$C_{60}F_{18}O$, the first characterised intramolecular fullerene ether

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A single-crystal X-ray structure determination of the main isomer of $C_{60}F_{18}O$ shows it to be an intramolecular fullerene ether rather than an epoxide, and thus the first example of an oxa-homo[60]fullerene.

Formation of oxides is a major feature of fullerene chemistry. Hitherto, these oxides have been either characterised (*e.g.* $C_{60}O$,[1] $C_{70}O$,[2] $C_{60}O_2$,[3] $C_{60}O_3$,[4] $C_{60}O_n$,[5] $C_{60}Me_5O_2OH$[6]), or conjectured (*e.g.* $C_{60}Ph_4C_6H_4O_2$,[7] fluorofullerene oxides[8,9]) as epoxides. Strong circumstantial evidence for the epoxy form of fluorofullerene oxides was provided by identification of components in the moisture-induced reactions: $C_{60}F_n \rightarrow C_{60}F_{n-1}OH \rightarrow C_{60}F_{n-2}O$ (for various values of n), HF loss being manifest also in container etching. It was also notable that the isolated oxides were associated with precursors which possessed two additional fluorine atoms. A further indication of the presence of epoxides was the dramatic increase in oxide content when either fluoro[60]- or [70]fullerenes were reacted with aq. MeOH.[9]

Recently we described the isolation and ^{19}F NMR characterisation of the main isomer of $C_{60}F_{18}O$.[10] This has C_s symmetry, and the data were consistent with the presence of an in-plane epoxy oxygen atom (addition across a 6,6-double bond, **1**), but we also considered the possibility of insertion into various 6,5-single bonds. Insertion of oxygen into 6,6- and 6,5-bonds of [60]fullerene is predicted to be quasi-isoenergetic,[11] though no example of the latter has been observed; one of us conjectured that this was the first step in the spontaneous formation of $C_{60}Ph_8O_4$ from $C_{60}Ph_8$.[12]

However, three features seemed somewhat anomalous regarding the structure **1**. First, for the oxide to be an epoxide, there should be evidence of a precursor $C_{60}F_{20}$ molecule, and although traces of a component of this formula were seen, the amount was very small.[10] Secondly, the necessary precursor structure required the addition of two fluorine atoms remote from the rest, which contradicts the pattern for which we are finding increasing evidence (see *e.g.* ref. 13), that addition take places in a contiguous fashion. Thirdly, although traces of other oxides appeared to be present, there was no obvious energetic reason for **1** to be preferred; indeed, calculations indicated that an epoxide was not the structure of overall lowest energy for the formula.

We recently have scaled up our production of $C_{60}F_{18}$ (100–200 mg yield) and found that substantial quantities (*ca.* 50 mg) of the previously described isomer[10] of $C_{60}F_{18}O$ are also produced. This was separated by HPLC as described previously, but using a larger column of 10 mm diameter and 4.7 mol min⁻¹ toluene flow rate. On standing, a toluene solution of this material deposited lemon-coloured plates, which single crystal X-ray characterisation† (Fig. 1) showed to be **2**.

This is thus the first intramolecular fullerene ether to be characterised and also the first having oxygen inserted into a 6,5-bond. The numbering of $C_{60}F_{18}$ is shown in **3** and hence this
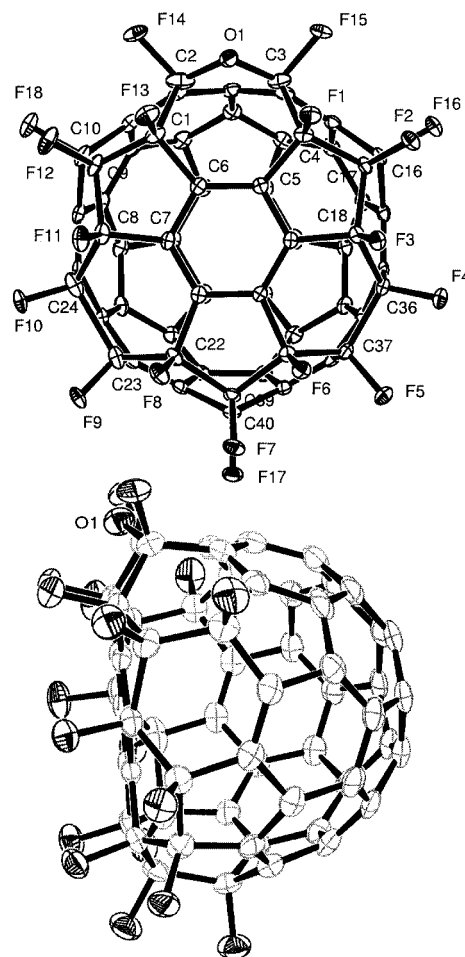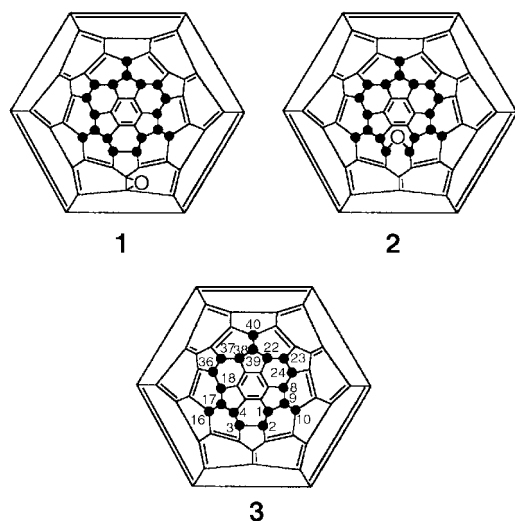

1

2

3

Fig. 1 Two projections (ORTEP) of $C_{60}F_{18}O$.

Table 1 Heats of formation (kcal mol^{-1}) for C_s $C_{60}F_{18}O$ structures

	MNDO	AM1
(i) Epoxides 6,6-bond to which oxygen is added		
5,6	*−63.9*	*17.8*
13,30	*−111.7*	*−18.0*
58,59	*−122.4*	*−27.3*
11,12	−113.5	23.2
28,29	−117.4	23.2
(ii) Ethers 6,5-bond in which oxygen is inserted		
20,21	*−56.7*	*21.2*
55,56	*−115.8*	*−29.2*
47,48	*−130.1*	*−41.7*
1,6	−43.9	−17.9
2,12	−113.5	−34.1
9,10	−122.8	−43.5
10,11	−129.2	−50.3
1,2	−129.3	−50.5
1,9	−142.3	−66.2
2,3	−150.9	−74.5

ether is 1,2,3,4,8,9,10,16,17,18,22,23,24,36,37,38,39,40-octadecafluoro-1,2,3,4,8,9,10,16,17,18,22,23,24,36,37,38,39,40-octadecahydro-2a-oxa-2(3)a-homo[60]fullerene. This compound complements the homofullerenes and aza-homofullerenes, which have -CR$_2$- and -NR-, respectively, inserted into 5,6-bonds; these were first reported in 1991–1993[14] and numerous examples are now known.

The preference for this insertion may have a simple rationalisation. Recently we reported the single crystal X-ray structure for $C_{60}F_{18}$[15] which showed that the lengths (Å) of the FC–CF bonds in the molecule are: 1.557 (1,2); 1.672 (2,3); 1.623 (1,9); 1.558 (9,10). Semi-empirical calculations on this structure give the same ordering of bond lengths with the 2,3-bond at 1.69 Å (AM1), 1.71 Å (MNDO) exceeding the 1,9-bond by 0.4 Å (AM1), 0.3 Å (MNDO). Thus the 2,3-bond being the longest should also be the weakest, and hence the most amenable to oxygen insertion. In **2** the long (2,3) bond of $C_{60}F_{18}$ has opened out by 0.53 Å. The fact that oxides are major by-products of fullerene fluorination suggests that the reaction is also enhanced by electron withdrawal.

Previously, we compared the experimental results with semi-empirical calculations of the stability of C_s $C_{60}F_{18}O$ isomers involving incorporation of oxygen at various epoxide and ether sites. For the latter we considered only those bonds which connect carbons having no fluorine addends. These calculations (italicised data) are reproduced in Table 1.

One epoxide and one ether, involving addition to the central benzenoid ring, were clearly ruled out by their extremely low stabilities. The remaining data showed that the ethers should be the more stable, but each was ruled out by the ^{19}F NMR data (which consisted of $8 \times 2 F + 2 \times 1 F$ peaks, as follows: (i) one of the 2 F peaks was shifted substantially downfield (*ca.* 40 ppm) and this could not be accounted for by the remote oxygen in the 47,48-isomer. (ii) The 55,56-isomer required a downfield shift of one of the 1 F peaks, which was not observed. The data were however fully consistent with the 13,30-epoxide (**1**).

We have now calculated the heats of formation for all of the possible epoxides and ethers, including for the latter, insertion between carbons each or both of which are bonded to fluorine. The results (non-italicised) are given in Table 1 and it is very satisfying to see that of all the possible isomers, the one that is isolated in by far the largest yield is the one that is predicted to be the most stable. MNDO has a known tendency to favour

ether over epoxide formation even in the bare [60]fullerene,[11] but the differences here should be more reliable indications of a real chemical preference, as they are much larger and stem from a clear geometric effect.

One unexpected feature however is the relatively small downfield shift for the resonances of the fluorines immediately adjacent to the oxygen. We have obtained significantly greater downfield shifts of some fluorine resonances in other fluorofullerene oxides, which may be attributable to differential electron withdrawal as a function of the number of sp^3 addend-bearing carbons. Further work on isolation and characterisation of oxides of fluorofullerenes is in hand.

Notes and references

† *Crystal data*: $C_{60}F_{18}O \cdot (C_7H_8)$, $M = 1170.7$, Monoclinic, $P2_1/n$ (no. 14), $a = 11.4675(4)$, $b = 21.2128(9)$, $c = 16.9247(6)$ Å, $\beta = 101.769(3)°$, $V = 4030.5(3)$ Å^3, $z = 4$, μ(Mo-Kα) = 0.17 mm^{-1}, $T = 173$ K. 27044 reflections measured on an Enraf-Nonius Kccd diffractometer, 5545 unique ($R_{int} = 0.103$), refinement on all F^2, $R^1 = 0.052$ [for 4276 reflections with $I > 2\sigma(I)$], $wR^2 = 0.114$ (for all reflections). CCDC 182/1682. See http://www.rsc.org/suppdata/cc/b0/b003753m/ for crystallographic data in .cif format.

1 K. M. Creegan, J. L. Robbins, W. K. Robbins, J. M. Millar, R. D. Sherwood, P. J. Tindall, D. M. Cox, A. B. Smith, J. P. McCaulay, D. R. Jones and R. T. Gallagher, *J. Am. Chem. Soc.*, 1992, **114**, 1103.
2 A. B. Smith, R. M. Strongin, L. Brard, G. T. Furst, J. H. Atkins, W. J. Romanov, M. Saunders, H. A. Jiménev-Vázquez, K. G. Owens and R. J. Goldschmidt, *J. Org. Chem.*, 1996, **61**, 1904; V. N. Bezmelnitsin, A. V. Eletskii, N. G. Schepetov, A. G. Avent and R. Taylor, *J. Chem. Soc., Perkin Trans. 2*, 1997, 683.
3 A. L. Balch, D. A. Costa, B. C. Noll and M. M. Olmstead, *J. Am. Chem. Soc.*, 1995, **117**, 8926.
4 T. Hamano, T. Mashino and M. Hiroba, *J. Chem. Soc., Chem. Commun.*, 1995, 1537; C. Fusco, R. Seraglia and R. Curci, *J. Org. Chem.*, 1999, **64**, 8363.
5 M. P. Barrow, N. J. Tower, R. Taylor and T. Drewello, *Chem. Phys. Lett.*, 1998, **293**, 302.
6 H. Al-Matar, P. B. Hitchcock, A. G. Avent and R. Taylor, *Chem. Commun.*, 2000, 1071.
7 A. G. Avent, P. R. Birkett, A. D. Darwish, H. W. Kroto, R. Taylor and D. R. M. Walton, *Chem. Commun.*, 1997, 1579.
8 R. Taylor, J. H. Holloway, E. G. Hope, G. J. Langley, A. G. Avent, T. J. Dennis, J. P. Hare, H. W. Kroto and D. R. M. Walton, *J. Chem. Soc., Chem. Commun.*, 1992, 665; R. Taylor, G. J. Langley, J. H. Holloway, E. G. Hope, A. K. Brisdon, H. W. Kroto and D. R. M. Walton, *J. Chem. Soc., Perkin Trans.2*, 1995, 181; O. V. Boltalina, J. H. Holloway, E. G. Hope, J. M. Street and R. Taylor, *J. Chem. Soc., Perkin Trans. 2*, 1998, 1845.
9 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.
10 A. G. Avent, O. V. Boltalina, P. W. Fowler, A. Yu. Lukonin, V. K. Pavlovich, J. P. B. Sandall, J. M. Street and R. Taylor, *J. Chem. Soc., Perkin Trans. 2*, 1998, 1319.
11 K. Raghavachari, *Chem. Phy. Lett.*, 1992, **195**, 221; K. Raghavachari and C. Sosa, *Chem. Phys. Lett.*, 1993, **209**, 223.
12 P. R. Birkett, A. G. Avent, A. D. Darwish, H. W. Kroto, R. Taylor and D. R. M. Walton, *J. Chem. Soc., Chem. Commun.*, 1995, 1869.
13 O. V. Boltalina, M. Bühl, A. Khong, M. Saunders, J. M. Street and R. Taylor, *J. Chem. Soc., Perkin Trans. 2*, 1999, 1475.
14 T. Suzuki, Q. Li, K. C. Khemani, F. Wudl and O. Almarsson, *Science*, 1991, **254**, 1186; M. Prato, Q. Li, F. Wudl and V. Lucchini, *J. Am. Chem. Soc.*, 1993, **115**, 1148.
15 I. S. Neretin, K. A. Lyssenko, M. Yu. Antipin, Y. L. Slovokhotov, O. V. Boltalina, P. Troshin, A. Lukonin, L. V. Sidorov and R. Taylor, *Angew. Chem., Int. Ed.*, in the press.