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Single crystal X-ray structure of tetrahedral $C_{60}F_{36}$: the most aromatic and distorted fullerene

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Received (in Cambridge, UK) 30th May 2002, Accepted 8th August 2002
First published as an Advance Article on the web 19th August 2002

Tetrahedral $C_{60}F_{36}$ is shown by its single-crystal X-ray structure to be the most aromatic (and distorted) fullerene derivative, having four planar hexagons with almost equal bond lengths, the average of which (1.373 Å) is the same as in $C_{60}F_{18}$; one exceptionally long FC–CF bond (1.665 Å) corresponds to the similarly long bond in $C_{60}F_{18}$ (a motif of *T* $C_{60}F_{36}$) and is likely to be the site of oxygen insertion in $C_{60}F_{36}O$

Previous work on fluorofullerenes has revealed structures having considerable distortion from sphericity. Thus $C_{60}F_{18}$ has one flattened and aromatic hexagon, the molecule being in effect a three-dimensional hexa-substituted benzene.[1] $C_{60}F_{20}$ ('Saturnene') has an equatorial band of 20 fluorine atoms and is flattened,[2] whilst $C_{60}F_{48}$ is slightly indented in the region of the six remaining double bonds.[3] The structure of $C_{60}F_{18}$ is particularly interesting because the bonds in the aromatic hexagon are of equal length indicating full delocalisation, and moreover they are shorter than in benzene due to compression from the adjacent fluorines. However, it is not the only aromatic fullerene, because one isomer of $C_{60}F_{36}$ has *T* symmetry as shown by its ^{19}F NMR spectrum, and this implies the presence of four delocalised benzenoid rings.[4] The bond lengths in such a structure have been calculated theoretically.[5] We have now obtained a crystalline sample of *T* symmetry $C_{60}F_{36}$ and have determined its single crystal X-ray structure.†

[60]Fullerene was fluorinated with MnF_3 at 0.01 bar by the general procedure described previously,[6] except that the temperature employed was 480 °C rather than 330 °C. This gave a substantially higher yield of the *T* isomer relative to that of the C_3 isomer, attributable to differences in entropy of formation arising from the very distorted structure of the *T* isomer. The pure *T* isomer was isolated from the crude fluorinated mixture by HPLC (high pressure liquid chromatography) as described previously,[4] and recrystallised from toluene as golden plates. The crystal structure contains two independent molecules; one disordered across a mirror plane and the other disordered unequally about a two-fold rotation axis. The single crystal molecular structure of *T* $C_{60}F_{36}$ is shown in Fig. 1.

The observed and calculated[5] bond lengths are assembled in Table 1, and notable features are:

(i) The agreement between calculated and observed bond lengths is very good with an average deviation between them of only 1%.

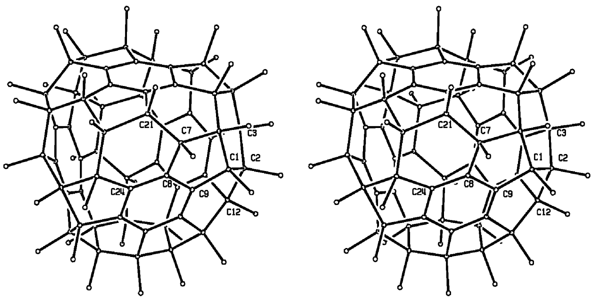

Fig. 1 A stereopair drawing of the molecular structure of *T* $C_{60}F_{36}$

(ii) The 8,9 and 8,24 bonds are almost equal in length showing that the four equivalent hexagonal rings that contain them are aromatic. The average length (1.373 Å) is exactly the same as in $C_{60}F_{18}$. The bonds within these hexagons are shorter than those in benzene due to compression from the surrounding fluorines. Similar compression causes bond shortening in both $C_{60}F_{18}$[2] and $C_{60}F_{48}$.[3]

(iii) The aromaticity of the hexagons is confirmed also by their planarity, the average root mean square deviation (over all four rings) of any one carbon from the mean hexagonal planes is < 0.02 Å.

(iv) The structure is highly distorted from the spherical norm usually associated with [60]fullerene and its derivatives, and indeed more so than any other derivative of which we are aware.

(v) The extremely long 2,12 bond corresponds to the 2,3 bond in $C_{60}F_{18}$ (almost identical length of 1.673 Å), and the identical location is shown (as a thickened bond) in the Schlegel diagram (Fig. 3). In $C_{60}F_{18}$ this bond is the one into which oxygen mainly inserts to give an ether.[7] The 2,12 bond is likely therefore to be the main site of oxygen insertion to give

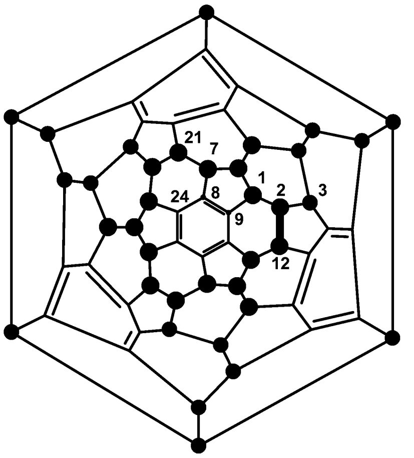

Fig. 2 Numbering used for *T* $C_{60}F_{36}$

Table 1 Observed and calculated bond lengths in *T* $C_{60}F_{36}$

Bond[a]	Observed/Å	Calculated[b]/Å	δ(Obs. − Calc.)/Å
8,9	1.379	1.351	0.028
8,24	1.366	1.359	0.007
1,2	1.559	1.545	0.014
1,9	1.489	1.459	0.030
2,3	1.591	1.586	0.005
2,12	1.665	1.690	−0.025
7,8	1.486	1.456	0.030
7,21	1.547	1.542	0.005

The length of all C–F bonds is 1.378 Å. [a] See Fig. 2 for bond identification. [b] Ref. 5.

DOI: 10.1039/b205286p

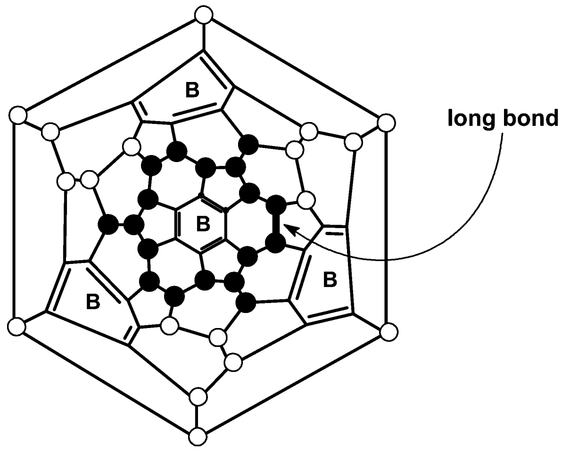

Fig. 3 Superimposed Schlegel diagrams of $C_{60}F_{18}$ (filled circles) and T $C_{60}F_{36}$ (filled plus open circles) showing (thickened) the common long bond (one of three for $C_{60}F_{18}$; one of six for $C_{60}F_{36}$); this is the main site of oxygen insertion in $C_{60}F_{18}$

$C_{60}F_{36}O$, which has been observed but not characterised in previous studies.[8]

We hope to be able to examine the potential of this aromatic fullerene for η^6 coordination to organometallic groups, and have prepared and purified 100 mg quantities for this purpose.

Notes and references

† *Crystal data*: $C_{60}F_{36}\cdot1.75C_7H_8$, $M = 1565.8$, monoclinic, $C2/m$ (no. 12), $a = 25.7592(7)$, $b = 30.5734(8)$, $c = 14.4709(4)$ Å, $\beta = 112.089(2)°$, $V = 10560.0(5)$ Å^3, $Z = 8$, $D_c = 1.97$ Mg.m^{-3}, μ(Mo-Kα) = 0.20 mm^{-1}, $T = 173$ K.

Data from a Nonius Kappa CCD diffractometer, 12644 unique reflections (R_{int}) = 0.077. There are two $C_{60}F_{36}$ molecules, both disordered; one unequally about a two-fold axis and the other about a mirror plane. C–C bonds within each set related by a molecular point group symmetry (T) were restrained to a free variable, and in addition, all C–F bonds were restrained to a single free variable. The toluene solvate molecules were also disordered and were included with the C_6 rings as rigid bodies where possible. Refinement on F^2 using SHELXL-97,[9] final residuals: $R1 = 0.090$ for 8278 reflections with $I > 2\sigma(I)$, $wR^2 = 0.267$ for all reflections.

The bond lengths given in this paper are the values to which the free variables refined. From the refinement the nominal esd associated with these free variables is 0.0003 Å, which is unrealistically low. The bond lengths are therefore listed to three decimal places and should be treated with caution.

CCDC 188250. See http://www.rsc.org/suppdata/cc/b2/b205286p/ for crystallographic data in CIF or other slectronic format.

1 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.
2 O. V. Boltalina, V. Yu Markov, P. A. Troshin, A. D. Darwish, J. M. Street and R. Taylor, *Angew. Chem., Int. Ed.*, 2001, **40**, 787.
3 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.
4 O. V. Boltalina, J. M. Street and R. Taylor, *J. Chem. Soc., Perkin Trans. 2*, 1998, 649.
5 S. Jenkins, M. I. Heggie and R. Taylor, *J. Chem. Soc., Perkin Trans. 2*, 2000, 2415.
6 O. V. Boltalina, A. Ya. Borschevskii, L. V. Sidorov, J. M. Street and R. Taylor, *Chem. Commun.*, 1996, 529.
7 O. V. Boltalina, B. de La Vaissière, P. W. Fowler, P. B. Hitchcock, J. P. B. Sandall, P. A. Troshin and R. Taylor, *Chem. Commun.*, 2000, 1325.
8 O. V. Boltalina, J. H. Holloway, E. G. Hope, J. M. Street and R. Taylor, *J. Chem. Soc., Perkin Trans. 2*, 1998, 1845.
9 G. M. Sheldrick, SHELXL-97, a program for crystal structure refinement, Univ. of Göttingen, Germany, 1997.