PERKIN 2

Aromaticity of [60]fullerene derivatives ($C_{60}X_n$, X = H, F; n = 18, 36) constrained to have planar hexagonal rings

Samantha Jenkins, Malcolm I. Heggie and Roger Taylor *

The Chemistry Laboratory, CPES School, Sussex University, Brighton, UK BN1 9QJ

Received (in Cambridge, UK) 22nd August 2000, Accepted 12th October 2000

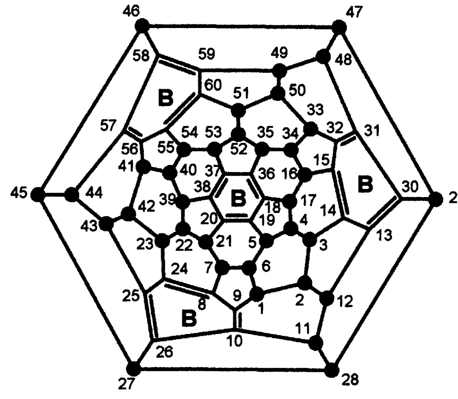
Density functional calculations accurately reproduce the known bond lengths for $C_{60}F_{18}$, shown recently (single crystal X-ray structure) to possess a fully aromatic hexagonal ring, and they correctly predict the planarity of this ring. Isostructural $C_{60}H_{18}$ is also calculated to have an aromatic benzenoid hexagonal ring, and to be marginally less planar. The four benzenoid hexagonal rings of T symmetry $C_{60}H_{36}$ and $C_{60}F_{36}$, and the three benzenoid rings of C_3 symmetry $C_{60}H_{36}$ and $C_{60}F_{36}$ are predicted to be aromatic, with both the T symmetry and the fluorinated species again having the slightly shorter bond lengths and the greater planarity; by these measures T-$C_{60}F_{36}$ is as aromatic as $C_{60}F_{18}$. In another C_{3v} isomer of $C_{60}H_{18}$, which had been predicted (AM1) to be thermodynamically more stable than the known isomer, density functional calculations show the central benzenoid ring to have slightly greater bond alternation, greater bond lengths, to be less planar and the molecule to be overall less stable than the known isomer; this is attributed to the greater strain in the three adjacent pentagonal rings. Sites for ether formation are conjectured based on the recent finding that oxygen inserts into long FC–CF bonds of fluorofullerenes.

Introduction

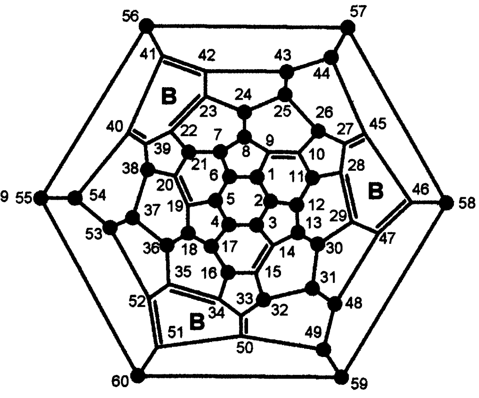
Fullerenes are relatively non-aromatic because of poor overlap of adjacent p-orbitals due to curvature[1] and because delocalisation in any given hexagon requires location of double bonds in the pentagons; this bond-shortening increases strain in the pentagons (Mills–Nixon effect) and is energetically unfavourable.[2] Thus [60]fullerene is comprised of sixty bonds of *ca.* 1.45 Å length and thirty bonds of *ca.* 1.40 Å length.[3] This strain is diminished if the hybridisation of any of the three carbons in the pentagonal ring adjacent to a given hexagon and *exo* to it is changed from sp^2 to sp^3. Thus it was predicted that the isolated isomer of $C_{60}H_{36}$ would have T symmetry (**1**, ● = H)[4] the underlying reason being that it should have four fully-delocalised benzenoid rings.[5] Calculations predicted that a C_3 symmetry isomer (**2**, ● = H) should also be stable,[6] and the symmetry of both these and the isostructural fluoro compounds have been characterised through the use of ^3He and ^{19}F NMR spectroscopy.[7]

Although simple models predict the planarity (and by implication the aromaticity) of the benzenoid rings of the T and C_3 isomers (labelled B in **1** and **2**) no bonding information has been available. In both **1** and **2** the benzenoid rings are created by the presence of six exocyclic sp^3-hybridised carbons which reduce strain in the adjacent pentagons so that these can then accommodate the bond-shortening necessary for delocalisation.

Experimental data have shown that compounds $C_{60}X_{18}$ (**3**, X = H, F) are isostructural and have a benzenoid ring central to the crown structure.[8] The *precise* structure of $C_{60}F_{18}$ has been determined very recently by single crystal X-ray studies (Fig. 1), which have revealed that the central ring is both planar and fully aromatic, having all bond lengths equal.[9] It was of interest therefore to determine: (a) if high-level calculations can predict accurately the cage bond lengths and benzenoid ring planarity in $C_{60}F_{18}$. (b) If there are predicted differences in structure between $C_{60}F_{18}$ and $C_{60}H_{18}$. (c) If, based on planarity and bond-length variation in the benzenoid rings, and assuming those in (a) are successful, the calculations predict the T and C_3 isomers of $C_{60}H_{36}$ and $C_{60}F_{36}$ to be aromatic. (d) What is the calculated degree of aromaticity for an alternative $C_{60}H_{18}$ structure **4**, which is predicted (AM1)[10] to be of lower energy (by 17.6 kcal mol^{-1}) than **3**? Structure **4** has not been isolated because hydrogenation (and fluorination) proceed *via* stepwise addition

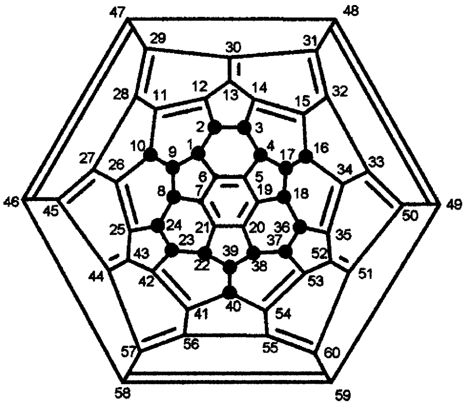


1, ● = H, F

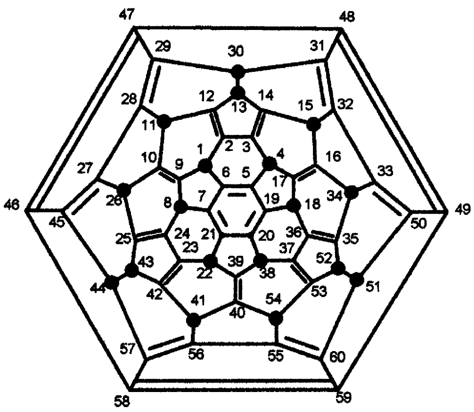


2, ● = H, F

DOI: 10.1039/b006858f



3, ● = H, F



4, ● = H

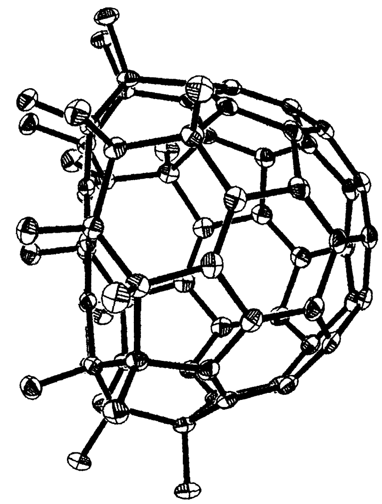


Fig. 1 Single crystal X-ray structure for $C_{60}F_{18}$.

dictated by localisation of adjacent double bonds following a first addition,[11] a process impossible for **4**.

Experimental

Calculation method

The calculations were made employing AIMPRO, a self-consistent density functional code running at local spin density approximation (LSDA) level.[12] Norm-conserving pseudopotentials[13] were used except for hydrogen. Molecular wave functions consist of n s, and m p_x, p_y and p_z symmetry Gaussian functions; the valence charge density is modelled by m s-functions. The values of (n,m) used here are C(4,4), F(5,5) and H(3,4). The calculations employed bond-centred orbitals, and structural optimisation to negligible forces was obtained by the conjugate gradient algorithm.

Planarity of the benzenoid rings

To further assess the aromaticity of the central benzenoid ring, the inversion or out-of-plane angle was measured. A value of 180° or 0° refers to a perfectly flat ring. To ascertain the planarity, four atoms were selected, *e.g.* C53, C35, C5 and C19 in **1**; this process was continued with six measurements being made all round the benzenoid ring.

$C_{60}F_{18}$. The carbon atoms employed were: 1,4,21,22; 1,6,18,38; 1,8,20,38; 4,5,22,38; 4,7,8,18; 8,18,19,22, giving an average angle of 179.7°.

$C_{60}H_{18}$. Using the same carbon atoms as for the fluorinated compound gave an average angle of 176.8°.

$C_{60}F_{36}$ (*T*). Here there are four equivalent rings, so that using for one ring the atoms: 1,7,25,43; 1,9,27,43; 1,11,23,24; 7,23,26,27; 10,11,23,43, and likewise for the others, gave an overall average inversion angle of 179.2°.

$C_{60}H_{36}$ (*T*). Using the same carbon atoms as for the fluoro analogue gave an overall average inversion angle of 176.5°.

$C_{60}F_{36}$ (C_3). The carbon atoms employed for a given benzenoid ring are 11,26,47,48; 11,28,44,58; 11,30,46,58; 26,27,48,58; 26,29,30,44; 30,44,45,48. Here the deviations from planarity show greater variation according to the four atoms chosen, ranging from 175.6 to 178.5°, the overall average value being 176.15°.

$C_{60}H_{36}$ (C_3). The atoms are used as for the fluorinated analogue, the deviations from planarity similarly showing a wider variation (from 174.0–175.5°) than in the corresponding *T* isomer, the overall average being 175.0°.

$C_{60}H_{18}$ isomer 4. Just as the calculated bond lengths indicate that the central hexagonal ring in this isomer is less aromatic, so this is confirmed by the inversion angle calculated to be 172.1°, compared to 176.8° for isomer **3**.

Results and discussion

The bond lengths in $C_{60}F_{18}$ 3

The observed[9] and calculated bond lengths are given in Table 1. Note that there are three equivalent bonds lying along or bisected by the symmetry planes and six equivalent bonds, which lie either side of the symmetry plane. In each case the symmetry-averaged values are given, the lowest bond numbers for equivalent bonds being shown.

There is excellent agreement between the observed and calculated bond lengths, the calculations tending to slightly underestimate the lengths by an average of 0.8%. They also accurately reproduce the bond length equivalence in the central benzenoid ring. Moreover, the benzenoid ring is calculated to have insignificant deviation from planarity (inversion angle of 179.7°) which is in complete accord with the X-ray structure,[9] and further emphasises its fully aromatic nature.

Given this result we may use the calculations with confidence in elucidating answers to (b)–(d) above.

Differences between calculated bond lengths in $C_{60}H_{18}$ and $C_{60}F_{18}$ 3

The calculated bond lengths for $C_{60}H_{18}$ are given in Table 2 together with the differences from the values calculated for $C_{60}F_{18}$. The calculated structure is given in Fig. 2.

Table 1 Observed and calculated bond lengths[a] (Å) for $C_{60}F_{18}$ **3**

Bond[b]	No. of bonds	Observed	Calculated	Obs. − calc.
1,2	6	1.557	1.556	0.001
1,6	6	1.476	1.455	0.019
1,9	6	1.623	1.628	−0.005
2,3	3	1.672	1.675	−0.003
2,12	6	1.500	1.479	0.021
5,6	3	1.372	1.357	0.015
5,19	3	1.373	1.364	0.009
9,10	3	1.558	1.549	0.009
10,11	6	1.524	1.505	0.019
11,12	6	1.363	1.359	0.004
11,28	6	1.435	1.422	0.011
12,13	6	1.428	1.418	0.010
13,30	3	1.386	1.384	0.002
27,28	3	1.438	1.430	0.008
27,45	6	1.386	1.381	0.005
29,30	6	1.435	1.418	0.017
29,47	6	1.452	1.435	0.027
46,47	3	1.388	1.388	0
46,58	3	1.447	1.426	0.021

[a] Average values for symmetry-equivalent bonds. [b] Lowest locant number for symmetry-equivalent bonds.

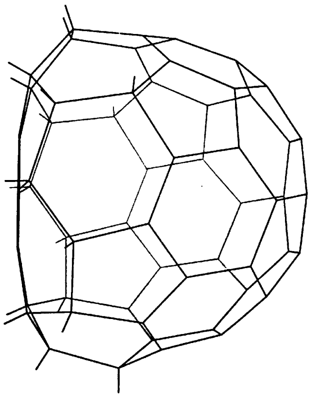


Fig. 2 Calculated structure for $C_{60}H_{18}$.

Table 2 Calculated bond lengths[a] (Å) for $C_{60}H_{18}$ and the differences from those for $C_{60}F_{18}$

Bond[b]	No. of bonds	Calculated	$C_{60}H_{18} - C_{60}F_{18}$
1,2	6	1.571	0.015
1,6	6	1.479	0.024
1,9	6	1.603	−0.025
2,3	3	1.630	−0.045
2,12	6	1.502	0.023
5,6	3	1.370	0.013
5,19	3	1.378	0.014
9,10	3	1.558	0.009
10,11	6	1.517	0.012
11,12	6	1.364	0.005
11,28	6	1.424	0.002
12,13	6	1.419	0.001
13,30	3	1.389	0.005
27,28	3	1.424	0.002
27,45	6	1.387	0.006
29,30	6	1.420	0.002
29,47	6	1.433	−0.002
46,47	3	1.390	0.002
46,58	3	1.430	0.004

[a] Average values for symmetry-equivalent bonds. [b] Lowest locant number for symmetry-equivalent bonds.

Table 3 Calculated bond lengths[a] (Å) in *T* symmetry $C_{60}H_{36}$ and $C_{60}F_{36}$

Bond[b]	No. of bonds	$C_{60}H_{36}$	$C_{60}F_{36}$	$C_{60}H_{36} - C_{60}F_{36}$
1,2	12	1.571	1.545	0.026
1,9	12	1.483	1.459	0.024
2,3	12	1.583	1.586	−0.003
2,12	12	1.625	1.690	−0.065
3,14	12	1.477	1.456	0.021
7,21	6	1.570	1.542	0.028
8,9	12	1.378	1.351	0.027
9,10	12	1.370	1.359	0.011

[a] Average values for symmetry-equivalent bonds. [b] Lowest locant number for symmetry-equivalent bonds.

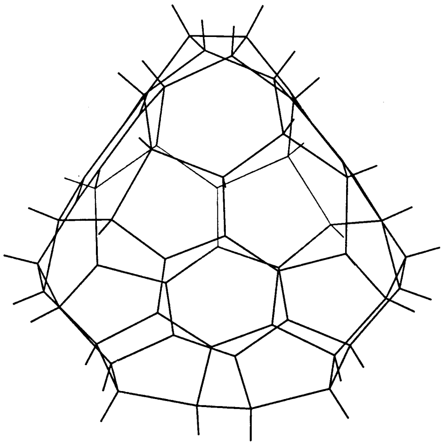


Fig. 3 Calculated structure for *T*-$C_{60}F_{36}$.

Points which emerge from these data are: (i) the bond lengths in the central hexagonal ring are very similar, showing that this ring too is aromatic. The bonds in this ring are *ca.* 2% longer than the corresponding ones in $C_{60}F_{18}$ which may reflect a compression effect (eclipsing strain) by the surrounding fluorines in the latter [see also (ii) and (iii)]. (ii) The 1,9- and 2,3-bonds are significantly shorter than in $C_{60}F_{18}$, attributable to compression between adjacent fluorines lengthening the bonds in the latter. This lengthening is for example responsible for facilitating oxygen insertion into the FC–CF bonds to form oxahomofullerenes.[14] (iii) Conversely, bonds (1,6, 2,12 and 10,11) between the compressed and other regions of the cage are longer in $C_{60}H_{18}$ because of the reduced compression in the addended region. (iv) On the side of the cage most remote from the addends, differences in the cage structure between the two derivatives are not significant. (v) The inversion angle 176.8° shows this compound to be slightly less aromatic than the fluorinated equivalent, even though the 'long'–'short' bond-length differences are calculated to be similar for each.

Calculated bond lengths for *T*-$C_{60}F_{36}$ and -$C_{60}H_{36}$

There are eight symmetry-equivalent C–C bonds in these *T* structures and these are shown for both the H- and F-compounds in Table 3. They demonstrate the following: (i) the bonds in the benzenoid rings for both compounds are predicted to be essentially identical in length, and also of the same lengths as those in the corresponding $C_{60}X_{18}$ compounds. Thus these rings are aromatic as was predicted earlier.[5] (ii) The 1,2-, 1,9-, 3,14-, and 7,21-bonds are all calculated to be longer in $C_{60}H_{36}$ (by an average of 0.025 Å) whereas the 2,12-bond is shorter in $C_{60}H_{36}$ (by 0.065 Å). These variations must arise from compression differences, though in a less evident way than for the $C_{60}X_{18}$ compounds. (iii) The inversion angle of 179.2° for *T*-$C_{60}F_{36}$ shows the benzenoid rings to be marginally less planar than the single ring in $C_{60}F_{18}$ in agreement with the prediction from bond lengths in these rings in each compound. Fig. 3 shows the calculated structure for the F-compound, which emphasises the distortion in structure from that of the parent [60]fullerene cage. (iv) The inversion angle of 176.5° for *T*-$C_{60}H_{36}$ shows that there is a greater deviation from planarity than is found with the

Table 4 Calculated bond lengths[a] (Å) in C_3 symmetry $C_{60}H_{36}$ and $C_{60}F_{36}$

Bond[b]	$C_{60}H_{36}$	$C_{60}F_{36}$	$C_{60}H_{18} - C_{60}F_{18}$	Bond[a]	$C_{60}H_{36}$	$C_{60}F_{36}$	$C_{60}H_{18} - C_{60}F_{18}$
1,2	1.564	1.564	0	23,42	1.384	1.365	0.019
1,6	1.566	1.573	−0.007	24,25	1.591	1.601	0.010
1,9	1.490	1.478	0.012	25,26	1.552	1.546	0.006
2,12	1.592	1.632	0.040	25,43	1.614	1.667	−0.053
7,8	1.590	1.605	−0.015	26,27	1.497	1.475	0.022
7,21	1.559	1.561	−0.002	42,43	1.479	1.452	0.027
8,9	1.486	1.469	0.017	27,45	1.368	1.360	0.008
8,24	1.572	1.569	0.003	40,41	1.383	1.369	0.014
9,10	1.319	1.314	0.005	40,54	1.483	1.460	0.023
10,11	1.507	1.498	0.009	41,42	1.370	1.358	0.012
10,26	1.514	1.516	−0.002	41,56	1.484	1.459	0.025
11,28	1.496	1.474	0.022	43,44	1.572	1.556	0.016
22,23	1.364	1.348	0.016	44,57	1.619	1.686	−0.067
22,39	1.390	1.384	0.006	55,56	1.583	1.582	0.001
23,24	1.483	1.450	0.033	56,57	1.567	1.547	0.020

[a] Average values for symmetry-equivalent bonds (three in each case). [b] Lowest locant number for symmetry-equivalent bonds.

Table 5 Calculated bond lengths[a] (Å) for $C_{60}H_{18}$ **4**

Bond[b]	No. of bonds	Calculated	Bond[b]	No. of bonds	Calculated
1,2	6	1.494	11,28	6	1.520
1,6	6	1.512	12,13	6	1.513
1,9	6	1.520	13,30	3	1.545
2,3	3	1.452	27,28	3	1.414
2,12	6	1.343	27,45	6	1.372
5,6	3	1.380	29,30	6	1.519
5,19	3	1.392	29,47	6	1.406
9,10	3	1.331	46,47	3	1.386
10,11	6	1.529	46,58	3	1.432
11,12	6	1.502			

[a] Average values for symmetry-equivalent bonds. [b] Lowest locant number for symmetry-equivalent bonds.

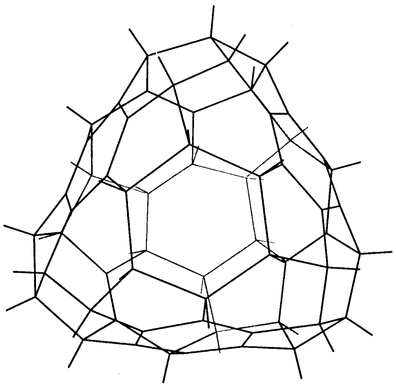


Fig. 4 Calculated structure for C_3-$C_{60}F_{36}$.

fluoro analogue, the planarity difference between the two compounds being 2.7°. This parallels the difference (2.85°) between $C_{60}F_{18}$ and $C_{60}H_{18}$.

Calculated bond lengths for C_3-$C_{60}F_{36}$ and -$C_{60}H_{36}$

These are given in Table 4, and show: (i) in the three benzenoid rings there is slightly greater bond alternation than for the *T* isomer. Thus for $C_{60}H_{36}$ the average lengths of the 'double' and 'single' bonds are 1.367 and 1.385 Å respectively, and for $C_{60}F_{36}$ they are 1.355 and 1.373 Å; again the bond lengths are shorter for the fluoro compound. The calculated bond length differences are 0.0018 Å in each case, and although these are *ca.* twice that calculated for the *T* isomer and for $C_{60}X_{18}$, these rings are essentially aromatic. (ii) As in the case of the *T* isomer, a number of bonds are significantly longer in C_3-$C_{60}F_{36}$ compared to C_3-$C_{60}H_{36}$ whereas others are shorter, attributable to differences in eclipsing strain in the two molecules. (iii) A significant feature is the short isolated 9,10 double bond (*ca.* 1.315 Å) which is shorter than a 'double bond' in [60]fullerene (1.40 Å) and even of a double bond in ethene (1.34 Å). (Using a range of basis functions in AIMPRO calculations we obtain a value of 1.32–1.33 Å for ethene.) A similar bond in the alternative isomer for $C_{60}H_{18}$ (below) is also very short. (iv) The inversion angle of 176.15° for C_3-$C_{60}F_{36}$ indicates that the benzenoid rings here are less aromatic than those in the corresponding *T* isomer. The same pattern is found with C_3-$C_{60}H_{36}$ where the inversion angle is 175.0°. Thus these results show that (a) the fluorinated compounds are the more aromatic, and (b) the *T* isomers are more aromatic than the corresponding C_3 isomers.

The calculated structure for C_3-$C_{60}F_{36}$ (Fig. 4) shows, as in the case of the corresponding *T* structure, the severely distorted [60]fullerene cage.

Calculated bond lengths for $C_{60}H_{18}$ 4

These bond lengths (Table 5) show the central benzenoid ring to be aromatic. However, the bond length differences in this ring (0.012 Å) are slightly greater than that (0.008 Å) for the alternative isomer **3**, which is consistent with the anticipated slightly greater strain in the three adjacent pentagons, causing delocalisation to be more restricted. The lower aromaticity of this ring is confirmed by the inversion angle of 172.1° compared to 176.8° for isomer **3**, and indeed our calculations show **4** to be less stable than **3** by 61.7 kcal mol^{-1}, which provides a further reason (see Introduction) for its failure to be isolated.

The 9,10 double bond is notably short (1.33 Å) *cf.* the C_3 isomer of $C_{60}X_{36}$.

Probable sites for ether formation

It has been shown recently that oxygen insertion, to give an ether, takes place readily in fluorinated $C_{60}F_{18}$ between the longest C–C bonds, this insertion being attributed to the weakness of these bonds.[14] Thus insertion takes place into the 1,2-, 1.9-, and 2,3-bonds, which have a calculated length of 1.556 Å or greater.

Given this, sites of possible ether formation in $C_{60}F_{36}$ to give $C_{60}F_{36}O$ can be conjectured. Many oxide derivatives from fluorinated [60]fullerene are evidently epoxides produced from nucleophilic substitution–elimination,[15] but recent work shows that ethers are also present.[14] For the *T* isomer, both the 2,3- and 2,12-bonds (and their equivalents) are longer than 1.55 Å. The latter bond is predicted to be longer even than the very long 2,3-bond in $C_{60}F_{18}$ and so must be considered a likely site for oxygen insertion. For the C_3 isomer, the 1,2-, 1,6-, 2,12-, 7,8-, 7,21-, 8,24-, 24,25-, 25,43-, 43,44-, 44,57-, and 55,56-bonds (and their equivalents) are each calculated to be longer than 1.55 Å, and so are also likely oxygen-insertion sites. This number makes it likely that isolation of specific derivatives will be very difficult, although that arising from insertion into the 25,43-bond (corresponding to the 2,12-bond for the *T* isomer) is likely to be present in highest yield.

Conclusion

Calculations correctly predict the structure and aromatic nature of $C_{60}F_{18}$, and show that $C_{60}H_{18}$, and both *T*- and C_3-$C_{60}X_{36}$ ($X = H$, F) contain essentially planar aromatic rings. The fluorinated compounds are more aromatic than their hydrogenated counterparts, and the aromaticity decreases slightly along the series; $C_{60}X_{18} > T\text{-}C_{60}X_{36} > C_3\text{-}C_{60}X_{36}$. Some exceptionally long FC–CF bonds indicate probable sites for oxygen insertion to give ethers.

References

1 R. C. Haddon, L. E. Brus and K. Raghavachari, *Chem. Phys. Lett.*, 1986, **131**, 165.

2 R. Taylor, *Tetrahedron Lett.*, 1991, 3731.

3 C. S. Yannoni, P. P. Bernier, D. S. Bethune, G. Meijer and J. R. Salem, *J. Am. Chem. Soc.*, 1991, **113**, 437; W. I. F. David, R. M. Ibberson, J. C. Matthewman, K. Prassides, T. J. Dennis, J. P. Hare, H. W. Kroto, R. Taylor and D. R. M. Walton, *Nature*, 1991, **353**, 156; K. Hedberg, L. Hedberg, D. S. Bethune, C. A. Brown, H. C. Dorn, R. J. Johnson and M. de Vries, *Science*, 1991, **254**, 410.

4 S. J. Austin, S. C. Batten, P. W. Fowler, D. B. Redmond and R. Taylor, *J. Chem. Soc.*, *Perkin Trans. 2*, 1993, 1383; A. Rathna and J. Chandrasekhar, *Chem. Phys. Lett.*, 1993, **206**, 217; B. I. Dunlap, D. W. Bremner and G. W. Schriver, *J. Phys. Chem.*, 1994, **98**, 1756; L. D. Bock and G. E. Scuseria, *J. Phys. Chem.*, 1994, **98**, 4283.

5 R. Taylor, *J. Chem. Soc.*, *Perkin Trans. 2*, 1993, 1383; R. Taylor, *Philos. Trans. R. Soc. London*, *A*, 1993, **343**, 87.

6 B. W. Clare and D. L. Keppert, *J. Mol. Struct.* (*THEOCHEM*), 1994, **315**, 71.

7 O. V. Boltalina, M. Bühl, A. Khong, M. Saunders, J. M. Street and R. Taylor, *J. Chem. Soc.*, *Perkin Trans. 2*, 1999, 1475. (Note: This work showed that the C_3 isomer of $C_{60}X_{36}$ is **2** rather than the other low energy alternative given earlier in ref. 11, p. 48.)

8 A. D. Darwish, A. G. Avent, R. Taylor and D. R. M. Walton, *J. Chem. Soc.*, *Perkin Trans. 2*, 1996, 2051; O. V. Boltalina, V. Yu. Markov, R. Taylor and M. P. Waugh, *Chem. Commun.*, 1996, 2549.

9 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.*, 2000, **39**, 3973.

10 B. W. Clare and D. L. Kepert, *J. Mol. Struct.* (*THEOCHEM*), 1996, **363**, 179.

11 R. Taylor, *Lecture Notes on Fullerene Chemistry: a Handbook for Chemists*, Imperial College Press, London, 1999, pp. 42–45.

12 R. Jones and P. R. Briddon, *Semicond. Semimet.*, 1998, **51A**, 287.

13 G. B. Bachelet, D. R. Hamann and M. Schluter, *Phys. Rev. B: Condens. Matter*, 1982, **26**, 4199.

14 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; O. V. Boltalina, B. de La Vaissière, P. W. Fowler, A. Yu. Lukonin, J. M. Street and R. Taylor, *J. Chem. Soc.*, *Perkin Trans. 2*, 2000, 2212.

15 O. V. Boltalina, J. H. Holloway, E. G. Hope, J. M. Street and R. Taylor, *J. Chem. Soc.*, *Perkin Trans. 2*, 1998, 1845.