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Isolation and spectroscopic characterisation of $C_{60}F_{18}CF_2$, the first difluoromethano[60]fullerene

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

[a] *The Chemistry Laboratory, CPES School, University of Sussex, Brighton, UK BN1 9QJ*
[b] *Chemistry Department, Moscow State University, Moscow 119899, Russia*
[c] *Chemistry Department, The University, Southampton, UK SO17 1BJ*

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From the fluorination of [60]fullerene by K_2PtF_6 at 465 °C under 0.1 bar, we have isolated and characterised $C_{60}F_{18}CF_2$ which has C_s symmetry and is isostructural with $C_{60}F_{18}O$; it co-elutes (HPLC) with a minor unsymmetrical isomer.

Numerous methano[60]fullerenes $C_{60}CR^1R^2$ have been prepared by methods which include the addition of carbenes or their diazo precursors, of α-halocarbanions, and the use of ylides.[1] 1′,1′-Dihalofullerenes $C_{60}CX_2$, have been formed either by pyrolysis of sodium chloroacetate in the presence of the fullerene ($X_2 = Cl_2$),[2] by generating a dihalocarbene from the haloform in the presence of a base ($X_2 = Br_2$, BrCl, I_2),[3] or by reacting the fullerene with $PhHgCBr_3$, $X_2 = CBr_2$.[4] However, no compounds with $X_2 = F_2$ are known, but mass spectrometry of fluorofullerenes has indicated that the CF_2 moiety may either be present in some mixtures of compounds, or is produced by fragmentation.[5] In a report describing HPLC purification of $C_{60}F_{18}O$, a component of 1112 amu (corresponding to $C_{60}F_{18}CF_2$) was detected in one fraction of the eluent.[6] We have now succeeded in isolating this component and characterising it fully.

[60]Fullerene (240 mg) was ground in a dry box with K_2PtF_6 (575 mg) and heated to 465 °C at *ca.* 0.01 bar in a glass tube contained within a furnace, as described previously.[6] The crude fluorofullerene mixture (300 mg, 85%) was partly prepurified by vacuum sublimation and a sample (*ca.* 280 mg) was dissolved in dry toluene (25 ml) and filtered under conditions which avoided moisture condensation. Purification by HPLC (10 × 250 mm Cosmosil Buckyprep column) with toluene elution at a flow rate of 4.7 ml min^{-1} (≡ 1 ml min^{-1} for a 4.6 mm diameter column), yielded recovered [60]fullerene (*ca.* 75 mg), $C_{60}F_{18}$[5] (*ca.* 100 mg) together with twenty other components in 1–5 mg yields, including $C_{60}F_{18}O$, described previously.[7]

The mass spectrum of the fraction (*ca.* 3 mg) eluting at 31 min (Fig. 1) shows the parent ion at 1112 amu ($C_{60}F_{18}CF_2$), with very prominent fragmentation by initial CF_3 loss. [This compound therefore elutes more rapidly than $C_{60}F_{18}$ and $C_{60}F_{18}O$ (36.5 and 45 min, respectively).] We have found such fragmentation (but on a lesser scale) to be a feature of EI mass spectrometry of fluorofullerenes (the mechanism being unclear), but here it is evidently enhanced by the presence of the CF_2 group. Moreover, the intensity of the 720 amu peak is much greater than is customary for fluorofullerenes and further indicates that the CF_2 group accelerates the fragmentation process. The presence of 18 fluorines shows that the compound is a derivative of the known $C_{60}F_{18}$.

The origin of the CF_2 group is indicated by the detection of numerous by-products containing both H and CF_3 species in the above fluorination. CF_3 radicals are produced by fragmentation of some of the cages as noted above, and these then attack other cages followed by the usual adventitious acquisition of hydrogen. The mass spectra of some (but not all) of the $C_{60}(H,CF_3)_n$ derivatives show loss of 20 amu (HF), which arises evidently when the H and CF_3 groups are adjacent, thereby producing the CF_2 group.

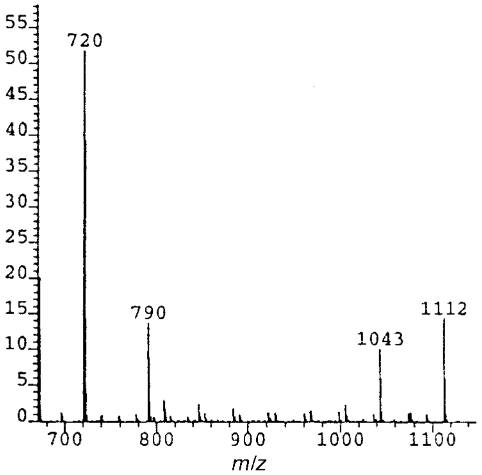


Fig. 1 EI mass spectrum (70 eV) for $C_{60}F_{18}CF_2$.

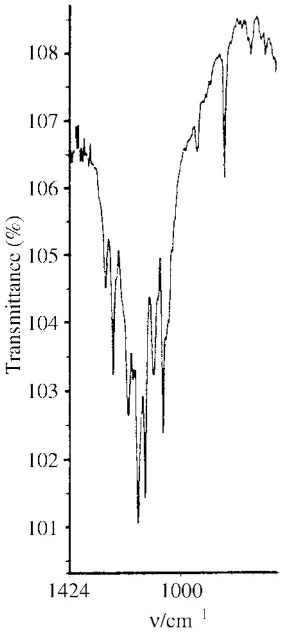


Fig. 2 IR spectrum (KBr) for $C_{60}F_{18}CF_2$.

The IR spectrum (bands at 1200, 1195, 1160, 1133, 1106, 1100 and 830 cm^{-1}, Fig. 2) shows the same fine structure characteristics of $C_{60}F_{18}$ and $C_{60}F_{18}O$ (*cf.* refs. 5, 6). However, there are additional bands at 1282 and 1254 cm^{-1} characteristic of aliphatic C–F bonds.

The ^{19}F NMR spectrum (Fig. 3, 376.4 MHz) consists of eleven peaks (some coincident) at δ_F −130.7 (2 F, d, 17.6 Hz),

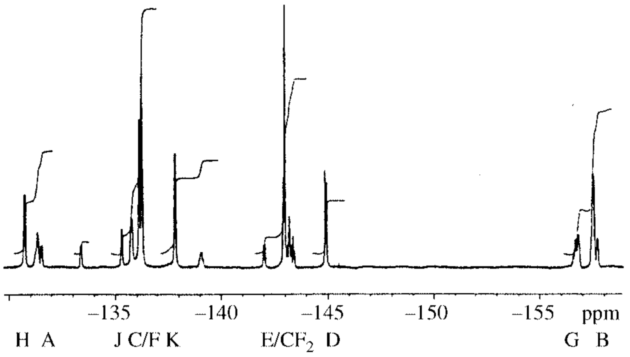


Fig. 3 ^{19}F NMR spectrum (376.4 MHz) for $C_{60}F_{18}CF_2$.

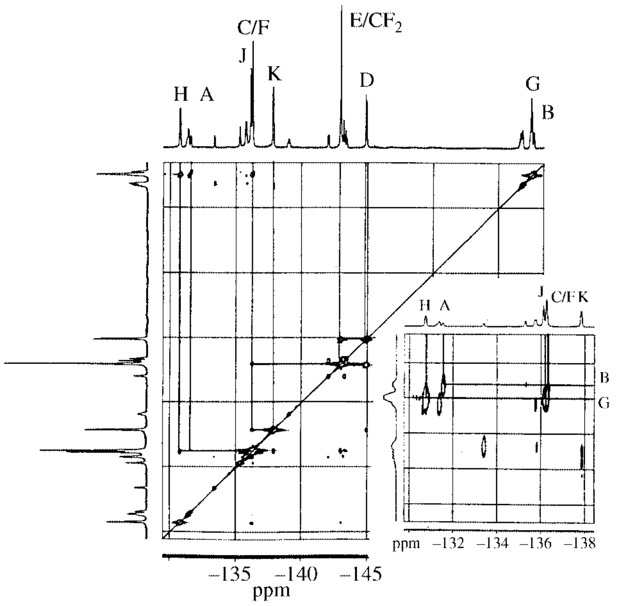
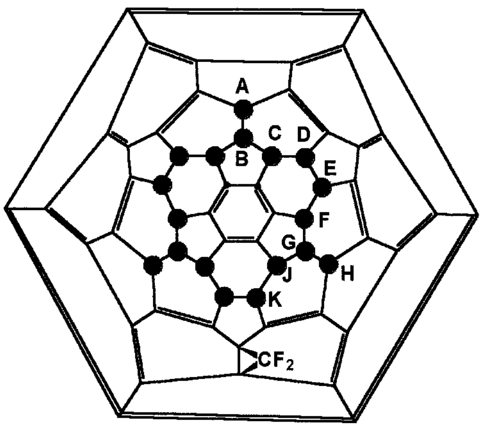


Fig. 4 2D ^{19}F NMR spectrum for $C_{60}F_{18}CF_2$ [inset shows expansion of the −130 to −138 ppm region].

−131.53 (1 F, d, 15.5 Hz), −136.11 and −136.25 (overlapping multiplets, 6 F), −137.82 (2 F, d, 17.8 Hz; additional minor peaks lie underneath here causing the integral to be approximately 25% too large—see below), −142.91 (2 F, m), −142.98 (4 F, m), −144.89 (2 F, d, 27 Hz), −157.50 (2 F, m) and −157.68 (1 F, m). Some minor peaks are also present and analysis (below) shows the product to consist of a mixture of a C_S isomer and an unsymmetrical one in *ca.* 65:35 ratio; the minor peaks (in approximately the same ratio) were reproduced in a second preparation.

The 2D ^{19}F NMR spectrum (Fig. 4) reveals the structure of the C_S isomer to be **1**; there are only three positions that the CF_2 group can occupy for a symmetrical structure and only one of them can give a singlet for the CF_2 group.



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(i) Previous ^{19}F NMR data for fluorofullerenes have indicated that upfield peaks are due generally to fluorines attached to carbon having three adjacent sp^3-hybridised carbon atoms, whilst downfield peaks are due to fluorines attached to carbons having only one adjacent sp^3-hybridised carbon atom.[7,8] This is due to the greater electronegativity of sp^2 carbons compared to sp^3 carbons.[6] Thus for structure **1**, there should be two upfield fluorines (G) coupled to two downfield fluorines (H), and likewise a single upfield fluorine (B) coupled to a single downfield fluorine (A). This is found (see inset to Fig. 4).

(ii) Fluorines G should be coupled to fluorines F and J, likewise fluorine B should be coupled to fluorines C, which locates these peaks in the spectrum (Fig. 4 inset). Note that fluorines C and F are coincident in the spectrum. Fluorines J are also coupled to fluorines K as required so these are also located. The 2D spectrum confirms that there are peaks underlying K (see above) and these are due to the minor isomer.

(iii) Fluorines D and E are coupled as required by the structure, but the integral for E is twice that for D due to the coincidence of the singlet due to the CF_2 group. The appearance of the latter at −143 ppm is entirely consistent with literature values (−143.2, −142.7, −143.2 ppm) for CF_2 forming part of a three-membered ring.[9] The coupling between fluorines C and F could not be seen; likewise in the 2D ^{19}F NMR spectrum for $C_{60}F_{18}O$ the couplings between fluorines G and either fluorines F and J were not found.

(iv) Fluorines D and E can be distinguished because E is coupled with F.

(vii) Both C and F are nearer to the central benzenoid ring than are D and E, and the resonances appear more downfield, this same pattern being found previously for $C_{60}F_{18}$ and $C_{60}F_{18}O$,[6,8] and may be a general feature for compounds of this type.

The minor isomer

The integrals for the fluorine content of the C_s isomer is 65% of the total observed. Those for the remainder, δ_F −131.2 to −131.4 (3 F, overlapping m), −133.38 (1 F, d), −135.28 (2 F, br s), −135.75 (3 F, br s), −139.1 (2 F, q), −142.05 (1 F, d), −143.19 (2 F, t), −143.36 (1 F, t), 156.5–156.9 (3 F, overlapping m), −157.4 (2 F, m), correspond to the presence of 20 fluorines (taking the smallest integral as 1 F), indicating that an unsymmetrical isomer is also present. Moreover it shows the same characteristics as the major isomer in having coupling between the low- and high-field fluorines, but with a difference in that there are at least four low-field fluorines. There is only one reasonable position for the CF_2 group to add, seen by reference to the labelled framework of **1**, *i.e.*, without the CF_2 group shown. This is to add to the double bond (which has localised electrons) in the ring with the A–D labels (or the five other equivalents). This is energetically less favourable than the addition which produces **1**, but is statistically favoured by a factor of 2:1. Such an addition now causes the carbon bearing fluorine D to be surrounded by three sp^3-hybridised carbons so that there are now four fluorines in such environments, requiring four upfield peaks.

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