The ^{3}He NMR spectra of $C_{60}F_{18}$ and $C_{60}F_{36}$; the parallel between hydrogenation and fluorination

Olga V. Boltalina,[a] Michael Bühl,[b] Anthony Khong,[c] Martin Saunders,[c] Joan M. Street[d] and Roger Taylor[e]

[a] *Chemistry Department, Moscow State University, Moscow 119899, Russia*
[b] *Organisch-Chemisches Institut, Universität Zürich, CH-8057 Zürich, Switzerland*
[c] *Department of Chemistry, Yale University, New Haven, Connecticut 06511, USA*
[d] *Chemistry Department, The University, Southampton, UK SO17 1BJ*
[e] *The Chemistry Laboratory, CPES School, University of Sussex, Brighton, UK BN1 9QJ*

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Both $i^3HeC_{60}F_{18}$ and $i^3HeC_{60}F_{36}$ have been prepared by fluorinating i^3HeC_{60}. The ^{3}He NMR spectrum of $i^3HeC_{60}F_{18}$ shows a single line at −16.66 ppm, very close to the value of −16.45 ppm, recorded previously for the isostructural $i^3HeC_{60}H_{18}$. Density functional calculations afford values of −15.0 and −16.2 ppm for the hydrogenated and fluorinated compounds, respectively. The ^{3}He NMR spectrum of $i^3HeC_{60}F_{36}$ consists of two almost coincident lines (intensity ratio of *ca.* 3:1), at −10.49 and −10.52 ppm, attributable respectively to the C_3 and T isomers shown previously to be the components (also in *ca.* 3:1 ratio) of $C_{60}F_{36}$. The spectrum is similar to that (lines at −7.8 and −7.9 ppm in a similar ratio) recorded previously for $i^3HeC_{60}H_{36}$, and provides compelling evidence that $C_{60}H_{36}$ also consists of a mixture of C_3 (major) and T (minor) isomers. The observed *ca.* 2–3 ppm upfield shift of the spectral lines for the $C_{60}F_{36}$ isomers compared to those for the $C_{60}H_{36}$ isomers is reproduced by both density functional and SCF calculations. The C_3 isomer involved has been identified by comparison of its 2D ^{19}F NMR spectrum with that for the T isomer. It is not the isomer calculated to be the most stable one, and its formation is believed to be favoured by contiguous activation of double bonds adjacent to those that have already undergone addition.

The use of ^{3}He NMR has proved to be a valuable tool for investigation of isomers of fullerenes and their derivatives, through incorporation of ^{3}He inside the cages. Each isomer, and each derivative, gives rise to a single and specific resonance. The technique has been described in reviews[1,2] and been used for example in analysing the adducts formed from reaction of [60]- and [70]fullerenes with cyclopropa[*b*]naphthalene, oxygen, and methylene,[3] in differentiating between isomers formed by bisaddition to [60]fullerene,[4] in the detection of five isomers of [78]fullerene and nine isomers of [84]fullerene,[5] and of isomers of $C_{60}H_4$.[6] Most recently it has been used to detect the presence of two helium atoms inside [70]fullerene[7] and to reveal the dramatic changes in aromaticities of the [60]- and [70]fullerene cages on formation of the hexa-anions.[8]

The first fullerene derivative to be made was $C_{60}H_{36}$,[9] but paradoxically its structure has remained unresolved. The initial proposal of a fully *non*-conjugated T_h-symmetry structure[7] contravened a fundamental rule of organic chemistry and an alternative T symmetry structure (possessing four fully delocalised benzenoid rings) was proposed.[10] This structure was supported subsequently by many theoretical calculations.[11,12] However, the problem of structure verification has proved intractable because of the ease with which $C_{60}H_{36}$ undergoes allylic oxidation during acquisition of the spectrum by ^{1}H NMR.[13] An alternative solution to the problem has come from the realisation that fluorination gives the same regiochemistry as hydrogenation (both are radical reactions). Thus just as [60]fullerene gives both $C_{60}H_{36}$ and $C_{60}H_{18}$ on hydrogenation,[7,14,15] so fluorination gives $C_{60}F_{36}$ and $C_{60}F_{18}$.[16,17] This remarkable parallel, theoretical aspects of which have been considered,[18] extends also to the products of these reactions with both [70]- and [84]fullerenes.[19]

Unambiguous evidence for the parallel between the two reactions was provided by the NMR proof that $C_{60}H_{18}$ and $C_{60}F_{18}$ are isostructural,[15,17] and have the C_{3v} structure predicted by earlier calculations.[20] A study of the spectroscopic and photophysical properties of $C_{60}H_{36}$ (produced by transfer hydrogenation from dihydroanthracene) showed the absorption spectrum to be consistent with a structure containing isolated benzenoid rings; this deduction is relevant to the conclusions obtained from the present work. The structure was conjectured as a single S_6 isomer, though both the T and D_{3d} isomers were also considered to be possible candidates.[21]

More recently ^{3}He NMR showed that $C_{60}H_{18}$ exhibited a single resonance at −16.45 ppm, in full agreement with the previous structural determination.[15] By contrast, $C_{60}H_{36}$ gave two resonances at −7.8 and −7.9 ppm (in *ca.* 2:1 ratio respectively). Thus $C_{60}H_{36}$ consists of two isomers, and it was proposed on the basis of calculations that the main isomer had D_{3d} symmetry.[22] The fluorinated equivalent, $C_{60}F_{36}$, also consists of two isomers and in a similar ratio (separated by HPLC), which ^{19}F NMR spectroscopy has shown unambiguously to be C_3 and T isomers, respectively, (though the specific C_3 was not identified).[16] It seemed likely therefore that the question of the structure of $C_{60}H_{36}$ could finally be solved by comparison of the ^{3}He spectra for the hydrogenated and fluorinated species, and by comparison of the results with theoretical calculations.

Experimental

$i^3HeC_{60}F_{18}$ was prepared by fluorinating i^3HeC_{60} with K_2PtF_6 as described previously.[17] It was dissolved in CD_2Cl_2 and the ^{3}He NMR spectrum obtained as shown in Fig 1. $i^3HeC_{60}F_{36}$ was prepared by fluorinating i^3HeC_{60} with MnF_3 as described

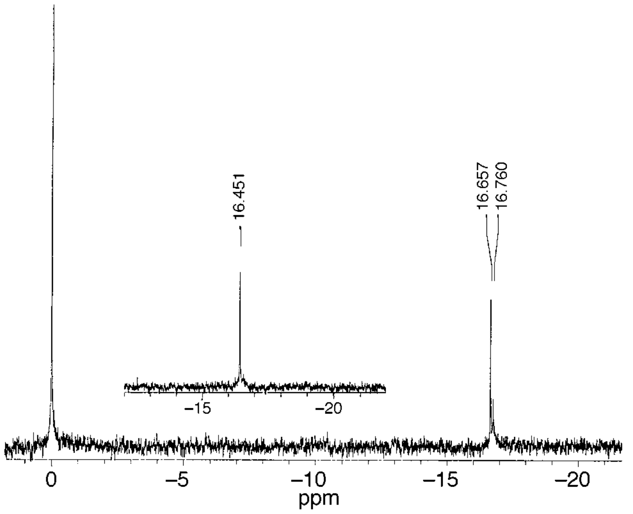

Fig. 1 ^{3}He NMR spectrum for $i^3\mathrm{HeC_{60}F_{18}}$ (inset shows the published spectrum for $i^3\mathrm{HeC_{60}H_{18}}$).

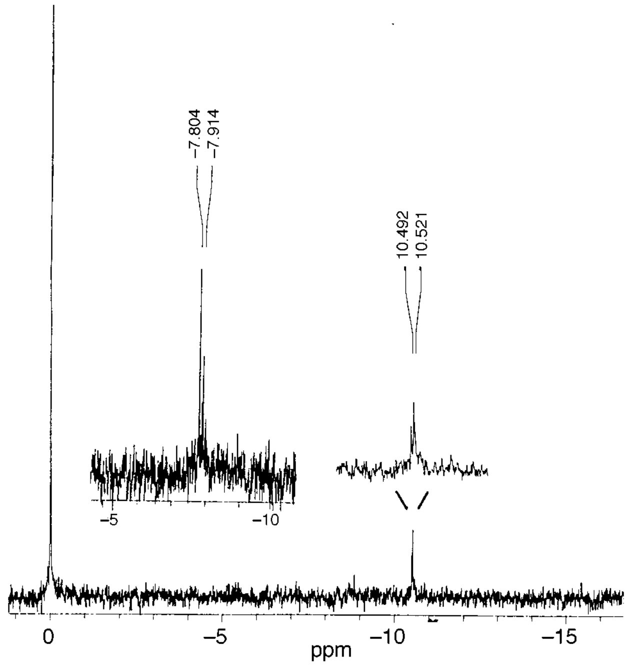

Fig. 2 ^{3}He NMR spectrum for $i^3\mathrm{HeC_{60}F_{36}}$ (inset shows the published spectrum for $i^3\mathrm{HeC_{60}H_{36}}$).

previously.[16] It was dissolved in methylnaphthalene–$\mathrm{CD_2Cl_2}$ (5 : 1), and the spectrum obtained is shown in Fig. 2. In order not to risk converting any of the small quantities of material available into hydroxy derivatives or epoxides, purification (HPLC) to remove minor impurities was not undertaken.

Computational details

Geometries of pristine fullerene derivatives were fully optimised in the given symmetry at the restricted Hartree–Fock level (or self-consistent field, SCF) using standard 3-21G basis sets.[23] Endohedral (incar) chemical shifts were evaluated (as negative of the absolute shieldings) at the centre of mass of the carbon framework, employing direct implementations[24] of the gauge-including atomic orbitals (GIAO-SCF) method, together with a polarised double-ζ basis on C and F and a double-ζ basis on H, denoted DZP.[25] It has been shown that endohedral (incar) shieldings computed in this way for fullerenes are virtually identical to $\delta(^3\mathrm{He})$ chemical shifts of the corresponding endohedral (incar) He compounds computed at the same level.[26] In order to estimate effects of He mobility, chemical shifts were also evaluated at various points up to 1 Å away from the centre. In addition, ^{3}He chemical shifts of the corresponding endohedral (incar) He compounds were computed at a gradient-corrected level of density-functional theory (DFT) employing Becke's exchange, and Perdew and Wang's[27] correlation functionals, denoted GIAO-BPW91 (no re-optimisation was undertaken and a polarised triple ζ basis was employed for He). Preliminary results at this level have been shown to improve the accord with experiment in most cases.[28] All computations were performed with the TURBOMOLE[29] and GAUSSIAN94[30] program packages, using the Silicon Graphics PowerChallenge and IBM RS600 workstations of the Organisch-Chemisches Institut.

Table 1 Chemical shifts (ppm)[a] of $i^3\mathrm{HeC_{60}X}_n$ species (X = H, F; n = 18, 36)

Compound	GIAO-SCF	GIAO-DFT[b]	Experiment
$\mathrm{C_{60}H_{18}}$ (C_{3v})	−18.1	−15.0	−16.45[c]
$\mathrm{C_{60}F_{18}}$ (C_{3v})	−20.0	16.2	−16.66
$\mathrm{C_{60}H_{36}}$ (T)	−10.6[d]	−8.8	−7.9[c]
$\mathrm{C_{60}H_{36}}$ (C_3, no. 64)	−9.0	−7.4	−7.8[c]
$\mathrm{C_{60}H_{36}}$ (C_3, no. 3)	−8.5	−7.0	−7.8[c]
$\mathrm{C_{60}H_{36}}$ ($D_{3d'}$)	−7.4[d]	−6.1	−7.8[c]
$\mathrm{C_{60}H_{36}}$ (C_3, no. 4)	−5.3	−4.4	−7.8[c]
$\mathrm{C_{60}F_{36}}$ (T)	−14.3	−12.0	−10.49
$\mathrm{C_{60}F_{36}}$ (C_3, no. 64)	−13.2	*ca.* −10.2[e]	−10.52
$\mathrm{C_{60}F_{36}}$ (C_3, no. 3)	−12.4	*ca.* −9.4	−10.52

[a] ^{3}He chemical shifts relative to free ^{3}He. [b] BPW91 functional. [c] From ref. 22. [d] Very similar values have been obtained[11] with a smaller basis set. [e] Estimated, see text.

Results and discussion

$\mathrm{C_{60}H_{18}}$ and $\mathrm{C_{60}F_{18}}$

These compounds provide a reference for the reliability of the method and analysis, since they are isostructural, the structure being fully established by NMR spectroscopy. The spectrum for $\mathrm{C_{60}F_{18}}$ (Fig. 1) consists of a peak at −16.66 ppm, together with a much smaller one at −16.76 ppm, the latter being due most probably to $\mathrm{C_{60}F_{20}}$ or $\mathrm{C_{60}F_{18}O}$ each of which has been detected as a minor by-product during the formation of $\mathrm{C_{60}F_{18}}$.[31] Thus both $\mathrm{C_{60}H_{18}}$ and $\mathrm{C_{60}F_{18}}$ give resonances at almost identical positions (see inset to Fig. 1), that for the fluoro compound being shifted very slightly upfield. This may be compared with calculated values for the shifts which are −15.0 and −16.2 ppm, respectively (DFT level, Table 1). SCF calculations also predict a more upfield value for the fluoro compound (−20.0 *vs.* −18.1 ppm) but, in accord with earlier findings,[32] these numbers are too strongly shielded with respect to experiment by *ca.* 2–3 ppm. Overall the agreement between experiment and the DFT data is very satisfactory.

$\mathrm{C_{60}H_{36}}$ and $\mathrm{C_{60}F_{36}}$

The spectrum of $\mathrm{C_{60}F_{36}}$ (Fig. 2) shows two main peaks in a *ca.* 3 : 1 area ratio at −10.49 and −10.52 ppm, together with a possible and much smaller peak at −8.84 ppm (if real, this latter is due very probably to the presence of some $\mathrm{C_{60}F_{38}}$ which is a by-product of the fluorination under these conditions, and would have been retained due to the absence of HPLC purification). The situation therefore parallels that obtained for the hydrogenated analogues (see inset to Fig. 2), providing compelling evidence that *the products from hydrogenation and fluorination are isostructural* as they are at the eighteen-fold addition level. Moreover, comparison of the peak areas with the relative yields in fluorination (determined by HPLC) shows that the peaks at −10.49 and −10.52 ppm for the fluoroisomers are due to the T and C_3 isomers, respectively. The minor peak

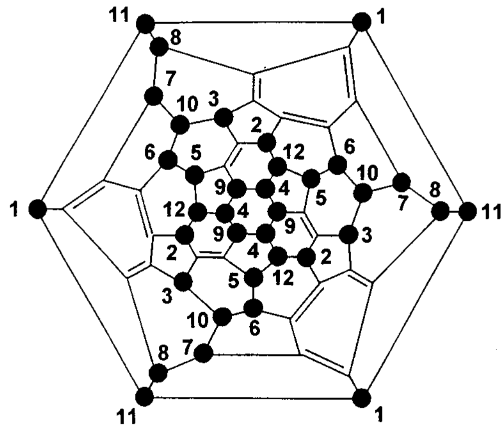

Fig. 3 Schlegel diagram for C_3 $C_{60}X_{36}$ (● = H, F), isomer no. 3.

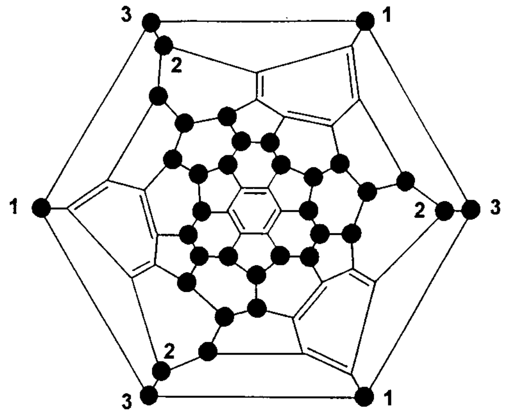

Fig. 4 Schlegel diagram for T $C_{60}X_{36}$ (● = H, F).

(−7.9 ppm) for $C_{60}H_{36}$ can thus reasonably be attributed to the T isomer, and the main one (−7.8 ppm) to a C_3 isomer.

It is instructive to compare the observed chemical shifts with those calculated. First we consider the T isomer of $C_{60}H_{36}$, earlier predictions for which have now been refined to −10.6 ppm (SCF) or −8.8 ppm (DFT, see Table 1), the latter in particular giving excellent agreement with the experimental value of −7.9 ppm. For the corresponding isomer of $C_{60}F_{36}$ the values calculated by these two methods are respectively −14.3 and −12.0 ppm, the DFT calculations again giving the best, and indeed excellent, agreement with the observed value of −10.49 ppm. For both molecules, the computed shieldings decrease off the centre (by less than 1 ppm) which would further improve the agreement with experiment if the He mobility were taken into account. We draw attention here to the almost constant difference between the two compounds of 2.7 ppm (observed), 3.2 ppm (DFT) and 3.6 ppm SCF. This similarity is applied below to calculations for the C_3 isomer.

Identification of the C_3 isomer

(i) Theoretical predictions. Two isomers, nos. 3 and 4 in the compilation of Clare and Kepert, were calculated (AM1) to have stabilities reasonably close to (but less than) that of the T isomer.[12] Isomer no. 4 (although less stable than no. 3) was provisionally favoured[16] on the basis that the disposition of the fluorine atoms found in $C_{60}F_{18}$ is found in isomer no. 4 (and the T isomer) but not in no. 3. More recently we have found that fluorination of $C_{60}F_{18}$ does indeed give $C_{60}F_{36}$ and with the same isomer composition as is obtained on direct fluorination of [60]fullerene.[19] Clare and Kepert have since discovered another C_3 isomer (their no. 64), which is calculated (AM1 level) to be more stable than any other isomer of $C_{60}H_{36}$.[33] This isomer differs from that of the T isomer (Fig. 3) only in that the double bonds in one benzenoid ring of the T isomer are exocyclic to this ring. (It can be derived from the T isomer by having three identical fluorine atoms carry out a single 1,3-shift; isomers nos. 3 and 4 are derived from the T isomer by making a single 1,3-shift by two sets of identical fluorine atoms.) This new isomer contains three 6,5-double bonds, usually regarded as being a destabilising feature, but at the AM1 level, it is more stable than the T isomer by 8 kcal mol^{-1}.[33] Though the same stability order is found with the SCF method (energetic separation 3 kcal mol^{-1}), T is calculated to be the more stable by 5.6 kcal mol^{-1} with BPW91. The theoretical methods thus agree that both isomers should be similar in energy. By contrast the C_3 isomers nos. 3 and 4 noted above are predicted to be substantially less stable than the T isomer (by between 30 and 45 kcal mol^{-1}, depending on the method). The relative stabilities of the T and C_3 (no. 64) isomers extends also to the fluorinated equivalents. AM1 calculations predict[33] that the C_3 isomer should be more stable than the T isomer by 28 kcal mol^{-1} whilst our SCF and DFT calculations give values of *ca.* 11 and −2.2 kcal mol^{-1}, respectively. The new C_3 isomer no. 64 was therefore evaluated as a potential candidate for the experimental C_3 species.

We now compare the calculated shifts with those obtained experimentally. For the hydrogenated species the DFT values are: −7.4 ppm (C_3 no. 64); −7.0 ppm (C_3 no. 3); −6.1 ($D_{3d'}$); −4.4 ppm (C_3 no. 4); the observed value is −7.8 ppm. The SCF data (which as seen above give values too negative), are in the same order (see Table 1). These results thus narrow the choice to isomers no. 3 and 64 and eliminate our earlier selection of no. 4. Moreover, each of isomers no. 3 and 64 have three benzenoid rings present (in contrast to the $D_{3d'}$ isomer which has only two) and are thus more consistent with the general structural conclusions (deduced from UV/vis studies) that the isomer must have a strong aromatic component.[21] Our new higher-level chemical-shift computations (Table 1) also disfavour the $D_{3d'}$ isomer implied previously.[22]

Unfortunately the lower symmetry of the C_3 isomers currently precludes the calculation of DFT chemical shifts for the fluoro analogues. Even the SCF computations are very time-demanding, so we have limited these to isomers no. 3 and 64. The resulting SCF values of −13.2 and −12.4 ppm are very close to that of the T isomer and again are consistent with the experimental observations. For the other fluoro compounds, the 'electron-correlation effect' (as assessed by the difference between the GIAO-SCF and DFT data in Table 1) is deshielding by *ca.* 3 ppm; thus one could anticipate respective DFT values around −10.2 and −9.4 ppm.

In summary, the ^3He results support identification of the C_3 isomer as either no. 3 or no. 64. Calculations of the overall stabilities (noted above) favour isomer no. 64, as do calculations (SCF) of the ^{19}F NMR shifts which are predicted to be in the range −(121.3–151.1 ppm, no. 64) and −(100.3–141.2 ppm, no. 3) compared to −(130–165.7 ppm, observed). However, despite these indicators, the C_3 isomer concerned turns out to be no. 3, the final proof of structure coming from the 2D ^{19}F NMR spectrum (shown but not solved, in a previous paper[16]).

(ii) 2D ^{19}F analysis. Previously we observed that three minor lines in the ^{19}F NMR spectrum of $C_{60}F_{36}$ were each upfield by 0.70 ppm from another three lines in the overall spectrum (peaks E and A respectively), suggesting a similarity of structure.[16] Subsequently we were able to identify the peaks E as due to the T isomer, and peaks A–D as due to a C_3 isomer.[16] Fig. 5 shows the connectivities in the 2D ^{19}F NMR spectrum of the T isomer, and should be viewed in conjunction with the Schlegel diagram (Fig. 4) on which we have labelled three of the non-identical peaks (1–3). Assignment of these peaks is based on the following:

(i) Peak no. 3 is identified because it is connected to the two other (different) peaks, and moreover is more upfield which

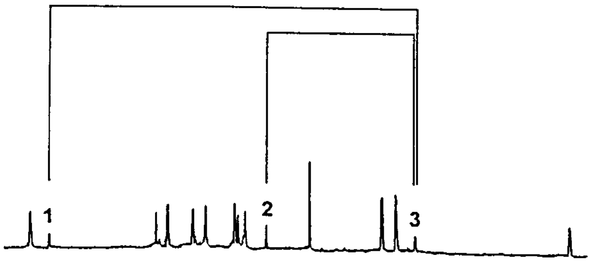

Fig. 5 Connectivity diagram deduced from the 2D ^{19}F NMR spectrum of T $C_{60}F_{36}$.

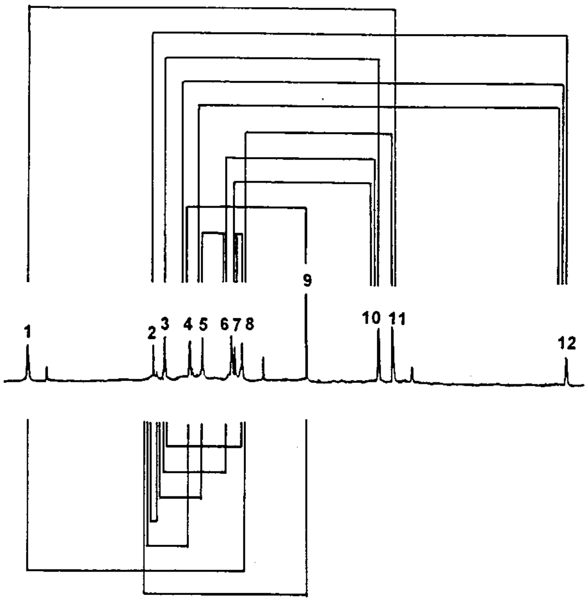

Fig. 6 Connectivity diagram deduced from the 2D ^{19}F NMR spectrum of C_3 $C_{60}F_{36}$; the upper connections are primary (1,2), the lower connections are secondary (1,3 or 1,4) (see text).

is commonly the case when the carbon to which fluorine is attached, is connected to three other sp^3 carbons (less electron-withdrawing than sp^2 carbons).[34] This effect is seen for example in the ^{19}F NMR spectra for $C_{60}F_{18}$ and $C_{60}F_{48}$.[15,17] Both SCF and DFT calculations confirm that fluorine no. 3 should give the most upfield resonance.

(ii) Fluorines 1 and 2 (each have two sp^3-hybridised carbons and one sp^3-hybridised carbon adjacent to the one to which they are attached) are assigned by both SCF and DFT calculations as shown in Figs. 4 and 5. This result is crucial to solving the C_3 structure.

(iii) Inspection of Schlegel diagrams shows that C_3 isomers 3, 4, and 64 are all related to the T isomer in having a common motif. This is shown for the isomer no. 3 in Fig. 3, where the outer nine fluorines have the same relative positions compared to the remainder of the structure as seen in the Schlegel diagram for the T isomer (Fig. 4). This accounts for the constant difference in position of three lines in the C_3 spectrum compared to those of the T isomer, since these nine fluorines are remote from the rest in each structure. This enables us to assign peaks 1, 8, and 11 in the spectrum of the C_3 isomer as these correspond to peaks 1, 2 and 3 in the T isomer. (SCF calculations predict that this shift should be upfield by an average of *ca.* 1 ppm relative to the corresponding peaks in isomer no. 64, and *ca.* 4 ppm relative to those for isomer no. 3.)

(iv) From the 2D spectrum one can derive, based on the spot intensities, a connectivity diagram for both the primary (1,2) connections and the secondary (1,3 and 1,4) connections (Fig. 6). It is a feature of 2D ^{19}F NMR spectra that secondary connections are readily seen, *e.g.* in the spectrum of $C_{60}F_{48}$.[35] There are two peaks in the spectrum that have primary connections to three others [and moreover are upfield, as described in (i) above], and these are fluorines no. 10 (connected to nos. 3, 6, and 7) and no. 12 (connected to nos. 2, 4 and 5). However, no. 7 is connected to no. 8 (already identified) and so we can distinguish between nos. 10 and 12.

(v) One of the peaks attached to no. 10 has only one connection, which must therefore be no. 3, and hence in turn we can assign no. 6. However, no. 6 is connected to no. 5 which is one of the three attached to no. 12, so it only remains to distinguish between nos. 2 and 4 attached to no. 12. Since no. 2 has no further connections, it is readily assigned and that just leaves the assignment of peak no. 9 to the remaining three identical fluorines in the central ring.

(vi) The secondary connections that are evident are 1–8, 2–3, 2–4 and 3–6 ('*meta*' connections) and 2–9, 3–5 and 3–8 ('para' connections with an intervening double bond which should aid conjugative interactions). These are all fully consistent with the structure of isomer no. 3.

We do not show the Schlegel diagrams for the other two C_3 structures considered (nos. 4 and 64), but the observed data cannot be made to fit either of them; indeed the data cannot fit any other C_3 structure since there can only be a unique solution for each 2D spectrum, given that the primary and secondary connections are clearly distinguished. The key features that distinguish isomers nos. 3 and 64 are as follows. In isomer no. 64, fluorine no. 9 would be 1,3-shifted to lie connected to fluorines nos. 2 and 3. This would require:

(i) A primary coupling between fluorines nos. 9 and 2 and a weak secondary one between fluorines nos. 9 and 4. This is the opposite of what is found, indeed in some 2D spectra the coupling between fluorines nos. 9 and 2 can barely be discerned.

(ii) A primary coupling between fluorines nos. 3 and 9. There is not even a hint of this in any of the spectra.

(iii) A different appearance for peak no. 9, which is outstandingly sharp, consistent with it being flanked by two identical fluorines (nos. 4) which presumably give rise to a small coupling constant. If however it were connected to the two different peaks nos. 2 and 3 (as in isomer no. 64) then it is improbable that *both* would give rise to small and identical coupling constants, so significant splitting could be expected.

Thus overall, our results prove that the two isomers in $C_{60}F_{36}$ are T and C_3 (no. 3), and that these are almost certainly the isomers present in $C_{60}H_{36}$.

Why isn't the most stable isomer formed?

It is necessary to account for the failure to obtain C_3 isomer no. 64 (competitive in energy with, if not more stable than, the T isomer) but also the $D_{3d'}$ isomer. This latter (denoted as no. 1 in Clare and Kepert's compilation[12]) is more stable than the T isomer *only* with semi-empirical methods, but is much higher in energy at *ab initio* and DFT levels.[11] Once fluorine attaches to one pair of double bonds, the partial aromaticity of the cage is such that increased localisation of the adjacent double bonds occurs, hence further addition takes place there preferentially, leading to 'T' and 'S' addition patterns.[15,36] This is seen for example in hydrogenation and epoxide formation. There will thus be contiguous activation of double bonds, with addition thus spreading through the molecule from a single commencement point (one double bond). Such a process cannot lead to the $D_{3d'}$ isomer, (nor in fact to C_3 isomer no. 4) because each has a 'non-addition' zone in the molecule. These could only be obtained if addition commences at two points in the molecule which would necessarily have to be the 'correct' ones if the final structure were to be obtained. Addition at a second point would also be disfavoured by the lowered activation energy for the other sites as noted above.

To obtain isomer no. 64, the addition process would need at some point to neglect the opportunity to add across an 'activated' 6,6-bond and instead add across a 6,5-bond.

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