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$C_{60}F_{36}$: there is a third isomer and it has C_1 symmetry

Anthony G. Avent,[a] Brian W. Clare,[b] Peter B. Hitchcock,[a] David L. Kepert[b] and Roger Taylor*[a]

[a] *The Chemistry laboratory, CPES School, Sussex University, Brighton, UK BN1 9QJ.*
E-mail: R.Taylor@sussex.ac.uk

[b] *Biomedical and Chemical Sciences School, University of Western Australia, Crawley, WA 6009, Australia*

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From fluorination of [60]fullerene with MnF_3/K_2NiF_6 at 480 °C we have isolated and characterised by both ^{19}F NMR spectrum and single crystal X-ray analysis, a C_1 isomer of $C_{60}F_{36}$; it has three planar delocalised aromatic rings, three short C=C bonds (due to compression from the adjacent fluorines), the longest FC–CF bond (1.684 Å) yet found in a fluorofullerene, and its stability is predicted by calculations.

Characterising polyaddition products is necessary for understanding the factors which govern the reactivity of fullerenes, but is hampered by the difficulty in identifying the isomers obtained out of the millions that are possible for a given addend level. Fullerene fluorination is particularly valuable in this respect, because the products can be separated by HPLC (high pressure liquid chromatography) and characterised by both mass spectrometry and ^{19}F NMR spectroscopy with, in a few cases, single crystal X-ray structures; moreover the reaction is only slightly hindered sterically. The problem of the number of derivatives is greatly simplified by the use of metal fluoride fluorination[1] *cf.* fluorine gas fluorination.[2]

The 36-addend level has been of particular interest in both fluorination and hydrogenation (which give isostructural products[3]); further studies on $C_{60}H_{36}$ have been reported very recently.[4] Previous work on $C_{60}F_{36}$ (produced by fluorination of [60]fullerene with MnF_3 at 330 °C)[5–7] produced C_3 and T isomers, the latter symmetry having been predicted.[8] Identification of the correct C_3 isomer[5–7] by ^{19}F NMR has been complicated by spurious long-range couplings, and absence of coupling by adjacent fluorines. An energetically-favoured structure (no. 64)[9] appeared to be incompatible with the 2 D ^{19}F NMR data,[7] but a higher sensitivity technique[10] has now indicated it to be the correct one. Our work, undertaken in order to obtain a single crystal X-ray structure of this isomer, has led instead to the discovery of another isomer.

Exploratory work, involving fluorination with MnF_3 at 470 °C yielded a small amount of a new product, preliminary ^{19}F NMR analysis of which showed *ca.* 30 unequal intensity lines, interpreted provisionally in terms of a mixture of C_2 and C_3 isomers.[11] The sample degraded through hydrolysis before analysis was completed, and so a much larger quantity was prepared by fluorinating [60]fullerene in batches (800 mg overall) with a mixture of MnF_3/K_2NiF_6 at 480 °C.[12] HPLC separation (10 × 250 mm Cosmosil Buckyprep column, 4.7 ml min^{-1} flow rate) involved elution with toluene and then 1:1 toluene:heptane (to remove $C_{60}F_{18}$ and other products). Early fractions (< 5 min retention times) were set aside in each case and processed with toluene–heptane (1:9). This yielded the C_3 (229 mg, 20%), T (47 mg, 4%) and C_1 (118 mg, 10%) isomers with retention times of 5.3, 5.95 and 7.9 min, respectively. The latter (white powder) crystallised very readily from toluene to give elongated golden yellow plates.

The EI mass spectrum (Fig. 1) indicates very pure $C_{60}F_{36}$. The ^{19}F NMR spectrum (Fig. 2, toluene/$CDCl_3$, 2 s delay and 33 μs pulse), comprises 36 equal-intensity peaks, four of which are coincident. The chemical shifts were dependent upon concentration and/or toluene/$CDCl_3$ ratio.

The single crystal X-ray structure† (Fig. 3) gives the cage C–C bond lengths (Table 1). Notable features are: (i) bonds are

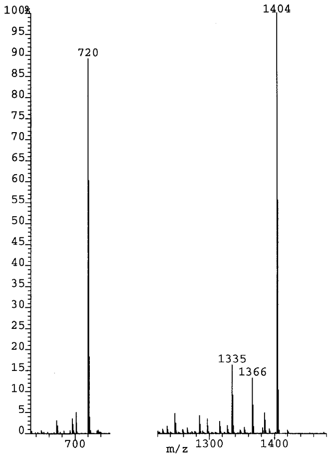

Fig. 1 EI mass spectrum (70 eV) of the 7.9 min fraction from processing with toluene–heptane (1:9).

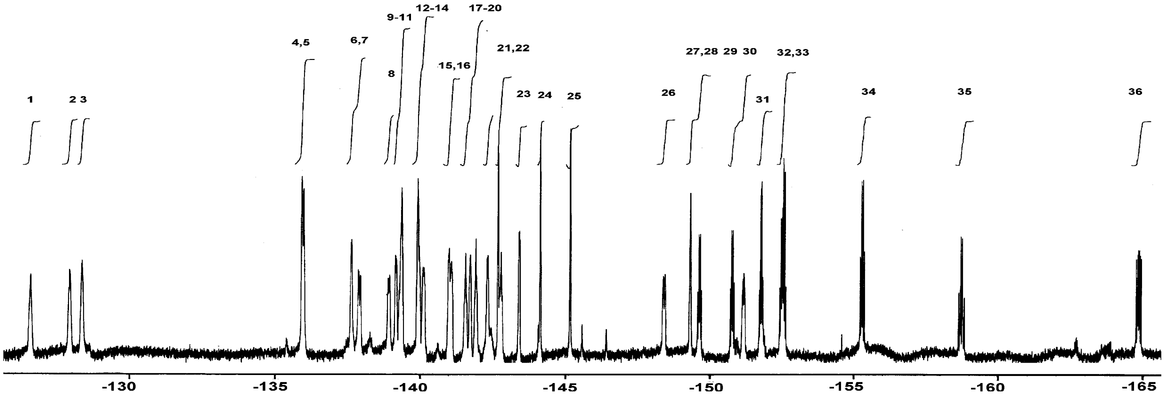

Fig. 2 ^{19}F NMR spectrum of the new isomer of $C_{60}F_{36}$.

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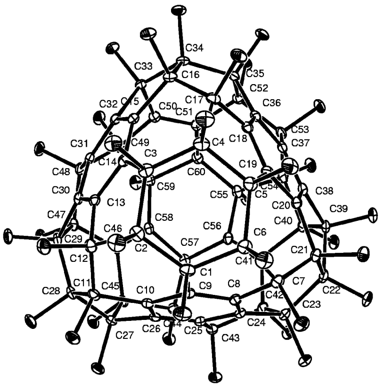

Fig. 3 ORTEP drawing (20% ellipsoids) for C_1 $C_{60}F_{36}$.

Table 1 Cage C–C bond lengths (Å) for C_1 $C_{60}F_{36}$

Bond		Bond		Bond	
C1–C2	1.575(6)	C18–C19	1.373(5)	C37–C53	1.486(5)
C1–C9	1.481(5)	C18–C36	1.377(5)	C38–C39	1.464(5)
C1–C6	1.579(6)	C19–C20	1.384(5)	C39–C40	1.548(6)
C2–C3	1.587(6)	C20–C38	1.379(5)	C40–C41	1.507(5)
C2–C12	1.657(5)	C20–C21	1.484(5)	C40–C54	1.647(5)
C3–C14	1.477(5)	C21–C22	1.651(6)	C41–C56	1.323(5)
C3–C4	1.561(6)	C22–C23	1.584(5)	C41–C42	1.485(5)
C4–C5	1.599(6)	C22–C39	1.610(6)	C42–C43	1.593(5)
C4–C17	1.661(5)	C23–C24	1.487(5)	C43–C44	1.571(5)
C5–C19	1.482(5)	C23–C42	1.579(6)	C44–C57	1.573(5)
C5–C6	1.573(6)	C24–C25	1.371(5)	C44–C45	1.639(5)
C6–C7	1.683(6)	C25–C26	1.369(5)	C45–C46	1.514(5)
C7–C8	1.489(5)	C25–C43	1.476(5)	C46–C58	1.316(5)
C7–C21	1.555(6)	C26–C27	1.474(5)	C46–C47	1.485(5)
C8–C24	1.370(5)	C27–C45	1.542(5)	C47–C48	1.577(5)
C8–C9	1.372(5)	C27–C28	1.605(5)	C48–C49	1.594(5)
C9–C10	1.375(5)	C28–C29	1.578(5)	C49–C50	1.537(5)
C10–C26	1.367(5)	C29–C30	1.493(5)	C49–C59	1.552(5)
C10–C11	1.484(5)	C29–C47	1.587(5)	C50–C51	1.319(5)
C11–C12	1.558(5)	C30–C31	1.370(5)	C51–C52	1.489(5)
C11–C28	1.654(5)	C31–C32	1.371(5)	C51–C60	1.494(5)
C12–C13	1.467(5)	C31–C48	1.504(5)	C52–C53	1.581(5)
C13–C14	1.379(5)	C32–C33	1.488(5)	C53–C54	1.578(5)
C13–C30	1.380(5)	C33–C50	1.502(5)	C54–C55	1.585(5)
C14–C15	1.381(5)	C33–C34	1.585(5)	C55–C56	1.492(5)
C15–C32	1.367(5)	C34–C35	1.578(5)	C55–C60	1.558(5)
C15–C16	1.483(5)	C35–C36	1.476(5)	C56–C57	1.486(5)
C16–C17	1.552(5)	C35–C52	1.591(5)	C57–C58	1.484(5)
C16–C34	1.654(5)	C36–C37	1.374(5)	C58–C59	1.498(5)
C17–C18	1.468(5)	C37–C38	1.367(5)	C59–C60	1.579(5)

effectively equal in each of the aromatic rings, the averages (Å) being 1.371 (**A**), 1.378 (**B**), 1.369 (**C**), *cf.* those (1.373 Å) found in the aromatic rings of T $C_{60}F_{36}$[12] and $C_{60}F_{18}$.[13] (ii) Rings **A**–**C** are planar (rms deviations of fitted atoms being 0.011, 0.011 and 0.013 Å, respectively). (iii) The C=C bonds (1.323, 1.316, 1.319 Å) are significantly shorter than that for a localised C=C bond (*ca.* 1.335 Å), attributable (as in $C_{60}F_{48}$ where they are even shorter)[14] to compression by the adjacent fluorines. (iv) Some FC–CF bonds, where one carbon is surrounded by three CF groups, are exceptionally long, *viz.* (Å) 1.651 (21,22), 1.654 (11,28; 16,34), 1.657 (2,12), 1.661 (4,17) and 1.683 (6,7). The latter is the longest found in a fluorofullerene[12,13] and longer than any in $C_{60}F_{48}$ (max. 1.604 Å); in the latter the C–C bonds cannot expand to compensate for the F$\cdots$F compression.

The Schlegel diagram (Fig. 4) shows the location of the three aromatic rings and the three isolated double bonds. The larger black circles indicate fluorines which have three fluorine neighbours, which in fluorofullerenes always give upfield multiplets. From the 2 D spectrum (not shown) some spectrum peaks can be assigned to structural positions, and the analysis (which is lengthy) will be given in a full paper.

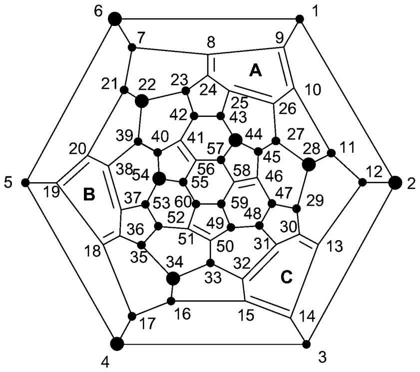

Fig. 4 Schlegel diagram for the C_1 $C_{60}F_{36}$ (● = F, see text).

Density functional calculations (B3LYP/6-31G*, Gaussian 98) gave the relative heats of formation (kcal mol^{-1}) for the three isolated isomers as 0 (T), 2.76 (C_3) and 4.40 (C_1) These are predicted to be significantly more stable than any other isomers for which the heats of formation have been calculated. The respective calculated dipole moments (Debye) are 0, 0.03 and 0.58, which parallels the observed elution order.

Nossal *et al.* believe there is no parallel between fluorination and hydrogenation becaue a C_1 isomer (uncharacterised) appears to be formed in hydrogenation.[4] However, our result *reinforces* the parallel; note that their presumed C_1 isomer has the C50–C51 bond placed across C51–C52 instead.

Notes and references

† *Crystal data*: $C_{60}F_{36}\cdot3.5(C_7H_8)$, $M = 1727.07$, monoclinic, $P2_1/n$ (no. 14), $a = 12.3151\ (1)$, $b = 36.9718(4)$, $c = 14.9318(2)$ Å, $\beta = 111.093(1)$, $V = 6343.1(1)$ Å^3, $Z = 4$, $D_c = 1.81$ Mg m^{-3}, μ(Mo-Kα) = 0.18 mm^{-1}, $T = 223$ K. $R_F = 0.059$ for 7389 reflections with $I > 2\sigma(I)$, $wR^2 = 0.157$ for 9500 independent reflections. CCDC 191455. See http://www.rsc.org/suppdata/cc/b2/b207580f/ for crystallograhic data in CIF or other electronic format.

1 O. V. Boltalina, A. Yu. Lukonin, A. A. Gorjunkov, V. K. Pavlovich, A. N. Rykov, V. A. Seniavin, L. V. Sidorov and R. Taylor, *Proc. Electrochem. Soc.*, 1997, **97–14**, 257.

2 R. Taylor, G. J. Langley, J. H. Holloway, E. G. Hope, H. W. Kroto and D. R. M. Walton, *J. Chem. Soc., Chem. Commun.*, 1993, 875; O. V. Boltalina, J. H. Holloway, E. G. Hope, J. M. Street and R. Taylor, *J. Chem. Soc., Perkin Trans. 2*, 1998, 1845.

3 P. W. Fowler, J. B. Sandall and R. Taylor, *J. Chem. Soc., Perkin Trans. 2*, 1997, 419.

4 J. Nossal, R. K. Saini, A. K. Sadana, H. F. Bettinger, L. B. Alemany, G. E. Scuseria, W. E. Billups, M. Saunders, A. Khong and R. Weisemann, *J. Am. Chem. Soc.*, 2001, **123**, 8482.

5 O. V. Boltalina, A. Ya. Borschevskii, L. N. Sidorov, J. M. Street and R. Taylor, *Chem. Commun.*, 1996, 529.

6 O. V. Boltalina, J. M. Street and R. Taylor, *J. Chem. Soc., Perkin Trans. 2*, 1998, 649.

7 O. V. Boltalina, M. Bühl, A. Khong, M. Saunders, J. M. Street and R. Taylor, *J. Chem. Soc., Perkin Trans. 2*, 1999, 1475.

8 R. Taylor, *J. Chem. Soc., Perkin Trans. 2*, 1992, 1667; R. Taylor, *Philos. Trans. R. Soc. London, A*, 1993, **343**, 87; S. J. Austin, R. C. Batten, P. W. Fowler, D. B. Redmond and R. Taylor, *J. Chem. Soc., Perkin Trans. 2*, 1993, 1383.

9 B. W. Clare and D. L. Kepert, *J. Mol. Struct. (THEOCHEM)*, 1999, **466**, 177; B. W. Clare and D. L. Kepert, *J. Mol. Struct. (THEOCHEM)*, 19994, **304**, 181; B. W. Clare and D. L. Kepert, *J. Mol. Struct. (THEOCHEM)*, 1994, **315**, 71.

10 A. A. Gakh and A. A. Tuinman, *Tetrahedron Lett.*, 2001, **42**, 7133.

11 A. G. Avent, P. B. Hitchcock and R. Taylor, *Proc. 100th Meeting of the Electrochemical Society*, in press.

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.