PERKIN 2

Some cycloadditions of dienes with $C_{60}F_{18}$: structures and relative stabilities derived from theoretical calculation

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The energies of various isomeric cycloaddition products of $C_{60}F_{18}$ with anthracene, buta-1,3-diene and benzene are calculated using a semi-empirical method. The energies are variously correlated with each other and with the Coulson free valence index and it is argued that the dominant effect that governs position of attack is electronic rather than steric in nature.

Introduction

The recent preparation and characterisation[1] of $C_{60}F_{18}$ in quantities of *ca.* tens of milligrams has opened up the possibility of systematic investigation of the chemistry of this fluorofullerene. The presence of the 18 fluorine addends, which are particularly resistant to loss of halogen, greatly increases the electron affinity of the parent fullerene and should give rise to interesting possibilities of donor–acceptor electronic interactions.[2] The cycloaddition reactions of [60]fullerene itself with electron rich species such as anthracene,[3] cyclopentadiene[4] and cyclohexa-1,3-diene[5] have already been investigated extensively. In general, these adducts are not thermally stable, multiple addition may take place, and characterisation has depended mainly on ^1H and ^{13}C NMR rather than X-ray crystallographic measurements. Since NMR measurements generally only give point group symmetries (*e.g.* C_{2v} for the C_{60}–anthracene monoadduct[3a,b]), it has usually been assumed, rather than demonstrated, that addition takes place to a fullerene double-bond at a hexagon–hexagon junction, *i.e.* that [4 + 2] cycloaddition takes place, although several crystal structures confirm[6,7] this mode of addition. This is a reasonable assumption – the chemistry of [60]fullerene generally resembles that of an electron-deficient olefin.[8] In fact no products seem to have been characterised in which C_{60} acts as a 4π component with addition occurring 1,4 across a fullerene hexagon, despite the ease with which 1,4-addition happens with simple addends such as bromine. Likewise, insertion of a diene at a pentagon–hexagon junction appears not to have been reported with [60]fullerene itself. This latter point has been examined *via* calculation[9–11] mainly at the semi-empirical level. Thus both the transition state for cycloaddition and the enthalpy of reaction are favoured by approximately 50 kJ mol^{-1} for 6,6- rather than 6,5-addition of the diene 2,3-dimethylidenebicyclo[2.2.2]-octane.[11]

The recent isolation[2] of two isomers of a $C_{60}F_{18}$–anthracene adduct (and the demonstration of the presence of a third) suggests that an examination of the reactivity of this fluorinated fullerene towards cycloaddition is timely. The authors of Ref. 2 assume [4 + 2] addition to a double bond at a 6/6 junction, in the 'curved' portion of the fullerene, by analogy with the behaviour of the parent compound, and certainly the NMR evidence is consistent with these products. However, simple extrapolation of parental behaviour to the fluorinated species is not always valid. Thus while the monoxides of both C_{60}[12] and C_{70}[13] have been shown to have an epoxide structure, the main isomer of $C_{60}F_{18}O$ is an intramolecular fullerene ether, with the oxygen atom inserted into a 6,5-FC–CF bond.[14] Semi-empirical calculations of the relative energies of the possible isomers showed this isolated compound to be the most stable by about 50 kJ mol^{-1} (AM1). In addition to the assumption of [4 + 2] cycloaddition in the curved region of this fluorinated fullerene, the authors of Ref. 2 suggest that the factor controlling relative extents of addition (to the four sites in $C_{60}F_{18}$ that they consider possible) is steric hindrance. Their argument is that adduct stability should decrease as the product is formed at positions nearer to the fluorinated region of the molecule. This is not a *necessary* consequence, since other, *e.g.* electronic, factors might contribute to, or even dominate, the stability of the product. Van der Waals repulsive terms should be important only if the addend and the fluorine atoms are separated by less than the appropriate sum of the Van der Waals radii.

We have therefore calculated the energies and structures of a series of isomeric [4 + 2] and [4 + 4] cycloaddition compounds to $C_{60}F_{18}$ for three different addends, buta-1,3-diene, benzene and anthracene, which have different steric requirements. In addition we have looked at the possibility of insertion into a 6,5-bond in the fluorinated fullerene, at the same site of attack as the oxygen atom and, for the sake of completeness, at the possibility of addition to the planar-hexagon region (Fig. 1). The reported lability[2] of the products at room temperature indicates that the reaction will be governed by thermodynamic rather than kinetic factors, and so we have not investigated transition states. Also, in an attempt to distinguish between electronic and steric factors, we have calculated the free valences[15,16] for the fullerene carbon atoms available for bonding to addends.

Results and discussion

Energies have been calculated using MOPAC Version 6.00[17] (AM1 Hamiltonian[18]). The AM1 method is preferred[19] when studying Diels–Alder type reactions, and for pericyclic reactions generally.[20] Full structural optimisations were carried out from different starting geometries in order to ensure that the final structure represented the most stable orientation of the diene relative to the fullerene moiety. A typical structure is given in Fig. 1 for a $C_{60}F_{18}$ benzene adduct.

The first task is to establish that the more stable positions for addition are situated in the 'curved' region of the fullerene and are for [4 + 2] cycloaddition to the fullerene rather than [4 + 4] addition. We have used benzene adducts for this purpose: benzene has a higher local symmetry than does butadiene and is

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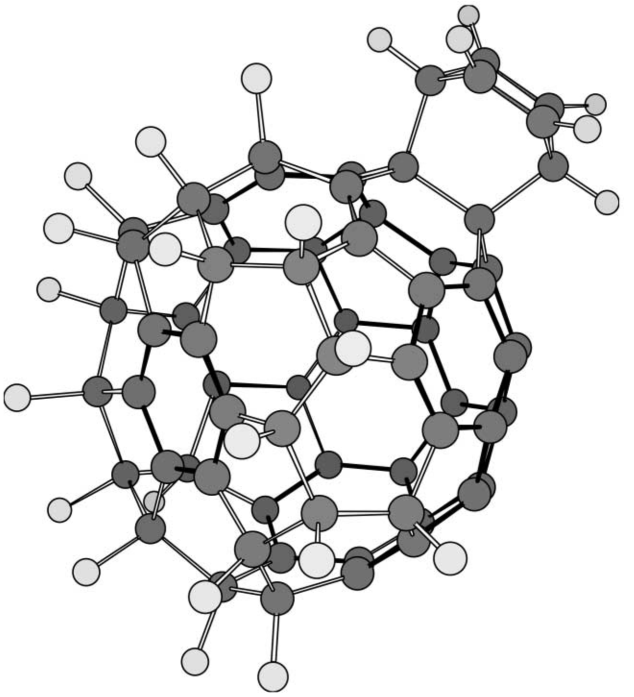

Fig. 1 Optimised (AM1) structure for a typical benzene–$C_{60}F_{18}$ adduct.

of smaller size than anthracene, which makes it easier to generate suitable starting structures. The isomers are identified with reference to the fixed numbering scheme given in Fig. 2

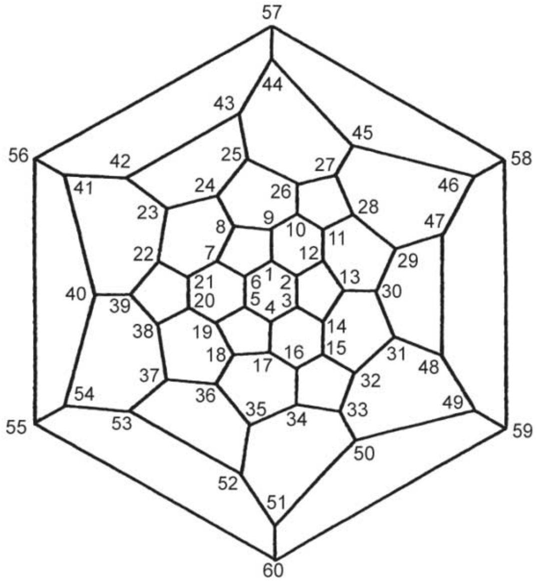

Fig. 2 Schlegel diagram of C_{60} with the numbering scheme used for the fullerene adducts. Fluorine atoms occupy positions 7–21, 24, 30, 36. The 'planar hexagon region' encompasses atoms 1–6; the 'curved region' of the $C_{60}F_{18}$ comprises all other non-fluorinated carbon atoms.

where the fluorine atoms occupy positions 7 to 21 inclusive and 24, 30 and 36. This approach to numbering is simpler than the full IUPAC scheme in cases where the locants of existing groups may change after each addition. Calculated AM1 heats of formation are given in Table 1.

The first four entries in the Table refer to addition at the four positions previously considered[2] possible for anthracene-adduct formation. Clearly, these are the most stable four positions for cycloaddition of benzene and one might infer that it is the same for anthracene. The next two entries refer to 1,4-addition across a hexagon in the 'curved' portion of the fullerene; it is obvious that, for the addition of this six-membered aromatic ring, [4 + 2] cycloaddition is strongly favoured over [4 + 4] cycloaddition. Interestingly, this preference is reversed when cycloaddition takes place in the planar aromatic ring of the fullerene (positions 1–6), although of course both types of addition in this area are strongly disfavoured when compared with reaction at the 'curved' region.

Table 1

Benzene adduct isomer	Fullerene addition mode	Energy/kJ mol^{-1}
56,57	1,2	7.7
43,44	1,2	27.2
27,45	1,2	58.1
25,26	1,2	135.0
43,56	1,4	203.3
41,44	1,4	186.9
1,6	1,2	306.0
2,5	1,4	302.1

In order to verify that the energy variation is indeed associated with a steric effect as the addend approaches the fluorine containing area of the fullerene, we have calculated the energies of the $C_{60}F_{18}$ adducts with buta-1,3-diene and anthracene as well as benzene. Butadiene will have a smaller steric requirement than benzene; anthracene a larger. In all three cases the four most stable adducts, in order of increasing energy, result from addition across positions 56, 57; 43, 44; 27, 45; and 25, 26.

The results are displayed graphically (Fig. 3) and show that the energies of both the benzene and anthracene adducts (*y*-axis) are well correlated (r^2 = 0.998, 0.993 respectively) with the energies of the corresponding butadiene adducts. There is no apparent deviation from linearity, and the slopes for the two adducts are similar (1.04, 1.18). This is strong evidence that the relative stabilities of these four adducts are mainly governed, not by steric factors as previously suggested,[2] but by electronic ones. Whilst the greater slope for the anthracene plot might be argued to suggest a small steric factor, this cannot be large, for even at the closest approach to the fluorinated area of the fullerene by the anthracene moiety the plot remains linear. It could be argued that all three adduct moieties have similar steric requirements, since the energy *differences* increase along each series, but this is physically implausible.

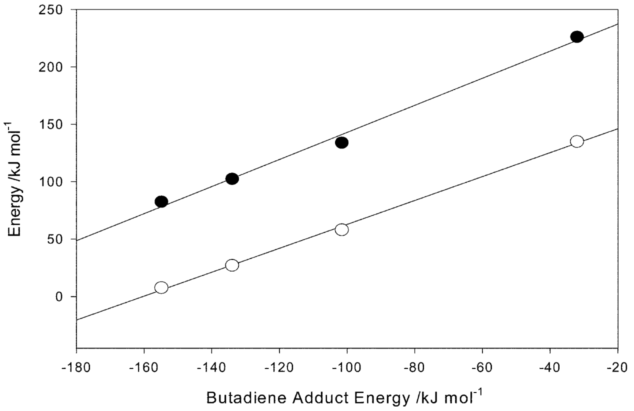

Fig. 3 Correlation of the calculated energies for addition to $C_{60}F_{18}$ of the four most stable anthracene (solid circles) and benzene (open circles) adducts (*y*-axis) with those of the corresponding buta-1,3-diene adduct (*x*-axis).

The corresponding calculations have also been carried out using the $C_{60}H_{18}$ crown structure where the fluorine atoms have been replaced by hydrogen (Fig. 4). Again the slopes are close to unity (0.906, 0.915 for benzene and anthracene respectively) and there is no sign of deviation from linearity even for the

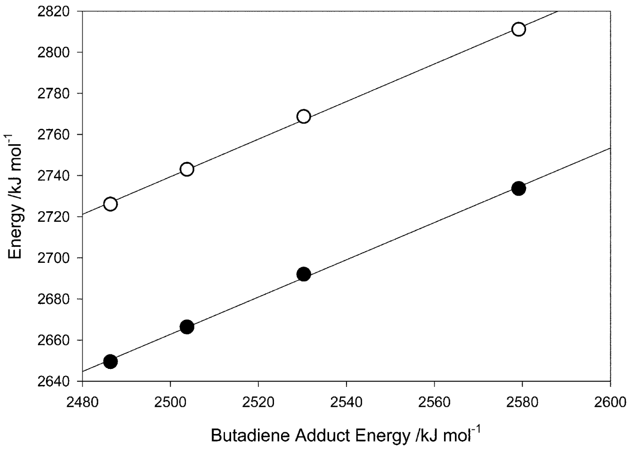

Fig. 4 Correlation of the calculated energies for addition to $C_{60}H_{18}$ of the four most stable anthracene (open circles) and benzene (closed circles) adducts (*y*-axis) with those of the corresponding buta-1,3-diene adduct.

most highly hindered adduct in each case. The smaller Van der Waals radius of hydrogen (120 pm, *cf.* 135 pm for fluorine) may account for the lower slope for addition to the hydrogenated fullerene.

Another possible approach to distinguishing steric and electronic factors is to examine the variation in the energy of a series of adducts with the Coulson free valence index,[15] F_r. This index is an approximate measure of the extent to which an atom in a molecule is not engaged in bonding: a free radical will have $F_r = 1.0$, a terminal carbon atom in an alkene has $F_r = 0.8$, an aromatic carbon atom $F_r = 0.4$, *etc.*[15] Fig. 5 shows the variation in energy of the four most stable anthracene adducts plotted against the sums of the free valences of the two carbon atoms in $C_{60}X_{18}$ on which addition takes place. The free valences were calculated by applying Hückel molecular orbital theory to a model [60]fullerene from which the non-sp^2 carbon atoms (those bearing the substituent X) had been removed.[16]

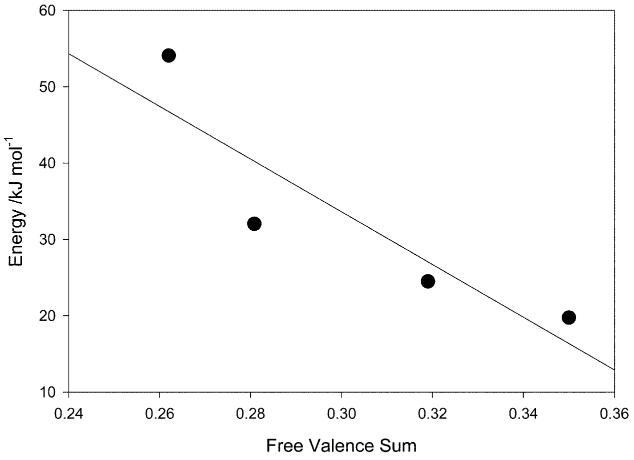

Fig. 5 Variation in energy of the four most stable anthracene adducts for $C_{60}F_{18}$ plotted against the sums of the free valences of the two carbon atoms in $C_{60}X_{18}$ on which addition takes place.

It is clear that the more stable the isomer, the greater the corresponding sum of the free valences of the pair of atoms to which the addend is attached. Thus one of the driving forces for this reaction is the distribution of free valence (effectively the 'available' π-electron density) which decreases as the fluorinated portion of the molecule is approached. One may further deduce that the markedly non-linear relation in Fig. 5 suggests that a steric effect may become important only with the least stable isomer (which is not observed[2] experimentally). A similar plot to that displayed in Fig. 5 may be obtained for the corresponding $C_{60}H_{18}$ isomers. These energies are displayed in Fig. 6 for the same four isomers of the benzene and anthracene adducts of $C_{60}H_{18}$. The plots are better correlated ($r^2 = 0.908$, 0.906) than that of Fig. 5 ($r^2 = 0.799$) suggesting either that steric effects may be less important for the hydrogenated fullerene, or that the electronic effect of the 18 fluorine atoms does slightly affect the energetics of addition.

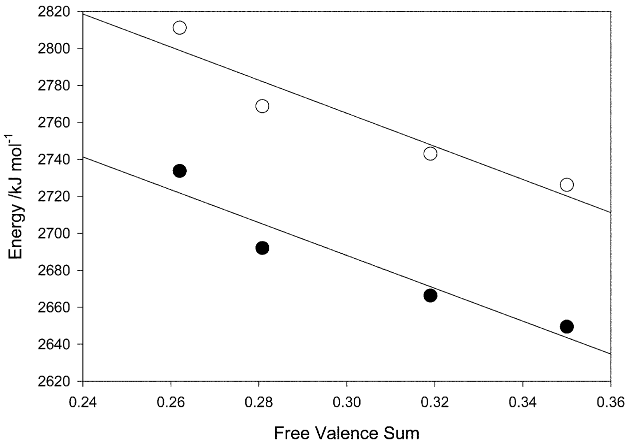

Fig. 6 Variation in energy of the four most stable benzene (closed circles) and anthracene (open circles) adducts for $C_{60}H_{18}$ plotted against the sums of the free valences of the two carbon atoms in $C_{60}X_{18}$ on which addition takes place.

A final example of the usefulness of the free-valence concept in the prediction of possible structures of addends is obtained by including the value for 1,2-addition to the 'aromatic ring' in the crown structure. If this is done, then the correlation is actually improved (Fig. 7, $r^2 = 0.960$ *cf.* Fig. 5, $r^2 = 0.799$). Clearly, the major variation in energy of the adducts is sufficiently explained by the free valences of the appropriate carbon atoms in the fullerene without invoking other factors. It is also noteworthy that the energetics of addition do not depend significantly on whether the crown structure of $C_{60}X_{18}$ is composed of hydrogen or fluorine atoms with their very different electronic effects – free valence values at this level depend only on the positions of addition of the X atoms. Thus the electronic effect that dominates addition is the variation in the degree of conjugation of the double bonds in the 'punctured' fullerene structure. This is one more example[21] of the way in which the structures of fullerene derivatives depend more on the *positions* of previous addends than on the *nature* of the addends themselves.

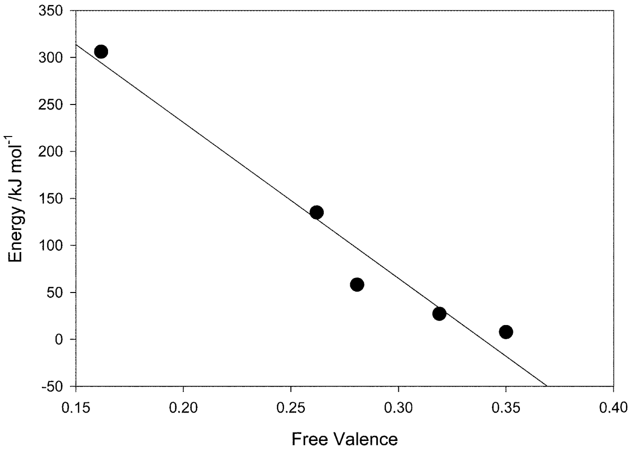

Fig. 7 Variation in energy of five benzene adducts of $C_{60}F_{18}$ plotted against the sums of the free valences of the two carbon atoms in $C_{60}X_{18}$ on which addition takes place.

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