Preparation of $C_{60}F_{36}$ and $C_{70}F_{36/38/40}$

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Fullerene fluorination parallels hydrogenation, the reaction of [60]- and [70]-fullerenes with MnF_3 giving $C_{60}F_{36}$ and $C_{70}F_{36/38/40}$; ^{19}F NMR spectroscopy indicates that $C_{60}F_{36}$ consists of four isomers, one of which has *T* symmetry.

The prospect that fluorofullerenes would be good lubricants[1] was diminished by the discovery that they are highly reactive towards nucleophiles,[2] though this commended them as synthons.[2] However, great difficulty has been encountered in producing fluorofullerenes of specific (and especially low) fluorine content; thus far only $C_{60}F_{48}$ has been prepared and characterized.[3]

Hydrogenation of [60]fullerene produces $C_{60}H_{36}$ and $C_{60}H_{18}$, whilst hydrogenation of [70]fullerene produces $C_{70}H_{36/38/40}$, but the structures of these derivatives have not been resolved by NMR due to their rapid oxidation.[4] A parallel between hydrogenation and fluorination was first indicated by the greater peak intensities for $C_{60}F_{18}$ and $C_{60}F_{36}$ and their mono-oxides amongst the wide range of fluoro products obtained from fluorination of [60]fullerene with fluorine gas.[5] Here we report that the reaction of [60]- and [70]-fullerenes with MnF_3 under vacuum at elevated temperatures gives high purity $C_{60}F_{36}$ and $C_{70}F_{36/38/40}$; the former of which has been partly characterized by 2D(COSY) ^{19}F NMR.

Initial experiments on fluorination of [60]fullerene were carried out using a Knudsen effusion cell incorporated in an MI-1201 magnetic-sector mass spectrometer. A mixture of [60]fullerene and MnF_3 (1 : 7) was placed in the effusion chamber, and the gas phase species produced under heating were monitored. At 560–650 °C an intense peak at 1404 amu ($C_{60}F_{36}^+$) was observed under EI conditions. Minor peaks assigned to $C_{60}F_{34}^+$, $C_{60}F_{32}^+$ and $C_{60}F_{36}^{2+}$ were observed with total intensities comprising less than 15% of that of $C_{60}F_{36}^+$. Pale yellow material deposited on the cold part of the ion source was collected and analysed on a VG Autospec mass spectrometer (Fig. 1), which confirmed that $C_{60}F_{36}$ is the main product. Use of the Knudsen cell technique at increased temperature led to the formation of a wide range of lower fluorinated species with $C_{60}F_{18}^+$ being especially prominent.

The IR spectrum of the $C_{60}F_{36}$ so produced (Fig. 2) reveals two sharp peaks at 1160 and 1132 cm^{-1} with shoulders at 1272 and 1074 cm^{-1}; by contrast $C_{60}F_{48}$ shows main bands at 1238, 1170 and 1142 cm^{-1}.[6]

To increase the yields, samples of [60]fullerene (*ca.* 25 mg) were ground intimately with MnF_3 (120 mg) and placed in a nickel tube (30 mm long × 5 mm diameter, closed at one end) contained in a glass tube which was evacuated to *ca.* 0.01 mbar (1 bar = 10^5 Pa) and placed in a furnace such that part of the glass tube was outside the heated zone. The temperature of the furnace was increased to 330 °C during 30 min, and maintained at this temperature for 24 h, during which pale lemon material deposited on the cool zone. After the tube had cooled the vacuum was released and the deposit (*ca.* 30% yield) analysed by EI mass spectrometry (inset to Fig. 1) and IR spectroscopy (insert, Fig. 2). In general the material produced within the mass spectrometer contained virtually no oxide, but a little $C_{60}F_{34}$, whereas the material produced in the heated tube contained a little $C_{60}F_{36}O$ but only a small amount of $C_{60}F_{34}$. However, only trivial differences were observed in the ^{19}F NMR spectra obtained from various samples. The IR spectra from the heated

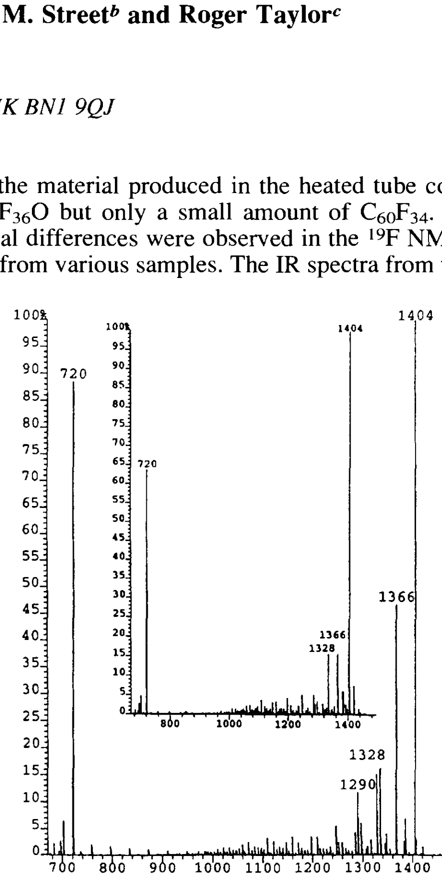

Fig. 1 Mass spectrum of $C_{60}F_{36}$ obtained from [60]fullerene and MnF_3 using a Knudsen cell; insert is the spectrum of the product obtained using a heated tube

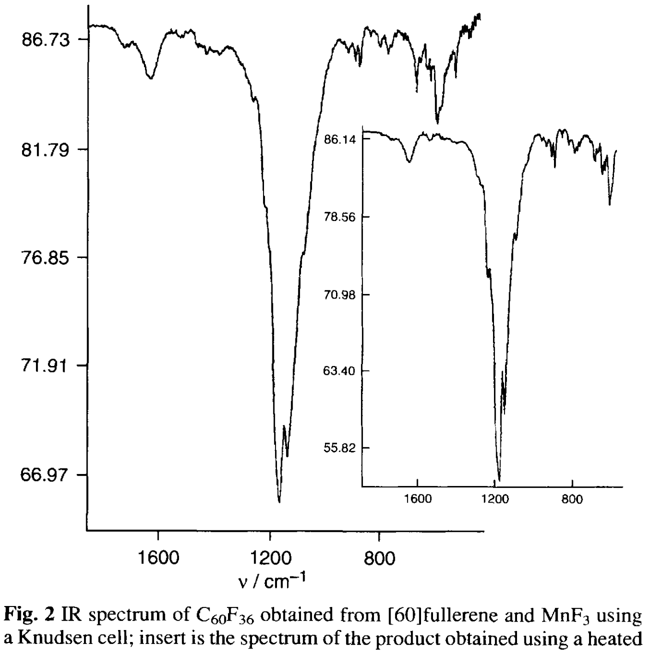

Fig. 2 IR spectrum of $C_{60}F_{36}$ obtained from [60]fullerene and MnF_3 using a Knudsen cell; insert is the spectrum of the product obtained using a heated tube

tube material show a very slight shift to higher wave numbers of the 1164 and 1133 cm^{-1} bands, consistent with the presence of a small amount of the oxide.

The structure of $C_{60}H_{36}$ was considered originally to contain all-isolated double bonds,[7] but subsequently a tetrahedral (*T* symmetry) aromatic structure was proposed,[8] and predicted by calculations to be the most stable.[9,10] A resolved ^1H NMR spectrum of $C_{60}H_{36}$ could not be obtained because of its extremely rapid reaction with oxygen; the same was true of $C_{70}H_{36/38/40}$.[4] The ^{19}F NMR spectrum of $C_{60}F_{36}$ (338.87 MHz, Bruker AM360, $CFCl_3$ reference, 295 K, Fig. 3) is therefore especially interesting. Although it is complicated by peak coincidences (which will require higher field for complete resolution) the main features, deduced by 2D(COSY) analysis, are: (*a*) There are four sets of coupled major peaks, *viz.* A, δ 130.1, 144.45, 154.25 (1 : 1 : 1); B, δ 139.35, 143.7, 144.0, 153.35 (1 : 1 : 1 : 1); C, δ 138.6, 140.9, 141.8, 165.9 (*ca.* 1 : 1 : 1 : 1 ratio); D, δ 140.9, 148.6 (*ca.* 1 : 2). The proportions of these isomers are *ca.* 30, 30, 30 and 10%, respectively. We concluded that $C_{60}F_{36}$ consists of a mixture of up to four isomers; set A corresponds to the *T* isomer (but could in principle also be either of isomers 2, 3, 6 or 8 given in ref. 9).[11] Set D corresponds to the T_h isomer, but the structures of isomers B and C are presently unclear. (*b*) Of the minor components, each peak of one set (E) is upfield of those of set A by an almost constant amount of 0.7 ppm and could be due to one of the isomers 2, 3, 6 or 8 noted above. Three other sets have approximate ratios of 1 : 1 : 1 : 1, and another a ratio of 2 : 1 : 1 but show intensity variations between spectra indicating that they are due to minor impurities. There are also three sets of coupled doublets (5% of the total material), due possibly to $C_{60}F_4$ isomers.

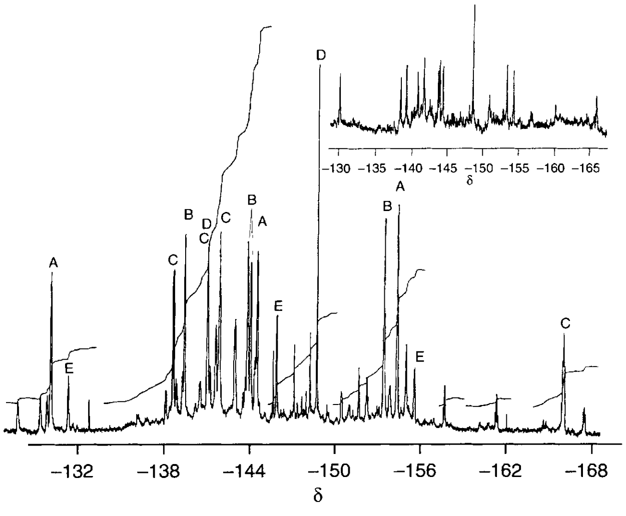

Fig. 3 ^{19}F NMR spectrum of $C_{60}F_{36}$; inset is the spectrum of the white material obtained after resublimation (see text)

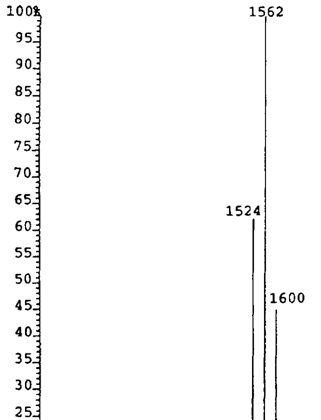

Fig. 4 Mass spectrum of the product from reaction of [70]fullerene with MnF_3

The sample of $C_{60}F_{36}$ was resublimed, giving a white material (more volatile) and a lemon one (less volatile). The mass- and IR-spectra of the former confirmed it as $C_{60}F_{36}$; the ^{19}F NMR spectrum (inset to Fig. 3) now contains only the peaks A, B, C and D. By contrast in the spectrum for the lemon material, the peaks for the minor components are now much more intense.

Fluorination of [70]fullerene was carried out by the heated tube method, higher temperature (390 °C) being employed. The mass spectrum (Fig. 4) is typical of that from many runs, with main peaks at 1524, 1562 and 1600 amu and shows the product to consist of $C_{70}F_{36/38/40}$, with $C_{70}F_{38}$ as the major component, which parallels the behaviour in hydrogenation.[4] The IR spectrum is broader than that for $C_{60}F_{36}$ (more components present), and has major bands at 1137 and 1163 cm^{-1} with shoulders at 1085 and 1212 cm^{-1}. The ^{19}F NMR spectrum consist of many lines, the resolution of which will be attempted subsequently.

Both mass spectra show a prominent peak due to CF_3 loss, *e.g.* at 1335 and 1493 amu (Figs. 1 and 4); the fragmentation pattern analysis will be described subsequently.

Preliminary experiments using CoF_3 gave comparable results, though it appears to be a more powerful fluorinating reagent; by contrast FeF_3 is less potent.

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