C_2 $C_{70}F_{38}$ is aromatic, contains three planar hexagons, and has equatorial addends

Peter B. Hitchcock,[a] Anthony G. Avent,[a] Natalia Martsinovich,[a] Pavel A. Troshin[b] and Roger Taylor*[a]

Received (in Cambridge, UK) 16th August 2004, Accepted 21st September 2004
First published as an Advance Article on the web 19th November 2004
DOI: 10.1039/b412599a

Single crystal X-ray analysis shows the main (C_2) isomer of $C_{70}F_{38}$ to contain three planar delocalised aromatic hexagons (two equivalent and one centred on the C_2 axis), together with seven C=C bonds (three pairs and one straddling the C_2 axis); $C_{70}F_{38}$ is the first high addition level [70]fullerene derivative to be fully characterised, is the first to have equatorial addends, and is calculated to have high stability.

Understanding the addition patterns of fullerenes and their origins is an integral part of fullerene chemistry. For [60]fullerene, numerous papers describe not only numerous fully characterised cycloadducts, but also the structures of derivatives (especially those containing H, F, Cl, Br) at a range of addition levels, enabling conjectures of the stepwise addition pathways.[1]

The situation for [70]fullerene is more complex,[2] and involves two main manifolds: additions/cycloadditions to the end caps giving *e.g.* $C_{70}H_{2/4}$, $C_{70}Me_2$, C_{70}benzyl$_2$, $C_{70}(OH)_2$, $C_{70}O$, and zig-zag equatorial addition giving $C_{70}Me_{4/6/8/10}$, $C_{70}Ph_{2/4/6/8/10}$, $C_{70}H_{8/10}$, $C_{70}Cl_{10}$, $C_{70}Br_{10}$, $C_{70}(O_2t\text{-Bu})_{10}$, $C_{70}Ph_9OH$, $C_{70}Ph_8(OH)_2$. Low addition-level products have also been obtained in reactions with benzyne, bromomalonate, Vaska's complex, and 2,2-bis(2,6-diisopropylphenyl)hexamethyltrisilane. In no reaction has equatorial addition ever been observed. (Reported equatorial silylation of [70]fullerene was based on ^{1}H NMR data, consistent however with equatorial *straddling*).[3]

Information on high levels of [70]fullerene radical-addition is sparse, and these have been obtained only in hydrogenation (which gave mainly uncharacterised $C_{70}H_{36/38}$ together with some $C_{70}H_{40-44}$),[4] and fluorination by MnF_3 (in which we isolated twenty-one highly fluorinated [70]fullerenes (mainly $C_{70}F_{36/38}$ with some $C_{70}F_{34-42}$), and many oxide derivatives.[5] However, the very complex ^{19}F NMR spectra precluded structural identification.

A feature of these additions is the absence of intermediate addition levels and the dominance of $C_{70}X_{36}$ and $C_{70}X_{38}$ (X = H, F). This led us to propose that $C_{70}H_{36}$ must be an aromatic compound, having benzenoid patches in the structure.[6] Aromatic structures were also proposed by Gerst *et al.*, and by Book and Scuseria.[7] However, subsequent MNDO calculations indicated that a structure having isolated double bonds would, for steric reasons, be much more stable than an aromatic one.[8] Clare and Kepert have calculated structures for $C_{70}X_{36/38}$ (X = H, F)[9] and predicted a number of structures for $C_{70}F_{38}$, including some having three aromatic rings and seven isolated double bonds. Since the 36 and 38 addition levels are clearly closely related, our target was to obtain a crystal structure to resolve both the aromaticity question and subsequently to deduce the formation route. We have now succeeded in our objective, and provide the first full characterisation of a highly addended [70]fullerene.

Fluorination of [70]fullerene by different fluorinating reagents was explored briefly, using a 5–10-fold weight excess of fluorinating reagent at *ca.* 520 °C; [70]fullerene is much less reactive than [60]fullerene. Each of $BaPbF_6$,[10] MnF_3, and CeF_4 showed $C_{70}F_{38}$ as the main product, with $BaPbF_6$ giving the highest relative yield. CeF_4 gave only $C_{70}F_{36}$ and $C_{70}F_{38}$, and very poor overall yields together with some unreacted fullerene. The other two reagents showed the presence of $C_{70}F_{40}$, whilst CoF_3 gave significant quantities of $C_{70}F_{40-50}$. Because of the extreme demands of the HPLC separations,[5] the products were combined and processed together. Numerous derivatives were obtained as before,[5] and also some new ones (due probably to the different fluorinating reagents, and the larger scale); this will be described in a full paper. As before, the main $C_{70}F_{38}$ isomer was no. 14,[5] which crystallised from toluene.

The single-crystal X-ray structure† (Figs. 1 and 2), reveals the structure to be aromatic, having three planar delocalised benzenoid rings, together with seven isolated double bonds. Their location is most easily seen from the Schlegel diagram (Fig. 3), which also gives the numbering. The view from the end caps (Fig. 2) shows a 'triangular' shape imparted by the presence of the three planar hexagons. Two of the benzenoid rings (Ar) are equivalent, whilst

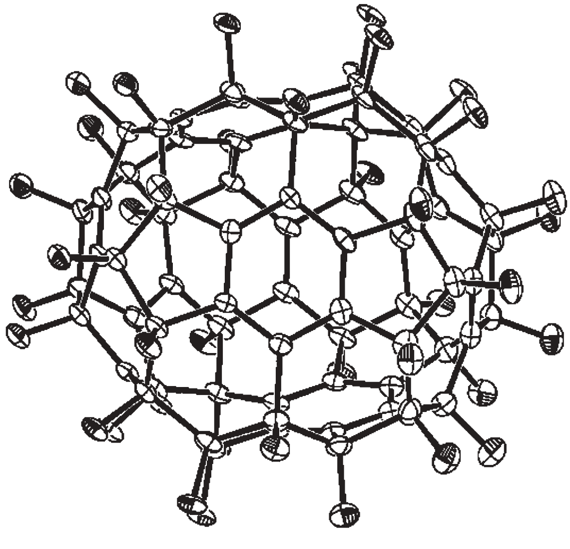

Fig. 1 ORTEP drawing (20% ellipsoids) for C_2 $C_{70}F_{38}$, viewed down the C_2 axis; the facing planar central hexagon is Ar* and the rear central C=C bond is C20–C21 (see Fig. 3).

---

*R.Taylor@sussex.ac.uk

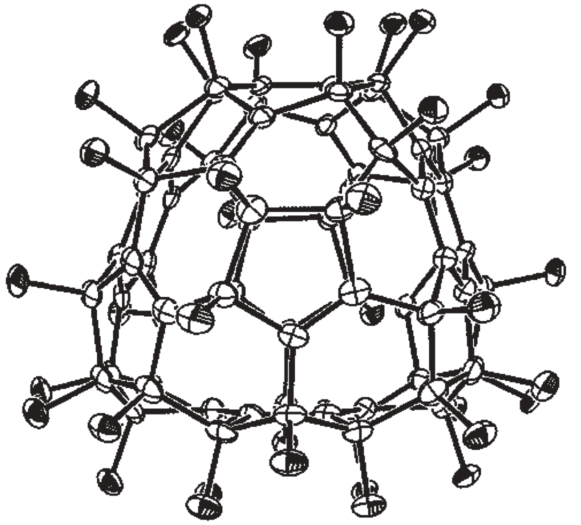

Fig. 2 ORTEP drawing (20% ellipsoids) for C_2 $C_{70}F_{38}$ viewed from an end cap, showing the 'triangular' shape imparted by the planar regions.

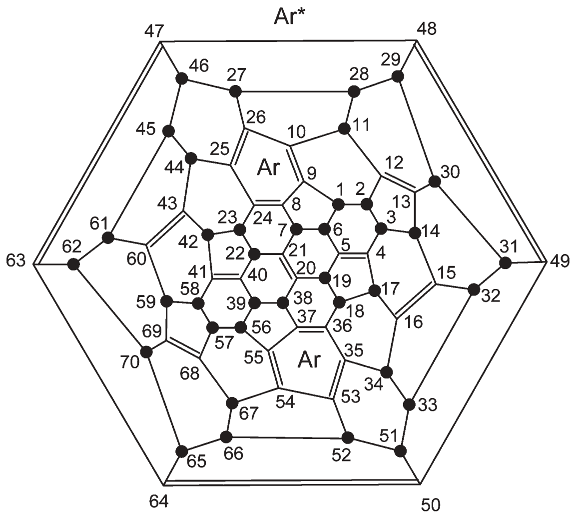

Fig. 3 Schlegel diagram for C_2 $C_{70}F_{38}$ showing the aromatic rings and the isolated double bonds (• = F). The C_2 axis bisects the C20–C21 bond and passes through the centre of the aromatic ring Ar*.

the third (Ar*) is unique and sits on the (non-crystallographic) C_2 axis. The double bonds comprise three equivalent pairs (C4–5/C40–41; C12–13/C68–69; C15–16/C43–60), and the unique C20–21 straddling the C_2 axis. A unique structural feature is the presence of two equatorial fluorines; equatorial addends on [70]fullerene have never been seen before.

The bond lengths (Table 1) are the average values for symmetry equivalent bonds given in terms of the lowest locant numbers. The average bond lengths (Å) in the three aromatic rings are 1.381(5), 1.384(5) and 1.382(5), confirming their aromaticity, *cf.* the values found in C_1 $C_{60}F_{36}$ (1.371, 1.378, 1.389),[11] T $C_{60}F_{36}$[12] and $C_{60}F_{18}$[13] (both 1.373). The C15=C16/C43=C60 double bonds are exceptionally short (1.313 Å average), attributed to compression produced by the neighbouring fluorines (*cf.* the short isolated double bonds in both C_1 $C_{60}F_{36}$[11] and $C_{60}F_{48}$).[14] As with C_1 $C_{60}F_{36}$ there is an exceptionally long FC–CF bond of 1.642 Å (27,28; 52,66), which arises as in the previous example, where a carbon is surrounded by three CF groups. The planarity of the benzenoid rings is shown by the valence angle sums for the aromatic carbons, which average 359.0° for Ar/Ar and 359.6° for Ar*.

Table 1 Cage C–C bond lengths (Å)[a] for C_2 $C_{70}F_{38}$

Bond		Bond		Bond	
C1–2	1.592	C10–C26	1.377	C25–C44	1.499
C1–6	1.580	C11–C12	1.507	C26–C27	1.505
C1–9	1.498	C11–C28	1.591	C27–C28	1.642
C2–3	1.555	C12–C13	1.328	C27–C46	1.547
C2–12	1.543	C13–C14	1.498	C28–C29	1.536
C3–4	1.509	C13–C30	1.478	C29–C30	1.585
C3–14	1.568	C14–C15	1.501	C29–C48	1.481
C4–5	1.343	C15–C16	1.313	C30–C31	1.565
C4–17	1.498	C15–C32	1.508	C31–C32	1.557
C5–6	1.470	C16–C17	1.492	C31–C49	1.496
C5–19	1.498	C16–C34	1.480	C32–C33	1.615
C6–7	1.574	C17–C18	1.552	C33–C34	1.587
C7–8	1.508	C18–C19	1.578	C33–C51	1.601
C7–21	1.500	C18–C36	1.510	C46–C47	1.481
C8–9	1.378	C19–C20	1.546	C47–C48	1.382
C8–24	1.398	C20–C21	1.335	C47–C63	1.375
C9–10	1.355	C24–C25	1.392	C48–C49	1.391
C10–11	1.478	C25–C26	1.395		

[a] These are the average values for symmetry equivalent bonds, and given as lowest locants; esd values are all 0.013 ± 0.001 Å.

Clare and Kepert proposed nineteen possible structures for $C_{70}F_{38}$ based on AM1 calculations, five of which had three aromatic rings and seven isolated double bonds,[9] though none correspond to the characterised structure. Previously, we isolated seven other isomers of $C_{70}F_{38}$ (all C_1) and it seems probable that these arise merely from 1,3-migrations of fluorines giving alternative locations of the double bonds (there are fourteen possibilities), producing C_1 structures. We hope to investigate this aspect further. We have calculated (AM1) the heat of formation of C_2 $C_{70}F_{38}$ and find it to be *ca.* 24 and 19 kcal mol^{-1} lower than the values for the most stable structures (nos. 1 and 2, respectively) in Table 4 of the Clare and Kepert paper.

The other highly fluorinated species $C_{70}F_{34/36}$ and $C_{40/50}$ are probably also aromatic, with more or fewer double bonds respectively, but retaining the locations of the benzenoid hexagons. The present structure thus presents a basis for extensive further calculations.

The ^{19}F NMR spectrum that we obtained previously for this isomer showed nineteen lines (confirmed here), two of which were upfield multiplets at δ −164.59 and −168.19. Our previous work with fluorinated fullerenes showed that upfield multiplets arise from fluorines attached to carbons having three CF neighbours, and are therefore assigned to fluorines at C28/C66, and C33/C45, which are *c*- and *d*-type[15] carbons, respectively. Since *c*-type carbons appear more downfield, we provisionally assign the δ −164.59 peak to F28/66. We hope to be able to assign all of the NMR peaks, and hence establish the peak positions of fluorines in specific locations in $C_{70}F_n$, and thereby solve all of the other structures.

Lastly, C_2 $C_{70}F_{38}$ does not contain the motif present in $C_{70}Cl_{10}$ *etc.*, suggesting that addition commences at the end caps, though isolation of intermediate structures would be necessary to support this conjecture.

Peter B. Hitchcock,[a] **Anthony G. Avent,**[a] **Natalia Martsinovich,**[a]
Pavel A. Troshin[b] **and Roger Taylor***[a]
[a]*Chemistry Department, University of Sussex, Brighton, UK BN1 9QJ.*
E-mail: R.Taylor@sussex.ac.uk; Fax: 44 1273 677196;
Tel: 44 1273 6768602
[b]*Chemistry Department, Moscow State University, Moscow 119899, Russia*

Notes and references

† *Crystal data*: $C_{70}F_{38}\cdot 2.5(C_7H_8)$, $M = 1793.0$, triclinic, space group $P\bar{1}$ (no. 2), $a = 12.1508(6)$, $b = 15.5160(7)$, $c = 18.0125(8)$ Å, $\alpha = 94.308(3)$, $\beta = 101.526(2)$, $\gamma = 106.457(2)^\circ$, $V = 3159.6$ Å^3, $Z = 2$, $D_x = 1.89$ Mg m^{-3}, μ(Mo-Kα) = 0.19 mm^{-1}, $T = 173$ K. Diffraction from the crystal was weak and limited. 11057 unique reflections ($R_{int} = 0.13$) measured on a KappaCCD diffractometer. Three disordered toluene solvate molecules included with restrained geometry. Refinement on F^2 using SHELX97, $R1 = 0.110$ for 5490 reflections with $I > 2\sigma(I)$, $wR2 = 0.324$ for all reflections. CCDC 247743. See http://www.rsc.org/suppdata/cc/b4/b412599a/ for crystallographic data in .cif or other electronic format.

1 R. Taylor, *Lecture Notes on Fullerene Chemistry: A Handbook for Chemists*, Imperial College Press, London, 1999, ch. 4, 7, 9, 11.
2 Leading references are collated in: R. Taylor, *J. Fluorine Chem.*, 2004, **125**, 359.
3 T. Akasaka, E. Mitsihida, W. Ando, K. Kobayashi and S. Nagau, *J. Am. Chem. Soc.*, 1994, **116**, 2627.
4 A. D. Darwish, A. K. Abdul-Sada, G. J. Langley, H. W. Kroto, R. Taylor and D. R. M. Walton, *J. Chem. Soc., Perkin Trans. 2*, 1995, 2359.
5 R. Taylor, A. K. Abdul-Sada, O. V. Boltalina and J. M. Street, *J. Chem. Soc., Perkin Trans. 2*, 2000, 1013.
6 R. Taylor, *J. Chem. Soc., Perkin Trans. 2*, 1994, 2497.
7 M. Gerst, H.-D. Beckhaus, C. Rüchardt, E. E. B. Campbell and R. Tellgman, *Tetrahedron Lett.*, 1993, **34**, 7729; L. D. Book and G. E. Scuseria, *J. Phys. Chem.*, 1994, **98**, 4283.
8 P. W. Fowler, J. P. B. Sandall, S. J. Austin, D. E. Manolopoulos, P. D. M. Lawrenson and J. M. Smallwood, *Synth. Met.*, 1006, **77**, 97; P. W. Fowler, J. P. B. Sandall and S. J. Austin, *Fullerene Sci. Technol.*, 1996, **4**, 369; P. W. Fowler, J. P. B. Sandall and R. Taylor, *J. Chem. Soc., Perkin Trans. 2*, 1997, 419.
9 B. W. Clare and D. E. Kepert, *J. Mol. Struct.: THEOCHEM*, 2002, **583**, 19–45.
10 P. A. Troshin, O. V. Boltalina, N. V. Polyakova and Z. E. Klinkina, *J. Fluorine Chem.*, 2001, **110**, 157.
11 A. G. Avent, B. W. Clare, P. B. Hitchcock, D. L. Kepert and R. Taylor, *Chem. Commun.*, 2002, 2370.
12 P. B. Hitchcock and R. Taylor, *Chem. Commun.*, 2002, 2078.
13 I. S. Neretin, K. A. Lyssenko, M. Yu. Antipin, Yu. L. Slovokhotov, O. V. Boltalina, P. A. Troshin, A. Yu. Lukonin, L. N. Sidorov and R. Taylor, *Angew. Chem., Int. Ed.*, 2000, **39**, 3273.
14 S. I. Troyanov, P. A. Troshin, O. V. Boltalina, I. N. Ioffe, L. N. Sidorov and E. Kemnitz, *Angew. Chem., Int. Ed.*, 2001, **40**, 2285.
15 R. Taylor, J. P. Hare, A. K. Abdul-Sada and H. W. Kroto, *J. Chem. Soc., Chem. Commun.*, 1990, 1423.