C_2 Isomers of $C_{84}F_{40}$ and $C_{84}F_{44}$ Are Cuboid and Contain Benzenoid and Naphthalenoid Aromatic Patches

Adam D. Darwish,[a] Natalia Martsinovich,[a] Joan M. Street,[b] and Roger Taylor*[a]

Abstract: A 1:1 mixture of $C_{84}F_{40}$ and $C_{84}F_{44}$, both derived from the D_2(IV) isomer, has been isolated from the fluorination of [84]fullerene with either MnF_3 or CoF_3 at 500 °C. The 1D and 2D COSY ^{19}F NMR spectra showed that each derivative is cuboid, having benzenoid rings at four of the six octahedral sites; the two remaining sites have naphthalenoid rings for $C_{84}F_{40}$, and two slightly offset benzenoid rings for $C_{84}F_{44}$. The benzenoid rings each have six adjacent sp^3-hybridised carbon atoms whilst the naphthalenoid moieties have eight, thus facilitating full delocalisation. In terms of the number and size of aromatic patches, $C_{84}F_{44}$ is the most aromatic fullerene derivative yet isolated.

Keywords: aromaticity · fluorine · fullerenes · NMR spectroscopy · structure elucidation

Introduction

The major driving force accounting for the regiochemistry and preferred addition levels in polyaddition to fullerenes is the formation of aromatic substructures. In the parent molecules, electron delocalisation is inhibited by the increase in strain that would arise on introduction of double bonds into pentagons. Fullerenes thus have a low intrinsic aromaticity.

Additions are therefore the main reactions and occur at the 6:6-bonds where the electrons are localised. This however reduces the strain in the pentagons through sp^2 to sp^3 transformations, and delocalisation is increased.[1] It is manifest in octahedral cycloadditions to [60]fullerene in which eight of the hexagons acquire increased delocalisation;[2] one reaction uniquely produces two such rings together with three groups of fused hexagons having some naphthalenoid character.[3] Triscycloaddition adjacent to the hexagonal end-caps of [78]fullerene isomers[4] may also be partly driven by the resulting increased aromaticity.

Delocalisation is, however, only partial in each of these examples, because only three of the carbon atoms adjacent to the "aromatic" rings (four in the case of the naphthalenoid rings) are sp^3 hybridised, so significant strain remains. By contrast, a range of halogenated fullerenes have been isolated and characterised, in which all six carbon atoms adjacent to the benzenoid rings are sp^3 hybridised. Delocalisation is effectively complete, the rings are planar and their bond lengths are equal. These comprise three isomers of $C_{60}F_{36}$,[5] two isomers of $C_{70}F_{38}$,[6] one isomer of $C_{60}Cl_{28}$,[7] one of $C_{70}Cl_{28}$[8] and two isomers of both $C_{60}Cl_{30}$[7] and $C_{78}Br_{18}$.[9] These compounds contain up to four planar benzenoid rings. The simple ^{19}F NMR spectrum of D_3-$C_{74}F_{38}$ was also interpreted in terms of a structure having six benzenoid rings.[10]

A very large amount of data, summarised recently,[11] is now available concerning fluorination of fullerenes, but few data are available for fluorination of higher fullerenes. A mass spectrometric study showed the preferential formation of $C_{76}F_{38}$, $C_{78}F_{38}$, $C_{82}F_{44}$, $C_{84}F_{40}$ (two isomers) and $C_{84}F_{44}$ but no structural information could be deduced because of the small sample sizes.[12] Fluorination of [76]- and [78]fullerenes gave $C_{76}F_n$: $n=32$, 36, 38 (main isomer of C_1 symmetry), 40 (five isomers, one of C_2 symmetry), 42, 44, together with $C_{76}F_{39}OH$, and $C_{78}F_n$: $n=38$, 42, together with $C_{78}F_{39}OH$.[13]

We now describe the isolation and structural characterisation of C_2 isomers of $C_{84}F_{40}$ and $C_{84}F_{44}$, both derived from [84-D_2(IV)]fullerene[14] through fluorination of [84]fullerene with either MnF_3 or CoF_3 at 500 °C.

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Results and Discussion

The EI mass spectrum (Figure 1, 70 eV) of HPLC-isolated fraction ii (see Experimental Section) showed the presence of $C_{84}F_{44}$ (1844 amu) and $C_{84}F_{40}$ (1768 amu), together with F_2 loss fragments. The relative concentration of $C_{84}F_{44}$ is exaggerated by its higher volatility; thus at high probe temperatures, the spectrum showed only $C_{84}F_{40}$.

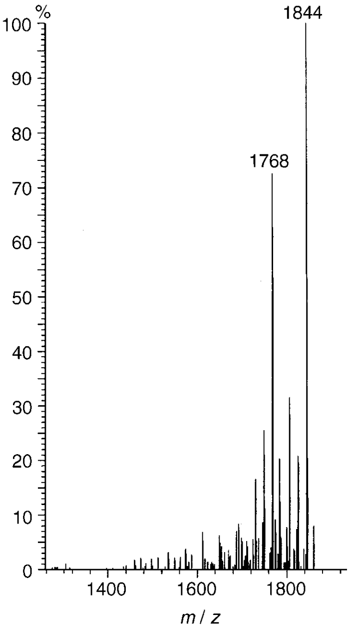


Figure 1. EI mass spectrum (70 eV) for the mixture of $C_{84}F_{44}$ and $C_{84}F_{40}$ (fraction ii, see Experimental Section).

The ^{19}F NMR spectrum (Figure 2) shows that both components are present in equal amounts, and comprises 42 equal intensity lines (some almost coincident), consistent only with a 1:1 mixture of C_2 isomers of $C_{84}F_{40}$ and $C_{84}F_{44}$. This was confirmed by a 2D COSY spectrum, the F–F couplings of which enabled separation into two series of lines: Twenty-two lines, no. 38, 37, 36, 35, 34, 33, 32, 31, 28, 27, 22, 21, 18, 15, 12, 11, 7, 5, 4, 3, 2, 1, assigned to $C_{84}F_{44}$; Twenty lines, no. 42, 41, 40, 39, 30, 29, 26, 25, 24, 23, 20, 19, 17, 16, 14, 13, 10, 9, 8, 6, assigned to $C_{84}F_{40}$. Thus both compounds are derived from the more abundant D_2(IV) isomer of [84]fullerene, as the minor D_{2d} isomer would give half the number of lines. The ^{19}F NMR spectrum exhibits some unique features that make it possible to solve the structures:

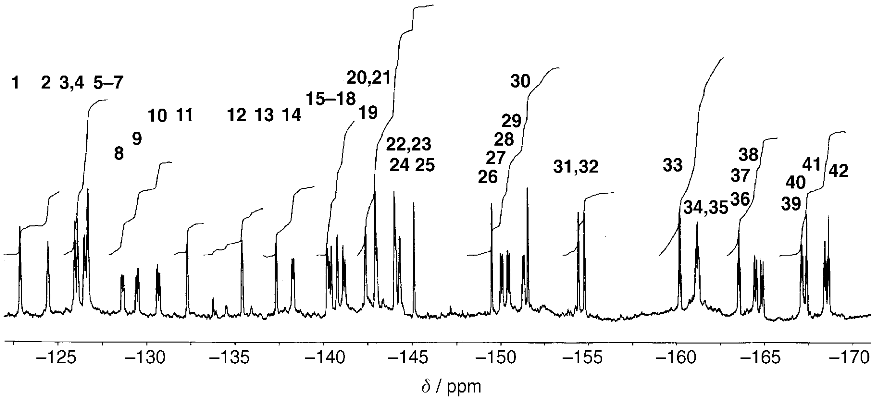
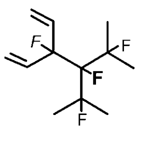


Figure 2. ^{19}F NMR spectrum (376 MHz) for the mixture of $C_{84}F_{44}$ and $C_{84}F_{40}$ (fraction ii, see Experimental Section), showing peak labelling (cf. Figure 3).

1) The spectrum comprises many pairs of very similar resonances, particularly the following: 42,41 versus 40,39; 38 versus 37; 35 versus 34; 32 versus 31; 28 versus 27; 23,22 versus 21,20; 12 versus 11. This shows that two components of either very similar structure or high symmetry are present, differing only in the location of the four additional fluorine atoms in $C_{84}F_{44}$.



A

2) There are ten upfield multiplets, six of which (38, 37, 36, 35, 34, 33) belong to $C_{84}F_{44}$, and four (42, 41, 40, 39) belong to $C_{84}F_{40}$. From numerous ^{19}F NMR spectra of fluorofullerenes obtained previously, we showed that upfield multiplets are due to the central fluorine in motif **A**. The solved structures contain six and four such motifs for $C_{84}F_{44}$ and $C_{84}F_{40}$, respectively; addition of the four extra fluorine atoms must occur at sites that result in formation of two additional motifs of **A**. $C_{84}F_{44}$ multiplets 37,38 couple to 34,35, which provides important evidence for the proposed structure.
3) In fluorofullerenes, fluorine atoms attached to carbon atoms having two sp^2 neighbours (*F* in **A**) are the most downfield peaks, and are always coupled to the most upfield peaks. This is precisely observed here: for $C_{84}F_{40}$ the four downfield peaks (6, 8, 9, 10) couple, respectively, to upfield peaks (39, 40, 42, 41), whilst for $C_{84}F_{44}$ the six downfield peaks (1, 2, 3, 4, 5, 7) couple , respectively, to upfield peaks (36, 33, 38, 37, 35, 34). The downfield peaks are coupled together in pairs (1–2, 3–4, 5–7, 6–8, 9–10), which is a key feature in elucidating the structure.
4) Given the ubiquitous formation of aromatic derivatives in highly addended fullerenes, the very specific 40 and 44 F addition levels obtained here and previously[12] indicated the formation of aromatic compounds. This requirement results in a perfect fit with the NMR data. All of the carbon atoms adjacent to the aromatic ring must have ad-

dends, and there are only two possible structures for each of $C_{84}F_{40}$ and $C_{84}F_{44}$ that meet this requirement; one set has C_2 symmetry (see Schlegel diagrams, Figure 3), the other has D_2 symmetry. (N.B. Because identification of the lowest locant pathway is formidable in these highly addended molecules, the numbering for the parent molecule[14] is retained here for simplicity). The D_2 option is further ruled out by the NMR data, by theoretical calculations that show that the C_2 isomer of $C_{84}F_{40}$ is much more stable than the D_2 isomer by 19.6 or 44.4 kcal mol^{-1} (DFT or AM1, respectively), and also by the options for addition (see below).

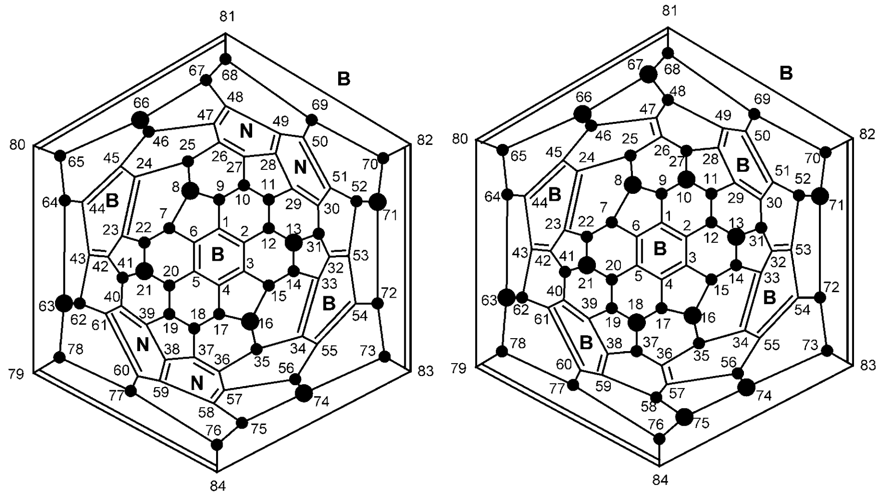


Figure 3. Schlegel diagrams for C_2-$C_{84}F_{40}$ (left) and -$C_{84}F_{44}$ (right) showing location of the benzenoid and naphthalenoid rings; ● = F, the larger circles (●) are for fluorine atoms (see bold F in **A**) that give upfield multiplets in the NMR spectrum. The C_2 axes pass through the central aromatic ring. (N.B. The cage numbering differs from the NMR peak numbering of Figure 2).

5) For $C_{84}F_{40}$ there are four pairs of symmetry-equivalent fluorine atoms that will give upfield peaks (39, 40, 41, 42) in the spectrum. These are attached collectively to positions 8 (=16), 13 (=21), 63 (=71) and 66 (=74) (Figure 3), and their very similar locations account for the similar positions in the spectrum. The corresponding downfield peaks in the spectrum (*F* in **A**) are due to fluorine atoms located on positions 25 (=35), 31 (=41), 62 (=52) and 46 (=56), and similar qualifications apply. Further confirmation of the structure comes from the couplings of the downfield peaks, namely 5 coupled to 6, and 7 coupled to 8, which is uniquely required by the structure, with 1,4-conjugated couplings as follows: 25–46 (≡35–56); 31–52 (≡41–62). The resultant structure is unique in not only being cuboid (see Figure 4), but also in having two naphthalenoid rings present. This latter feature would not be feasible in a lower fullerene, but the lower curvature in the larger fullerene now makes this possible. A related result is the optimised molecular structure for $C_{80}H_{44}$ which is cuboid with six planar benzenoid rings at the octahedral sites.[15] Another structural feature is the resemblance of the motifs surrounding the aromatic rings centred on the C_2 axis to that found in $C_{60}F_{18}$.[16]

6) For $C_{84}F_{44}$, addition of the four extra fluorine atoms to $C_{84}F_{40}$ with minimum loss of aromaticity can occur only in the naphthalenoid ring. There are a number of options and constraints: the feasible addition patterns in naphthalene are either 1,4-, 2,3- 2,6-, 1,5- or 9,10 (see **B**), the added fluorine atoms must have two sp^2 neighbours in order to account for their downfield location in the spectrum and they must be coupled and non-equivalent. The neighbour requirement rules out both 2,3-addition and 9,10-addition, and only 1,4-addition will give the maximum aromaticity in the product (six benzenoid rings). This conjecture was confirmed by the calculated (DFT) lower stability (41.4–47.8 kcal mol^{-1}) of the structure resulting from addition to the 1,5-naphthalene-like positions (i.e., positions 27, 50, 37, 60), compared with the 1,4-addition alternatives. These latter involve either positions 27 and 48 (=37 and 58) or 29 and 50 (=39 and 60). The product of the former option is calculated (DFT) to be more stable than that from the latter by 6.3 kcal mol^{-1}, so that only one isomer of $C_{84}F_{44}$ should be formed. As these fluorine atoms are 1,4-conjugated, they should be coupled, just as is found for the two additional downfield peaks. A consequence of the addition of the four extra fluo-

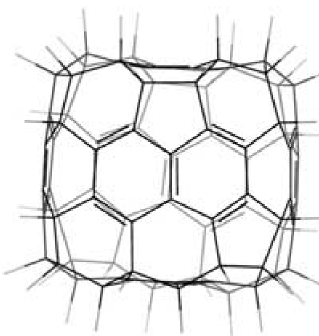
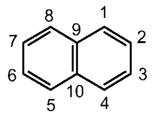


Figure 4. Structure of C_2-$C_{84}F_{40}$ viewed along the axis that bisects the central bonds of the naphthalenoid rings.



B

rine atoms to sites 27/48 and 37/58 is to create two equivalent pairs of motifs **A** on positions 10 (=18) and 67 (=75). Not only is this precisely observed, but the new multiplets should be either 1,3- or 1,2-coupled to the fluorine atoms on positions 8 (=16) and 66 (=74), respectively. This is seen also in the NMR spectrum, with coupling between multiplets (37, 38)/(34, 35), as noted above.

Note that if $C_{84}F_{44}$ involved location of the two additional benzenoid rings on carbon atoms (26, 27, 28, 49, 48, 47) = (36, 37, 38, 59, 58, 57) (giving a D_2 product) then addition of the additional fluorine atoms to the 1,4-naphthalene-like positions would, according to calculations (DFT), give two structures of approximately equal energy, so that two isomers of $C_{84}F_{44}$ would have been expected rather than the one observed.

Conclusion

In summary, we have isolated and characterised a mixture of C_2 isomers of $C_{84}F_{40}$ and $C_{84}F_{44}$, shown that they each contain six aromatic patches, two of which in $C_{84}F_{40}$ are uniquely naphthalenoid, the remainder are all benzenoid. These aromatic rings occupy octahedral sites making these derivatives cubic, a shape not observed previously in fullerene derivatives.

Experimental Section

[84]Fullerene was provided by Hoechst in a crude mixture comprising approximately 95% higher fullerenes. It was separated by using high-pressure liquid chromatography (HPLC) with a 250×10 mm Cosmosil 5 PYE column and toluene/heptane (1:1) elution. A total of 75 mg was fluorinated with MnF_3 (1.42 g) in three batches at 500 °C by the general method described previously.[1] The reactivity of [84]fullerene is low and a 50% recovery (HPLC of a toluene extract) of unreacted fullerene was obtained. A further 28 mg of recovered [84]fullerene was fluorinated with CoF_3 (615 mg) at 500 °C; this is a more vigorous fluorinating reagent, so only a 20% recovery of unreacted fullerene was obtained. This low reactivity reinforces our recent observation[6] that fluorination of [70]fullerene is significantly slower than that of [60]fullerene, that is, reactivity of fullerenes decreases with increasing size.

HPLC of the product, using the 5 PYE column (1:1 toluene/heptane at 4.2 mL min^{-1}) gave fractions (i–iv) eluting at the following times: i) 4.0 min (mainly $C_{84}F_{44}$); ii) 4.4 min (a mixture of $C_{84}F_{44}$ and $C_{84}F_{40}$); iii) 5.1 min (a mixture of $C_{84}F_{40}$ and $C_{84}F_{38}$); iv) 7.4 min ($C_{84}F_{40}$).

Of these fractions (some of which contained traces of oxides), only fraction ii was of a quantity (ca. 2 mg) sufficient to give a satisfactory ^{19}F NMR spectrum, with resonances (all 1F multiplets unless indicated) at $\delta = 122.89$ (t, $J = 18$ Hz), 124.45 (t, $J = 16$ Hz), 125.98, 126.14, 126.52, 126.70 (2F), 128.77 (dd, $J = 8$, 39 Hz), 129.55 (dd, $J = 19$, 47 Hz), 130.65 (dd, $J = 20$, 48 Hz), 132.34 (s), 135.45 (t, $J = 10$ Hz), 137.36 (d, $J = 23$ Hz), 138.23 (d, $J = 37$ Hz), 140.27 (dd, $J = 11$, 24 Hz), 140.48 (d, $J = 42$ Hz), 140.82 (dd, $J = 5$, 18 Hz), 141.20 ($J = 43$ Hz), 142.42, 142.98, 143.08, 144.05, 144.13, 144.35 (d, $J = 14$ Hz), 145.14 (d, $J = 6$ Hz), 149.52, 150.08 (d, $J = 39$ Hz), 150.47 (d, $J = 45$ Hz), 151.33 (dd, $J = 6$, 33 Hz), 151.59, 154.46 (d, $J = 5$ Hz), 154.80 (d, $J = 7$ Hz), 160.23 (9, $J = 19$ Hz), 161.22 (m, 2F), 163.59 (dt, $J = 8$, 25 Hz), 164.51 (dt, $J = 12$, 45 Hz), 164.90 (dt, $J = 12$, 45 Hz), 167.13 (dt, $J = 10$, 25 Hz), 167.36 (dt, $J = 7$, 21 Hz), 168.43 (dt, $J = 8$, 25 Hz), 168.63 ppm (dt, $J = 6$, 21 Hz).

Density functional theory (DFT) calculations were by performed using the AIMPRO program[17] in the cluster approach. The program uses pseudopotentials and basis sets consisting of atom-centred Gaussian orbitals (s, p for carbon; s, p, d for fluorine). Semiempirical AM1[18] calculations were carried out by using the program MOPAC.[19]

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