Structural parallels in hydrogenated and fluorinated [60]- and [70]-fullerenes

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Semi-empirical molecular orbital calculations (MNDO) have been carried out on isomers of $C_{60}X_{36}$ and $C_{70}X_{36}$ (X = H, F) in order to investigate the underlying cause of the parallel behaviour of the two addends towards [60]- and [70]-fullerenes. In both series the driving force for reaction (in addition to C–X bond formation) appears, on the MNDO model, to be relief of steric strain in the fullerene cage, rather than the electronic effects on the carbon framework of the addition of hydrogen and fluorine atoms. The formation of hydrogenated and fluorinated compounds with 36 added atoms from both [60]- and [70]-fullerene appears to be coincidental, arising essentially from the fact that in both cases this number of added atoms is sufficient to maximise the relief of strain in the appropriate cage. While a *T* point-group structure appears significantly more stable than others for $C_{60}F_{36}$, the differences amongst isomers of $C_{60}H_{36}$ are small. The MNDO predicted structures of C_{70}, $C_{70}X_{40}$ (X = H, F) are analysed to determine the major contributions to strain energy.

Introduction

Early evidence[1] that fluorination of [60]fullerene parallels hydrogenation was provided by the greater intensity of peaks for $C_{60}F_{18}$ and $C_{60}F_{36}$ (and their epoxides) in the mass spectrum of the products of treatment of [60]fullerene with fluorine gas. Many studies had previously indicated[2] that $C_{60}H_{18}$ and $C_{60}H_{36}$ are the most stable products of hydrogenation, but, owing to their rapid oxidation, the structures were not elucidated at the time. Further evidence for the stability of $C_{60}F_{18}$ and $C_{60}F_{36}$ was obtained subsequently.[3] Some confirmation of this parallelism between hydrogenation and fluorination has now been obtained through the isolation and characterisation of $C_{60}F_{18}$[4] and partial characterisation of $C_{60}F_{36}$.[5] The former appears to be iso-structural with $C_{60}H_{18}$, which has recently been confirmed[6] to be a crown-shaped molecule of C_{3v} point-group symmetry. This pattern of hydrogenation is a sub-structure of a previously proposed[7] isomer **I** of $C_{60}H_{36}$ which has chiral *T* point group symmetry. The choice of this chiral *T* structure was based mainly on the expectation that its four arene rings would give rise to a high delocalisation energy. Semi-empirical calculations[8] (AM1) have established the relative stability of this structure for $C_{60}H_{36}$ and suggested a second, D_{3d}, close competitor **II** which is predicted to be more stable by 3 kJ mol^{-1} despite its containing only two arene rings. The ^{19}F NMR spectrum of $C_{60}F_{36}$ suggests[5] that one of the three major products does indeed have *T* symmetry. Other structural proposals for $C_{60}H_{36}$ have included[2d] a molecule of S_6 point-group symmetry (with two benzenoid rings, **III**) a D_{3d} isomer (also with two benzenoid rings **IV**); and an early suggestion[2a] of T_h symmetry (completely non-conjugated, **V**). Calculations using a uniform self-consistent method (LDF) on four of these structures (**I**, **III**, **IV**, **V**) have been reported,[9] predicting relative stabilities: *T*, 0.0; S_6, 42; T_h, 203; D_{3d}, 227 kJ mol^{-1}. From these figures it is difficult to argue a strict relationship between the number of arene rings and the stability of the hydrogenated species. Another report[10] has suggested an energy difference (calculated using the BLYP density functional method) of 407 kJ mol^{-1} between the *T* and T_h isomers. While the preliminary assignment[5] of the ^{19}F NMR spectrum of $C_{60}F_{36}$ is inconsistent with the presence of any species with S_6, T_h or D_{3d} point-group symmetries, the pub-

lished spectrum contains nine resonances, other than the three ascribed to the *T* isomer, variously coupled to each other, eight of approximately equal intensity and one with doubled intensity, as well as several minor resonances, so that it is not yet possible to rule out the presence of species of other symmetries.

Interestingly, the addition of 36 hydrogen atoms has also been reported[2c] for [70]fullerene. However, hydrogenation does not stop cleanly at $C_{70}H_{36}$ as with [60]fullerene; $C_{70}H_{38}$ and $C_{70}H_{40}$ are also produced.[5] Calculations (MNDO, AM1, PM3) of the energies of various isomers have shown[11,12] that the principle of increasing aromaticity, which is consistent with the correct structure of $C_{60}H_{18}$ and the *T* structure of $C_{60}H_{36}$, fails altogether for [70]fullerene: aromaticity is negatively correlated with stability. In the MNDO model, a structure with isolated double bonds was ultimately predicted to have much lower energy than any of the previously suggested 'aromatic' species. This semi-empirical approach also predicts that hydrogenation should go on to generate species with 38 and 40 added atoms. Fluorination of [70]fullerene also parallels hydrogenation at least in so far as the stoichiometries $C_{70}F_{36}$, $C_{70}F_{38}$ and $C_{70}F_{40}$ are produced.[5] Since semi-empirical molecular orbital calculations have been used[13] successfully to confirm the relative stability of the experimentally observed[14] isomer of $C_{60}F_{48}$, it appears that the MNDO fluorine parameters, as well as those for hydrogen, may be validly applied in fullerene systems.

The enormous number[15] of theoretically possible isomers and the experimental problems of purification and characterisation of these addition compounds make the study of structure-energy relationships an essential adjunct of any investigation of fullerene chemistry. It is clearly useful at this stage to use present experimental knowledge, sparse though it is, to help calibrate semi-empirical methods for the investigation of possible structures of compounds arising from hydrogen and fluorine addition to fullerenes. The semi-empirical model can be tested to see whether the experimental parallels between hydrogenation and fluorination are replicated in calculation. The use of more sophisticated density functional or *ab initio* methods for these systems (approximately 100 heavy atoms), at a sufficiently high level of theory, will be too expensive for any extensive search of the isomer population. Semi-empirical and *ab initio* (HF/6-31G*) methods agree[16] on the energetics of

Table 1 Energies (kJ mol^{-1}), E_x, of five isomers of C$_{60}$X$_{36}$ (X = H, F) with given symmetries. Drawings of the structures may be found in the references cited in the text. The quoted energies are heats of formation predicted within the MNDO model

Isomer	C$_{60}$H$_{36}$ E_H/kJ mol^{-1}	C$_{60}$F$_{36}$ E_F/kJ mol^{-1}
T **I**	958.3	−3999.4
D_{3d} **II**	944.3	−3920.0
S_6 **III**	958.6	−3872.8
T_h **IV**	974.5	−3837.7
D_{3d} **V**	1105.9	−3600.4

Table 2 Six of the 'aromatic' isomers of C$_{70}$F$_{36}$ that may be generated by pairwise fluorination of some of the formal double bonds of the C$_{70}$ structure. Isomers are identified by $\{n\}$, the set of four defects (unfluorinated double bonds) with respect to the list given in ref. 1(a). G is the point symmetry, E_{HMO} the simple Hückel resonance energy per π electron in units of the bond integral and E_F the heat of formation (kJ mol^{-1}) calculated using MNDO. Isomer **2** is a fluorinated version of structure **I** of ref. 3

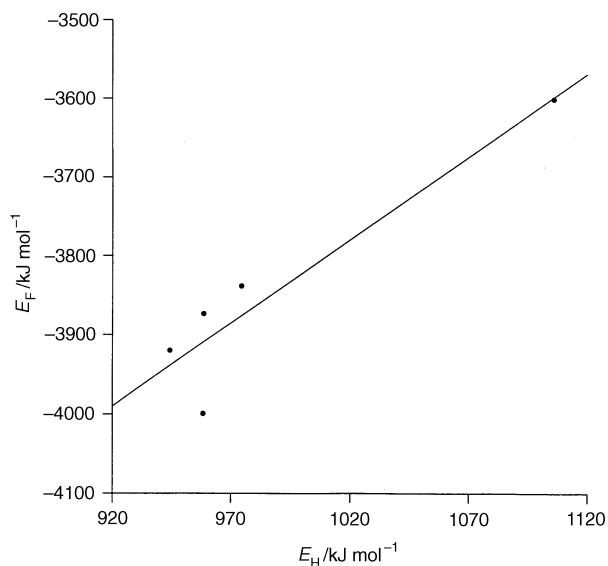| Isomer	$\{n\}$	G	E_{HMO}	$-E_F$/kJ mol^{-1}
1	9,19,28,29	C_s	0.414 76	2425
2	5,6,31,32	C_s	0.413 33	2484
8	11,12,16,17	C_s	0.382 19	2702
12	3,14,16,17	C_s	0.364 92	2705
13	1,2,13,30	C_s	0.351 04	2797
14	11,12,59,60	C_{2v}	0.351 04	2943

Fig. 1 Correlation of MNDO calculated standard heats of formation (E_H and E_F) for corresponding pairs of hydrogenated and fluorinated isomers of C$_{60}$ (see Table 1)
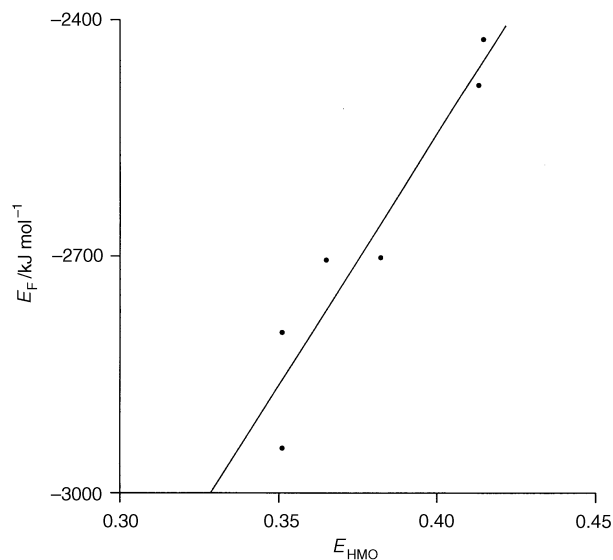

Fig. 2 Anti-correlation of stability of isomers of C$_{70}$F$_{36}$ and nominal π aromaticity. E_F is the total (MNDO) energy and E_{HMO} is the resonance energy as given in Table 2.

addition of two and four atoms of hydrogen to within 20 kJ mol^{-1} for both [60]- and [70]-fullerenes. We have already shown[11,17] that the relative stabilities computed with the MNDO, AM1 and PM3 Hamiltonians are approximately linearly related in similar systems.

Results and discussion

Calculations have been carried out using MOPAC version 6.0 (MNDO parameterisation) on hydrogen and fluorine derivatives of both [60]- and [70]-fullerene.

[60]Fullerene
Table 1 displays the energies (kJ mol^{-1}) of five pairs of isomers of C$_{60}$H$_{36}$ and C$_{60}$F$_{36}$. These were chosen from the ~10^{13} possible isomers on the basis of previous appearance in the literature (see introduction) as structures likely to have low energy. The energies of the corresponding isomers follow a roughly linear trend (see Fig. 1) but the fluorinated derivative of the T structure, with its four intact arene rings, appears to be relatively more stable than its hydrogenated counterpart. The slope of the plot is 2.0, significantly greater than the mean bond enthalpy ratio C–F/C–H (1.06), suggesting that whatever is the major factor for stabilisation in this series (presumably relief of steric strain in the cage) it is more sensitive to fluorine addition than to hydrogen.

The extra stability of the fluoro derivative with T symmetry is somewhat unexpected, since fluorine is overall electron-withdrawing compared to hydrogen and will decrease the electron density in the four arene rings; but in fact the MNDO model predicts that these rings are more closely sixfold symmetric (bond lengths 1.40 ± 0.01 Å) for the fluorine analogue

than for hydrogen (1.40 ± 0.02 Å). Whilst the MNDO stability order for the hydrogenated compounds follows that of the LDF calculations,[9] the correlation is poor. The major difference is that in the MNDO model the T_h structure, with its completely non-conjugated double bonds and even spread of steric strain over the molecule, is stabilised relative to the value expected from the density functional treatment.

[70]Fullerene
Calculations have also been carried out on a series of six C$_{70}$F$_{36}$ isomers chosen to cover the full range of nominal aromaticity investigated in our previous work.[11] To avoid confusion, isomer numbering and definition is taken over from that reference. The results (standard heats of formation, E/kJ mol^{-1} and Hückel energies, E_π/β) are given in Table 2; the essential anti-correlation of these quantities is demonstrated in Fig. 2; this is the same finding as for the hydrogenated species which implies that again the energetics are dominated by steric considerations, i.e. relief of strain in the cage structure. The most stable arrangement according to the MNDO method is that in which the areas of conjugation are minimised, not because 'aromaticity' is not a stabilising factor (albeit an inefficient one in a non-planar system), but rather because it is outweighed by the steric factor: in C$_{70}$ the equatorial area for instance, with its planar hexagons, is a strained system. This is confirmed[18] by the relatively favourable energy of addition of two hydrogen atoms 1:4 across an equatorial hexagon. That strain rather than 'aromaticity' dominates the total energy in the MNDO model is shown clearly by isomers **13** and **14** which are identical in terms of 'aromatic

Table 3 Bond lengths (Å) for the eight different C–C bonds in the $D_{5h}C_{70}$ cages (C_{70} itself, $C_{70}H_{40}$ and $C_{70}F_{40}$)

Bond	Type	C_{70}	$C_{70}H_{40}$	$C_{70}F_{40}$
a–a'	5 : 6	1.47	1.57	1.65
a–b	6 : 6	1.40	1.56	1.63
b–c	5 : 6	1.47	1.51	1.54
c–c'	6 : 6	1.39	1.34	1.33
c–d	5 : 6	1.48	1.52	1.55
d–d'	5 : 6	1.44	1.57	1.63
d–e	6 : 6	1.43	1.52	1.55
e–e'	6 : 6	1.48	1.37	1.36

−3592 kJ mol⁻¹

−3434 kJ mol⁻¹

Fig. 4 Two low-energy isomers generated by nominal defluorination of $C_{70}F_{40}$ (isomer **B**). Energies (kJ mol⁻¹) are the heats of formation calculated by MNDO.

1   2

8   12
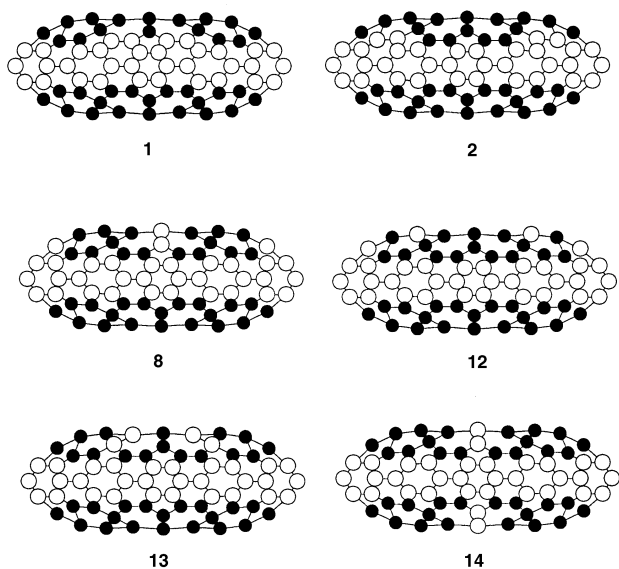

13   14

Fig. 3 Six of the 16 possible isomers reachable by successive fluorination of 18 of the 20 'Stone–Wales' double bonds in C_{70}.[11] Isomers were chosen to cover the widest possible range of nominal (Hückel) aromaticity, consonant with high symmetry.

Fig. 5 Relationship between the energies (kJ mol⁻¹) calculated by MNDO, for isostructural fluorinated (E_F) and hydrogenated (E_H) $C_{70}X_{36}$ cages

character' (the central penta-phenylene belt) but whose calculated standard heats of formation differ by nearly 150 kJ mol⁻¹. The structures are illustrated in Fig. 3.

The parallel between the total energy-delocalisation energy relationships of corresponding hydrogen and fluorine isomers is thus far reasonable. Clearly, hydrogen and fluorine at this level of modelling have similar structural and energetic effects in spite of their markedly different electronic effects.

Is it then possible to extend the analogy further and to use our previous approach to find a good candidate for the most stable isomer of $C_{70}F_{36}$? The most stable hydrogenated species was found[11] by rejecting preconceived ideas and looking at three highly symmetrical isomers of $C_{70}H_{40}$ with extremely different patterns of substitution. By far the most stable was the one in which there is no conjugation whatsoever. The complete localisation of all the double bonds in this isomer is effectively a consequence of an arrangement of hydrogen atoms that gives rise to the most even distribution of steric strain. We have investigated the same three structures (**A**–**C** in ref. 11) substituting fluorine for hydrogen. The energies of these three isomers of $C_{70}F_{36}$ are -2950, -3900 and -3562 kJ mol⁻¹, respectively. Again we observe the marked stability of **B** with 20 isolated double bonds. Modification of this structure by removing variously four fluorine atoms gives rise to a large series of isomers all of which are likely to be more stable than the 'aromatic' isomers listed previously. Two examples are given in Fig. 4, with energies of -3434 and -3592 kJ mol⁻¹, both much more stable than the best isomer of Table 2, **14**, which has energy -2943 kJ mol⁻¹. Fig. 5 shows a strong correlation in energy between isostructural examples of $C_{70}X_{36}$ cages where X = H and F. Note that the slope of this plot (~2.4) is again much greater than the
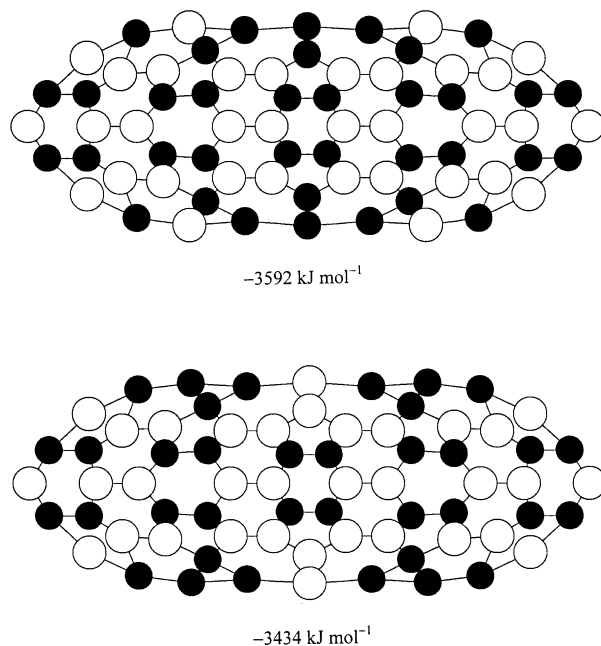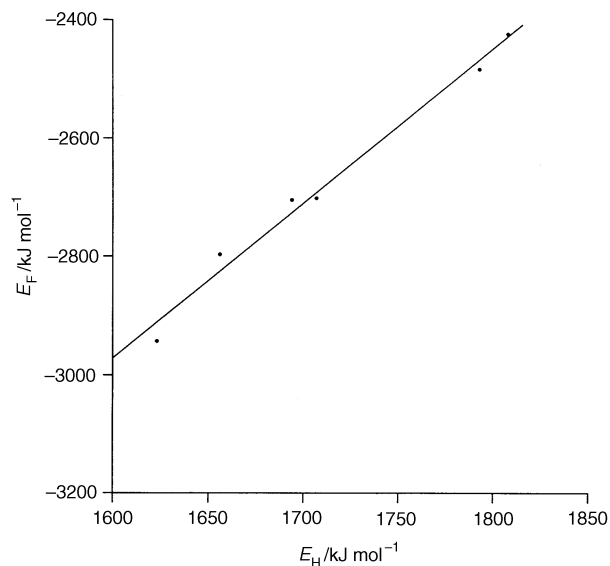
ratio of typical C–F and C–H bond energies and even higher than the corresponding figure in the [60]fullerene derivatives. This implies first that the relief of steric strain in the cage is more marked with fluorination than with hydrogenation and second, that the reduction in steric strain is more marked for [70]fullerene than for [60]fullerene, which in turn suggests the importance of reduction in strain in the equatorial area, unique to [70]fullerene.

It is tempting to look for the explanation of this much greater relief of strain in terms of the structural parameters calculated by MNDO. This is possible for the high symmetry D_{5h} isomers. The simplest approach is to compare the eight different C–C bond lengths (Å) in each of the D_{5h} structures C_{70}, $C_{70}H_{40}$ **B** and $C_{70}F_{40}$ **B** (Table 3). The three symmetry distinct C–H bond lengths are calculated to be equal (1.12 Å) as are the three C–F lengths (1.35 Å). Examination of the carbon–carbon bond lengths in Table 3 for the parent fullerene shows the expected

Table 4 Calculated and ideal bond and torsion angles in D_{5h} C_{70}, $C_{70}H_{40}$ and $C_{70}F_{40}$

Bond angles	C_{70} Calculated	C_{70} Strain-free	$C_{70}H_{40}$ Calculated	$C_{70}F_{40}$ Calculated	$C_{70}X_{40}$ Strain-free
a,a′,a″	108.0	120.0	108.0	108.0	109.5
b,c,d	108.5	120.0	111.7	111.5	120.0
c,b,c′	106.9	120.0	98.6	96.2	109.5
c,d,d′	108.1	120.0	103.8	102.2	109.5
Torsion angles					
a,a′,a″,b	38.4	0.0	42.3	45.5	60.0
a,a′,b,c	43.0	0.0	55.0	58.5	60.0
a,b,c,d	37.2	0.0	22.7	17.3	—
b,c,c′,d	42.0	0.0	15.0	8.0	0.0
c,d,d′,e	32.5	0.0	57.5	61.5	60.0
d,e,e′,d[a]	30.5	0.0	0.0	6.6	0.0

[a] Atom beyond 'equator' with reference to previous three atoms.
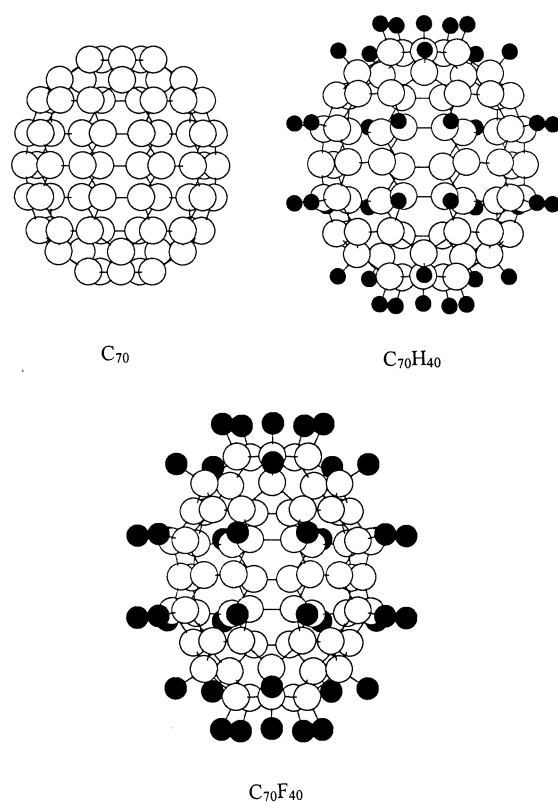
C_{70} $C_{70}H_{40}$

$C_{70}F_{40}$

Fig. 6 MNDO optimal structures (drawn to scale) for C_{70}, $C_{70}H_{40}$ and $C_{70}F_{40}$

variation with type, *i.e.* bonds at pentagon–hexagon junctions are generally longer than those at hexagon–hexagon junctions; the only anomaly is the e–e′ bond which is rather longer (by 0.05 Å) than the calculated (MNDO) value for the central bond in pyrene, presumably in partial compensation for strain. On hydrogenation, there are obvious changes: C–C bonds where both carbon atoms are now sp³ hybridised (a–a′, a–b, d–d′) achieve the normal single bond length and the bonds where the enforced bond order is two shorten to values close to a typical double bond length. On fluorination, the effects are even more marked, the typical single bond length increasing to about 1.64 Å (close to the C–C distance in hexafluoroethane) and the fixed double bonds (c–c′ and e–e′) decreasing in length to the usual value of about 1.34 Å. Clearly, in the fluorinated cage structure, the approach of the bond lengths to their normal values suggests lower strain. The major source of strain energy in a cage structure is, however, bond angle distortion and torsion angle distortion. Complete analysis of these parameters is difficult since an objective assessment of the normal values is not easy in systems with both sp² and sp³ carbon atoms. We

have, however, listed in Table 4 those calculated bond and torsion angles (°) that are most obviously highly strained in the parent C_{70} cage, together with the corresponding expected values for carbon atoms with the same nominal hybridisation in a locally strain-free situation. Also listed are the new values after hydrogenation and fluorination again, where possible, with their expected normal values.

The most obvious sources of strain in the parent fullerene are the enforced pentagonal bond angles of sp² hybridised carbon atoms and the torsion angles of ~37° in the non-planar fused ring systems. In the derivatives the new bond angles approach the ideal more closely, varying from it in some cases by only one or two degrees, and never more than ten. This improvement is even more marked for the torsion angles, which now lie much closer to the strain-free value, the average deviation falling from 37° to 8.0° for the hydrogenated compound and 4.4° for the fluorinated product. It is perhaps this that is the major factor in the stabilisation. It also may be noted that for both hydrogen and fluorine, the typical H–H (2.11, 2.11, 2.29 Å) and F–F (2.35, 2.36, 2.59 Å) distances for atoms attached to contiguous carbons are a little smaller than the sum of their Van der Waals' radii (2.40 and 2.70 Å, respectively). This suggests some residual repulsive effect between the attached atoms, but this should not be large, since 1,2 is favoured over 1,4 addition for both addends.

The structures calculated for the three species are illustrated in Fig. 6 where the marked elongation of the molecule on addition may be observed. The pole-to-pole carbon–carbon distances are 8.39, 9.09 and 9.50 Å for the three cage structures; there is a corresponding narrowing across the equator where the diameters fall (7.16, 6.86 and 6.83 Å).

We may conclude then that, at least on the MNDO model, patterns of addition of H and F are very similar in C_{70} and that, just as with hydrogen, we would expect on this model that fluorination would not stop at exactly 36 added atoms—species with 38 and 40 atoms should be more stable still. The driving force for the reaction, over and above C–X bond formation, seems to be the release of steric strain in the fullerene cage. This factor may account for the very different patterns of addition for C_{60} and C_{70}; the latter species is unique in possessing the equatorial pentaphenylene belt which constitutes a region of greater strain. For [60]fullerene the stability, on the MNDO model, of the *T* isomer is much more marked for fluorine substitution than for hydrogen; but the formation of a mixture of species in fluorination experiments does imply that other structures must be considered. It is possible of course that the stability of the *T* structure arises particularly from the near planarity achievable by the four arene rings, rather than from considerations of aromaticity; the relatively greater stability of the fluorinated structure favours this interpretation. The MNDO calculated energies for hydrogenation lie much closer together than for fluorination and choice of a particular structure here

may be premature. Finally, it is worth noting that the MNDO model gives a relatively high stabilisation energy to the non-conjugated isomer **IV** of $C_{60}H_{36}$ compared with the LDF model. It may be that this bias is also present in calculations on the [70]fullerene compounds, and that **B** would appear as relatively less stable in the LDF model. The parallel demonstrated between hydrogenated and fluorinated fullerene derivatives is however likely to remain a useful tool in exploration of the complex structural problems posed by these compounds.

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