] but was prepared for this work in two ways:

1) K_2PtCl_6 (Aldrich) was converted by reacting with fluorine gas, into K_2PtF_6, an intimately ground mixture of the latter was then heated with [60]fullerene (3:1 weight ratio) to 460 °C under vacuum by the method described previously.[23] The crude material (65 % yield) was then purified by HPLC to give a 63.5 % yield of the 1:1 $C_{60}F_{18}$:toluene solvate (41 % overall). In some experiments this was used without further treatment, though in these cases some mixed arylation resulted from the toluene present. A portion of the sample was dissolved in dichloromethane and concentrated to dryness in a rotary evaporator; this procedure was repeated three times to remove any toluene. The dried solid was then heated under vacuum for 2 h at 110 °C. This resulted in an overall 10 % weight loss (approximately that calculated for the weight of toluene in the 1:1 solvate), and no further loss occurred on additional heating (up to 110 °C). The overall yield of pure $C_{60}F_{18}$ was thus 37 %.

2) An intimately ground mixture of [60]fullerene (80 mg), MnF_3 (270 mg) and K_2NiF_6 (160 mg, Apollo Fluorochemicals) was placed in a Pyrex glass tube (120 × 8 mm i.d), and distributed evenly along it; it is essential to avoid having a "plug" of material present as this can cause its ejection on pre-heating. Packing of the tube is easier (and the yields are higher) if "old" tubes are re-used, probably due to deactivation of hydroxy sites on the glass. They are then placed in a larger tube (300 × 11 mm i.d.) inside a silica tube contained within a tube furnace. After application of vacuum (two-stage pump), the temperature was raised successively to 60, 150, 220 and 280 °C and kept at each temperature until the pressure returned to 0.005 mBar. The temperature was then raised rapidly to 520 °C (setting the furnace initially to 600 °C to get the most rapid heating) and then ramping back when the temperature had reached 470 °C to avoid overshoot. Fluorination is complete in about 20 min, and during release of fluorine by the fluorinating reagents, the pressure increases to 0.1 mBar. This increase is disadvantageous to the formation of $C_{60}F_{18}$ because it is not swept efficiently away from the reaction zone, thereby affording opportunity for further fluorination to give the unwanted $C_{60}F_{36}$. Notably, little product is deposited in the cold zone until the higher vacuum is restored, and yields are reduced if larger quantities of reagents are taken, because a larger degradation of the vacuum occurs during fluorination. Higher yields should be obtainable by using a ballasted system coupled with a pump of higher efficiency than that presently available to us, and this is to be investigated.

The tubes were removed, cooled rapidly, and the product was extracted with toluene (sonication), filtered, concentrated and purified by HPLC. The whole contents of each run were purified in one injection (6–7 mL) using a 250 × 20 mm Cosmosil Buckyprep column, (18 mL min^{-1} toluene flow rate). The average yield per run of pure $C_{60}F_{18}$:toluene solvate was 16–17 mg (14 %). Three runs were routinely carried out per day (using fast cooling of the furnace at the end of each run), giving weekly yields of about 250 mg for this and other ongoing work. At full capacity our HPLC system is able to purify 400 mg of $C_{60}F_{18}$ per week.

Arylation: In previous work using benzene as the aromatic compound,[15] the reagents ($C_{60}F_{18}$/benzene/$FeCl_3$) were mixed together, one batch being left at room temperature, the other was heated to 70 °C for 1 h. The solutions were then left (for logistical reasons) to evaporate to dryness over a period of about three months. On the assumption that the reaction was occurring whilst the reagents were in solution, we repeated this procedure but analysed the solutions, and found very little reaction to occur. They were concentrated for $C_{60}F_{18}$ recovery using a rotary evaporator at 40 °C, when it was discovered that reaction then took place. Subsequent experiments confirmed that reaction under these conditions occurred only when the reagents were evaporated essentially to dryness, and would seem to be a concentration effect. All subsequent preparations were performed using two regimes: 1) a mixture of the aromatic compound (excess), $C_{60}F_{18}$ (3–5 mg) and (except where otherwise indicated) $FeCl_3$ (10 mg, excess) was heated to 40 °C and concentrated to dryness using a rotary evaporator; use of catalytic quantities of $FeCl_3$ gave lower yields. Solid aromatic compounds were dissolved first in either benzene or toluene, and this resulted in some mixed substitution, which also provided information on the relative reactivities of the aromatic compounds; 2) the aromatic compound was dissolved in 1,2-dichlorobenzene and heated to 90 °C with $C_{60}F_{18}$/$FeCl_3$ and then evaporated to dryness under vacuum. This gave a better yield of tris adducts in some cases, but also produced accompanying substitution into 1,2-dichlorobenzne. $SnCl_4$ was a less effective catalyst giving greater recovery of unreacted $C_{60}F_{18}$, whilst use of $AlCl_3$ resulted in polyarylation, and loss of all of the $C_{60}F_{18}$.

We briefly investigated the use of other solvents: poor yields were obtained by using CCl_4, CH_2Cl_2, C_6F_6 and 1,2-dichloroethane (the most satisfactory of the non-aromatic compounds). Overall, benzene, toluene and 1,2-dichlorobenzene were best.

At the end of reaction, toluene was added to the solid mixture which was filtered and the products were separated by HPLC using a Cosmosil 5

PYE column with toluene elution at 4 mL min^{-1}, and then examined by mass spectrometry (EI, 70 eV), ^{1}H and ^{19}F NMR spectroscopy. Because of the small scale used in this work, products were each obtained in about 1 mg yields.

In common with many other fullerene derivatives, some compounds showed instability towards EI mass spectrometry, with loss of some or all of the aryl groups, leaving the fluorinated fragment from which the nature of the parent species was determined (confirmed by the NMR spectra). The fluorofullerene fragments that indicated the parent species were: 1005 amu ($C_{60}F_{15}$); 1024 ($C_{60}F_{16}$); 1043 ($C_{60}F_{17}$), and these are evident in typical examples of the mass spectra that are shown.

Spectroscopic data

Mass spectra: These were all EI and run at 70 eV.

^{1}H and ^{19}F NMR spectra: ^{1}H and ^{19}F NMR spectra were run at 500 and 377 MHz (CDCl3), respectively.

Benzene: The mass spectrum of the eluent with a retention time of 6.1 min showed peaks (amu) at 1005 (30%), 1082 (5%), 1159 (20%), 1278 (55%), 1326 (6%) and 720 (100%), confirming the presence of phenyl and tolyl groups.

Toluene: The mass spectrum of the fraction with a retention time of 6.0 min (Figure 9) showed the parent ion at 1278 amu [$C_{60}F_{18}(tol)_3$], and fragmentation ions at 1187, 1096 and 1005 amu due to the loss of the three aryl groups. The ^{19}F NMR spectrum comprised three peaks at $\delta =$ −137.43 (bs, 3F), −138.44 (bs, 6F) and −145.17 ppm (bs, 6F), and the ^{1}H NMR spectrum (500 MHz, $CDCl_3$) showed $\delta = 7.61$ (d, ^3J(H,H) = 8 Hz, 2H, *meta* to Me), 7.43 (d, ^3J(H,H) = 8, 0.5 Hz, 2H, *ortho* to Me), and 2.48 ppm (s, 3H, Me). Irradiation of the latter collapsed the upfield peaks to a doublet showing them to be due to the hydrogen atoms adjacent to the methyl group, and this is also consistent with the location of the more downfield pair, which are *ortho* to the electron-withdrawing cage.

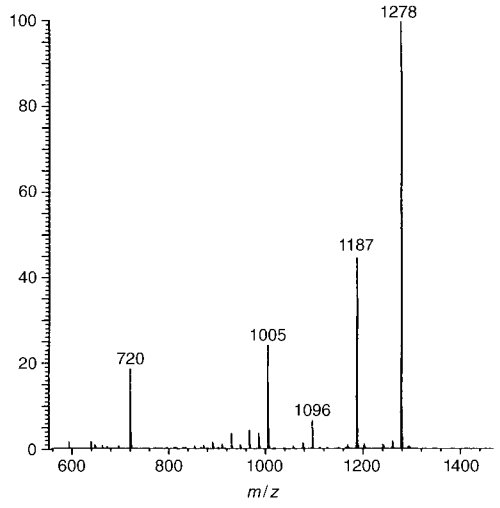


Figure 9. EI mass spectrum for $C_{60}F_{15}(tolyl)_3$.

The mass spectra of the fractions with retention times of 8.9 and 15.5 min gave parent ions at 1206 amu [fragmentation ion at 1024 amu ($C_{60}F_{16}$)], and 1134 amu [fragmentation ion at 1043 amu ($C_{60}F_{17}$)], respectively. Both spectra showed fragmentation ions at 904 and 812 amu due to loss of all the fluorine atoms.

Anisole: The mass spectra of the fractions with retention times of 6.85, 9.75, and 17.7 min gave parent ions at 1326, 1238, and 1150 amu (Figure 10). The latter shows the main fragmentation ion at 1043 amu ($C_{60}F_{17}^+$, due to loss of the aryl group) and 828 amu (C_{60}anisyl$^+$, due to loss of all of the fluorine atoms).

Diphenyl ether: The mass spectra of the fractions with retention times of 4.8, 7.85 and 15.1 min showed parent ions in the mass spectra at 1513 (Figure 11), 1362 and 1212 amu due to $C_{60}F_{15}(C_6H_4OPh)_3$, $C_{60}F_{16}(C_6H_4OPh)_2$, $C_{60}F_{17}(C_6H_4OPh)$, respectively.

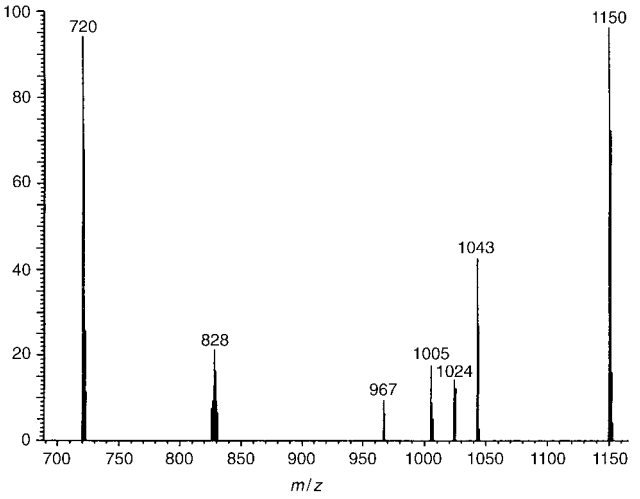


Figure 10. EI mass spectrum for $C_{60}F_{17}$(anisyl).

Biphenyl: The fractions with retention times of 6.1 and 7.8 min gave EI mass spectra showing parent ions at 1465 amu [$C_{60}F_{15}$(biphenyl)$_3$] with fragments at 1311, 1158 and 1005 amu due to aryl loss. By analogy with the results with toluene, the fractions are assigned to *para*- and *ortho* substitution. The 16.6 min fraction gave parent/fragmentation ions at 1196/1043 amu ($C_{60}F_{17}$(biphenylyl)), and the 7.3 min fraction gave parent/fragmentation ions at 1481/1326 amu, [$C_{60}F_{15}$(biphenyl)$_2$O] (either an ether or fluoroxy derivative).

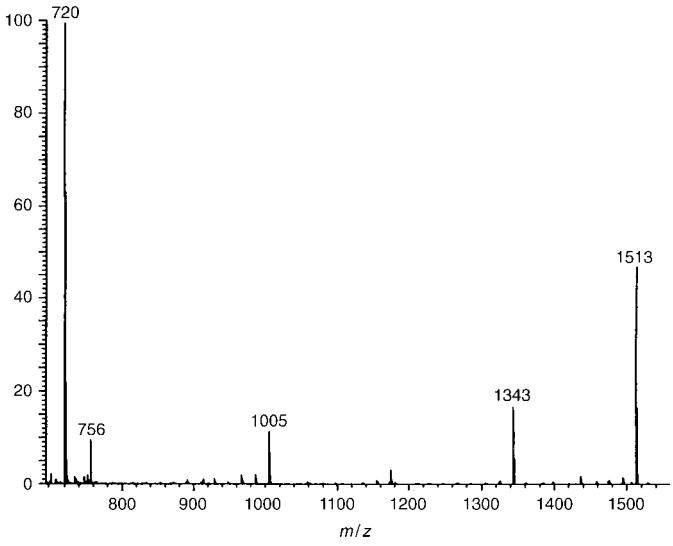


Figure 11. EI mass spectrum for $C_{60}F_{15}(C_6H_4OPh)_3$.

Fluorene: The ^{19}F NMR spectrum of the tris-derivative shows three peaks at $\delta_F = -136.1$ (bs, 3F), −137.8 (bs, 6F) and −144.0 ppm (bs, 6F). The ^{1}H NMR spectrum (328 K) gave $\delta = 8.04$ (s, 1H, H^1), 7.89 (dd, ^3J(H,H) = 7.8, 2.2 Hz, 1H, H^3), 7.74 (d, ^3J(H,H) = 7.8 Hz, 1H. H^4), 7.73 (d, ^3J(H,H) = 7.7 Hz, 1H, H^5), 7.34 (d, ^3J(H,H) = 7.6 Hz, 1H, H^8), 7.25, (m, H^{6,7} 2H, m), 3.54 ppm (s, 2H, s CH_2). H^1 and H^8 were identified by nOe between them and the methylene group, and the 2.2 Hz coupling of H^3 is due to interaction with the nearby fluorine on the cage.

On lowering the temperature to 280 K, restricted rotation of the asymmetric 2-fluorenyl group caused the methylene peak to split into three peaks at $\delta = 3.40$, 3.52 and 3.56 ppm in a ratio of about 1:4:4.

Naphthalene: The tris-naphthyl derivatives eluting at 7.25 and 7.95 min gave parent ions at 1387 amu.

^{1}H NMR spectrum for $C_{60}F_{17}$(2-naphthyl): $\delta = 8.09$ (d, ^3J(H,H) = 8.7, 1H, H^4), 8.07 (d, ^3J(H,H) = ca. 2 Hz, 1H, H^1), 7.95–8.00 (bm, 2H, H^{5,8}), 7.77 (d, ^3J(H,H) = 8.4, 2.1 Hz, 1H, H^3), 7.65–7.63 ppm (bm, 2H, H^{6,7}). were identified by decoupling. The nine-line ^{19}F NMR spectrum (Figure 12), proves the C_s symmetry and that the 2-naphthyl group rotates freely. The

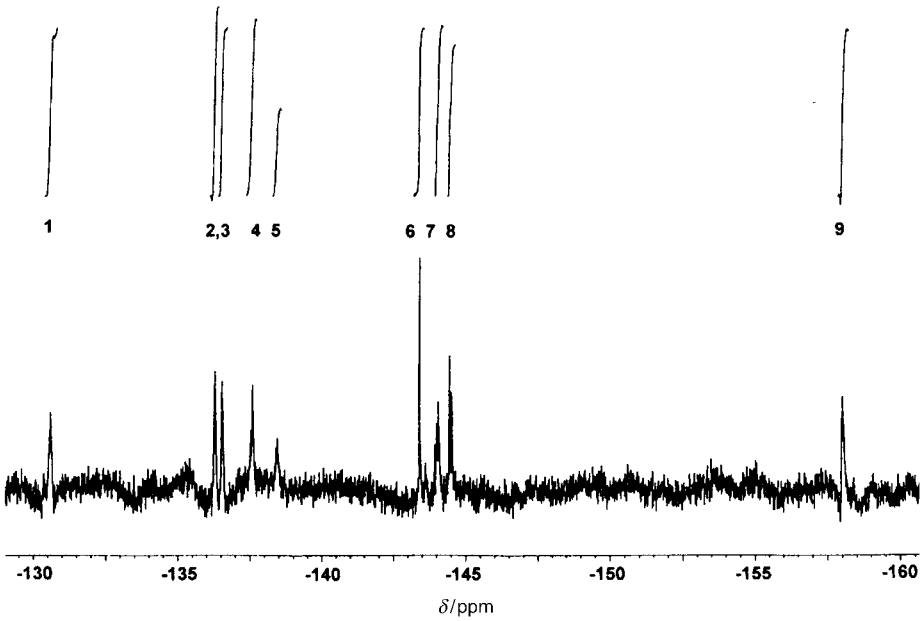


Figure 12. ^{19}F NMR spectrum of $C_{60}F_{17}$(2-naphthyl); for peak assignments see Figure 4.

peaks (all 2F multiplets except no. 5 which is 1F) appear at $\delta_F = 130.60$, 135.26, 135.41, 137.54, 137.59, 143.42, 144.46, 144.52, 158.01 ppm and are assigned (Figure 4) from experience with $C_{60}F_{18}$ derivatives.

Figure 13 is the EI mass spectrum for $C_{60}F_{17}$(1-naphthyl). The NMR spectrum shows seven equal-intensity lines, assigned through multiplicity and de-coupling, at $\delta = 8.87$ (dm, ^3J(H,H) = 7.7 Hz, H^8), 8.04 (d, ^3J(H,H) = 7.9 Hz, H^4), 8.02 (d, ^3J(H,H) = 8.2 Hz, H^5), 7.90 (d, ^3J(H,H) = 6.9 Hz, H^2)

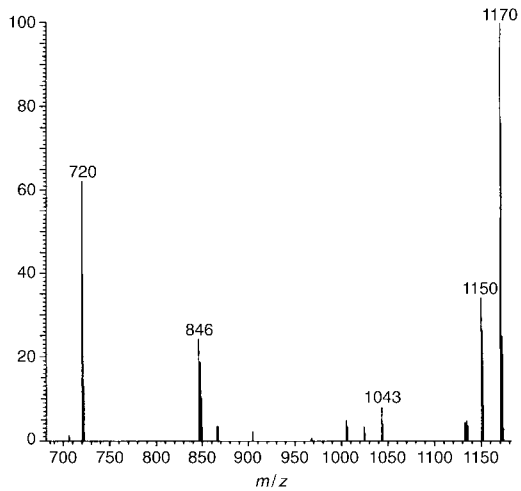


Figure 13. EI mass spectrum of $C_{60}F_{17}$(1-$C_{12}H_7$).

7.74 (t, ^3J(H,H) = 8.3 Hz, H^7), 7.648 (t, ^3J(H,H) = 7.0 Hz, H^6), 7.642 ppm (t, ^3J(H,H) = 7.9 Hz, H^3).

The ^{19}F NMR spectrum shows seventeen peaks (all 1F multiplets except where stated) at $\delta_F = -130.39$, −130.68, (*a*-type fluorine atoms); −136.30 (2F), −136.43, −136.62, −137.32, −137.67 (*c*-type fluorine atoms); −138.84 (*d*-type fluorine atoms); −141.70, −143.63 (2 F), −144.45, −145.73, −148.16 (all *e*-type fluorine atoms); −158.03, −158.38 ppm (*g*-type fluorine atoms). These peaks all fall in the ranges found generally for $C_{60}F_{18}$ derivatives, except for peak *d* (and likewise peak 5 for the 2-naphthyl isomer), which is shifted downfield due to loss of an adjacent fluorine and its electron-supplying lone pair.

Pyrene: ^{19}F NMR data for $C_{60}F_{17}$(1-pyrene): $\delta_F = -130.33$ (d, ^3J(F,F) = 19.7 Hz, 1F), −130.55 (d, ^3J(F,F) = 18 Hz, 1F), −136.20 (bs, coincident, 2F), −136.30 (bs, 1F), −136.50 (bs, 1F), −137.22 (bs, coincident, 2 F), −137.37 (m, 1F), −141.73 (d, ^3J(F,F) = 31 Hz, 1F) , −143.53 (s, coincident, 2F), −144.25 (d, ^3J(F,F) = 24 Hz, 1F), −145.71 (d, ^3J(F,F) = 27 Hz, 1F), −144.80 (d, ^3J(F,F) = 27 Hz), −157.95 (m 1F), −158.26 ppm (m, 1F).

^{1}H NMR data for $C_{60}F_{17}$(1-pyrene): $\delta = 9.11$ (dt, ^3J(H,H) = 9.4, 2 Hz, 1H), 8.40, (d, ^3J(H,H) = 8.2 Hz, 1H), 8.37 (d, ^3J(H,H) = 9.4 Hz, 1H), 8.34 (d, ^3J(H,H) = 8.2 Hz, 1H), 8.332 (d, ^3J(H,H) = 7.5 Hz, 1H), 8.327 (d, ^3J(H,H) = 6.9 Hz, 1H), 8.23 (d, ^3J(H,H) = 8.9 Hz, 1H), 8.152 (d, ^3J(H,H) = 8.9 Hz, 1H), 8.133 ppm (t, ^3J(H,H) = 7.7 Hz, 1H).

Acknowledgement

We thank Dr Peter Fearon for running the fluorescence spectra, and the EPSRC and the Royal Society (Joint Project Award) for financial support.

[1] S. H. Hoke, J. Molstad, G. L. Payne, B. Kahr, D. Ben-Amotz, R. G. Cooks, *Rapid Commun. Mass Spectrom.* **1991**, *5*, 472.
[2] O. V. Boltalina, J. M. Street, R. Taylor, unpublished work.
[3] G. A. Olah, I Bucsi, . C. Lambert, R. Aniszfeld, N. J. Trevedi, D. K. Sensharma, G. K. S. Prakash, *J. Am. Chem. Soc.* **1991**, *113*, 9387; G. A. Olah, I. Bucsi, D. S. Ha, R. Aniszfeld, C. S. Lee, G. K. S. Prakash, *Fullerene Sci. Technol.* **1997**, *5*, 389; A. G. Avent, P. R. Birkett, R. Taylor , unpublished work.
[4] R. Taylor, G. J. Langley, M. F. Meidine, J. P. Parsons, A. K. Abdul-Sada, T. J. Dennis, J. P. Hare, H. W. Kroto, D. R. M. Walton, *J. Chem. Soc. Chem. Commun.* **1992**, 667.
[5] A. D. Darwish, P. R. Birkett, G. J. Langley, H. W. Kroto, R. Taylor, D. R. M. Walton, *Fullerene Sci. Technol.* **1997**, *5*, 705.
[6] A. G. Avent, P. R. Birkett, H. W. Kroto, R. Taylor, D. R. M. Walton, *Chem. Commun.* **1998**, 2153; P. R. Birkett, M. Bühl, A. Khong, M. Saunders, R. Taylor, *J. Chem. Soc. Perkin Trans. 2* **1999**, 2037.
[7] A. G. Avent, P. R. Birkett, J. D. Crane, A. D. Darwish, G. J. Langley, H. W. Kroto, R. Taylor, D. R. M. Walton, *J. Chem. Soc. Chem. Commun.* **1994**, 1463; A. D. Darwish, A. G. Avent, P. R. Birkett, H. W. Kroto, R. Taylor, D. R. M. Walton, *J. Chem. Soc. Perkin Trans. 2* **2001**, 1038.
[8] P. R. Birkett, A. G. Avent, A. D. Darwish, I. Hahn, J. O'Loughlin, H. W. Kroto, G. J. Langley, R. Taylor, *J. Chem. Soc. Perkin Trans. 2* **1997**, 1121.

[9] P. R. Birkett, A. G. Avent, A. D. Darwish, H. W. Kroto, R. Taylor, D. R. M. Walton, *J. Chem. Soc. Perkin Trans. 2* **1997**, 457.
[10] A. K. Abdul-Sada, A. G. Avent, P. R. Birkett, A. D. Darwish, H. W. Kroto, R. Taylor, D. R. M. Walton, O. B. Woodhouse, *Chem. Commun.* **1998**, 307.
[11] A. D. Darwish, A. G. Avent, H. W. Kroto, R. Taylor, D. R. M. Walton, *J. Chem. Soc. Perkin Trans. 2* **1999**, 1983.
[12] A. G. Avent, P. R. Birkett, A. D. Darwish, H. W. Kroto, R. Taylor, D. R. M. Walton, *Tetrahedron* **1996**, *52*, 5235.
[13] P. R. Birkett, A. G. Avent, A. D. Darwish, H. W. Kroto, R. Taylor, D. R. M. Walton, *Chem. Commun.* **1996**, 1231.
[14] P. R. Birkett, A. G. Avent, A. D. Darwish, H. W. Kroto, R. Taylor, D. R. M. Walton, *J. Chem. Soc. Perkin Trans. 2* **2001**, 68.
[15] O. V. Boltalina, J. M. Street, R. Taylor, *Chem. Commun.* **1998**, 1827.
[16] A. P. Laws, R. Taylor, *J. Chem. Soc. Perkin Trans. 2* **1987**, 591.
[17] J. M. Blatchly, R. Taylor, *J. Chem. Soc.* **1964**, 4641.
[18] Crystal data for $C_{72}H_7F_{17}.C_7H_8$, $M_r = 1298.9$, triclinic , $P\bar{1}$ (no. 2), $a = 11.2748(3)$, $b = 11.4746(3)$, $c = 19.7087(7)$ Å , $\alpha = 95.348(1)$, $\beta = 98.313(1)$, $\gamma = 108.960(1)°$, $V = 2359.2(1)$ Å^3, $T = 223$ K, $Z = 2$, $\rho_{calcd} = 1.81$ Mg m^{-3}, μ ($Mo_{K\alpha}$) $= 0.15$ cm^{-1}, crystal size $0.1 \times 0.05 \times 0.02$ mm^3. Data collected on a KappaCCD diffractometer, 8127 unique reflections ($R_{int} = 0.12$). Refinement on F^2, final residuals $R1 = 0.074$ (for 4573 reflections with $I > 2\sigma I$), $wR2 = 0.174$ for all data. CCDC-228315 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/consts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB12 1EZ, UK; fax: (+44)1223-366-033; or e-mail: deposit@ccdc.cam.ac.uk.
[19] K. C. C. Bancroft, G. R. Howe, *J. Chem. Soc. B* **1970**, 1541.
[20] R. Taylor, *Electrophilic Aromatic Substitution*, Wiley, Chichester, **1990**, Tables 3.17 and 11.1).
[21] J-C. Lee, T-Y. Kim, S. H. Kang, Y. K. Shim, *Bull Acad. Korean Chem. Soc.* **2001**, *22*, 257.
[22] O. V. Boltalina, V. Yu. Markov, R. Taylor, M. P. Waugh, *Chem. Commun.* **1996**, 2549.
[23] O. V. Boltalina, A. Yu. Lukonin, A. A. Gorjunkov, V. K. Pavlovich, A. N. Rykov, V. A. Seniavin, L. V. Sidorov, R. Taylor, *Proc. Electrochem. Soc.* **1997**, *97–14*, 257.

Received: January 13, 2004
Revised: April 2, 2004
Published online: August 2, 2004

