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$C_{60}F_2$ exists!

Olga V. Boltalina,[a] Andrei Yu. Lukonin,[a] Joan M. Street[b] and Roger Taylor[c]*

[a] *Chemistry Department, Moscow State University, Moscow 119899, Russia*
[b] *Chemistry Department, The University, Southampton, UK SO17 1BJ*
[c] *The Chemistry Laboratory, CPES School, University of Sussex, Brighton, UK BN1 9QJ.*
E-mail: R.Taylor@sussex.ac.uk

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From the fluorination of [60]fullerene with K_2PtF_6 at 470 °C under *ca.* 0.01 bar we have isolated (HPLC) 1,2-F_2C_{60}, the structure of which is confirmed by ^{13}C NMR and a single ^{19}F NMR line at -148.3 ppm.

As synthons, halogenofullerenes containing very few halogen atoms are desirable, but thus far they have been unattainable. Both chlorination and bromination involve a radical cascade process which necessitates, for steric reasons, contiguous *para* (1,4) halogenation. This is terminated by *ortho* (1,2) halogenation only as a necessity for the formation of a non-radical product such as $C_{60}X_6$ (X = Br, Cl)[1,2] or $C_{70}Cl_{10}$.[3] The adjacency of the bulky halogens creates instability, and these are preferentially lost for example either in subsequent reactions[4,5] or through rearrangement *e.g.* the conversion of $C_{60}Br_6$ to $C_{60}Br_8$ on standing.[1] In $C_{60}Br_8$ (and also in $C_{60}Br_{24}$)[6] all of the bromines are in either a 1,4- or a 1,3-relationship. Thus no 1,2-dibromo- or 1,2-dichlorofullerene has been either isolated or inferred from subsequent substitutions.

By contrast, the lack of steric hindrance in fluorination permits 1,2-addition which results in contiguous activation of adjacent double bonds (through increased bond localisation). The ensuing halogenation cascade tends to cease only when a product is obtained of enhanced aromaticity (such as $C_{60}F_{18}$ or $C_{60}F_{36}$)[7,8] *i.e.* containing delocalised benzenoid rings.

Characterisation of bromo- and chlorofullerenes is rendered difficult by their instability towards mass spectrometry, which becomes greater the fewer halogens that are present; so far, only a FAB spectrum of $C_{60}Cl_{24}$ has been obtained.[9] Fluorofullerenes are more stable towards mass spectrometry and the existence of $C_{60}F_n$ (n = 18, 36 or 48)[8–10] shows that fluorines can be attached to adjacent carbon atoms without introducing undue strain. Nevertheless, as with the other halogenofullerenes noted above, *the stability decreases the fewer the number of attached fluorines*, seen for example by the appearance of lower fluorinated species (through fragmentation) in the EI mass spectrum of $C_{60}F_{18}$.[8] In fluorination by fluorine gas, the EI mass spectrum showed a continuous spectrum of derivatives from $C_{60}F_2$ up to *ca.* $C_{60}F_{42}$ (and numerous oxygenated derivatives).[11–13] However, it was unclear if the lower fluorinated species were compounds or merely fragmentation ions.

We now report the successful isolation and characterisation of $C_{60}F_2$.

[60]Fullerene (240 mg) was fluorinated with K_2PtF_6 (575 mg) and a toluene solution of the product (280 mg after prepurification by sublimation) was filtered with precautions to minimise interaction with atmospheric moisture, all as described previously.[14] HPLC separation of the product was carried out using a 10 mm × 250 mm Cosmosil Buckyprep column with elution by toluene at 4.7 ml min^{-1}. This yielded mainly $C_{60}F_{18}$[8] (elution time 37 min) together with a large number of other components, most of which are ethers. A fraction (*ca.* 1.5 mg) which eluted at 10.5 min (*cf.* 7 min for [60]fullerene) was shown by the mass spectrum (Fig. 1) to contain $C_{60}F_2$ (758 amu). The spectrum also gave peaks at 858 [$C_{60}(CF_3)_2$], 840 ($C_{60}C_2F_5H$), and 790 amu ($C_{60}CF_3H$). [Formation of CF_3 radicals by fragmentation is well-known to accompany fluorination of [60]fullerene,[13,15] and is especially marked when using K_2PtF_6; the radicals then attack other [60]fullerene molecules.] The mass spectrum is however very misleading (as the ^{13}C and ^{19}F spectra show) because it *greatly* underestimates the concentration of $C_{60}F_2$ in the sample due to fragmentation (as described above), and which is severe at this fluorination level. This is shown (Fig. 1) by the peak at 720 amu being 960 × the intensity of the 758 amu peak, *yet no [60]fullerene was present in the sample*. The same effect was evident in the spectra of $C_{60}F_nO$, (n = 8,6,4) which due to increasing fragmentation with lower addend level, showed increased amount of [60]fullerene relative to the parent ion, along this series.[14]

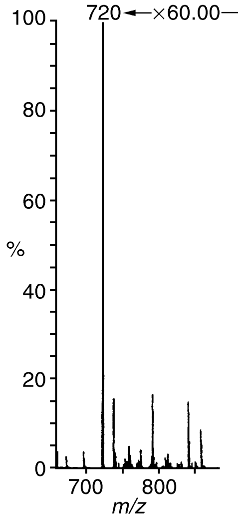

Fig. 1 EI mass spectrum (70 eV) for $C_{60}F_2$.

The IR spectrum (KBr, Fig. 2) shows two sharp peaks at 1070 and 1035 cm^{-1} in the C–F stretching region, and also sharp bands at 770, 724, 648, 594, 527 and 500 cm^{-1}. The very simple spectrum is consistent with a highly symmetrical structure, and the strong band at 527 cm^{-1} is characteristic of unaddended [60]fullerene,[16] which the present structure closely resembles.

The ^{19}F NMR spectrum (Fig. 3, 338.9 MHz, $CDCl_3$) showed a singlet at -148.3 ppm together with two very small peaks at -67.9 and -69.7 ppm, which are typical of CF_3-containing [60]fullerenes. The peak area intensities indicate that these derivatives constitute *ca.* 6% of the total fluorinated fullerene present, which further emphasises the misleading nature of the EI mass spectrum (see above).

This singlet thus falls in the range obtained for fluorinated [60]fullerenes, *e.g.* $-(132–158)$ for $C_{60}F_{18}$ and $-(130–166)$ ppm for $C_{60}F_{36}$. 1,2-Isomers of [60]fullerene are more stable than 1,4-isomers, since the latter contain a destabilising double bond in a pentagon and are obtained only when the addend is large. Thus due to the difference in addend size, methylation gives a mixture of 1,2- and 1,4-dimethyl derivatives, whereas benzylation gives 1,4-addition.[17] Since fluorine is smaller than

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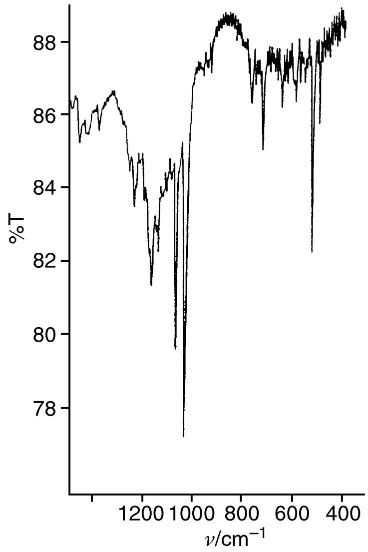

Fig. 2 IR spectrum (KBr) for $C_{60}F_2$.

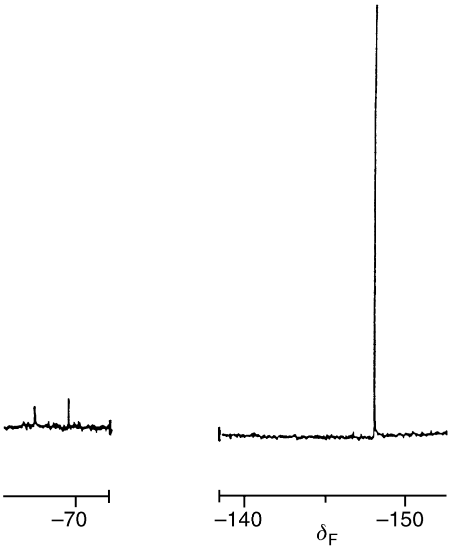

Fig. 3 ^{19}F NMR spectrum (338.9 MHz) for $C_{60}F_2$.

carbon, there is no advantage, either thermodynamic or kinetic, in forming the 1,4-isomer.

The location of the ^{19}F NMR peak is also consistent with a 1,2- rather than the 1,4-isomer. In the latter, each sp^3-hybridised carbon bearing the fluorine is surrounded by *three* sp^2-hybridised carbons (which are more electron withdrawing than sp^3), whereas there are only *two* in the 1,2-isomer. This differential effect is clearly seen in the $C_{60}F_{18}$ peak positions which are -132, -140 (av.) and -158 ppm for C–F bonds having 2, 1, and 0 sp^2 neighbours,[9] or in T $C_{60}F_{36}$ where they are -138 (av.) and -155 ppm for C–F bonds having 1 and 0 sp^2 neighbours.[18] Thus for the 1,4-isomer the peak would be expected to appear more downfield, the above data suggesting a value of $-(120–130)$ ppm.

Final proof that we have isolated the 1,2-isomer comes from the ^{13}C NMR spectrum (Fig. 4). Obtaining such spectra for F-containing compounds requires F-decoupling which is unavailable, nevertheless for $C_{60}F_{18}$ we obtained a spectrum showing singlets for γ-carbons (and those more remote) relative to the (F)C$_\alpha$ carbons. Whereas 1,4-F_2C_{60} (C_s symmetry) requires in the sp^2 region (29–3) = (26 $\times$ 2 C lines, 1,2-F_2C_{60} (C_{2v} symmetry) requires 3×2 C and $(13 - 1) = 12 \times 4$ C lines. Our spectrum (which required 90 h acquisition time) shows 12×2 C lines at 146.54, 146.50, 146.24, 145.08, 145.01, 144.54 (two coincident), 142.53, 142.23, 142.14, 141.62, 139.32, 137.85. Lines of 2 C intensity appeared at 141.16 and 138.35. Other lower intensity lines at δ_C 144.23, 143.79, 143.36, 141.29 and 141.20 were barely above background and may not be real. The compound is thus fully confirmed as the 1,2-isomer. No peak is seen in the sp^3 region due to coupling with fluorine.

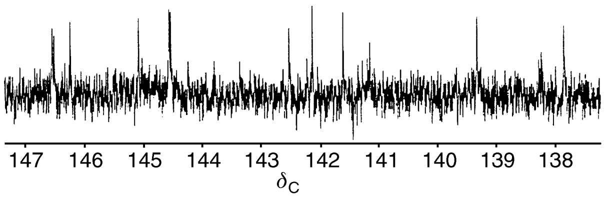

Fig. 4 ^{13}C NMR spectrum for $C_{60}F_2$.

In early work with F_2-fluorinated [60]fullerene, treatment of the crude product with either acetone or THF gave a product showing a single ^{19}F NMR line at *ca.* -150.5 ppm, and two sharp IR bands at 1067 and 1035 cm^{-1}; a single line NMR was also obtained by treatment of $C_{60}F_{48}$ with diethyl ether.[10] We conjectured that this line could be due to $C_{60}F_{60}$,[11] but later work showed this to be unlikely.[19] Since both the NMR line and especially the IR peaks for $C_{60}F_2$ are remarkably similar to those described above, $C_{60}F_2$ could conceivably be the species responsible in the earlier work. However, the availability now of a defined HPLC retention time for $C_{60}F_2$ means that repetition of the earlier work and separation of the products may provide an answer. We plan to undertake this work.

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