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Isolation and characterisation of $C_{60}F_{16}$; a key to understanding fullerene addition patterns

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From the reaction between [60]fullerene and K_2PtF_6 at 465 °C we have isolated C_s symmetric $C_{60}F_{16}$, the structure of which provides fundamental information concerning the manner in which addition takes place to fullerenes.

Introduction

Fullerenes have some aromatic character, hence the double bonds are not fully localised. Addition to one bond therefore increases localisation and thus the π-density of the remaining double bonds of the hexagon in which the first addition occurs.[1] In the absence of steric hindrance further 1,2-addition will be directed into the same hexagon, and continued addition will give rise to 'S' and 'T' addition patterns.[2] Where steric hindrance is greater, as in the case of bromination,[3] chlorination[4] and alkylation[5], 1,4-addition predominates instead in a regular progression around the cage.[6] Steric hindrance also affects cycloaddition, consequently addition at the double bond adjacent to the first addend (*cis*-1 addition) takes place in low yield, if at all.[7]

A second factor resulting also from the partial aromaticity of the cage, is the tendency to form derivatives in which relief of strain (through the presence of sp^3-hybridised carbons adjacent to hexagonal rings) permits increased delocalisation in these 'benzenoid' rings. This shows up not only in the octahedral pattern observed in some cycloadditions,[8] but also in, for example, the formation of T and C_3 isomers of $C_{60}F_{36}$,[9] and, of particular relevance to the present work, of the C_{3v} (crown) isomer of $C_{60}F_{18}$.[10]

For fundamental understanding of the factors governing polyaddition, it is necessary to have a reaction essentially free of steric effects. Both hydrogenation and fluorination meet this requirement, and hydrogenation fits the above conjecture concerning the addition pattern in that the preferred tetrahydrofullerenes have all four hydrogens adjacent. However, the reaction has major disadvantages in the ready oxidation of hydrofullerenes to fullerenols, and the difficulty of dissecting the complex spin–spin coupling patterns. By contrast, fluorination is only encumbered by the low availability of ^{13}C NMR instruments having fluorine-decoupling facilities. However, it is often possible (as is the case here) to solve the structures without recourse to ^{13}C NMR.

As a result of our being able to scale up the fluorination of [60]fullerene using K_2PtF_6, and the availability to us of a larger (10 mm diameter) Cosmosil HPLC column, we have been successful in isolating a number of components that were not evident in the original small-scale preparation of $C_{60}F_{18}$.[10] We now report therefore the isolation and characterisation of $C_{60}F_{16}$, the structure of which throws considerable light on the stepwise nature of the addition pathway in [60]fullerene.

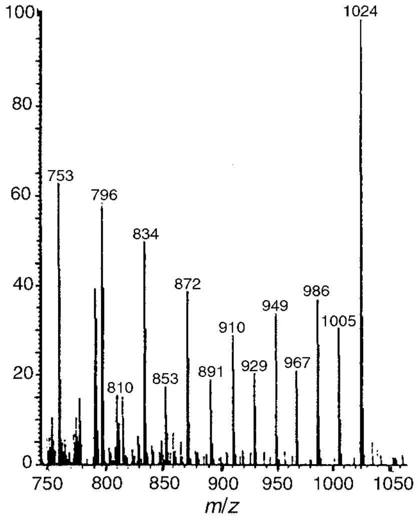

Fig. 1 EI mass spectrum (70 eV) for $C_{60}F_{16}$.

Experimental

[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. The crude fluorofullerene mixture (300 mg, 85%) was partly pre-purified by vacuum sublimation and a sample (*ca.* 280 mg) was dissolved in dry toluene and filtered under conditions which avoided moisture condensation. Purification by HPLC, (10 mm × 250 mm Cosmosil Buckyprep column) with toluene elution at a flow rate of 4.7 ml min^{-1} yielded recovered [60]fullerene (*ca.* 75 mg), $C_{60}F_{18}$[5] (*ca.* 100 mg) together with twenty other components. $C_{60}F_{16}$ (*ca.* 2 mg) eluted after 84 mins and was mixed with some $C_{60}F_{20}O_3$ which was largely solvent-separated by the use of toluene (in which the oxide is more soluble).

Mass spectrum (70 eV, EI)

This (Fig. 1) shows the parent ion at 1024 amu, the fragmentation pattern resembling very strongly that which we obtained

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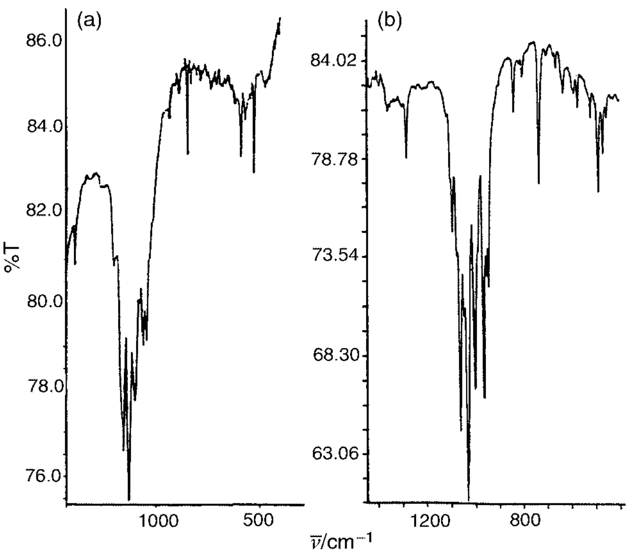

Fig. 2a,b IR spectra (KBr) for $C_{60}F_{16}$ and $C_{60}F_{18}$ respectively.

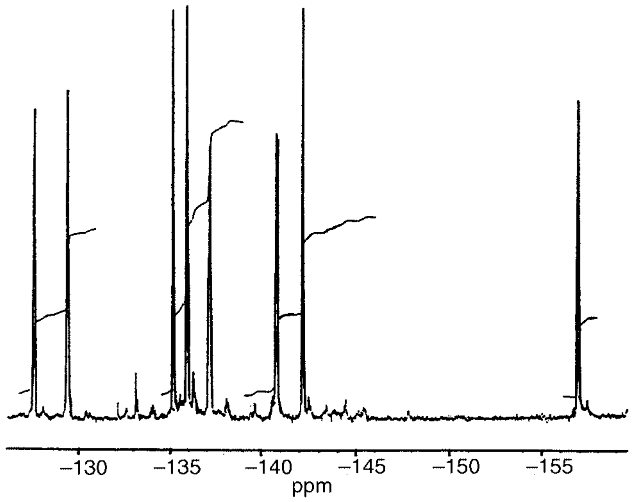

Fig. 3 ^{19}F NMR spectrum (339 MHz) for $C_{60}F_{16}$.

previously for $C_{60}F_{18}$,[8] with high and alternating intensities of the fragmentation ions.

IR (KBr)

The spectrum (Fig. 2a) shows main bands appearing at 1154, 1129, 1101, 1062, 1046, 840, 588 and 528 cm^{-1} and thus shows similarities to that for $C_{60}F_{18}$ which shows bands at 1163, 1133, 1103, 1067, 1045, 833 and 589 cm^{-1} (Fig. 2b), the main difference being the appearance of the band at 528 cm^{-1}.

^{19}F NMR

The 1D spectrum is shown in Fig. 3 and consists of eight lines of equal intensity, which appear at δ_F −127.8 (A), −128.5 (B), −135.2 (C), −136.0 (D), −137.1 (E), −140.8 (F), −142.2 (G) and −157.0 (H), (for notation see Figs. 4 and 5a) compared to −131.6, −136.0, −143.4 and −158.1 in $C_{60}F_{18}$. The 2D spectrum is shown in Fig. 4 and from this the structure can be readily solved as follows:

1. From other work, we have established that fluorine atoms attached to carbons surrounded by three sp^3 carbons (less electron-withdrawing than sp^2 carbons) appear most upfield in ^{19}F spectra. There is a pair of such fluorines (H, Fig. 5a) in the $C_{60}F_{16}$ motif, and the chemical shift (−157.0 ppm) is similar to that (−158.1 ppm) of the corresponding position in $C_{60}F_{18}$.

2. For the same reasons, fluorine atoms attached to one sp^3 carbon together with two sp^2 carbons tend to be the most downfield in the spectrum. There are two pairs of such fluorines (A and B) in the $C_{60}F_{16}$ motif.

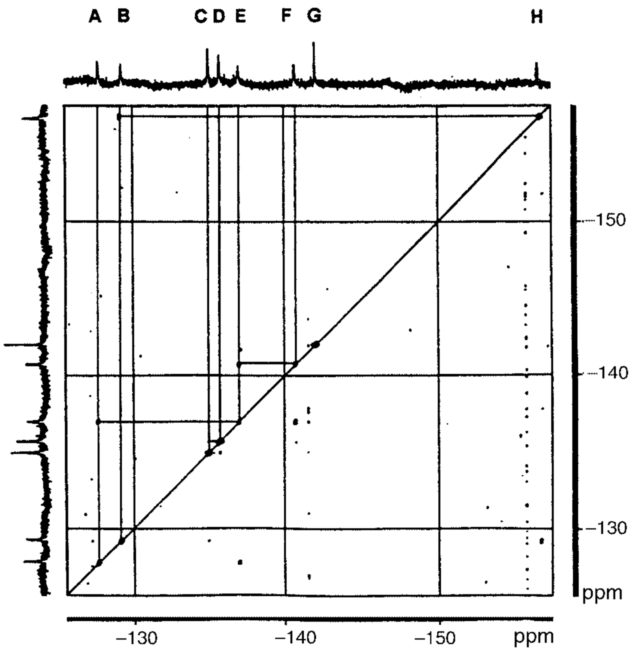

Fig. 4 2D COSY ^{19}F NMR spectrum (376 MHz) for $C_{60}F_{16}$.

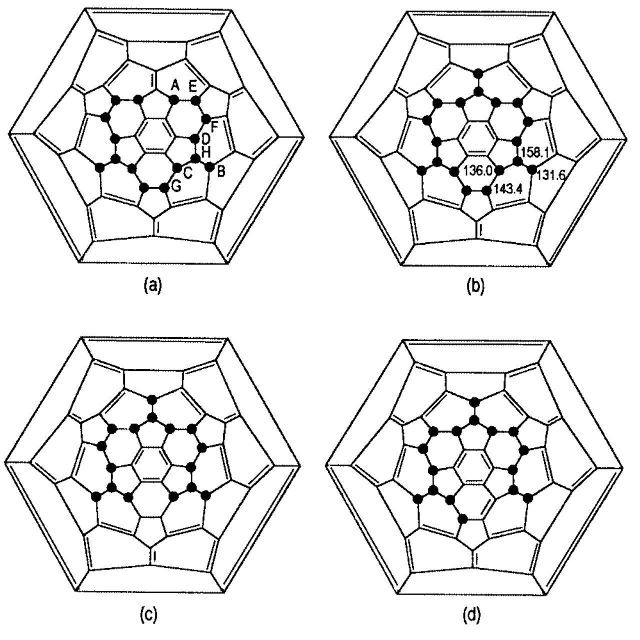

Fig. 5 Schlegel diagrams for (a) $C_{60}F_{16}$, showing peak assignments; (b) $C_{60}F_{18}$, showing chemical shifts; (c) an alternative structure for $C_{60}F_{16}$ which cannot be formed by contiguous addition of 6,6-bonds; (d) an alternative structure for $C_{60}F_{16}$ which can be formed by contiguous addition across 6,6-bonds but does not have a fully aromatic central hexagon.

3. The 2D spectrum shows that B is attached to H and so this distinguishes and defines A and B. The chemical shift of B (−128.5 ppm) is similar to that of the corresponding position (−131.6 ppm) in $C_{60}F_{18}$.

4. A, thus defined, is shown by the 2D spectrum to be coupled to E, which in turn is coupled to F. This places E and F as shown in Fig. 5a.

5. C and D are also coupled (1,3-coupling); their positions shown in Fig. 5a could in principle be reversed, but this does not affect the analysis.

6. G occupies the remaining position. We note that in $C_{60}F_{18}$ (Fig. 5b) of the fluorines attached to hexagons adjacent to the benzenoid ring, those nearer to the ring have a more downfield

chemical shift. Likewise in $C_{60}F_{16}$, C and D appear more downfield than either E, F, or G. The data are therefore all self-consistent.

Discussion

The mechanism of addition

The isolation of $C_{60}F_{16}$ provides important information concerning the mechanism of addition. As described in the introduction, it is our view that in the absence of steric constraints, addition to fullerenes takes place in a stepwise fashion with contiguous activation of double bonds adjacent to the site of initial addition. Thus if addition takes place across any of the 6,6-bonds (which ultimately undergo addition) in $C_{60}F_{18}$ then with eight further pairs of additions it is possible to arrive at the overall structure.

Further contiguous addition of fluorine pairs (beyond the 18F level) will become energetically less favourable because although the aromaticity of the central ring is retained (addition there is very costly in energy), significant eclipsing steric hindrance will start to occur. The free energies of the products resulting from the successive addition of pairs of fluorine atoms will therefore rise to a maximum, falling only when further aromatic rings are created, as in the case of $C_{60}F_{36}$. Thus $C_{60}F_{18}$ and $C_{60}F_{36}$ represent islands of stability. This accounts for the fact that we have seen no evidence for the separate existence of compounds of the structure of *e.g.*, $C_{60}F_n$ ($n = 24, 26, 28$ *etc.*).

The significance of the isolation of $C_{60}F_{16}$ is that it is evidently the precursor for $C_{60}F_{18}$ but like the latter, possesses a complete benzenoid central ring, this being surrounded completely by sp^3-hybridised carbons. Thus it is stable enough to be readily isolable. Moreover:

(i) it can be formed by the step-wise adjacent-pair mechanism enunciated above;

(ii) whereas one other structure (see Fig. 5c), can have a central benzenoid ring, this cannot be formed by the stepwise-pair mechanism (which requires addition across 6,6-bonds);

(iii) whereas one other structure can be formed by the stepwise-pair mechanism (see Fig. 5d) this no longer has a fully benzenoid central ring (one *exo* carbon is sp^2 hybridised), and therefore will be less stable.

Alternative formation process

We have also been able to form $C_{60}F_{16}$ by *loss* of F_2 from $C_{60}F_{18}$. The procedure involves addition of ferric chloride to a solution of $C_{60}F_{18}$ in anisole, and allowing to stand for 3–4 weeks. Work up with HPLC separation produced a product of 1024 amu in the mass spectrum. There was insufficient material for proper characterisation, but we hope eventually to obtain larger samples for this purpose.

Acknowledgements

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