# $C_{60}F_{18}O$: Isolation, spectroscopic characterisation and structural calculations

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**$C_{60}F_{18}O$, obtained as a byproduct of fluorination of [60]fullerene with $K_2PtF_6$, has $C_s$ symmetry, the oxygen being located in one of the symmetry planes of $C_{3v}$ $C_{60}F_{18}$. $C_{60}F_{20}$, isolated in low yield, also has $C_s$ symmetry arising from addition of $F_2$ either across or (more probably) in the symmetry plane of $C_{60}F_{18}$. The results are compared with theoretical predictions of the structures. $C_{60}F_{18}{\cdot}CF_2$ has also been obtained as a byproduct of the production of $C_{60}F_{18}$ and provides further confirmation of the parallel between fluorination and hydrogenation (which correspondingly gives methylene adducts), the adducts being produced by cage fragmentation in each case. A 790 amu species (as yet uncharacterised but which may be either $C_{60}F_2O_2$ or $C_{60}CF_3H$) is detected in some samples.**

The stability of $C_{60}F_{18}O$ was first indicated by the EI mass spectrum of the product of the reaction of methanol with a mixture of fluorinated [60]fullerenes,[1] and also by the fluorination work of Cox and co-workers.[2] Oxide formation is very widespread in fullerene chemistry, especially when halogenated fullerenes are involved in syntheses, indicating that the oxides are formed by nucleophilic substitution of halogen by water, with subsequent Hhal elimination, resulting in an epoxide structure,[1] (though six-centre elimination of Hhal with accompanying ring opening and $>$C=O formation could participate in some circumstances).[3] The ready loss of HF from fluorofullerenes is manifest in etching of glass containers of fluorofullerenes, especially when the latter are in solution. Oxides are also formed by direct oxygenation,[4,5] and the epoxide structure has been confirmed in some cases by either $^{13}C$ NMR spectroscopy or X-ray crystallography.[5] Calculations have indicated that oxygen insertion into a 6,5-bond should also be a favourable process,[6] though indirect experimental evidence for this occurrence has been forthcoming only in one example.[7]

We now report the isolation of $C_{60}F_{18}O$, and trace quantities of $C_{60}F_{20}$, $C_{60}F_{18}CF_2$, and either $C_{60}F_2O_2$ or $C_{60}CF_3H$, together with theoretical predictions of the favoured site for addition of either an oxygen atom or two fluorines to $C_{60}F_{18}$.

## Experimental

### Isolation of $C_{60}F_{18}O$

[60]Fullerene was fluorinated with $K_2PtF_6$ at 500–600 K to produce mainly $C_{60}F_{18}$ as described previously.[8] The product was dissolved in HPLC-grade toluene, filtered and then subjected to HPLC separation using a 4.6 mm × 25 cm Cosmosil Buckyprep column with toluene as eluent at a flow rate of 1 ml min$^{-1}$. $C_{60}F_{18}$ eluted after 37 min, slightly faster than that (44.4 min) which we described previously, due apparently to differences in ambient temperature and column condition. A significant peak with a retention time of 58 min was also obtained, and this proved to be $C_{60}F_{18}O$ as shown by the EI mass spectrum (Fig. 1). Traces of $C_{60}F_{18}{\cdot}CF_2$ (Fig. 2) and what may be another isomer of $C_{60}F_{18}O$ were obtained at 30 and 50 min retention times, respectively. The mass spectrum of $C_{60}F_{18}{\cdot}CF_2$ showed the presence of a 790 amu species which was detected also in fractions with retention times of 10–12, 21 and 54 min. It is possible therefore that in some (or possibly all) of these fractions this species (which may be either $C_{60}F_2O_2$ or $C_{60}CF_3H$) is produced from a less stable one during EI mass spectrometry.

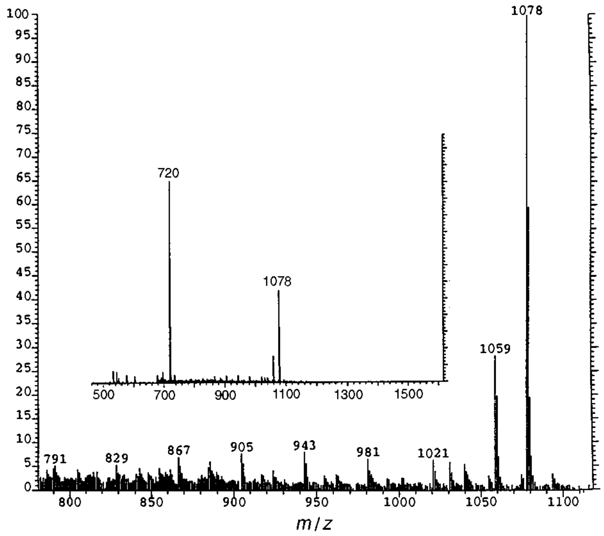

**Fig. 1** EI mass spectrum (70 ev) of $C_{60}F_{18}O$

From the product of reaction of [60]fullerene with $MnF_3$ at 350 °C, a trace of a component of *ca.* 42 min retention time was obtained under the above conditions, which the EI mass spectrum (1100 amu, Fig. 3) showed to be $C_{60}F_{20}$.

## Results and discussion

### The structure of $C_{60}F_{18}$

Through the use of $^{19}F$ NMR spectroscopy, it was deduced previously that $C_{60}F_{18}$ consists of a $C_{3v}$ crown (inset to Fig. 4).[8] Use of $^{13}C$ NMR spectroscopy for identification of fluorofullerenes is limited by the need to decouple the fluorine, a facility currently unavailable to us. However, the structure of $C_{60}F_{18}$ with the fluorines concentrated at one end of the molecule permitted the obtaining of a meaningful undecoupled $^{13}C$ NMR spectrum. The spectrum is predicted (see Fig. 4) to consist in the sp$^2$-hybridised region of five singlets (3 × 6 C and 2 × 3 C) due to the respective carbons being at least two bond lengths removed from fluorine, and three multiplets (3 × 6 C). This is

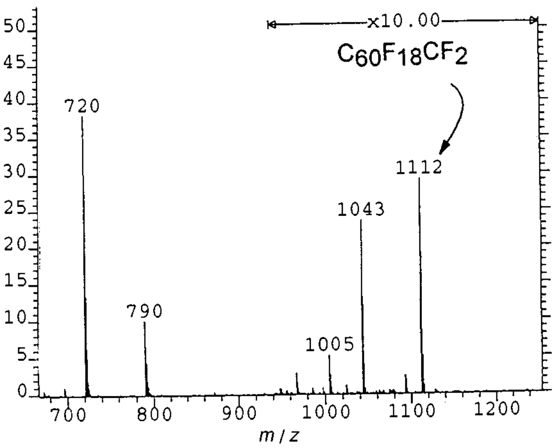

**Fig. 2** EI mass spectrum (70 ev) of $C_{60}F_{18}{\cdot}CF_2$, showing also the presence of the 790 amu species (see text)

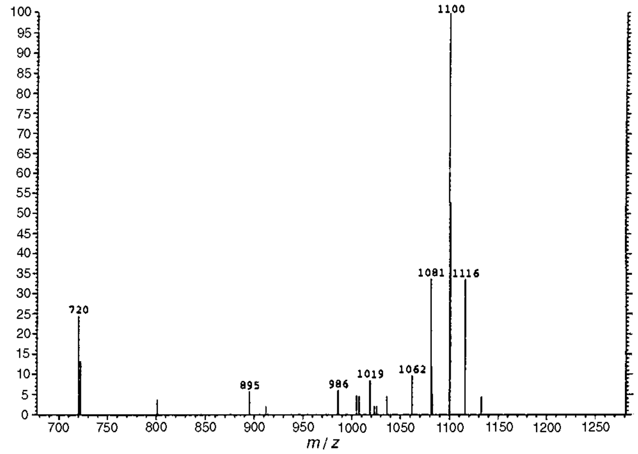

**Fig. 3** EI mass spectrum (70 ev) of $C_{60}F_{20}$

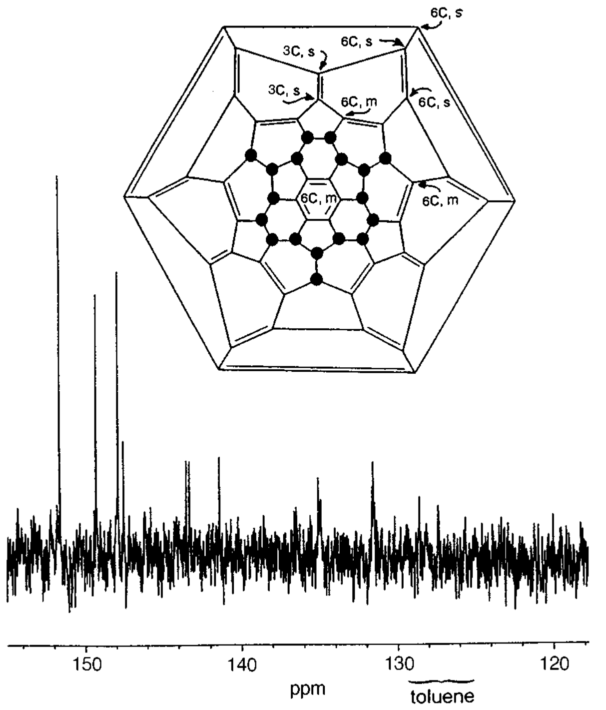

**Fig. 4** $^{13}C$ NMR spectrum ($sp^2$ region, 125 MHz, $CDCl_3$) of $C_{60}F_{18}$, showing (Schlegel diagram, inset) the predicted $^{13}C$ NMR pattern for the various $sp^2$-hybridised carbons

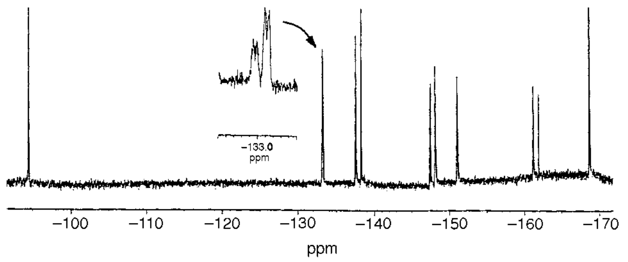

**Fig. 5** $^{19}F$ NMR spectrum (338.9 MHz, $CDCl_3$, $CFCl_3$) for $C_{60}F_{18}O$; insert shows resolution of the peak at −133 ppm through the use of deuteriobenzene as solvent

observed (Fig. 4), with one of the multiplets (probably due to the $sp^2$ carbons in the central benzenoid ring) appearing as a clear doublet: $\delta_C(CDCl_3)$, 151.77 (s, 6 C), 149.42 (s, 6 C), 148.02 (s, 6 C), 147.68 (s, 3 C), 143.55 (d, 6 C, *J* 24.8 Hz), 141.57 (s, 3 C), 135.10 (m, 6 C), 131.76 (m, 6 C); peaks at 128.74 and 127.53 are due to traces of the HPLC eluent toluene, which is retained in the lattice. As required by the structure, four multiplet peaks were observed in the $sp^3$-region at $\delta_C$ 91.15, 89.20, 86.28 and 84.01, but these latter are considered provisional in the absence of an F-decoupled spectrum (which would also allow accurate determination of peak intensities).

## The structure of $C_{60}F_{18}O$

**The $^{19}F$ NMR spectrum.** The location of the oxygen is of considerable importance in aiding our understanding of how addition patterns are built up in fullerenes. If oxygen is incorporated either along or across the symmetry plane (three possibilities) then the $^{19}F$ NMR spectrum should consist of ten lines: $8 \times 2$ F + $2 \times 1$ F. If however it is incorporated anywhere else, then the spectrum should increase to eighteen lines because of the loss of symmetry. The observed spectrum (338.9 MHz, $CDCl_3$, $CFCl_3$ reference, Fig. 5) consists of nine multiplets at $\delta_F$ −94.60 (2 F), −133.30 (*ca.* 3 F), −137.62 (2 F), −138.37 (2 F), −147.60 (2 F), −148.21 (2 F), −151.0 (2 F), −161.27 (1 F) and −168.81 (2 F). The $\delta_F$ −133.30 multiplet was resolved into two multiplets of *ca.* 2:1 ratio by using deuteriobenzene as solvent (inset to Fig. 5); in some samples a small peak at −162 ppm appeared, due it is believed, to traces of HF. The oxygen is therefore incorporated to give a $C_s$ symmetric product, and the significantly longer HPLC retention time of the oxide suggests that the oxygen is incorporated to give a highly polar product and is therefore near to the fluorines. This conjecture is consistent with the 2-D COSY $^{19}F$ NMR spectrum (Fig. 6), which shows on the Schlegel diagram, the assignments of the spectrum together with the oxygen location. The following features are evident.

(1) The positions of the resonances for the ten different fluorines are as follows, with the values for the corresponding positions in $C_{60}F_{18}$ in parentheses: A, −133.1 (−131.6); B, −161.3 (−158.1); C, −138.4 (−136.0); D, −137.6 (−143.4); E, −147.6 (−143.4); F, −137.6 (−136.0); G, −168.8 (−158.1); H, −132.9 (−131.6); J, −151.0 (−136.0); K, −94.6 (−143.4). It is seen that for positions A–F and H, there are very little changes for the corresponding resonances because these positions are remote from the added oxygen. By contrast, the resonances for fluorines K, which are in the immediate vicinity of the oxygen, are drastically moved downfield. This produces polarisation of the carbon–carbon bond to which fluorines J and K are attached, consequently, the resonance for fluorines J (and also fluorines G) move upfield.

(2) The coupling constants between fluorines corresponding to A and B in $C_{60}F_{18}$ are *ca.* 20 Hz. Likewise in the oxide, the A/B and G/H couplings are *ca.* 18 and 21 Hz, respectively. Other identifiable couplings are 8, 11, 21, 25 and 8 Hz for C/D, E/F, K/J, D/E and B/C, respectively.

These resonances are consistent only with oxygen located in the symmetry plane. The mass spectrum and previous work on

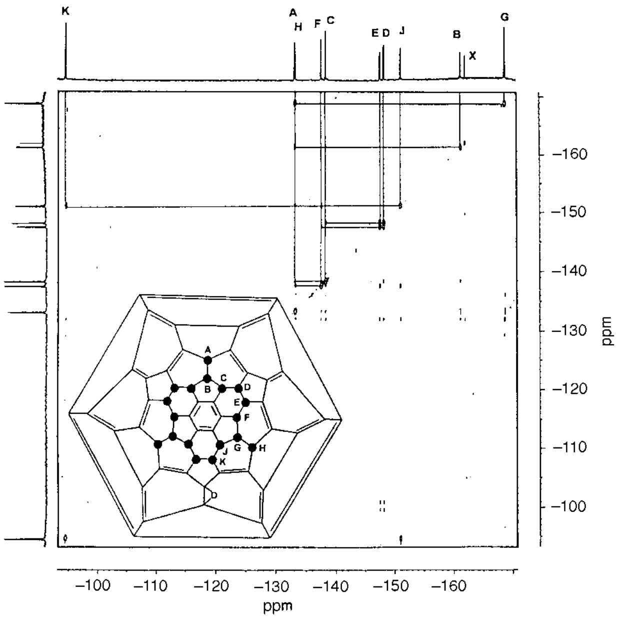

**Fig. 6** 2D-COSY spectrum of $C_{60}F_{18}O$, showing inset the assignment of peaks

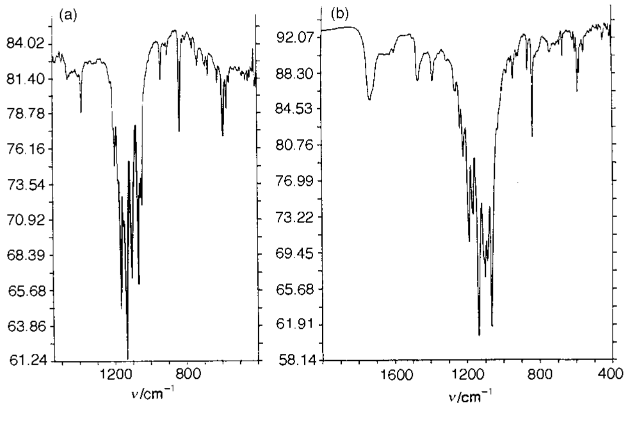

**Fig. 7** IR spectra (KBr disc) for (a) $C_{60}F_{18}$ and (b) $C_{60}F_{18}O$

[60]fullerene are consistent with oxygen addition across a 6,6-bond, rather than insertion into a 6,5-bond.[5] If the addition were in the aromatic hexagon at the centre of the crown, then fluorines J would experience a large downfield shift, and other fluorines in the vicinity would also be affected. If on the other hand the oxygen was located in the hexagon at the other pole, then the shifts would be small (and only fluorine A would be significantly affected).

**The IR spectrum.** The respective IR spectra [Fig. 7(a), (b)] are consistent with the relatively small perturbation in the proposed oxide structure (inset to Fig. 4) compared to $C_{60}F_{18}$. Main bands at 1163, 1133, 1103, 1067, 833 and 589 $cm^{-1}$ for $C_{60}F_{18}$ appear closely similar at 1166, 1136, 1101, 1065, 836 and 590 $cm^{-1}$ in the oxide.

Notably, the IR spectrum shows a broad band at 1731 $cm^{-1}$, and we note that some 45% of epoxides given in a standard compilation also show bands in this region.[9] Although the band could imply that a ketonic group is present in $C_{60}F_{18}O$, this may reasonably be discounted by arguments based on energetics and symmetry, and by the mass spectrum which shows normal fragmentation down to [60]fullerene (Fig. 1, inset). It is possible that the band originates from traces of fullerenols produced by hydrolysis of C–F bonds, since these are known to give rise to bands in this IR region.[10]

The origin of the oxygen in the present sample of $C_{60}F_{18}O$ is unclear, but it seems likely that it is formed by reaction with oxygen traces during the fluorination process. The alternative would be for it to be derived from $C_{60}F_{20}$ through addition of water and elimination of HF. Although traces of $C_{60}F_{20}$ have been isolated, there are no reasons to believe that it is sufficiently stable to be present in the substantial quantities needed for it to be the $C_{60}F_{18}O$ precursor.

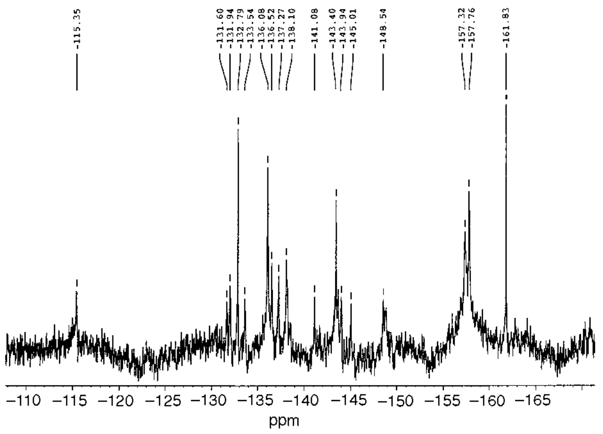

**Fig. 8** $^{19}F$ NMR spectrum of $C_{60}F_{20}$

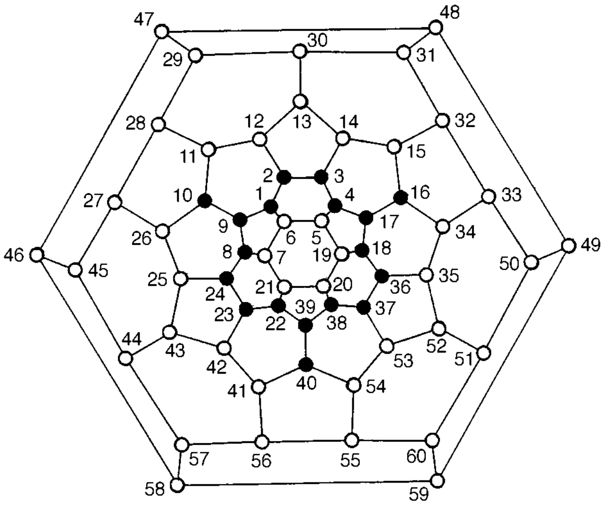

**Fig. 9** Numbering for $C_{60}F_{18}$; ● = location of fluorines

### Other compounds obtained in the fluorination

**The structure of $C_{60}F_{20}$.** At this stage we consider possible structures based only upon addition of $F_2$ to $C_{60}F_{18}$. If addition occurs in one of the symmetry planes (three equivalent double bonds), then there should be twelve lines in the $^{19}F$ NMR spectrum (4 × 1F + 8 × 2F) and if addition occurs across a plane (two sets of three equivalent double bonds) there should be eleven lines (2 × 1F + 9 × 2F). Addition elsewhere (two sets of six equivalent bonds) would give twenty lines since all symmetry is then lost. The observed preliminary spectrum (not shown) consists of seventeen lines (Fig. 8), four of which (at $\delta_F$ −131.6, −136.1, −143.4 and −157.8, *cf.* ref. 8) may be attributed to the presence of some $C_{60}F_{18}$, and a prominent singlet at −161.8 is due most likely to HF. This indicates that $C_{60}F_{20}$ is one of the first two possibilities. It is noteworthy that one peak at $\delta_F$ −115.4 is well downfield from the remainder which appear between −132 and −158, and this shows a parallel with the oxide. We hope in due course to be able to isolate larger quantities of this material and so obtain a more detailed spectrum. Theoretical predictions of the structure are described below.

**$C_{60}F_{18}$·$CF_2$.** The mass spectrum for this compound (Fig. 2) is of particular interest because it shows a further extension of the parallel between hydrogenation and fluorination. Hydrogen-

**Table 1** Heats of formation (kcal mol$^{-1}$) for $C_s$ $C_{60}F_{18}X$ structures[a]

| | | MNDO | AM1 |
|---|---|---|---|
| (a) X = O | | | |
| (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 |
| (ii) Ethers | 6,5-bond in which oxygen is inserted | | |
| | 20,21 | −56.7 | 21.1 |
| | 55,56 | −115.8 | −29.2 |
| | 47,48 | −130.1 | −41.7 |
| (b) X = $F_2$ | 6,6-bond to which $F_2$ is added | | |
| | 5,6 | −115.1 | |
| | 11,12 | −170.1 | |
| | 13,30 | −188.4 | |
| | 55,60 | −197.9 | |
| | 58,59 | −205.5 | |

[a] Numbering of the precursor $C_{60}F_{18}$ is according to the lowest locant rule (Fig. 9); $C_{60}F_{18}$ is thus 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[60]fullerene. The common mirror plane bisecting the 5,6 bond is used for both sets.

ation of fullerenes is accompanied by the formation of methylene adducts the origin of which was uncertain,[11] but the possibility that they are derived from fragmentation of a highly hydrogenated cage to give methylene radicals was reinforced by subsequent identification of cage fragmentation during hydrogenation.[12] Likewise it has been shown previously that the fullerene cage can hyperfluorinate (*i.e.* to give cages comprised of CF and $CF_2$ groups),[13] so that subsequent fragmentation to give difluoromethyl radicals which then attack another cage, accounts readily for the observed result.

**The 790 amu species.** This is evident in the spectrum of fractions as described in the Experimental. Both $C_{60}CF_2O_2$ and $C_{60}CF_3H$ are likely candidates for the structure, but cannot be distinguished by accurate mass measurement because the difference between their masses is insignificant. We consider that $C_{60}CF_3H$ is the less probable species because there is no M − 1 fragmentation peak at 789 amu[14] in any of our spectra; we hope to isolate this component in spectroscopically analysable quantities in due course.

### Theoretical calculations

**$C_{60}F_{18}O$.** The experimental results are compared with semi-empirical predictions of the stability of $C_{60}F_{18}O$ based upon the preferred site for incorporation of oxygen into $C_{60}F_{18}$. These have been calculated by both MNDO and AM1 methods [Table 1(a), all isomers run in $C_s$ symmetry] for both oxygen addition to a 6,6-bond (giving an epoxide) or oxygen insertion to a 6,5-bond (giving an ether). In each case there are three possibilities that produce a symmetrical product. Both calculation methods predict: (i) ether formation should be preferred over epoxide formation, thereby paralleling predictions for the parent fullerenes,[6] (ii) incorporation into the benzenoid ring at the centre of the crown should be very unfavourable, which is consistent with the loss of aromaticity that would result, (iii) incorporation should take place in the antipodal hexagon. That it does not points to the importance of kinetic factors, as yet not understood. One possibility is that electron withdrawal favours oxygen addition, so this occurs as near to the fluorines as possible, (though not of course in the unfavourable benzenoid ring). Certainly the large number of oxide derivatives of fluorofullerenes that have been detected by mass spectrometry supports this conjecture.[15]

**$C_{60}F_{20}$.** Whilst the structure of this compound is not yet known, the preliminary spectrum indicates that fluorine adds to $C_{60}F_{18}$ so as to give a symmetrical product. The MNDO calculated heats of formation for addition to the five distinct formal double bonds (no enforced symmetry) are given in Table 1(b). The overall prediction is that addition is more favourable, the further away it is from the crown, but there is no pronounced preference for either symmetrical or unsymmetrical addition. The favourability of addition to the 58,59-bond and its equivalents, and the unfavourability of addition to the 11,12 bond and its equivalents, are consistent with the formation of *T* and $C_3$ $C_{60}F_{36}$ which are presumed to occur *via* $C_{60}F_{18}$ as intermediate.[16]

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## References

1 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; 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.

2 S. W. Chowdhury, S. D. Cameron, D. M. Cox, K. Kniaz, R. A. Strongin, M. A. Cichy, J. E. Fischer and A. B. Smith, *Org. Mass. Spectrom.*, 1993, **28**, 860.

3 R. Taylor, *Russ. Chem. Bull.*, in the press.

4 J. M. Wood, B. Kahr, S. H. Hoke, L. Dejarme, R. G. Cooks and D. Ben-Amotz, *J. Am. Chem. Soc.*, 1991, **113**, 5907; W. A. Kalsbeck and H. H. Thorp, *J. Electroanal. Chem.*, 1991, **314**, 363; D. Heymann and L. P. F. Chibante, *Chem. Phys. Lett.*, 1993, **207**, 339; R. Malhotra, S. Kuma and A. Satyan, *J. Chem. Soc., Chem. Commun.*, 1994, 1339.

5 K. M. Creegan, J. L. Robbins, W. K. Robbins, J. M. Millar, R. D. Sherwood, P. J. Tindall, D. M. Cox, A. B. Smith and J. P. McCauley, *J. Am. Chem. Soc.*, 1992, **114**, 1103; Y. Elemes, J. K. Silverman, S. Chen, M. Kao, C. S. Foote, M. M. Alvarez and R. L. Whetten, *Angew. Chem., Int. Ed. Engl.*, 1992, **31**, 351; A. L. Balch, D. A. Costa, J. W. Lee, B. C. Noll and M. M. Olmstead, *Inorg. Chem.*, 1994, **33**, 2071; A. B. Smith, R. M. Strongin, L. Brard, G. F. Furst, J. H. Atkins, W. J. Romanov, M. Saunders, H. A. Jiménez-Vázquez, K. G. Owens and R. G. 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.

6 K. Raghavachari, *Chem. Phys. Lett.*, 1992, **195**, 221; 1993, **209**, 223.

7 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.

8 O. V. Boltalina, Y. Yu Markov, R. Taylor and M. P. Waugh, *Chem. Commun.*, 1996, 2549.

9 Aldrich Library of FTIR Spectra, Aldrich Chemical Co., 1985, vol. 1.

10 L. Y. Chiang, in *The Chemistry of Fullerenes*, ed. R. Taylor, World Scientific, Singapore, 1995.

11 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.

12 A. D. Darwish, H. W. Kroto, R. Taylor and D. R. M. Walton, *J. Chem. Soc., Perkin Trans. 2*, 1996, 1415.

13 O. V. Boltalina, A. K. Abdul-Sada and R. Taylor, *J. Chem. Soc., Perkin Trans. 2*, 1995, 981; A. A. Tuinman, A. A. Gakh, J. L. Adcock and R. N. Compton, *J. Am. Chem. Soc.*, 1993, **115**, 5885.

14 H. P. Fritz and R. Hiemeyer, *Carbon*, 1995, **33**, 1601; J. D. Crane, H. W. Kroto, G. J. Langley, R. Taylor and D. R. M. Walton, unpublished work.

15 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; 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, 511.

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

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