Preparation and characterisation of $C_{60}F_{18}$

Olga V. Boltalina,*[a] Vitaly Yu. Markov,[a] Roger Taylor*[b] and Martin P. Waugh[b]

[a] *Chemistry Department, Moscow State University, Moscow 119899, Russia*
[b] *School of Chemistry and Molecular Sciences, University of Sussex, Brighton, UK BN1 9QJ*

$C_{60}F_{18}$ has been prepared by reaction between [60]fullerene and potassium hexafluoroplatinate in a Knudsen cell contained within a mass spectrometer; characterisation by ^{19}F NMR spectroscopy shows that the molecule has C_{3v} symmetry and is isostructural with $C_{60}H_{18}$.

Fluorinated fullerenes are very soluble and readily undergo nucleophilic substitution,[1,2] which commends them as valuable synthons. However, preparation of fluorinated fullerenes having a specific (and in particular low) fluorine content is very difficult, because reaction has to be carried out heterogeneously, whence fluorine does not readily penetrate the fullerene lattice. Thus, attempted partial fluorination of [60]fullerene by fluorine gas produced a mixture of highly fluorinated and unfluorinated material.[3] Fluorination with fluorine gas at high temperature produces mainly $C_{60}F_{48}$ which has been isolated and characterised.[4,5]

Previously, we found that use of a bulky fluorination reagent, *e.g.* MnF_3 (coupled with removal under vacuum of the volatile reaction products from the metal fluoride to avoid further reaction) resulted in limited fluorination and the successful formation of both $C_{60}F_{36}$[6] and $C_{70}F_{36-40}$; the *T* isomer is the major component of $C_{60}F_{36}$.[6] These products are notable because the most stable species produced on hydrogenation of [60]fullerene is $C_{60}H_{36}$, whilst [70]fullerene gives $C_{70}H_{36-40}$.[7] The results confirmed that fluorination parallels hydrogenation, an earlier mass spectroscopic study having shown that both $C_{60}F_{36}$ and $C_{60}F_{18}$ (and their epoxides) were prominent amongst the numerous species obtained on fluorination of [60]fullerene with fluorine gas at 70 °C;[3] $C_{60}F_{18}$ and $C_{60}F_{36}$ were also found to be the most stable species (by mass spectrometry) on fluorination of [60]fullerene by ClF_3.[8] $C_{60}H_{18}$ has been detected as a high stability species in a number of hydrogenation studies.[7]

Recently, one of us has shown[9] that $C_{60}H_{18}$ has the crown-shaped C_{3v} structure predicted[10] to be of high stability. We now report the formation of $C_{60}F_{18}$, the fullerene of lowest fluorine content yet produced, by fluorination of [60]fullerene with potassium hexafluoroplatinate. Characterisation by ^{19}F NMR shows it to be isostructural with $C_{60}H_{18}$.

A mixture of [60]fullerene (20 mg) and potassium hexafluoroplatinate (60 mg) was ground intimately and placed in a Knudsen cell incorporated within an MI-1201 magnetic sector mass spectrometer; a collection plate was situated *ca.* 8 mm from the outlet of the cell. The temperature was raised to 500–600 K and the recorded spectra showed that $C_{60}F_{18}$ was being produced. The instrument was left running for 8 h, and the deposit (*ca.* 10% yield) was then removed from the collection plate. Mass spectrometry (VG Autospec) showed the combined crude product to consist of unreacted [60]fullerene together with $C_{60}F_{18}$, a smaller amount of $C_{60}F_{36}$ (which is more volatile) and traces of other minor components such as $C_{60}F_{18}O_2$. The fluorofullerenes can be separated partly from the unreacted [60]fullerene by extraction with chloroform. Final purification was carried out by HPLC (toluene eluent) using a 4.6 mm × 25 cm Cosmosil column; at 0.85 ml min^{-1} flow rate the retention times of C_{60} and $C_{60}F_{18}$ are 9.37 and 44.4 min, respectively. The very long retention time of $C_{60}F_{18}$ is consistent with high polarity resulting from its structure. By contrast, the retention time of the effectively nonpolar $C_{60}F_{36}$ is 3.35 min, and notably, that of $C_{70}F_{36-40}$ is slightly shorter at 3.29 min; this latter behaviour parallels that of the corresponding hydrogenated fullerenes.[7]

Pure $C_{60}F_{18}$ is a green–yellow microcrystalline solid and is readily soluble in a range of solvents, *e.g.* hexane, toluene and chloroform. Dilute solutions in toluene are green–yellow, more concentrated solutions being deep yellow. $C_{60}F_{18}$ may also be obtained by HPLC separation of the products formed by fluorination of [60]fullerene with MnF_3.

Numerous apparently polymeric products (soluble in either acetone or chloroform) were obtained from the HPLC separation but contained neither fullerene nor fluorine. They appeared to have been produced from the toluene solvent, possibly by a reaction involving traces of HF.

The EI mass spectrum of $C_{60}F_{18}$ (Fig. 1) and shows greater fragmentation compared to that for $C_{60}F_{36}$,[6] but this does not necessarily indicate that $C_{60}F_{18}$ is of lower stability; the lower volatility of $C_{60}F_{18}$ compared to $C_{60}F_{36}$ requires the use of higher probe temperatures. Of particular note is that fragmentation takes place by F loss down to $C_{60}F_8$, and by F_2 loss thereafter. This feature was evident from a number of spectra recorded on different samples, and suggests that the $C_{60}F_n$ (n = 2,4,6,8) species may be relatively stable. The spectrum indicates the presence of *ca.* 2% of $C_{60}F_{20}$ in the sample.

The ^{19}F NMR spectrum of $C_{60}F_{18}$ (376.4 MHz, $CDCl_3$, Fig. 2) shows just four lines at δ −131.6, −136.0, −143.4 and −158.1, with intensity ratios 1:2:2:1, respectively. The splittings, evident from expanded spectra (not shown), and couplings derived from 2D-COSY analysis are given along the top of the spectrum; the inset motif shows the only possible locations of the four distinct fluorine atoms on a carbon backbone. Threefold repetition of this motif gives C_{3v} symmetric $C_{60}F_{18}$, shown in the Schlegel diagram (Fig. 3), and this structure contains a benzenoid ring in which full delocalisation of electrons can occur through reduction of angle strain in the three adjacent pentagons; notably, this is a substructure of *T*

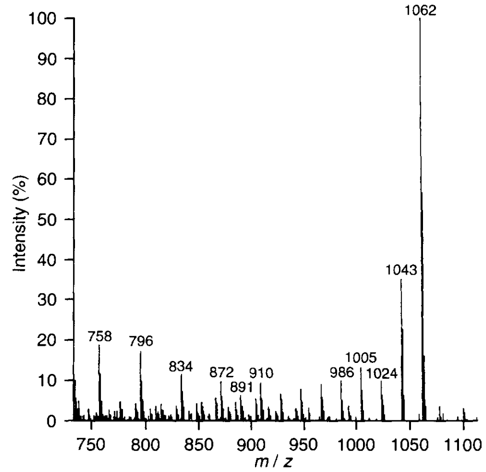

Fig. 1 EI mass spectrum (70 eV) of $C_{60}F_{18}$

symmetric $C_{60}F_{36}$. The same structural pattern has been confirmed for $C_{60}H_{18}$ by its ^1H NMR spectrum which likewise shows four lines of 1 : 2 : 2 : 1 intensity ratio; the only difference being that for the hydrogenated compound the resonance for atom C occurs upfield of that for atom B.[9] The positions of the resonances depend on two factors: the number of adjacent electron-withdrawing sp^2-hybridised carbons, and the electronegativity of the elements attached to the adjacent sp^3-hybridised atoms. The different relative dispositions of the resonances in $C_{60}F_{18}$ compared to those in $C_{60}H_{18}$ derive from this latter factor. In both compounds the resonance for atom A is the furthest downfield, and this would seem to be due to the fact that the cage atom to which A is attached is the only one with *two* adjacent sp^2-hybridised carbons.

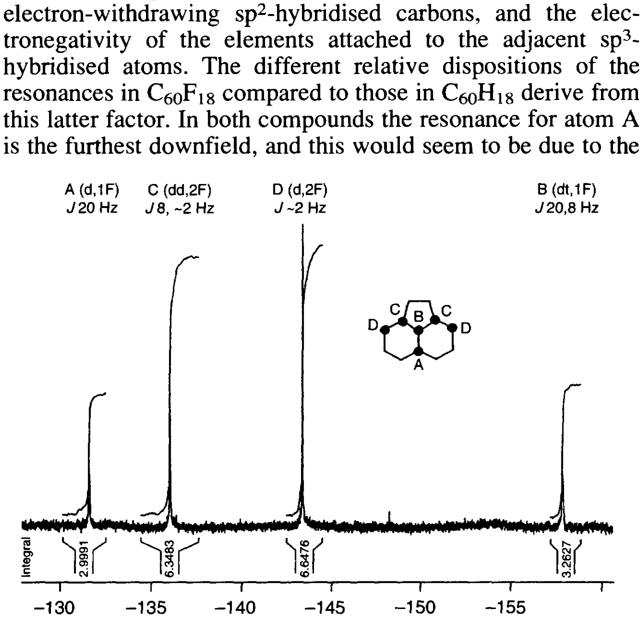

Fig. 2 ^{19}F NMR spectrum (376.4 MHz) for $C_{60}F_{18}$, showing integration, splitting and couplings (from 2D-COSY analysis)

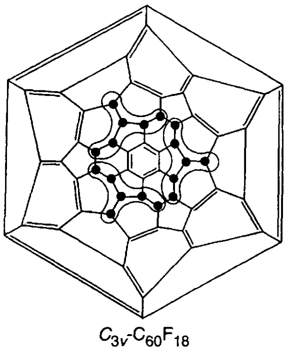

Fig. 3 Schlegel diagram for $C_{60}F_{18}$, with filled circles showing the location of the fluorines; the threefold motif that gives rise to the observed NMR spectrum is encircled

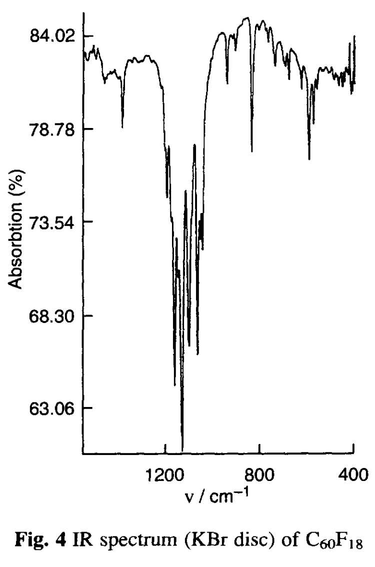

Fig. 4 IR spectrum (KBr disc) of $C_{60}F_{18}$

Although the motif could be inverted about the $F_AC–CF_B$ bond and give the same NMR pattern, the resultant $C_{60}F_{18}$ is not a substructure of $C_{60}F_{36}$; it would have very low polarity, and the equivalent structure for $C_{60}H_{18}$ has been disproved.

The IR spectrum (Fig. 4) consists of a number of very sharp bands at 1385, 1196, 1163, 1133, 1103, 1067, 1045, 939, 833, 733, 673, 589 and 570 cm^{-1}. This provides confirmation (see NMR above) for the existence of a single isomer. By contrast, the spectrum of $C_{60}F_{36}$ was less sharp due to the presence of four isomers.[6] The spectrum, and the simple structure of the compound, should provide a useful basis for refinement of theoretical calculations[11] of IR spectra for fluorofullerenes.

The UV–VIS spectrum of $C_{60}F_{18}$ in hexane shows sharp bands at 221, 247, and 339 nm, and weak shoulders at *ca.* 365 and 445 nm. The spectrum shows some similarities to that of $C_{60}H_{18}$,[9] which has maxima at 232, 261 and 343 nm, and this is consistent with the identical addend-free UV-active portion of the cage in each molecule. In toluene the band at 339 nm suffers a small bathochromic shift to 348.6 nm (the weak shoulders appear to shift by a similar amount) indicating a small charge transfer interaction, but the effect is much smaller than that observed with $C_{60}F_{48}$,[5] as expected.

At present we have insufficient material for a comprehensive study of the nucleophilic reactivity of $C_{60}F_{18}$. An addition–elimination mechanism for nucleophilic substitution of the fluorinated cage is probable since the S_N2 mechanism is impossible and the S_N1 mechanism unlikely.[1] $C_{60}F_{18}$ could be more susceptible to such elimination, since there is a greater availability of double bonds adjacent to the fluorines than is the case in either $C_{60}F_{36}$ or $C_{60}F_{48}$, and addition to most of these does not require loss of aromaticity (*cf.* $C_{60}F_{36}$). It is notable therefore that the ^{19}F NMR spectrum of a solution in THF showed complete removal of fluorine from the cage (confirmed by IR), only HF being detected; no component having a singlet around δ −150 was produced, in contrast to the behaviour of either $C_{60}F_{36}$,[5] $C_{60}F_{48}$[4] and $C_{60}F_{>48}$.[12] We plan further investigations in this area.

We thank the Royal Society for a Joint Project Grant, the Russian Foundation for Fundamental Science and the Russian Research Programme 'Fullerenes and Atomic Clusters'.

References

1 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, *Nature*, 1992, **355**, 27; *J. Chem. Soc., Chem. Commun.*, 1992, 665.

2 E. G. Hope and J. H. Holloway, in *The Chemistry of Fullerenes*, ed. R. Taylor, World Scientific, Singapore, 1995.

3 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.

4 A. A. Gakh, A. A. Tuinman, J. L. Adcock, R. A. Sachleben and R. N. Compton, *J. Am. Chem. Soc.*, 1994, **116**, 819.

5 O. V. Boltalina, L. N. Sidorov, V. F. Bagryantsev, V. A. Seredenko, A. S. Zapol'skii, J. M. Street and R. Taylor, *J. Chem. Soc., Perkin Trans, 2*, 1996, 2275.

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

7 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 and references therein.

8 A. S. Alikhanyan, I. P. Malkerova, D. V. Sevastyanov, S. P. Ionov, V. P. Sukhoverkov and N. G. Spitsina, *Zh. Neorg. Khim.*, 1995, **40**, 1502.

9 A. D. Darwish, A. G. Avent, R. Taylor and D. R. M. Walton, *J. Chem. Soc., Perkin Trans. 2*, 1996, 2051.

10 B. W. Clare and D. L. Kepert, *J. Mol. Struct.*, 1994, **303**, 1.

11 S. J. Austin, P. W. Fowler, J. P. B. Sandall and F. Zerbetto, *J. Chem. Soc., Perkin Trans. 2*, 1996, 155.

12 O. V. Boltalina, A. K. Abdul-Sada and R. Taylor, *J. Chem. Soc., Perkin Trans. 2*, 1995, 981.

Received, 28th August 1996; Com. 6/05925B