Is Aromaticity a Useful Concept for C_{60} and its Derivatives? Aromatisation of C_{60} by Regioselective Addition

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Qualitative symmetry arguments, evidence from bondlengths and energies, and from the addition chemistry of C_{60} point to a localised description of the π system of this molecule. Regioselective saturation of six double bonds in C_{60} is predicted to lead to an alternant delocalised (aromatic) π system that is realised in at least one well characterised compound.

The aromaticity or lack of it in C_{60} has been a talking point amongst chemists since the first days of fullerene research. The molecule has been labelled aromatic, non-aromatic and 'ambiguously aromatic' by different workers at the same time and by the same workers at different times. Both molecular-orbital and valence-bond approaches appear at first sight to encourage an idea of C_{60} as a 3D analogue of benzene. In VB theory there are some 12 500 Kekulé structures for C_{60},[1] and in MO theory the symmetry-adapted π orbitals are delocalised over the sphere, suggesting the idea of a σ framework encased in a double skin of π density.[2] Since it is hard to know exactly what to expect of a curved and closed π system, experimental[3,4] and theoretical[5-8] examinations of the magnetic properties of the molecule have not produced a clear resolution of the debate. It would be presumptuous to claim that we can decide the question in this short note, but it does seem that a growing body of experimental evidence is compatible with a 'non-aromatic' interpretation of C_{60}, and we offer some qualitative theoretical arguments that point in the same direction. Qualitative calculations also predict regiospecificity in the addition chemistry of C_{60}, since they show that saturation of six octahedrally disposed double bonds at hexagon–hexagon junctions leads to an aromatic π system, thus rationalising the occurrence of this pattern in several compounds of C_{60}.

Bondlengths.—One fact militating against a fully delocalised structure for C_{60} is the inequality of the C–C bondlengths. Measurements and calculations show the 60 pentagon edges to be longer than the 30 edges shared by hexagon pairs. The pentagon edges have length r_p and the hexagon edges r_h where $r_p = 1.45 \pm 0.015$ Å, $r_h = 1.40 \pm 0.015$ Å (^{13}C NMR[9]); $r_p = 1.458(6)$ Å, $r_h = 1.401(10)$ Å (electron diffraction[10]); $r_p = 1.467(21)$ Å, $r_h = 1.391(18)$ Å (neutron powder diffraction[11]). *Ab initio* calculations at various levels give values close to these,[12-14] and formal π bond orders of *ca.* $\frac{1}{3}$ for r_p and *ca.* $\frac{2}{3}$ for r_h have been suggested.[15] Even the simplest Hückel treatment assigns a higher bond order to the r_h edges, correctly implying bond lengths $r_p > r_h$.

Resonance Structures.—A clear distinction can be drawn between C_{60} and the archetypal aromatic, benzene. Benzene has sixfold rotational symmetry but the two Kekulé structures have only threefold symmetry and other VB structures are even less symmetric. In order to construct a fully symmetric charge density it is therefore necessary to mix at least two VB structures, leading to the equivalence of all six bonds in the usual picture of benzene as below.
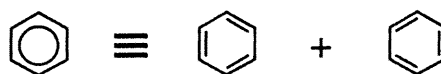
For C_{60}, however, there is already a VB structure with the full (I_h) symmetry of the nuclear framework; the Kekulé structure with single bonds along all pentagon edges and double bonds along all hexagon–hexagon edges is the only one of the 12 500 to satisfy this criterion and is likely to be a good approximation to the electronic structure. Some mixing in of other resonance structures may improve the energy, but it is not forced by symmetry as it is in the case of benzene. The observed bondlengths suggest that the degree of mixing is indeed small and that aromaticity is not a characteristic of C_{60}.

It is interesting to note that in C_{60} we may have the only unambiguous example of the Mills–Nixon effect. It was proposed many years ago[16] that fusion of five- and six-membered rings in a π-system would result in bond localisation, with the double bonds lying *exo* to the pentagon. Whilst the original rationalisation was based on faulty data,[17] and evidence for the effect in small hydrocarbons has proved elusive,[18] it certainly appears that in C_{60} there is significant localisation of double bond character in precisely the 30 bonds *exo* to the pentagons. Taylor[19] has proposed that single bond localisation in the pentagons will be an important stabilising factor for some isomers of the higher fullerenes. A molecular-orbital interpretation of this model is also possible.[20]

Energies.—Calculations of total energies have been performed for C_{60} and related molecules using various levels of empirical, semi-empirical and *ab initio* theory. From the published data, various measures of aromaticity can be computed. One traditional index is the bond localisation energy. This is not well defined in the *ab initio* context, but the simple Hückel model gives a value of 33.16 β for the π stabilisation of C_{60} with respect to 30 isolated double bonds,[2] and if the effect of non-planarity in reducing β is taken into account,[21] this falls to 27.71 in units of the ethylene β. Ninety benzenoid bonds would imply a stabilisation of 60 in these units.

A related quantity available from *ab initio* calculation is the bond separation energy. This is defined for C_{60} by eqn. (1)

$$C_{60} + 120\,CH_4 \longrightarrow 30\,C_2H_4 + 60\,C_2H_6 \qquad (1)$$
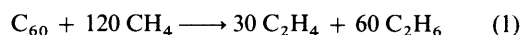
which is isodesmic[22] (*i.e.* it preserves the number of formal single and double bonds between heavy atoms). Using the SCF
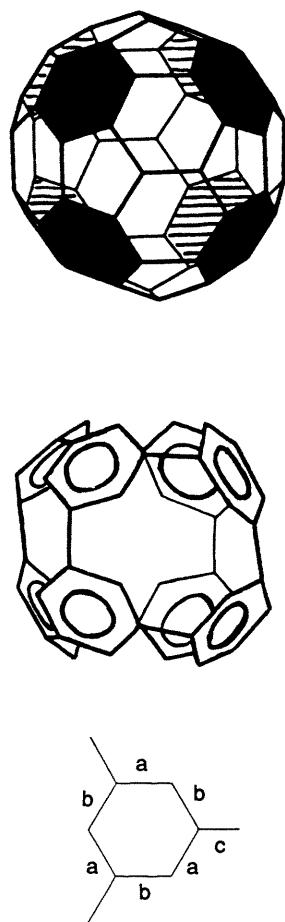
Fig. 1 $C_{60}X_{12}$, a 48-electron alternant π system produced by saturation of six double bonds in C_{60}, leaving eight linked benzenoid hexagons. Bonds a and b within the hexagons have Hückel order 1.623, and the linking bond c has order 1.366. In C_{60} itself a and c would have order 1.476 and b would have order 1.601.

energies for molecules frozen at their equilibrium geometries,*[23] the cost of separating the bonds in a C_{60} molecule is predicted to be 0.855 E_h (2245 kJ mol⁻¹), compared with 0.112 E_h (294 kJ mol⁻¹) calculated in the same way for benzene using eqn. (2).

$$C_6H_6 + 6\,CH_4 \longrightarrow 3\,C_2H_4 + 3\,C_2H_6 \qquad (2)$$
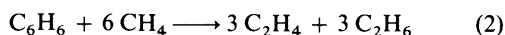
Bond for bond it is significantly easier to break up the C_{60} framework than an aromatic model would suggest—separation of 90 benzenoid bonds would cost twice as much energy as for C_{60}.

Estimates of hydrogenation energies are also available. The energy of this process is not uniformly described at the STO-3G level,[22] and so the numerical values should be treated with caution. The energy change for molecules frozen at equilibrium is $-1.768\ E_h$ (-4641 kJ mol⁻¹) for $C_{60} + 30H_2 \longrightarrow C_{60}H_{60}$, compared with $-0.239\ E_h$ (-627 kJ mol⁻¹) for $C_6H_6 + 3H_2 \longrightarrow C_6H_{12}$, and $-0.115\ E_h$ (-301 kJ mol⁻¹) for $C_2H_4 + H_2 \longrightarrow C_2H_6$, all calculated in the STO-3G basis. These results indicate a stabilisation per 'double' bond in C_{60} about half that in benzene, though the caveat about absolute accuracy should be borne in mind.

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* In the STO-3G basis, the energies for the optimised structures are (in E_h): $-1.117\ 51$ (H₂), $-39.726\ 86$ (CH₄), $-77.073\ 95$ (C₂H₄), $-78.306\ 18$ (C₂H₆), $-227.891\ 36$ (C₆H₆), $-231.482\ 67$ (C₆H₁₂), $-2244.221\ 25$ (C₆₀), $-2279.514\ 09$ (C₆₀H₆₀). These values are taken from the GAUSSIAN archive,[23] were computed specially (C₆H₁₂) or are given in ref. 12 (C₆₀, C₆₀H₆₀).

Chemistry.—Chemical evidence for bond localisation in C_{60} is also accumulating. Several organometallic complexes of C_{60} have been characterised,[24] and share the common feature of η^2 coordination of the fullerene by a metal moiety adding across one or more of the hexagon–hexagon edges. C_{60} plays the role of a coordinated alkene, and indeed displaces ethene in the synthesis of $[(C_6H_5)_3P]Pt(\eta^2\text{-}C_{60})$ from $[(C_6H_5)_3P]Pt(\eta^2\text{-}C_2H_4)$. Birkett *et al.*[25] note that the general addition chemistry of C_{60} with metals, dipolar molecules, radicals and amines is closer to 'super alkenic' than 'super aromatic'. Fagan *et al.* have described C_{60} as an electron-deficient alkene.[24]

If C_{60} itself is not aromatic, then it is pertinent to ask what is the minimum number, and the disposition, of double bonds that must be saturated to generate an aromatic derivative. We note also that addition of electrons to the neutral molecule to give C_{60}^{3-} or C_{60}^{6-} is predicted to equalise r_h and r_p bondlengths,[26] and to cause an increase in magnitude of mean diamagnetic magnetisability.[5,6] On either criterion, both of these I_h anions would be more aromatic than the neutral molecule.

An exploratory simple Hückel calculation shows that selective addition to (saturation of) six double bonds at hexagon–hexagon edges located on octahedral axes leads to a network of eight 1,3,5-linked benzene rings (Fig. 1); this 48-electron π system is an alternant, with 24 bonding and 24 antibonding orbitals, and predicted bond orders as marked in Fig. 1. The effective symmetry of the adjacency matrix is fully octahedral (rather than the T_h symmetry of the geometric structure) and all bonds within the hexagons have equal order. The eight rings are therefore benzenoid in character, and within the Hückel picture one factor driving sixfold substitution is the generation of an aromatic system from the non-aromatic C_{60}. Taylor[27] has noted the stability of this arrangement of rings, and the present structure is in fact his Fig. 3(b). A fully characterised derivative of C_{60} which fits this picture is the hexasubstituted $[(Et_3P)_2Pt]_6C_{60}$. In this molecule[24] each Pt has added in η^2 fashion across one of the hexagon–hexagon edges (formal double bonds in the dominant Kekulé structure) so that the six attached platinum atoms are octahedrally arranged on the C_{60} surface to give a complex with overall T_h symmetry. The crystal structure[24] shows that bond alternation within the six 'benzene' rings is reduced to 0.037 (± 0.020) Å, half the value in C_{60} itself, supporting the idea that the π system has become more delocalised.

In our view the important factor leading to the octahedral addition of six platinum units is electronic, although in this case steric factors[24] may well inhibit *further* addition. On the basis of our qualitative calculation it may reasonably be proposed that the reported products of sixfold addition of morpholine[28] and of diphenylcarbene[29] to C_{60} also have pseudo-octahedral symmetry with a residual π system of eight 1,3,5-linked benzene rings.

Many molecules with this aromatic π framework can be imagined. For example, partial hydrogenation of C_{60} might afford $C_{60}H_{12}$, though at the cost of introducing six pairs of eclipsing C–H bonds in the idealised T_h symmetry. An equally attractive goal is the hexa-epoxide of this symmetry. Although the known mono-epoxide[30,31] is readily deoxygenated with regeneration of C_{60},[30] it is possible that the aromatic π system in the notional octahedral hexa-epoxide would make it less labile. Would the rapid addition of a six mole ratio of dimethyldioxirane to C_{60} yield $C_{60}O_6$? It is interesting to note that with the use of only one mole of dimethyldioxirane, it was reported that polyoxygenated material (presumably including 1,3-dioxolanes) accompanied the low yield of the mono-epoxide.

Other stoichiometries may also be compatible with molecules that are more aromatic/delocalised than C_{60} itself. The formula $C_{60}H_{20}$ is compatible with a system of four linked 'naphthalene' fragments in a strip spanning the surface of the cage (Fig. 2),
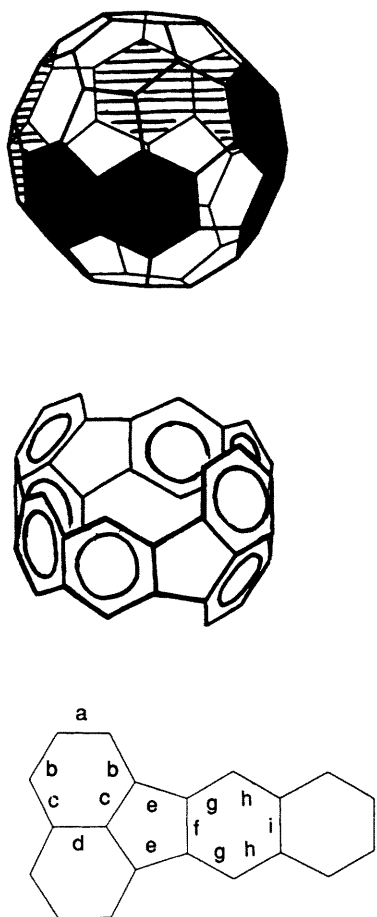
Fig. 2 $C_{60}X_{20}$, saturation of two naphthalene-like patches on the C_{60} surface leaves four linked naphthalene systems with two distinct sets of hexagons. Bonds **a, b, c, d** within the three-coordinate hexagons form an allylic pattern (1.634, 1.651, 1.519, 1.537) and in the two-coordinate hexagons the bonds **f, g, h, i** form a butadiene pattern (1.511, 1.675, 1.557, 1.504). The linking pentagon edge **e** has order 1.390.

Though not an alternant, this π system has a respectable HOMO–LUMO gap of 0.416 β; bond alternation is however still pronounced, and better candidates with this stoichiometry may exist. A candidate[32] for the structure of the reported[33] $C_{60}H_{36}$ has four isolated benzenoid hexagons, derivable by saturation of alternate benzene rings in the $C_{60}H_{12}$ structure with retention of T_h symmetry.

Conclusions

The available evidence points to a picture of the electronic structure of C_{60} in which the two types of carbon–carbon bond retain a separate chemical identity. Approach to aromaticity may be an important feature in the addition chemistry of C_{60}. We suggest that the octahedral addition pattern described here is more likely to be produced in sterically unhindered addition reactions that are rapid and do not involve ionic intermediates. The regiochemistry of the brominated fullerenes $C_{60}Br_6$, $C_{60}Br_8$ and $C_{60}Br_{24}$[25] is affected by the fact that 1,2-addition of Br_2 is precluded by the unfavourable eclipsing interaction on a rigid spherical surface;[34] a sequence of conjugate additions to bromonium ions and allylic shifts can be invoked to rationalise the observed products[25] in this case.

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