$C_{60}F_{36}$ Consists of two isomers having T and C_3 symmetry

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$C_{60}F_{36}$ has been obtained by fluorination of [60]fullerene with MnF_3 at 350 °C under vacuum. HPLC separation involving elution first with toluene (to separate highly polar $C_{60}F_{18}$which has a much longer retention time, and in one run, $C_{60}F_{20}$ which has a retention time similar to that of $C_{60}F_{18}$), then with toluene–hexane mixtures, and finally hexane, produces two main fractions of $C_{60}F_{36}$, each giving a 1404 amu mass spectrum. The ^{19}F NMR spectrum of the first fraction (which is also the major and more volatile component) consists of 12 lines of equal intensity showing it to have C_3 symmetry. The spectrum of the second fraction consists of three lines of equal intensity, indicating it to be the T isomer, confirmed by ^{13}C NMR spectroscopy which shows two lines of equal intensity in the sp^2 region; the ratio of the two fractions is *ca.* 3 : 1, respectively. Both the T isomer and a low energy C_3 isomer contain the $C_{60}F_{18}$ moiety as a subset. A reason for the failure to observe any of the predicted D_{3d} isomer is conjectured. The mass spectrum of purified $C_{60}F_{36}$ shows the presence of a trace of $C_{60}F_{38}$ (which is more volatile).

The longest unresolved problem in fullerene chemistry is the structure of $C_{60}H_{36}$, the first derivative to be made.[1] Spectroscopic confirmation has not been forthcoming because of the rapidity with which the material oxidises in solution, causing precipitation during spectrum acquisition. Degassing of NMR solvents is of no advantage since the fullerenes readily occlude oxygen in the lattice, and heating to remove the oxygen results in dehydrogenation. The ^1H NMR spectrum thus consists of a broad band with few distinguishing features, consistent also with the presence of more than one isomer.[2] Numerous attempts have been made to predict the structure of $C_{60}H_{36}$ with general agreement that the T isomer is a most likely candidate.[3–5] Indirect spectroscopic studies indicated that $C_{60}H_{36}$ might have either D_{3d} or S_6 symmetry,[6,7] though the conclusions were based on the assumption that only one isomer was present. Most recently (and pertinent to our results), ^3He NMR studies showed $C_{60}H_{36}$ to consist of two isomers (in *ca.* 2 : 1 ratio), with very similar chemical shifts of δ −7.7 and −7.8.[8] The authors concluded on the basis of theoretical predictions of chemical shifts that one isomer could be of D_{3d} symmetry (this is isomer no. 1 of the compilation of Clare and Kepert[5] and was designated D_{3d}' in earlier publications[4,8]).

A solution to the problem lies with fluorination. Both fluorination and hydrogenation are radical reactions, steric effects are similar (fluorine is smaller than carbon) and all the existing evidence points to these reactions giving identical products. Thus each gives three levels of addition of X (X = H, F) with [60]fullerene: $C_{60}X_{18}$, the products being isostructural;[9,10] $C_{60}X_{36}$;[10,11] and $C_{60}X_{48}$.[12,13] Furthermore, both fluorination and hydrogenation of [70]fullerene give a mixture of $C_{70}X_{36/38/40}$, the component with 38 addends being dominant in each case.[10,11] The isostructural nature of hydrogenation and fluorination has been analysed recently.[14] Fluorofullerenes are sufficiently stable to allow their full spectroscopic analysis, and here we report on the structure of $C_{60}F_{36}$, some details having been given in a preliminary publication.[11]

Fluorination of fullerenes by metal fluorides under vacuum at high temperature has a distinct advantage over F_2 gas fluorination, namely that the volatile fluorofullerenes are swept away from the reaction zone, thereby limiting the extent of addition. Recently, we described the use of MnF_3 for the preparation of $C_{60}F_{36}$, which preliminary characterisation by ^{19}F NMR spectroscopy indicated to consist of at least four main isomers.[11] The off-white material consisted of 15 lines, seemingly divided (2D-COSY) into five separate sets (which were labelled A–E), together with other background material. Compound E, present in low concentration only, consisted of three lines in a 1 : 1 : 1 ratio, each of which was upfield by *ca.* 1.3 ppm (incorrectly quoted as 0.7 ppm in ref. 11) from those of another 1 : 1 : 1 ratio set (set A) present in higher concentration, suggesting that they were structurally related.

Purification by sublimation yielded a white material, the ^{19}F NMR spectrum of which now contained only the 12 main lines present in the crude material. However, the relative proportions of components A–D were approximately the same in both crude and sublimed material. Sublimation is in general not a very satisfactory purification process because it is not very efficient at separating components of a similar structure, and material losses occur, a factor of considerable importance when dealing with the valuable fluorofullerenes. Having now larger quantities of material available we decided to examine the possibility of using HPLC for purification, given that the fluorofullerenes are reasonably soluble in a range of solvents.

Experimental

$C_{60}F_{36}$ was prepared by grinding together (in a dry box) a mixture of [60]fullerene (*ca.* 25 mg) and MnF_3 (120 mg) which was placed in a nickel tube (30 mm long × 5 mm diameter, closed at one end) contained in a glass tube. This was evacuated to *ca.* 0.1–0.01 mmHg and placed in a furnace such that *ca.* 15 cm protruded outside. The furnace was then heated to 350 °C during 30 min and maintained at this temperature for 24 h during which material ranging from pale brown through orange–yellow to almost white deposited on the cold zone. After the tube had cooled, it was opened and the deposit (*ca.* 30% yield) removed by scraping. After HPLC purification (below) the yields of the two isomers totalled *ca.* 10 mg. ^{19}F NMR spectra were obtained at 338.87 MHz ($CFCl_3$ reference) using $CDCl_3$ as solvent, and mass spectra were obtained under EI conditions (70 eV) using a VG Autospec instrument.

HPLC purification

$C_{60}F_{36}$ was purified by high pressure liquid chromatography using an extensive multisolvent regime (described below) employing a 4.6 mm × 25 cm Cosmosil (Buckyprep) column with either toluene or hexane (or a mixture of both) as eluents. $C_{60}F_{36}$ is very soluble in toluene, and slightly soluble in hexane.

We found that with this column and solvent combinations it is possible to separate $C_{60}F_{36}$ from oxides and other impurities. It is essential to use a solvent progression series commencing with use of the more polar solvent, in order to avoid having very polar material (in particular traces of $C_{60}F_{18}$) retained on the column. Nevertheless, the column and filter tended to block periodically, the column being cleared by back-flushing with methanol which did not impair its subsequent performance. Solvent compositions were standardised using a refractometer. Some of the oxide fractions described below are believed to be formed during processing, as a result of reaction with traces of moisture present in the solvents. The isolation of these fractions may not therefore be reproducible from batch to batch, but the results described are typical observations.

(1) Toluene eluent (1 ml min^{-1} flow rate). Four peaks were obtained with the following retention times: (1*a*) 3.5 min, 1404 amu. This is mainly $C_{60}F_{36}$. It was necessary to avoid excessive heating on removal of the toluene, as degradation was liable to occur giving oxygen-containing derivatives. It was repurified under (2) below. (1*b*) 8.8 min, 720 amu. Traces of unreacted [60]fullerene. (1*c*) 12.3, 14.1, 15.7, 17.5 min. None of these components contained any fullerene and they are believed to be various polymers produced from toluene by the action of traces of HF arising from degradation of the fluorinated fullerene. (1*d*) 44.9 min, 1062 amu. We have recently fully characterised this as $C_{60}F_{18}$.[3] In one batch, the isolated component of approximately this retention time was $C_{60}F_{20}$ as shown by the mass spectrum (not shown). (1*e*) 49.8 min. No fullerene detected; IR spectroscopy showed bands at 2960, 2929, 2858, 1736, 1460, 1175 and 1736 cm^{-1}. (1*f*) 53.7 min. No fullerene detected; insufficient material to run IR spectrum.

(2) Toluene–hexane eluent (50:50, 1.0 ml min^{-1}). Fraction (1*a*) above was repurified and gave peaks with the following retention times: (2*a*) 3.6 min. Yellow, retained for reprocessing [see (3), below]. (2*b*) 4.7 min. Colourless, retained for reprocessing [see (3), below]. (2*c*) 5.9 and 7.3 min. The intensities of these seemed to increase with successive injections, indicating that they are decomposition products. They were poorly resolved and so were combined and mixed with the earlier fraction for reprocessing with solvent 3, below. (2*d*) 12 min. This broad peak consisted of oxygen-containing derivatives, analysis of which will be described elsewhere.

(3) Toluene–hexane eluent (10:90, 1.0 ml min^{-1}). Peaks (2*a*) and (2*b*) were reprocessed and gave similar peak patterns except that (2*a*) gave more of peak (3*b*) and peak (2*b*) gave more of peak (3*c*). The retention times of the fractions were as follows: (3*a*) 3.1 min. Colourless and oily, and believed to be dioctyl phthalate concentrated from the solvent. (3*b*) 4.0 min. The main peak from reprocessing (2*a*). Yellow, and indicated by its IR spectrum to be mainly $C_{60}F_{36}$. The colour in the presence of toluene is due to charge-transfer complex formation. (3*c*) 8.1 min. Pale yellow. The mass spectrum indicated the presence of $C_{60}F_{36}$ (due to substantial tailing from peak 3*b*), together with smaller amounts of $C_{60}F_{34}O$ and $C_{60}F_{36}O$ in a *ca.* 3:1 ratio; analysis of these components is deferred. (3*d–f*) 12, 21 and 24.5–28.5 min. These consisted of various oxygen-containing components, to be described subsequently.

(4) Hexane eluent (1 ml min^{-1}). Fraction (3*b*) was further purified with this solvent, and yielded peaks with the following retention times: (4*a*) 3.9 min. No residue on evaporation. (4*b*) 5.8 min. Colourless oil, probably traces of dioctyl phthalate. (4*c–g*) 9.2, 11.5, 14.1, 16.6, 18.7 min. Minor components, some of which are oxygen containing. We hope also to describe these subsequently. (4*h*) 24.9 min. This is $C_{60}F_{36}$ (white). The mass, IR and ^{19}F NMR spectra for this compound (component 1) are shown in Figs. 1(*a*), 2(*a*) and 3(*a*), respectively. (4*i*) 33.2 min. This is also $C_{60}F_{36}$ (white). The mass, IR and ^{19}F NMR spectra for this compound (component 2) are shown in Figs. 1(*b*), 2(*b*) and 3(*b*), respectively. The yields of components 1 and 2 are approximately in the ratio 3:1, respectively.

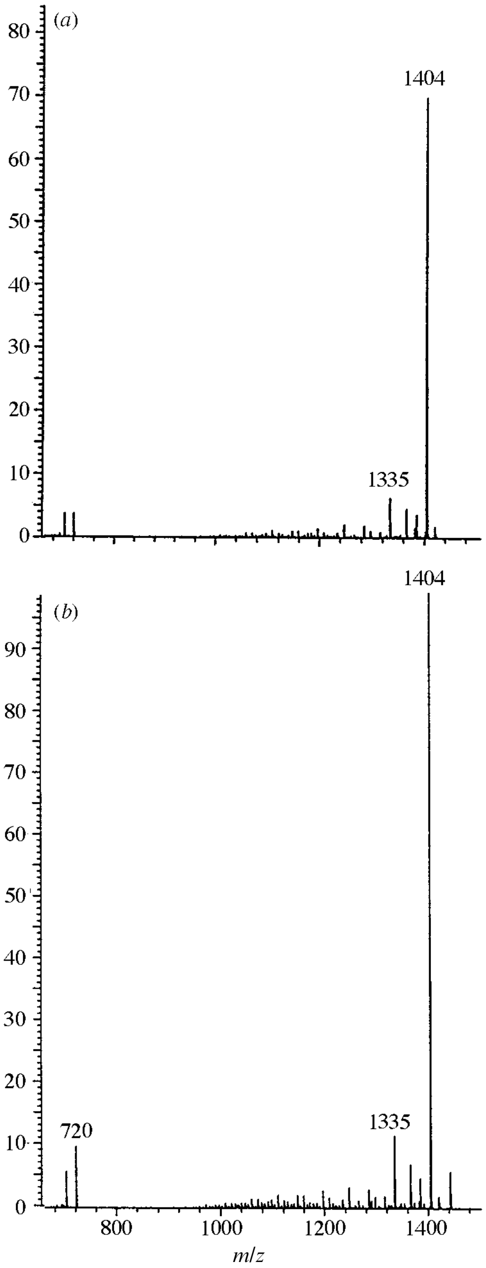

Fig. 1 EI mass spectra (70 eV) of the $C_{60}F_{36}$ isomers (*a*) 1 and (*b*) 2

Apart from the spectroscopic differences, described below, we observed that the isomer of longer retention time appeared to be more soluble in hexane than the other isomer. We also found that the fluorofullerene oxides were more soluble in hexane than $C_{60}F_{36}$ and this property could be used to improve the quality of crude material. This was confirmed by MS analysis of the undissolved material, which showed very little oxide to be present.

Because of the evident value of HPLC separation of fluorofullerenes, we investigated briefly the behaviour of more-highly fluorinated material. Whilst we were unable to separate $C_{60}F_{48}$[10] using toluene as solvent (because it forms a charge-transfer complex which evidently binds strongly to the column), with hexane as solvent and under the above conditions, it elutes very quickly (3.5 min).

In summary, the approximate elution sequence so far established for fluorofullerenes is $C_{60}F_{48} > C_{60}F_{36} > C_{60}F_{18}$. HPLC thus promises to be a valuable tool for future separation of fluorofullerenes, thereby permitting evaluation of their structure and properties.

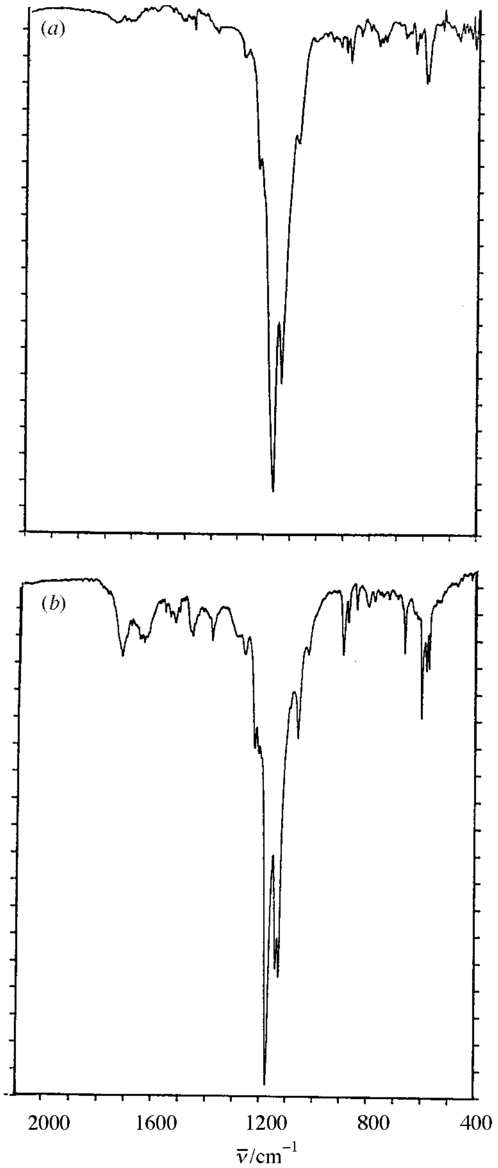

Fig. 2 IR spectra (KBr disc) of the $C_{60}F_{36}$ isomers (*a*) 1 and (*b*) 2

Results and discussion

Mass spectra

The mass spectra of the two $C_{60}F_{36}$ components are shown in Fig. 1(*a*) and (*b*). It is evident that there is no significant difference in the spectra. There was some indication that of the two isomers, the one of longer retention time may degrade to [60]-fullerene more readily. However, it is difficult to be certain of this because of the difficulty of reproducing the mass spectrometry *vs.* probe temp. conditions. Each component produces a degradation peak at 1335 amu due to $C_{59}F_{33}^{\bullet}$ arising from loss of $CF_3^{\bullet}$, a common feature of EI mass spectra of fluorinated fullerenes (see *e.g.* ref. 15), and as in the present case, is always accompanied by a peak at 1285 amu due to a further loss of CF_2. The traces of $C_{60}F_{38}$ evident in the mass spectra were slightly stronger at lower probe temperatures, showing that $C_{60}F_{38}$ is more volatile than $C_{60}F_{36}$ and this follows the general trend for fluorofullerenes, namely that volatility increases with increasing level of fluorine addition.

IR spectra

The $C_{60}F_{36}$ that elutes first from the HPLC (isomer 1) shows a main band at 1163 cm^{-1}, a secondary one at 1133 cm^{-1} and a weak feature at 1074 cm^{-1} [Fig. 2(*a*), KBr disc]. The $C_{60}F_{36}$ with the longer retention time (isomer 2) shows a main band at 1175 cm^{-1}, two smaller peaks at 1140 and 1127 cm^{-1} and a small but sharp band at 1060 cm^{-1} [Fig. 2(*b*)]. In crude material the latter component is evident as a slight shoulder in the spectrum reported in the preliminary publication (and was responsible for the main band appearing slightly shifted at 1166 cm^{-1}).[11]

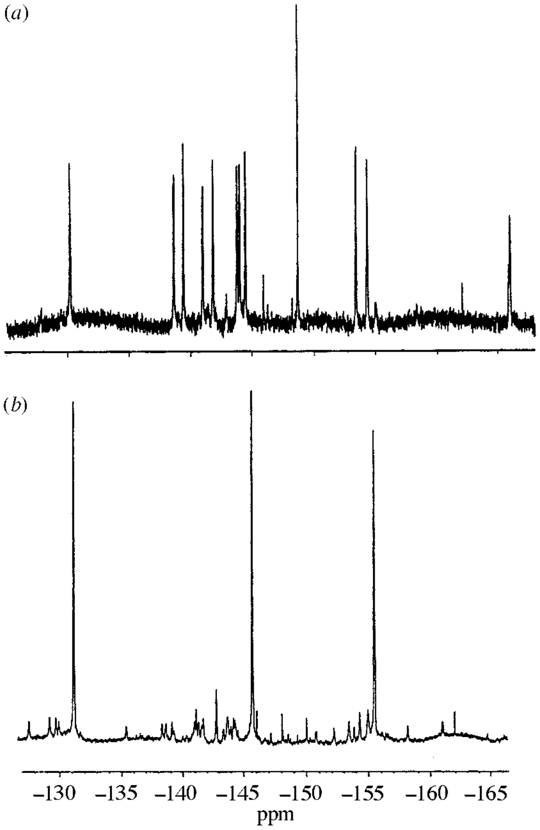

Fig. 3 ^{19}F NMR spectra of the $C_{60}F_{36}$ isomers (*a*) 1 and (*b*) 2

^{19}F NMR spectrum

The spectrum for component 1 [Fig. 3(*a*)] is substantially better than the preliminary one that we obtained from sublimed material.[11] Furthermore, the peak area integration now shows that the 12 peaks present each have an intensity equal to within ±5%. This is a very significant feature in deducing the structure as described. The spectrum for component 2 [Fig. 3(*b*)] shows just three lines of equal intensity; the minor lines in the background are due to traces of isomer 1 and oxide impurities. We have now successfully reproduced the isolation of component 2 from three separate batches.

Structure of component 1

The question to be answered here is: is this a single isomer or a mixture of four isomers as we suggested in the preliminary publication? Our reasoning previously was substantially influenced by the 2D-COSY spectrum which indicated that there were four groups of peaks with no apparent connection between them. The new 2D-COSY spectrum (Fig. 4) now shows more clearly that there are connections between peak D and two peaks of the C group, between one or more of the B peaks and one of the C group, and between one peak of the A and B groups. These facts now show that ‘constituents’ A–D are all part of a single isomer, and this is confirmed by the following reasoning.

(*a*) Given that we have isolated a different isomer (component 2) which has quite different volatility and polarity from component 1, it would be extremely surprising if each of the other presumed four isomers comprising component 1 showed no difference at all in either of these properties. It is evident for example from our preliminary investigation[11] that on sublimation, the proportions of the supposed constituents A, B, C and D were unchanged. (*b*) The probability that each component

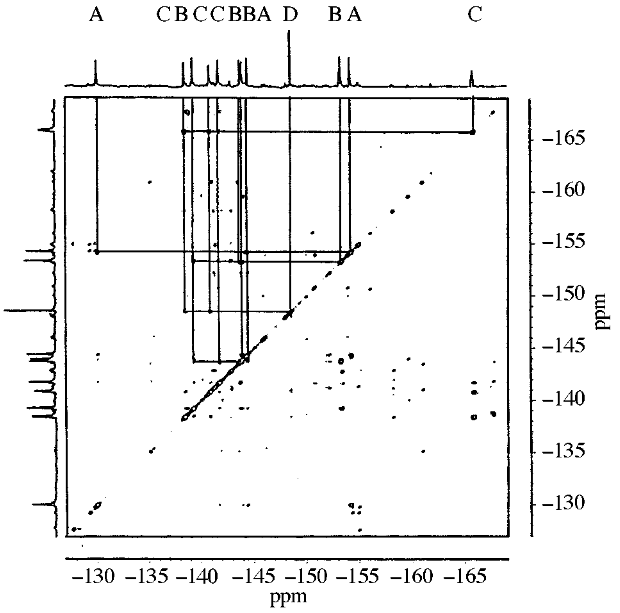

Fig. 4 2D-COSY spectrum of isomer 1

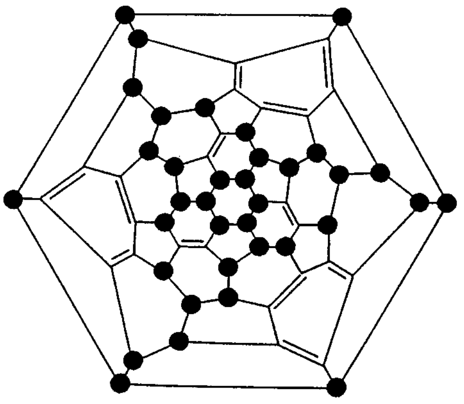

Fig. 5 Schlegel diagram of C_3 $C_{60}F_{36}$ (isomer no. 3 of ref. 4)

isomer would be present in amounts that would give equal intensities for each line in the NMR spectrum is exceedingly low. (*c*) Previously we conjectured that 'constituent A' was the *T* isomer since it gave three lines of equal intensity. But this created an unresolvable problem in that the residual 'constituents' B and C each give four line spectra, which is impossible for any $C_{60}F_{36}$ isomer. (*d*) The analysis of the spectra comprising peaks A–D was influenced by the expectation of a 1 : 1 : 1 three line spectrum required by a *T* symmetry isomer. However, we now have firm evidence for this isomer, which is component 2, and have identified this as giving rise to the set of peaks labelled E in the spectrum shown in the preliminary publication.[11]

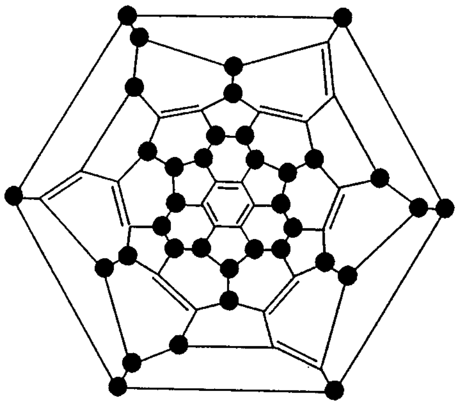

Fig. 6 Schlegel diagram of C_3 $C_{60}F_{36}$ (isomer no. 4 of ref. 4)

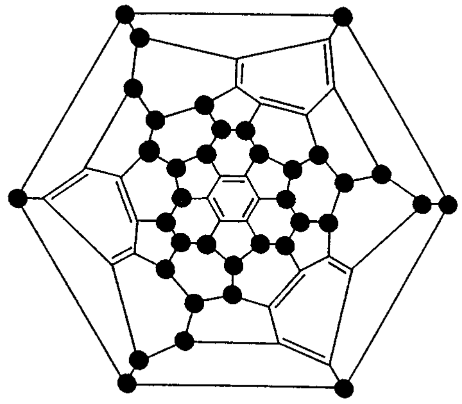

Fig. 7 Schlegel diagram of *T* $C_{60}F_{36}$ (isomer no. 2 of ref. 4)

Component 1 is therefore a single isomer, and the 12 equal intensity lines shows that it has C_3 symmetry. Clare and Kepert have reported AM1 calculations on 63 isomers of $C_{60}H_{36}$ and the predicted heats of formation indicate that the two most stable isomers should have D_{3d} and *T* symmetry, followed by two isomers of C_3 symmetry (Figs. 5 and 6). One of these latter (no. 4, Fig. 6) contains the $C_{60}F_{18}$ moiety as a substructure, and both are built up from '*S*' and '*T*' arrangements of six addends which one of us proposed would be involved in the formation of $C_{60}H_{18}$.[10] Each isomer will give 12 lines of equal intensity in the ^{19}F NMR spectrum. There appears to be no way to distinguish these isomers at present, for each will give eight lines in the sp^2 region of a ^{13}C NMR spectrum. However, we favour isomer no. 4 because of its relationship to $C_{60}F_{18}$, which almost certainly lies on the pathway to formation of $C_{60}F_{36}$. Moreover, for the hydrides at least, heating $C_{60}H_{36}$ causes it to degrade to $C_{60}H_{18}$.[2] Isomer no. 3 is a precursor of $C_{60}F_{48}$, but this is probably not significant, because at the temperature of formation of $C_{60}F_{48}$,[12] the fluorines are labile and must therefore undergo significant re-organisation on the cage surface to reach the final structure.

Although we are unable at present to fully analyse the ^{19}F NMR spectrum for component 1, the precise relationship between the peaks at −130.1, −144.45 and −154.25 ppm and those of component 2 (at −131.25, −145.82 and −155.47 ppm, which are thus upfield by 1.24, 1.37 and 1.22 ppm, respectively) suggests that there is a strong structural similarity between the two isomers. Such a similarity can be seen by comparing the Schlegel diagram for the *T* isomer (Fig. 7) with those for either of the C_3 isomers (Figs. 5 or 6). A three-fold shift of pairs of addends from a 1,2- to a 3,4-position transforms Fig. 5 into Fig. 7, and a related shift transforms Fig. 7 to Fig. 6.

The paucity of connections on the 2D-COSY spectrum is consistent with the preferred structure, since there are two groups of fluorine atoms separated from each other by at least two bond lengths.

Structure of component 2

The spectrum of three lines of equal intensity for this isomer is consistent with either the *T* isomer (no. 2 in ref. 4) or two D_{3d} isomers (nos. 11 or 60 in ref. 4). However, each of these latter two isomers are predicted to be substantially less stable than either the *T* or C_3 isomers, and moreover, neither of them contain the F_{18} moiety. Confirmation that component 2 is the anticipated *T* symmetry isomer (Fig. 7), comes from the ^{13}C NMR spectrum which shows just two equal-intensity lines (broad, because we are unable at present to decouple from fluorine) in the sp^2 region, at δ 136.6 and 137.5. By contrast, the D_{3d} isomers require three lines of intensity ratio 1 : 1 : 2.

The absence of any evidence for the formation of the D_{3d} isomer (no. 1 in ref. 4), predicted to give a 1 : 1 : 2 : 2 ^{19}F NMR pattern, indicates either the failure of theoretical predictions, or, more probably, the importance of kinetic control in determining the preferred isomers. It is reasonably certain that $C_{60}F_{18}$ is the precursor of $C_{60}F_{36}$ and the structure of the former is firmly established.[9] Addition of F_2 to $C_{60}F_{18}$ can take place in a number of ways. For symmetrical addition, fluorine can add either along or across one of the symmetry axes. If symmetrical addition is favoured, and it occurs furthest away from the concentration of 18 fluorines (*i.e.* in the hexagon at the opposite pole), further progress to the D_{3d} isomer (which consists of two F_{18} moieties at opposite ends of the molecule) is precluded. Theoretical calculations may provide further insight into this problem.

Finally we comment further on the relationship between hydrogenation and fluorination. We suggest that both reactions give the same isomers, and certainly the ^{3}He NMR work supports this view, two isomers of $C_{60}H_{36}$ being found in approximately the same ratio as we observe, with shifts of −7.7 and −7.8 ppm. The computed values for the C_3 isomers (Figs. 5 and 6) and T isomer (Fig. 7) are −8.4, −5.7 and −10.3 ppm respectively.[16] On this basis, the preferred C_3 structure is that shown in Fig. 5 since the shift is closer to that calculated for the T isomer. Lastly, the UV–VIS spectroscopic interpretation of the structure of $C_{60}H_{36}$ was based on the indication that aromatic patches are present. This is wholly consistent with a mixture of T and C_3 isomers as may be seen from the Schlegel diagrams.

Acknowledgements

We thank the Royal Society for support of this work through a Joint Project Award, Julian Keates for assistance with the NMR spectroscopy, Dr Michael Bühl for the ^{3}He NMR calculations, and Professor P. W. Fowler for providing MNDO-optimised coordinates for $C_{60}H_{36}$

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Paper 7/07286D
Received 8*th October* 1997
Accepted 28*th November* 1997