Fluorination of Buckminsterfullerene

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Fluorination of solid C_{60} with fluorine gas proceeds in a stepwise manner to give, after twelve days (10 mg scale), a colourless derivative indicated by a single line ^{19}F NMR spectrum to be $C_{60}F_{60}$; reaction time is quantity dependent.

Ever since spectroscopic evidence for the existence of C_{60} was obtained[1] there has been speculation as to the possible lubricant properties of the fully fluorinated derivative. We now report preliminary results on C_{60} fluorination.

Pure C_{60}, prepared by the arc-discharge[2,3] and purification procedure,[4] was freed from traces of solvent by heating at 170 °C (3 mmHg) during 2 h. Initial fluorination with XeF_2 in dichloromethane (C_{60} is insufficiently soluble in more suitable fluorocarbon solvents), produced after 2 h a deep-yellow material which was readily soluble in acetone and chloroform. This was highly polar and could not be eluted on either alumina (anhydrous), silica or cellulose, and gave an intense broad C–F stretching band centred at 1126 cm^{-1} (shoulder at 1250 cm^{-1}) and C–H stretching bands. The ^{19}F NMR spectrum showed a very broad band centred at δ −140 and together with the IR data indicated that a mixture of partially fluorinated derivatives had been produced with solvent involvement probable.

Subsequent fluorinations were carried out with fluorine gas using *ca.* 10 mg batches of solid C_{60}, and reaction for varying lengths of time at 70 °C. There initially was no evidence for reaction other than an increase in volume, then, after 3–4 days the material turned dark brown quite quickly. This colour was in turn retained for a further 3–4 days before turning pale brown during a short period. After further fluorination this material very slowly became almost white. We interpret these

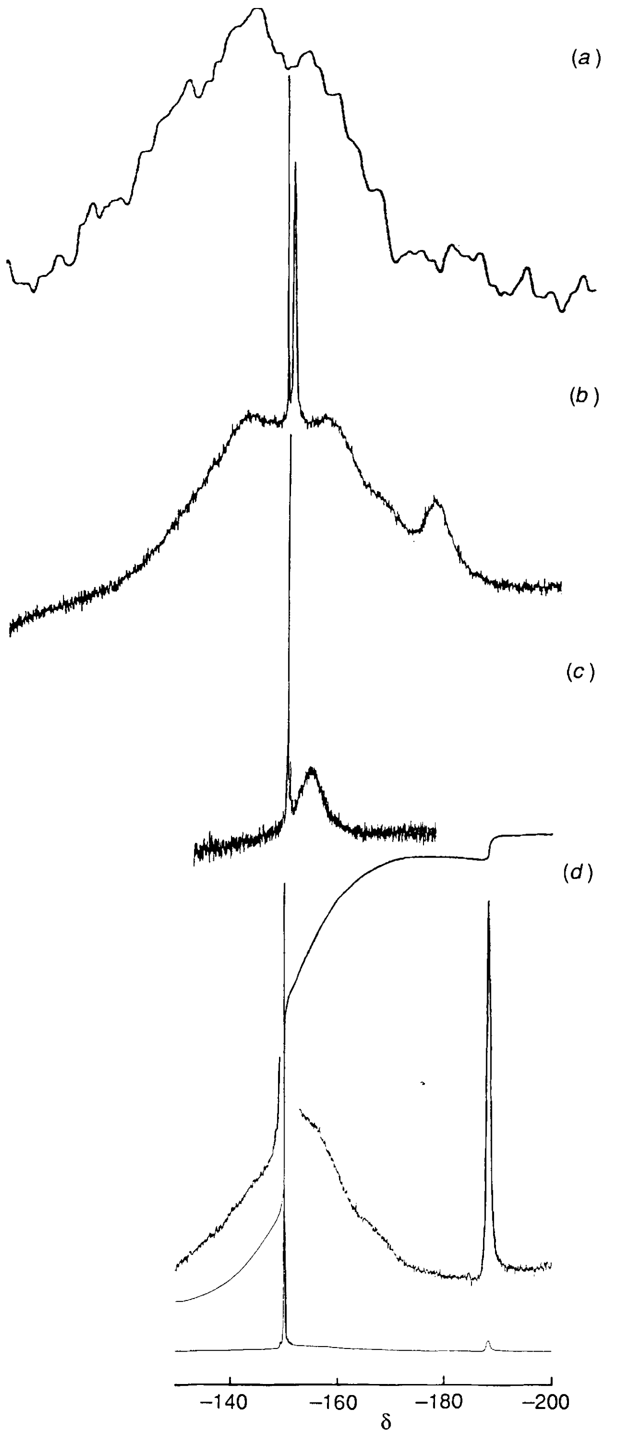

Fig. 1 ^{19}F NMR spectra of C_{60} after fluorination for *ca.* 4, 8, 10 and 12 days (*a–d*), respectively

results in terms of stepwise addition of fluorine molecules, the two brown materials consisting largely of partially fluorinated derivatives that are particularly stable; mass spectrometric results (below) support this view.

The material from each fluorination was removed from the reaction vessel with acetone [in some cases a THF (tetrahydrofuran) pre-wash removed small amounts of yellow by-products]. The extracted material contained some fluorosilicate material from fluorination of the reaction vessel, and this was separated by filtration through a 3 mm square of tissue (using a Pasteur pipette) to give clear solutions. The results of these fluorinations are as follows.

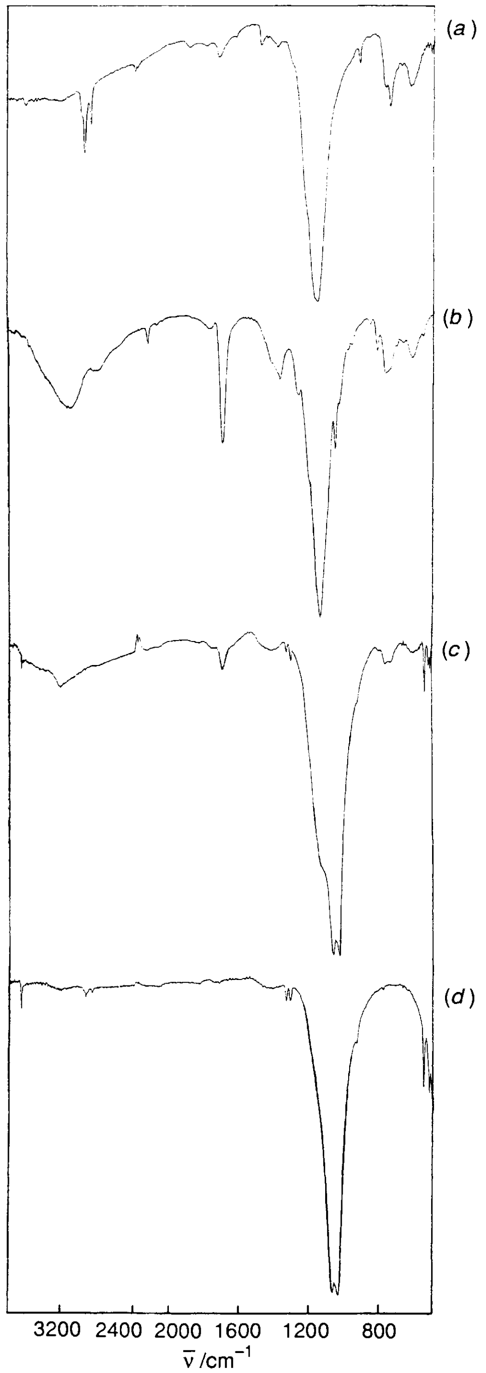

Fig. 2 IR spectra (*a–d*) corresponding to the samples in Fig. 1

The ^{19}F NMR spectra of the unprocessed product from each fluorination are shown in Figs. 1(*a*)–(*d*), which represent increasing reaction time; along this series the products were paler in colour. Each spectrum shows a broad background, which diminishes in intensity the greater the reaction time owing, we believe, to variation in the number of non-equivalent fluorines in partially fluorinated material. Each of the products from longer fluorinations [Figs. 1(*b*)–(*d*)] show a singlet peak at either *ca.* δ −150.5, −152.7, or both. We believe that one, and possibly both, of these peaks is due to $C_{60}F_{60}$ since the singlets require that all the fluorines are equivalent; this is further discussed below. In 1-fluorobicyclo[2,2,2]octane the ^{19}F NMR peak appears at δ −148,[5] and the environment of the fluorines is similar to that expected for $C_{60}F_{60}$; adjacent fluorines in $C_{60}F_{60}$ would produce a downfield shift.

The IR spectra of samples deposited from acetone solution onto a KBr plate and corresponding to those above, are given in Figs. 2(*a*)–(*d*). All show a very strong C–F stretching band, and a pattern is evident. With increasing fluorination, the broad band at *ca.* 1148 $\mathrm{cm^{-1}}$ (which we attribute to a mixture of partially fluorinated material) diminishes, whilst the sharp bands at 1060 and 1035 $\mathrm{cm^{-1}}$ (ascribed to the fully fluorinated material) intensify. The pale-brown material from incomplete fluorination is very polar, is soluble in diethyl ether, acetone and chloroform, and the IR spectra of samples containing this material consistently show additional bands at 1698 (C=C?), *ca.* 1375, 910, 767sh, 742, and 620 $\mathrm{cm^{-1}}$ [the OH band in Fig. 2(*b*) is due to moisture contamination].

Further confirmation that the IR band at 1148 $\mathrm{cm^{-1}}$ is associated with material that is more soluble, was provided by deposition of a drop of acetone solution of the crude material onto a KBr plate. Evaporation occurs mainly at the expanding edge of the drop, the more soluble material being deposited last. The 1148/1060, 1035 $\mathrm{cm^{-1}}$ band ratio was greatest in the edge material and lowest in the centre. It was subsequently found that the two components can be cleanly separated with chloroform, which dissolves exclusively the 1148 $\mathrm{cm^{-1}}$ material.

Material giving the NMR singlet at δ −150.5 (+/− 0.15 ppm depending upon the sample studied) was not clearly crystalline, and melted at >315 °C. However, from a slowly evaporating acetone solution in a 5 dram vial, colourless plates were deposited on the sides of the vessel. These melted sharply at 287 °C, were soluble in THF and especially so in acetone, but were insoluble in chloroform. They gave a sharp singlet at δ −153.9 in the ^{19}F NMR spectrum (Fig. 3; adjacent peaks are spinning side bands). This peak occurred in a number of other spectra of partly processed material, and appeared downfield (by up to 2.2 ppm) the less pure the sample.

The IR spectrum of the crystalline material is shown in Fig. 4, and is evidently very similar to Fig. 1(*d*), which is of the material giving the NMR peak at δ −150.5. The two main bands appear at 1067 and 1027 $\mathrm{cm^{-1}}$; the less pure the sample, the smaller the separation between them, and the closer they are in peak height. Bands occur consistently at 1337, 1312 and 550 $\mathrm{cm^{-1}}$, and variously at 466, 461 and 451 and 446 $\mathrm{cm^{-1}}$.

The NMR spectrum Fig. 1(*d*) (and also the THF pre-wash of other samples) shows a small peak at *ca.* δ −188.5 indicative of the presence of HF.[6] The batch giving rise to the spectrum in Fig. 1(*d*) spontaneously turned dark brown during NMR analysis; the main peak was unaffected. The THF pre-wash material on heating also suddenly turned dark brown and solidified, due possibly to an HF-catalysed polymerisation of a by-product.

Mass spectrometric analysis was attempted using EI (electron impact) conditions (positive ionisation), and various FAB (fast-atom bombardment) matrices with both positive and negative ionisation. Only the latter (mNBA *m*-nitrobenzylamine) produced a signal, and then only for the partially fluorinated residue from which crystalline material as described above had been removed. The spectrum showed a continuum of mass numbers attributable to partially fluorinated material and fragments, with masses peaking at *ca.* 834 and 1518, corresponding to $\mathrm{C_{60}F_6}$ and $\mathrm{C_{60}F_{42}}$, respectively. Masses greater than $\mathrm{C_{60}F_{60}}$ observed could correspond to association of fragments (which can occur under FAB conditions). In one sample, intense peaks at m/z = 513 and 619 suggested some fragmentation of the fullerene cage.

Incomplete combustion occurred on attempted microanalysis (carbon content *ca.* 5, and 12% in the presence of a catalyst), understandable in view of the $\mathrm{C_{60}F_{60}}$ structure.

Our provisional interpretation of these results is that fluorination is initially slow owing to the high stability of the fullerene cage, but once the first fluorine molecule has been added, the two other bonds in a given benzenoid ring will fluorinate more rapidly to give $\mathrm{C_{60}F_6}$; this may be the dark-brown material that is formed after an induction period. (Methylation of $\mathrm{C_{60}}$ produces predominantly the hexamethyl derivative.[7]) If $\mathrm{C_{60}F_6}$ is relatively stable then the further induction period can be accounted for, following which fluorination proceeds rapidly to give a second derivative of enhanced stability, possibly $\mathrm{C_{60}F_{42}}$; this would correspond to the light-brown material. Various structures for this can be proposed *e.g.* all positions fluorinated except a triphenylene-like cap, feasible if fluorination 'spreads' through $\mathrm{C_{60}}$. Another isomer would have the equatorial ring (hexagonal pole) of carbons unfluorinated, though this would place double bonds in the five-membered rings, which is unfavourable.[8]

Further slow fluorination (steric hindrance becomes increasingly severe) then gives the colourless fully fluorinated derivative characterised by the single peak ^{19}F NMR spectrum, at δ −150.5. This derivative may be associated with hydrogen fluoride (arising from the reaction of fluorine with adventitious water), which is lost on slow crystallisation of the material from acetone, with a consequent upfield shift of the

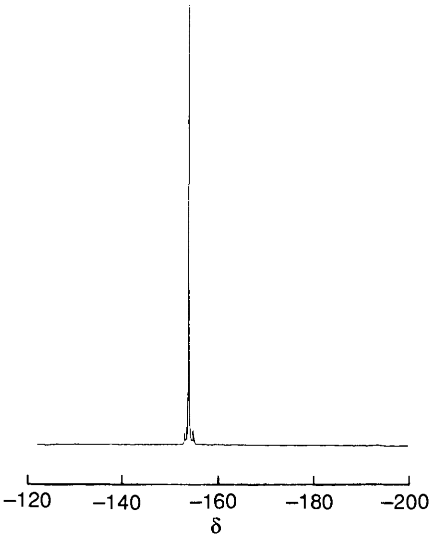

Fig. 3 ^{19}F NMR spectrum of colourless crystalline material, m.p. 287 °C extracted from 12 day fluorination sample

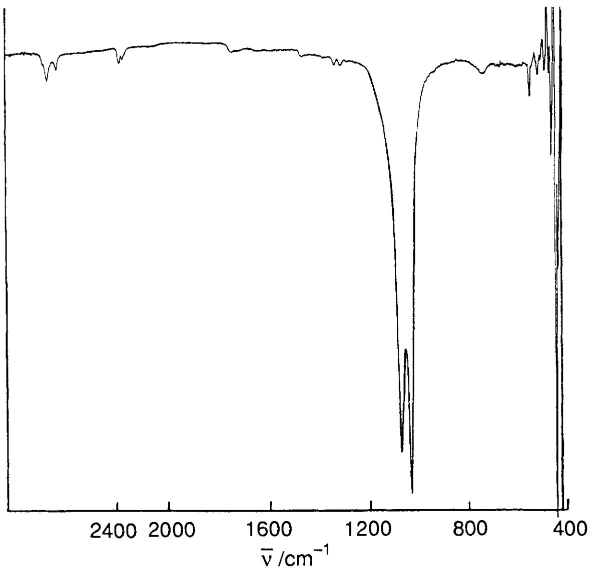

Fig. 4 IR spectrum of the material giving Fig. 3

spectrum; significantly, etching of the vials containing the evaporating acetone solution is observed. The extent to which HF is lost could then account for the variability of the position of the singlet for this 'derivative'. Hydrogen fluoride may be produced either from adventitious water during the fluorination process or, more probably, from the reaction of occluded fluorine with water present in the work-up acetone. It is significant that in two samples (one pre-washed with THF, the other with chloroform), the NMR singlet appeared at *ca.* δ -153, with 6% or less of the δ -150.5 peak present. An alternative explanation of the interconversion of these two singlets arises from the fact that two $C_{60}F_{60}$ isomers are possible, having I_h and I symmetry, the latter (which is chiral) being expected to be the more stable.[9]

A number of partially fluorinated derivatives with fluorines in identical environments [*e.g.* $C_{60}F_6$, $C_{60}F_{12}$, $C_{60}F_{18}$ and $C_{60}F_{20}$ (fluorines equatorial), $C_{60}F_{24}$ (fluorines in benzenoid rings at the apices of a tetrahedron)] may account for the other small singlets that appeared in the ^{19}F NMR spectra of two samples. One singlet was 0.41 ppm upfield of the peak at δ -150.5 [see Fig. 2(*c*)], and the other was 0.06 ppm downfield of the peak at δ -153.9.

The fluorinated product caused aldol-type condensation of the deuteriated acetone, used to obtain the ^{19}F NMR spectra. This was not brought about by the fluorosilicate by-product; catalysis by HF traces is probably responsible.

Lastly, we note that colourless crystalline material is discernible in a chloroform solution of partially fluorinated C_{60}. We believe that colour is lost before fluorination of C_{60} is complete.

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