ARTICLE

OBC
www.rsc.org/obc

The energies of some isomers of $C_{60}F_8$: the use of experimental and theoretical considerations to limit candidate structures

John P. B. Sandall and Patrick W. Fowler
School of Chemistry, University of Exeter, Stocker Road, Exeter, UK EX4 4QD

Received 21st November 2002, Accepted 29th January 2003
First published as an Advance Article on the web 24th February 2003

A survey of possible structures for the $C_{60}F_8$ molecule has been carried out, using both experimental (^{19}F NMR data) and theoretical (structure–energy correlation) considerations to limit the number of isomers to be regarded as candidates for the previously isolated species. Several isomers are suggested as likely, with one low-energy structure in particular appearing to fulfil all the criteria better than the literature suggestion. Both this predicted isomer and that previously suggested have in common a sub-structure of a single fluorinated carbon atom surrounded by three *vicinal* fluorine neighbours together with a further pair of fluorine atoms added so as to generate a T-shaped motif.

Introduction

The most extensive set of characterised and partly characterised halogeno[60]fullerenes is that comprising the fluoro derivatives. Over the past eight years, no fewer than eleven have been prepared[1–13] and purified and, of these, five ($C_{60}F_{18}$,[4,5,7] $C_{60}F_{20}$,[9] $C_{60}F_{36}$[3,5,8,12] (*T* isomer), $C_{60}F_{36}$[13] (C_1 isomer) and $C_{60}F_{48}$[1,2]) are well characterised. The other products, $C_{60}F_2$,[11] $C_{60}F_4$,[10] $C_{60}F_6$,[10] $C_{60}F_8$,[10] $C_{60}F_{16}$,[6] and $C_{60}F_{36}$[3,5,8] (C_3 isomer), have each had a structure assigned that is consistent with, variously, ^{19}F, ^{13}C or ^{3}He NMR spectra and also consistent with a mechanism of sequential, contiguous atom addition[5,6,11,15,18,20] which is considered to be common to sterically undemanding addends such as hydrogen and fluorine. In addition, a series of fluorinated fullerene oxygen derivatives has been identified,[14–18] first thought to be epoxides[14,16] and more recently shown to be ethers.[15,17,18] Another derivative, $C_{60}F_{17}CF_3$, has also been completely characterised[21] by X-ray diffraction. The problem of isomer identification is not simple since, even for a species with only 8 identical addends on the [60]fullerene, there is a total of 21 330 558 possible isomers,[22] and thus huge scope for multiple solutions compatible with any given set of spectral data.

Since fluorination at high temperatures of different mixtures of species ranging from $C_{60}F_{16}$ to $C_{60}F_{42}$ gives the unique $C_{60}F_{48}$ isomer, as also does fluorination of *both* the isomers of $C_{60}F_{36}$, despite the fact that none of the postulated or known structures for these contain fluorine atoms in the same positions as in $C_{60}F_{48}$, Gakh and Tuinman[23] were led to suggest that a rapid fluorine migration must occur on the [60]fullerene surface. Likewise, fluorination of $C_{60}F_{18}$ generates[5] the two $C_{60}F_{36}$ isomers in exactly the same ratio as does fluorination of C_{60}, although one of these isomers cannot be derived from its precursor by simple 1,2 addition without rearrangement of fluorine atoms. In turn this implies that the nature of the products is governed, at least to some extent, by thermodynamic rather than kinetic factors. The very recent observation[24] of the room-temperature migration of fluorine converting $C_{60}F_{36}$ (C_1) to $C_{60}F_{36}$ (C_3) again demonstrates the lability of individual fluorine atoms and hence thermodynamic control of the fluorination process.

On the other hand, it has been stated[10] that one requirement for the structure of $C_{60}F_8$ is that it should be compatible with a mechanism of successive 1,2 additions, postulated to account for a possible sequence required to generate $C_{60}F_{18}$. The addition of a sterically small addend, *e.g.* H or F, is thereby supposed to take place as a 1,2 addition across a 6,6 'double' bond and this addition to one bond in the hexagon is suggested[15] to increase the π-density of the adjacent double bonds in the same hexagon. Thus the next pair of addends will generate a 1,2,3,4 pattern around the hexagon and further addition of 1,2 pairs gives rise to 'S' and 'T' addition patterns,[25] since the presence of six addends in a single hexagon is considered de-stabilising. This interpretation is open to question: in the case of hydrogen, the 1,2 isomer is accompanied by up to 40% of the 1,4 isomer[19] and the material isolated[26] as $C_{60}H_4$ gives a complex mixture of six isomers of which only 50% is the 1,2,3,4 species, the others comprising more distant additions of 1,2 pairs or isomers of unknown structure. Although this mechanism of successive 1,2 additions has been formulated[25] in kinetic terms (products are governed by changes in the π-density of the fullerene double bonds) it appears that the amounts of the three identified $C_{60}H_4$ isomers also parallel their thermodynamic stabilities[26] determined by *ab initio* calculation. More recent work[27] on the $C_{60}H_4$ isomers suggests the presence of at least five of the eight possible isomers generated by addition of two 1,2 pairs. It may also be significant that there appears to be a similarity in the structures of $C_{60}F_{18}$ and $C_{60}H_{18}$ as well as in the corresponding $C_{60}X_{36}$ (X = H, F) isomers; again this has been interpreted[28] in terms of thermodynamic stability. Thus the material isolated from the complex mixture of isomers arising during fluorination may not be comprised only of isomers arising from successive 1,2 contiguous additions of fluorine.

While mechanistic control, leading to successive 1,2 additions, accounts for the known structure[7] of $C_{60}F_{18}$ (and structure[9] of $C_{60}F_{20}$), there is no guarantee that the mechanism could not generate other isomeric structures of the same molecular formula. Also, in the case of $C_{60}F_8$, the successive 1,2 addition of fluorine had to be abandoned[10] and a unique process, 1,8 addition, is necessary as the final step to generate the reported isomer. Further, it would appear unlikely, in view of the lability of these fluoro derivatives, that a relatively unstable $C_{60}F_8$ intermediate species would be formed merely because it lies on one particular path to a known stable structure. Arguments based on energetic considerations should have some relevance at each stage of $C_{60}F_X$ formation.

^{19}F NMR chemical shifts and coupling constants

The deductions concerning the structures of these isomers have been based on the application of spectroscopic methods. The most important technique used has been ^{19}F NMR, especially comparisons of chemical shift and coupling constants together with connectivity data obtained from 2D COSY spectra. The single most important datum obtainable from the ^{19}F spectrum

DOI: 10.1039/b211371f

Table 1 ^{19}F chemical shifts (δ) and ^{19}F–^{19}F coupling constants reported for known fluorinated [60]-fullerenes, classified according to the number of *vicinal* fluorine neighbours

Compound	3 Neighbours	2 Neighbours	1 Neighbour	Coupling constants/Hz
$C_{60}F_{48}$[a]	−153 to −170	−131 to −139		Not reported
$C_{60}F_{36}$ (T)[b]	−156	−131, −146		Not reported
$C_{60}F_{36}$ (C_1)[c]	−152 to −165	Not reported	Not reported	Not reported
$C_{60}F_{20}$[d]		−133		
$C_{60}F_{18}$[e]	−158	−136, −143	−132	^3J = 20, 8, 2
$C_{60}F_{18}O$[f]	−161, −169	−138 to −151	−133, −134	^3J = 25, 21, 20, 11, 8

[a] Ref. 1,2. [b] Ref. 5,8. [c] Ref. 13. [d] Ref. 9. [e] Ref. 5,7. [f] Ref. 16.

is the point group of the observed species. If the group is non-trivial, significant simplification can occur. Thus the presence in the spectrum of three lines of equal intensity for one of the $C_{60}F_{36}$ isomers[5,8] reduces the 3.0 × 10^{14} possibilities immediately to four of point-group symmetry T; one of these structures has now been proved by X-ray analysis.[12] $C_{60}F_{20}$ gives rise to a single fluorine resonance, clear evidence that of the 3.5 × 10^{13} possible isomers for this molecular formula, only two D_{5d} isomers need to be considered; one of these is calculated[9] to be of much lower energy than the other. On the other hand, the presence of at least 32 peaks in the spectrum of another isomer of $C_{60}F_{36}$[13] implies C_1 symmetry and reduces the possibilities only from 300 436 595 453 640 to 300 436 529 264 126.[22]

The magnitudes of the chemical shifts and coupling constants, and connectivities between fluorine atoms are of course related to the structure. However, these relations are not precise in the way that the relation of peak numbers and integral ratio to symmetry is precise; they depend on the development of empirical ideas concerning how these experimental observations might vary with structure. The nearest structural analogues to the fluorofullerenes are the fluoro-substituted aromatic compounds where the geometry is fixed. Here there are two obvious major effects: the number of near fluorine neighbours to the observed fluorine atom, and the electron-withdrawing or donating effect of more distant substituents. Thus fluorobenzene resonates at $\delta = -112$, 1,2-difluorobenzene at −140 (2F), 1,2,3,5-tetrafluorobenzene has resonances at −108 (1F), −124 (2F) and −156 (1F), pentafluorobenzene at −139 (2F), −162 (2F) and −154 (1F) while C_6F_6 resonates at −163 (6F) (data from ref. 29). A single fluorine neighbour thus gives an upfield shift of about 30 ppm, and two such neighbours give a further 25–30 ppm, doubtless due to the extra screening by the lone pairs of the contiguous fluorine atom(s). The effect of more distant substituents on ^{19}F shifts is demonstrated[29,30] by the many correlations with Hammett substituent constants; shifts of up to 30 ppm are observed on changing from strongly electron-attracting substituents (*e.g.* NO_2) to electron-releasing ones (*e.g.* $N(CH_3)_2$) in *p*-substituted fluorobenzenes,[30] with smaller shifts of up to 7 ppm on substitution in the *m*-position, where resonance effects are of less importance. Clearly, in the fluorofullerenes the effect of further fluorine substitution on the observed ^{19}F shift will not be easily predictable, and an effect over and above those already mentioned also will be noticeable:[11] the hybridisation of the carbon atoms changes from sp^2 to sp^3 as addition of fluorine atoms takes place. It is noteworthy that the two major nuclear shielding effects in the polyfluoro-[60]fullerenes, the extra screening by vicinal fluorine atoms and the de-shielding by the electron-withdrawing effects of the more distant fluorines, must roughly cancel, leaving the shifts of many of the fluorine atoms in the same region, regardless of the extent of substitution.

^{19}F–^{19}F coupling constants for 1,2 fluorine atoms in aromatic systems (^3J) are generally of the order of 18–22 Hz; for 1,3 atoms (^4J) 0–5 Hz and for 1,4 atoms (^5J) somewhat larger again at 4–10 Hz, thus often making it possible to identify contiguous fluorines. Although at first sight the connectivities obtained from 2D COSY spectra are obviously useful, it has been pointed out[31] that long-range scalar couplings in fluorofullerenes may be larger than vicinal ^3J constants. Thus the case for one particular C_3 isomer[8] of $C_{60}F_{36}$ rather than another[5] rests partly on the basis that the ^4J and ^5J couplings through the π system are larger than the vicinal ^3J couplings.

Correlations of ^{19}F parameters in fluorofullerenes should be derived only from absolutely known structures; we are therefore limited to $C_{60}F_{18}$, $C_{60}F_{20}$, $C_{60}F_{36}$ (T and C_1 isomers) and $C_{60}F_{48}$, together with the ether derivative, $C_{60}F_{18}O$, to analyse the relation between structure and parameters. In principle, $C_{60}F_{17}CF_3$[21] could be added to these, but the chemical shifts are in fact within 4 ppm of the corresponding ones in $C_{60}F_{18}$ and coupling constants are not reported; the ^{19}F NMR spectrum of the C_1 isomer of $C_{60}F_{36}$ has not yet been completely assigned. These structures have been elucidated either by X-ray crystallography or are sufficiently symmetrical for only a very small number of isomers to be consistent with the NMR spectrum. In Table 1 we have tabulated the range of positions of the ^{19}F resonances, together with coupling constants where these have been reported, classified according to the number of vicinal fluorine atom neighbours for a given fluorine atom.

First we may note that the variability of coupling constants rules out their use as primary evidence for definitive structure prediction. It could be argued that some of the couplings reported as vicinal ^3J may arise in fact from more distant interactions; this would require changes to the assignments of certain of the fluorine atoms. The chemical shifts are less variable, and it would seem that any observed chemical shift with $\delta < -152$ probably arises from a fluorine atom surrounded by three others; no firm conclusions can be drawn from shifts in the range $-130 > \delta > -150$ except that a shift in the range −140 to −150 is more likely to arise from a fluorine with two neighbours than a fluorine with only one neighbour. Likewise a shift in the range −130 to −120 is more likely to arise from a fluorine with fewer than two neighbours, but these are merely probability based conclusions in quite highly fluorinated systems. That large high-field shifts are possible in compounds with few fluorine atoms may be deduced from the reported ^{19}F chemical shift of $C_{60}F_2$ ($\delta = -148.3$) where obviously the fluorine atom has a maximum of one vicinal fluorine neighbour.

Possible structures for $C_{60}F_8$

We now discuss the possible structures of $C_{60}F_8$. The published data[10] consists of an EI mass spectrum (parent ion for $C_{60}F_8$ at 872 amu, with stepwise loss of 4 × F_2) and a ^{19}F NMR spectrum with 5 peaks: δ_F −124.5 (A, 1 F, dm, J = 26 and 4 Hz), −134.9 (B, 2 F, d, J = 27 Hz), −136.2 (C, 2 F, s), −137.8 (D, 2 F, d, J = 4 Hz), −153.2 (E, 1 F, dt, J = 27.3 Hz). Thus E is coupled strongly to both A and B; A is coupled less strongly to D and C is not coupled at all. Together with three assumptions, which may be labelled: A(1), that addition of fluorine atoms always takes place contiguously; A(2), that the isomer should 'most probably be an intermediate on the path to $C_{60}F_{18}$'; and A(3), 1,8 addition of fluorine is allowed as the final step; the data allows the following structure to be deduced[10] (isomer 1, Fig. 1).

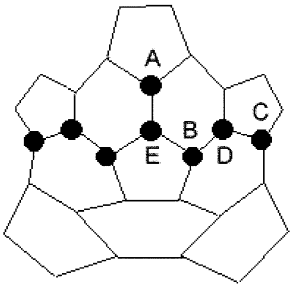


Fig. 1 Isomer 1. Structure previously assigned[10] to isolated $C_{60}F_8$. Structures are given as partial Schlegel diagrams showing the relevant part of the fullerene framework with fluorine added at the positions marked with black dots.

This structure is certainly compatible with the data (although the absence of any observable C–D coupling is unusual) but in view of the huge number of theoretically possible isomers, it is of interest to check whether it is the *only* possibility that is compatible with the data and further, whether assumptions A(1) to A(3) are necessary or sufficient to prove the structure.

The most logical approach in view of the difficulties outlined above is to consider all possible isomers, reducing their number by taking known facts into account, or, when this is not possible, to make assumptions based on thermodynamic stability, since there is much evidence that previously isolated species have been the most stable at least in a restricted group of isomers.[32,33] Only as a final step shall we make use of ^{19}F NMR shifts and coupling constants, since these appear to us to be at present the least reliable evidence for structure. The two assumptions, A(1) and A(2), concerning the contiguity of addition of fluorine atoms and the path to the $C_{60}F_{18}$ structure will then be considered separately.

(i) Assignment of symmetry

We start therefore with the NMR signal intensity ratios, which are consistent only with a structure with C_s point-group symmetry which has two fluorine atoms on the mirror plane and three pairs lying symmetrically across it. The intensities 1,2,2,2,1 indicate a point group with orbit sizes 1 and 2; of the sub-groups of the I_h symmetry of the pristine fullerene, only in C_s does the decomposition of the 60-orbit of I_h contain orbits of both sizes; in C_s the set of 60 atom positions falls into 4 × 1 and 28 × 2, symbolically represented $O_{60} \longrightarrow 4O_1 + 28O_2$, and hence there are 4 sites in the mirror plane, and 28 pairs of sites related by reflection across it. The observation of C_s point-group symmetry reduces the number of isomers from 21 330 558 to 10 027 distinct candidates;[22] the fact that exactly *two* atoms are on the mirror plane reduces the number further to 4 888 by explicit construction and symmetry reduction of all cases in which 2 out of 4 O_1 orbits and 3 out of 28 O_2 orbits are fluorinated. For this purpose, every isomer is represented by a vector of 60 positions, $\boldsymbol{X}$, each containing 1 for a fluorinated site and 0 for a bare carbon atom; the 120 operations of the parent I_h group and the C_s subset then correspond to permutations of these vector entries that can be used to project out redundant repetitions, assign site symmetries and check compatibility with orbit structure. However, 4 888 is still a very large number even for semiempirical calculation; to reduce it further, some qualitative energetic considerations are introduced.

(ii) Energetics of local addition patterns

We therefore investigated the total energies of the 23 isomers arising from addition of a pair of fluorine atoms to [60]fullerene. The energies, calculated semiempirically (AM1), of the six most stable difluoro species are listed in Table 2.

Table 2 MOPAC (AM1) energies for the six most stable $C_{60}F_2$ isomers

Mode of addition	AM1 energy/kJ mol^{-1}
1,2 'double'	3618
1,4 across hexagon	3636
1,2 'single'	3695
1,4 over 2 hexagons	3764
1,3 across hexagon	3831
1,3 across pentagon	3859

Here 1,2 'double' implies addition across the formal double bonds in the fullerene at a hexagon–hexagon junction; 1,2 'single' implies addition at a pentagon–hexagon junction. The entries in the table suggest that we may, with reasonable safety, restrict our consideration to only those isomers where the fluorine atoms are added in combinations involving the first three types of addition only. Therefore all isomers, under this restriction, have every single fluorine atom involved in *at least* one 1,2 *or* one 1,4 combination with some other fluorine atom. This is a relaxation of assumption A(1) of contiguity of fluorine addition, in that 1,4 addition is now allowed, and it is not prescribed that all addition must take place in pairs. Thus, for example, the isomer illustrated in Fig. 1 is allowed, even though it cannot be generated by pairwise 1,2 or 1,4-addition, since *each* of its fluorine atoms forms half of a 1,2 or 1,4 pair. Applying this restriction to the 4 888 isomers reduces the total number to be considered to 559, a number for which it is reasonable to perform a complete calculation of fully optimised structures and energies using semiempirical methods.

It is worth noting at this point that we have made a tacit assumption of approximate additivity of effect: it is possible in principle that some combinations of our stable set of 1,2 and 1,4 interactions may give rise to de-stabilising factors or that other less stable pairwise interactions may accidentally combine to generate a particularly stable structure. We shall return to this aspect later.

(iii) Total energy calculations

Starting structures for the 559 isomers were generated and the energies (AM1, MNDO, PM3), at fully optimised geometries, were calculated using the MOPAC package.[34] The AM1–PM3 correlation ($r^2 = 0.99$) for the full set of isomers is illustrated in Fig. 2; the AM1–MNDO correlation is similar but less precise ($r^2 = 0.94$).

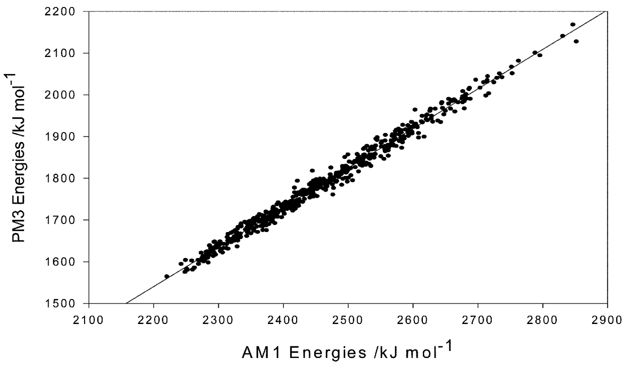


Fig. 2 Correlation of MOPAC PM3 and AM1 energies calculated with full geometry optimisation for 559 isomers of $C_{60}F_8$.

In view of the good correlation between the three methods of calculation, most discussion will be limited to the AM1 energies. In fact all three Hamiltonians give the same lowest energy structure: this isomer is illustrated below (Fig. 3, isomer 2). The calculated AM1 energy is 2 220 kJ mol^{-1}, no less than 148 kJ mol^{-1} (AM1) more stable than isomer 1. The corresponding relative stabilities for the other Hamiltonians are

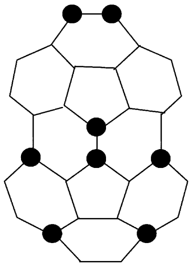


Fig. 3 Isomer 2. Structure of the most stable (AM1) $C_{60}F_8$ isomer of the set of 559.

211 kJ mol^{-1} (MNDO) and 112 kJ mol^{-1} (PM3). The energy gaps to the second most stable isomer are 22.0 (AM1), 11.2 (PM3) and 4.0 (MNDO) kJ mol^{-1} respectively.

The reason for the extra stability of this isomer over that of isomer 1 is easy to see: a group of six fluorine atoms take up the experimentally determined[35] pattern of the only $C_{60}Cl_6$ isomer yet isolated, in which the cyclic grouping gives rise to five 1,4 interactions. In fact, if addition of chlorine is limited to 1,2 and 1,4 partnerships, then this is the most thermodynamically stable (AM1) of all possible hexachloro-[60]fullerene isomers;[36] the same pattern is incidentally also predicted by kinetic arguments based on a free-valence/spin-quenching model[37] for bulky addends.

(iv) Compatibility with more highly fluorinated structures

Of the 559 candidates compatible with the NMR spectrum, no fewer than 136 are predicted to be more stable than isomer 1. Before examining these isomers more closely, a brief discussion of the second assumption, A(2), *i.e.* that $C_{60}F_8$ probably lies on the pathway to the $C_{60}F_{18}$ structure (Fig. 4), is given. This 'crown' structure of $C_{60}F_{18}$ consists of a connected set of sp^3 carbon atoms which separate the cage into a benzenoid hexagon and a large non-fluorinated area of 36 sp^2 carbon atoms.

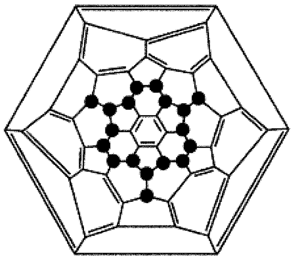


Fig. 4 Structure of $C_{60}F_{18}$.[7]

The implication is that fluorine atoms add once and for all to the cage and do not migrate, and that, under the appropriate conditions, $C_{60}F_{2n}$ (n = 1,8) will fluorinate to give the next species on the path. We have shown in the Introduction that this assumption is not completely valid for hydrogen addition at low levels of coverage. Another area where it may be tested is at higher levels of fluorination, where some structures are reliably known. We have therefore investigated whether any of the published structures for the known species $C_{60}F_{18}$,[7] $C_{60}F_{20}$,[9] $C_{60}F_{36}(T)$,[12] $C_{60}F_{36}(C_3)$,[5] $C_{60}F_{36}(C_3)$,[8] $C_{60}F_{36}(C_1)$,[13] $C_{60}F_{48}(S_6)$[1] and $C_{60}F_{48}(D_3)$[1] are compatible. We have included both suggested structures for the C_3 isomer of $C_{60}F_{36}$. Compatibility in this sense is defined exactly as above: *i.e.* it is the situation where a more highly fluorinated fullerene may be derived from a less highly fluorinated one by the addition of further fluorine atoms anywhere on the cage, assuming that the original fluorine atoms do not migrate. An automated check of compatibility may be made using the vector representation of isomers outlined earlier. If $C_{60}F_A$ is upwardly compatible with $C_{60}F_B$ (A < B), then the scalar product of the vector $\boldsymbol{X}_A$ with one of the 120 images of $\boldsymbol{X}_B$ under the operations of the I_h group is exactly A, *i.e.* all A atoms are on fluorinated sites in $C_{60}F_B$. There are 21 pairs of compounds in the test set; only in one pair is compatibility found—$C_{60}F_{18}$ is compatible with $C_{60}F_{36}$ (T). It is seems that it is the exception rather than the rule to find one fluorinated product directly on the pathway to another.

(v) Isomers on the path to the $C_{60}F_{18}$ crown

It is, however, possible that less highly fluorinated species such as $C_{60}F_8$ are less susceptible to fluorine migration and so it may be useful to examine the concept of a pathway from one lightly fluorinated species to another and to identify the isomeric $C_{60}F_8$ structures that are compatible with $C_{60}F_{18}$. Of the 4 888 isomers that are compatible with the C_s point-group symmetry and have exactly two fluorine atoms in the mirror plane, 56 lie on the path to the crown in the sense that their fluorine atoms correspond in position to some set of eight in the $C_{60}F_{18}$ crown structure. This set of 56 isomers divides into 36 where all fluorine atoms are present in either 1,2 or 1,4 pairwise structures, and 20 isomers which lack any such feature. It is instructive to examine these two sets statistically. The set of 36 has a mean energy of 2 410 kJ mol^{-1}, a standard deviation of 87 kJ mol^{-1}; the most stable isomer has an energy of 2 263 kJ mol^{-1}. For the set of 20 we have a mean energy of 2 543 kJ mol^{-1}, a standard deviation of 123 kJ mol^{-1}, and the most stable isomer has an energy of 2 377 kJ mol^{-1}. Making the null hypothesis that the two samples are drawn from the same population and applying Student's t-test to the difference of the two means gives the highly significant, low probability of the hypothesis being correct of 2.08×10^{-5} (54 degrees of freedom). Essentially this confirms our earlier suggestion that restricting consideration to candidates generated from 1,2 and 1,4 addition gives a class of isomers that is significantly more stable than the general set. The isomer of lowest energy in the group of 20, lies 9 kJ mol^{-1} higher than isomer 1. The structure of the most stable isomer of the set of 36 is given in Fig. 5 (isomer 3).

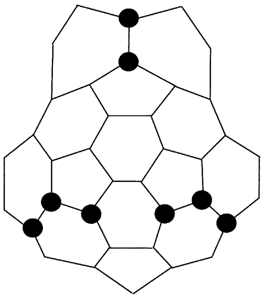


Fig. 5 Isomer 3. Structure of the most stable $C_{60}F_8$ isomer that lies on the 'path to the crown', *i.e.* is compatible with the known structure of $C_{60}F_{18}$.

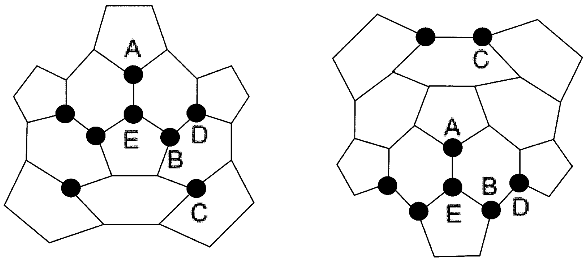
This isomer is 43 kJ mol^{-1} less stable than the best isomer (Fig. 3) but still 105 kJ mol^{-1} more stable than that first proposed[10] (isomer 1, Fig. 1) and does indeed lie on the pathway to $C_{60}F_{18}$. However, since the assumption that a less fluorinated fullerene should lie on the path to a more highly fluorinated one has not been validated, there seems no *a priori* reason to accept any of these 36 isomers on that basis alone.

As a check on our method of generating the isomer structures and also to confirm that the hypotheses[10] of contiguous fluorine atom addition (A(1)) and the existence of a pathway to the crown (A(2)) generate a unique $C_{60}F_8$, we have also calculated the number of possible isomers generated by picking all the different patterns of 8 atoms from the 18 of the $C_{60}F_{18}$ crown structure: there are 7 356. Of these, only 8 have their fluorine atoms connected as a series of *contiguous* atoms and only 3 of these are of C_s point-group symmetry. Of these 3, only one, isomer 1, has the requisite 2 atoms in the mirror plane.

Taylor *et al.*[10] are therefore correct in asserting that there is only one $C_{60}F_8$ isomer with the correct symmetry, on the path to $C_{60}F_{18}$, that has every fluorine atom as part of a 1,2 pair (even though this isomer is obtainable only by invoking a 1,8 final addition (assumption A(3))).

(vi) Evidence from chemical shifts and coupling constants

We may now return to the question of which of our set of 559 isomers is compatible with the ^{19}F NMR spectrum—not only in the number and relative heights of peaks but also in the chemical shifts and couplings. Comparison of the observed parameters for $C_{60}F_8$ with those in Table 1 yields strong evidence for the presence of a fluorine atom with three contiguous fluorine neighbours. Evidence for this sub-structure is the chemical shift of the high-field fluorine atom (E, −153) and the fact that it is coupled to both the low-field fluorine (A, −124.5) and a pair of atoms (B, −134.9) with coupling constants of 27 Hz. The chemical shift is comparable with other fluorine atoms known to be so surrounded, and it is difficult to envisage coupling constants of this magnitude unless the atoms are indeed *vicinal*. Taking this as valid, we may turn our attention to the sub-set of the 559 isomers which have exactly one such structure. There are 114 of these of which 14 are more stable than isomer 1. The two most stable of these isomers are illustrated below (Fig. 6, isomers 4 and 5).



Isomer 4 Isomer 5

Fig. 6 The two most stable (AM1) isomers of the set of 559 that contain exactly one fluorine atom with three vicinal fluorine atom neighbours.

Isomer 4 has energy 2 260 kJ mol^{-1} and isomer 5 has energy 2 284 kJ mol^{-1} (AM1), 108 and 84 kJ mol^{-1} respectively more stable than isomer 1. In addition to the ABE sub-structure, both of these isomers contain the pair of fluorine atoms, corresponding to the signal D, in the identical positions on the fullerene that were previously suggested[10] (isomer 1), giving the T-shaped motif.[25] This T-shaped motif was originally suggested as arising from contiguous addition, but it is clearly also a very thermodynamically stable arrangement for six atoms that are sterically less demanding than chlorine, since the positioning of the three 1,2 fluorine pairs across contiguous Stone–Wales bonds[38] gives rise to two stabilising 1,4 patterns across hexagons. Exactly the same set of interactions arise in the S-shaped motif, the pattern of which accounts for the $C_{60}F_6$ (C_2) structure.[10] Although *vicinal* to B, the B–D coupling constant is only 4 Hz; this may be compared with 2 Hz in $C_{60}F_{18}$, 8 Hz in $C_{60}F_{18}O$ and 30 Hz in $C_{60}F_6$ for the corresponding fluorine atoms; examples of the variability of *vicinal* couplings.

The final question to be answered is with what pattern is the signal C ($\delta = -136.2$, singlet; the other signals are as assigned in isomer 1) consistent? Perhaps the most important fact concerning this peak is that it shows no coupling to fluorine D. This CD coupling is not observable in $C_{60}F_{18}$ (the two corresponding atoms are magnetically equivalent) but in $C_{60}F_{18}O$, with its lower symmetry, the coupling for the corresponding pair of atoms is observed[15] to be 25 Hz. The absence of *any* coupling suggests that it is more consistent with either the isolated 1,4 pair in isomer 4 or the isolated 1,2 pair in isomer 5. Since a difluoro[60]fullerene has been prepared[11] with a chemical shift of −148.3, and assigned as a 1,2 isomer, then perhaps isomer 4, the lower energy species with the 1,4 pair, is indicated. The most stable species, isomer 2, is an unlikely candidate since it lacks the pattern of the T-shaped motif of six fluorine atoms as does isomer 3.

Table 3 Reduction scheme for the candidate isomers of $C_{60}F_8$

Compatible with molecular formula	21 330 558
Compatible with C_s symmetry	10 027
Compatible with NMR intensities	4 888
Compatible with 1,2 and 1,4 pairing	559 (MOPAC full optimisation)
Compatible with motif ABE	114

(vii) Refinement of energies by *ab initio* calculation

The combination of semiempirical calculations and NMR data has reduced the number of likely candidates for the structure of $C_{60}F_8$ to a small number. Of the NMR-compatible structures, isomers 4 and 5 are picked out by AM1 as having low total energies, improving by about 95 kJ mol^{-1} on the literature proposal.[10] Semiempirical energetics alone predict some species to be even more stable than these isomers. However it is interesting to note that more refined calculations of the energetics suggest that the stability of isomer 2 is over-estimated by the AM1 method and hence strengthen the case for isomer 4.

In RHF calculations using the minimal STO-3G basis the total energies (in atomic units) of the optimised structures are: isomer 1, −3028.5819; isomer 2, −3028.6107, isomer 4, −3028.6355 and isomer 5, −3028.6151. Isomer 4 is therefore predicted to be the most stable of this set, ~65 kJ mol^{-1} more stable than the AM1-optimal isomer 2 and ~140 kJ mol^{-1} below isomer 1. Improvement in the basis, to the 6-31G* level, increases the gap between isomers 4 and 2 to ~71 kJ mol^{-1}, and a separation of ~97 kJ mol^{-1} between isomers 4 and 1. Thus isomer 4 is not only NMR compatible but appears to be the most stable isomer of $C_{60}F_8$ at the best available level of calculation. The relative costs of semiempirical and *ab initio* RHF calculations support the strategy of using the former as a coarse filter to produce mangeable sets of structures before application of the more sophisticated techniques.

Conclusion

We have conducted a thorough survey of the possible isomeric structures for the $C_{60}F_8$ molecule, limiting the enormous number of possible species by applying various constraints based both on the observed properties of the isolated compound and calculated energies for various patterns of addition. Our reduction procedure is summarised in Table 3.

If, as seems likely, the structure of the isolated compound depends on its thermodynamic stability, rather than on its mechanism of formation by contiguous addition of fluorine on a pathway leading to the $C_{60}F_{18}$ structure, then we suggest that the most probable species is one of isomers 4 or 5, rather than isomer 1,[10] with isomer 4 complying best with current knowledge of ^{19}F NMR shifts and coupling constants in fluorofullerenes as well as being the most stable at the 6-31G* level of the final restricted set. Isomers 2 and 3, although significantly more stable than isomer 1, are unlikely candidates on the basis of their ^{19}F NMR spectra. The most likely candidate, isomer 4, contains a thermodynamically stable T-shaped pattern of six fluorine atoms, first suggested by Taylor[25] to be a consequence of a mechanism of contiguous addition. All of the possible candidates given by consideration of the available evidence differ only in the placement of two fluorine atoms.

Note: Re-examination of the original ^{19}F NMR spectrum for $C_{60}F_8$ has revealed further couplings that support assignment of the isomer 4 structure to the isolated material.[39]

References

1 A. A. Gakh, A. A. Tuinman, J. L. Adcock, R. A. Sachleben and R. N. Compton, *J. Am. Chem. Soc.*, 1994, **116**, 819.

2 O. V. Boltalina, L. N. Sidorov, V. F. Bagryantsev, V. A. Seredenko, A. S. Zapolsk'ii, J. M. Street and R. Taylor, *J. Chem. Soc., Perkin 2*, 1996, 2275.

3 O. V. Boltalina, A. Ya Borschevskii, L. N. Sidorov, J. M. Street and R. Taylor, *Chem. Commun*, 1996, 529.

4 O. V. Boltalina, V. Yu. Markov, R. Taylor and M. P. Waugh, *Chem. Commun*, 1996, 2549.

5 O. V. Boltalina, M. Bühl, A. Khong, M. Saunders, J. M. Street and R. Taylor, *J. Chem. Soc., Perkin 2*, 1999, 1475.

6 A. G. Avent, O. V. Boltalina, A. Yu. Lukonin, J. M. Street and R. Taylor, *J. Chem. Soc., Perkin 2*, 2000, 1359.

7 I. S. Neretin, K. A. Lyssenko, M. Yu. Antipin, Yu. L. Slovokhotov, O. V. Boltalina, P. A. Troshin, A. Yu. Lukonin, L. N. Sidorov and R. Taylor, *Angew. Chem., Int. Ed. Engl.*, 2000, **39**, 3273.

8 A. A. Gakh and A. A. Tuinman, *Tetatrahedron Lett.*, 2001, **42**, 7133.

9 O. V. Boltalina, V. Y. Markov, P. A. Troshin, A. D. Darwish, J. M. Street and R. Taylor, *Angew. Chem., Int. Ed. Engl.*, 2001, **40**, 787.

10 O. V. Boltalina, A. D. Darwish, J. M. Street, R. Taylor and X-W. Wei, *J. Chem. Soc., Perkin 2*, 2002, 251.

11 O. V. Boltalina, A. Yu. Lukonin, J. M. Street and R. Taylor, *Chem. Commun.*, 2000, 1601.

12 P. B. Hitchcock and R. Taylor, *Chem. Commun.*, 2002, 2078.

13 A. G. Avent, B. W. Clare, P. B. Hitchcock, D. L. Kepert and R. Taylor, *Chem. Commun.*, 2002, 2370.

14 O. V. Boltalina, A. Yu. Lukonin, A. G. Avent, J. M. Street and R. Taylor, *J. Chem. Soc., Perkin 2*, 2000, 683.

15 A. G. Avent, R. Taylor, O. V. Boltalina, A. Yu. Lukonin, B. de la Vaissière, P. W. Fowler and J. M. Street, *Recent Adv. Chem. Phys. Fullerenes Relat. Mater.*, 2000, **7**, 109.

16 A. G. Avent, O. V. Boltalina, P. W. Fowler, A. Yu. Lukonin, V. K. Pavlovich, J. P. B. Sandall, J. M. Street and R. Taylor, *J. Chem. Soc., Perkin 2*, 1998, 1319.

17 O. V. Boltalina, B. de La Vaissière, P. W. Fowler, A. Yu. Lukonin, A. K. Abdul-Sada, J. M. Street and R. Taylor, *J. Chem. Soc., Perkin 2*, 2000, 2212.

18 O. V. Boltalina, B. de La Vaissière, P. W. Fowler, P. B. Hitchcock, J. P. B. Sandall, P. A. Troshin and R. Taylor, *Chem. Commun.*, 2000, 1325.

19 A. G. Avent, A. D. Darwish, D. K. Heimbach, H. W. Kroto, M. F. Meidine, J. P. Parsons, C. Remars, R. Roers, O. Ohashi, R. Taylor and D. R. M. Walton, *J. Chem. Soc., Perkin 2*, 1994, 15.

20 A. D. Darwish, A. G. Avent, R. Taylor and D. R. M. Walton, *J. Chem. Soc., Perkin 2*, 1996, 2051.

21 O. V. Boltalina, P. B. Hitchcock, P. A. Troshin, J. M. Street and R. Taylor, *J. Chem. Soc., Perkin Trans. 2*, 2000, 2410.

22 S. Fujita, *Bull. Chem. Soc. Jpn.*, 1991, **64**, 3215.

23 A. A. Gakh and A. A. Tuinman, *Tetrahedron Lett.*, 2001, **42**, 7137.

24 A. G. Avent and R. Taylor, *Chem. Commun.*, 2002, 2726.

25 R. Taylor, *Lecture Notes on Fullerene Chemistry*; a Handbook for Chemists, Imperial College Press, 1999, p. 43.

26 C. C. Henderson, C. M. Rohlfing, R. A. Assink and P. A. Cahill, *Angew. Chem., Int. Ed. Engl.*, 1994, **33**, 786.

27 W. E. Billups, W. M. Luo, A. Gonzalez, D. Arguello, L. B. Alemany, T. Marriott, M. Saunders, H. A. Jimenez-Vazquez and A. Khong, *Tetrahedron Lett.*, 1997, **38**, 171.

28 P. W. Fowler, J. P. B. Sandall and R. Taylor, *J. Chem. Soc., Perkin Trans. 2*, 1997, 419.

29 *Progress in Nuclear Magnetic Resonance Spectroscopy*, ed. J. W. Emsley, J. Feeney and L. H. Sutcliffe, Pergamon Press, Oxford, 1971.

30 H. Spiesecke and W. G. Schneider, *J. Chem. Phys.*, 1961, **35**, 731.

31 Y. G. Gakh, A. A. Gakh and A. M. Gronenborn, *Magn. Reson. Chem.*, 2000, **38**, 551.

32 S. J. Austin, R. C. Batten, P. W. Fowler, D. B. Redmond and R. Taylor, *J. Chem. Soc., Perkin Trans. 2*, 1993, 1383.

33 B. W. Clare and D. L. Kepert, *J. Mol. Struct. (THEOCHEM)*, 1994, **303**, 1.

34 MOPAC, Microsoft Windows Version, Victor Lobanov, University of Florida, 1996.

35 P. R. Birkett, A. G. Avent, A. D. Darwish, H. W. Kroto, R. Taylor and D. R. M. Walton, *J. Chem. Soc., Chem. Commun.*, 1993, 1230.

36 J. P. B. Sandall and P. W. Fowler, unpublished calculations.

37 K. M. Rogers and P. W. Fowler, *Chem. Commun.*, 1999, 2357.

38 A. J. Stone and D. J. Wales, *Chem. Phys. Lett.*, 1986, **128**, 501.

39 R. Taylor, personal communication.