A model for pathways of radical addition to fullerenes

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A sequential π-electronic model that simulates addition of large radicals to fullerenes yields pathways to the experimental structures of $C_{60}X_6$ (X = Cl, Br) and $C_{70}Cl_{10}$ and predicts structures for $C_{60}X_{12}$ and $C_{60}X_{18}$.

The fullerenes behave as giant electron-deficient alkenes[1] and possess a rich addition chemistry. Derivatives in which the addends are halogen atoms were among the first to be fully characterised: $C_{60}Cl_6$,[2] $C_{60}Br_6$,[3] $C_{60}Br_8$[3] and $C_{70}Cl_{10}$[4] have all been synthesised and their structures identified. Analogous derivatives have been made by replacing some or all of the halogen addends with aryl[5] and allyl[6] groups. Six nitro groups add to C_{60} to give a derivative that is thought to be isostructural with $C_{60}Br_6$.[7] Direct alkylation, haloalkylation and arylation *via* radical species have also been studied.[8,9] Whilst benzylation of fullerenes, for example, clearly involves radical species, often leading to relatively stable radical products,[8,9] halogenation leads directly to products with even numbers of addends and stable electronic configurations. However, it is believed that addition of halogen atoms also occurs *via* a radical mechanism.[10]

The present communication describes a simple model based on topology alone that is designed to predict the most likely sites for addition of large radicals to an extended carbon π system. Application of the model to C_{60} and C_{70}, the two fullerenes for which data exist, generates addition pathways that lead to stable addend patterns isostructural with experimentally produced compounds. The potential for generalisation of the approach when new fullerenes become available in quantity is clear.

The model is based on Hückel molecular-orbital (HMO) theory, which is often used to provide simple qualitative π-electronic information of fullerenes. The background is given in many textbooks.[11] In the simplest ('topological') approximation, Coulomb integrals α are equal for all atoms, resonance integrals β are equal for all σ-bonded pairs and all more distant interactions are neglected. Diagonalisation of the adjacency matrix gives the dimensionless eigenvalues $\lambda = (\varepsilon - \alpha)/\beta$ (where ε is an orbital energy) and their corresponding eigenvectors. One useful feature of the Hückel model is that topological coordinates of the atoms of a fullerene can be generated from the eigenvectors of its adjacency matrix.[12] The model developed here generates several π-electronic properties of fullerenes from their Hückel eigenvectors.

One property readily derived from HMO eigenvectors is p_{rs}, the π *bond order* between two atoms r and s in an extended π system. It is a sum over the partial mobile bond orders contributed by all molecular orbitals [eqn. (1)],

$$p_{rs} = \sum_j n_j c_{jr} c_{js} \tag{1}$$

where c_{jr} is the coefficient of the p_π orbital of atom r in the jth molecular orbital and n_j is the *occupation number*.

The model applied here is based on two further properties. The first, *free-valence index*, was used in early work by Coulson and coworkers on radical addition to small unsaturated hydrocarbons.[13] The free-valence index F_r, defined by Coulson,[14] measures ease of attack by species, particularly free radicals, at an atom r in a conjugated π system [eqn. (2)].

$$F_r = N_{\max} - N_r \tag{2}$$

N_r is the sum of π bond orders over all bonds joining atom r to the remainder of the π system. $N_{\max}$ is the maximum value of this sum and depends on how many other sp^2 carbons are attached to the atom in question; $N_{\max}$ is $\sqrt{m}$ for an sp^2 carbon attached to m others.[15] The second property, *spin density*, $\rho_{(\pi)r}$, measures the amount of unpaired electron density on an atomic site of a molecule in an open-shell state [eqn. (3)],

$$\rho_{(\pi)r} = \sum_j v_j (c_{jr})^2 \tag{3}$$

where v_j is the *spin number* of the jth molecular orbital. In this model, empty and full (doubly occupied) orbitals have spin number zero and the spin number may be non-integral for a partially filled, degenerate HOMO.

The two properties are used in combination to create a model for simulation of free-radical attack, specified as follows. Assume that addends are attached to a fullerene framework sequentially, in a game with two rules. Attack of the first addend on the closed-shell molecule obeys *rule (i)*: attach to a position of maximum free valence. This produces a radical product, which is attacked in the next addition, under *rule (ii)*: attach to an available position of maximum spin density amongst all those that will quench the radical. If steric effects are ignored, all sites are 'available', but for a bulky addend such as Cl, Br or $PhCH_2$, neighbours of sp^3 sites can be taken to be unavailable unless their occupation becomes necessary for radical quenching. It turns out that in the examples investigated here, the position of maximum free valence is never adjacent to an sp^3 site [hence the omission of the term 'available' from rule (i)], although this may not be the case for other examples.

Addition to C_{60}: following rules (i) and (ii), addition to C_{60} occurs in a straight-forward sequence. After one addition, the site of maximum spin density is at the other end of the attacked formal double bond (hexagon–hexagon edge), but the preference for *non-adjacent* attack leads to attachment at the 1,4 position of a hexagon. Successive brominations continue to make 1,4 patterns, winding around a central pentagon [Fig. 1(a)]. By the addition of the fifth Br atom, the pentagon in question is isolated and is effectively a cyclopentadienyl radical in the Hückel model (although in more sophisticated theory, the radical moiety would interact weakly with the rest of the cage *via* homoconjugation[16]). The only way to quench the radical at the next step is by addition within the surrounded pentagon, giving the experimental $C_{60}X_6$ (X = Cl, Br) pattern with a single sp^3–sp^3 adjacency.[2,3] This addition sequence, summarised in Fig. 1(a), is compatible with more sophisticated calculations and the ESR measurements on known radical additions such as benzylation,[8] where the long lifetime of the intermediate allyl and cyclopentadienyl radicals makes direct observation possible. Such radical intermediates are stabilised by the hyperconjugation and steric protection provided by the bulky organic addends.[8,9] Neither of these features is provided by atomic halogen addends; hence any radical intermediate is susceptible to rapid further addition.

Extended application of the model to C_{60} leads to incorporation of two further sets of six addends, indicating possible stability for derivatives with 12 and 18 bulky ligands. The pattern of addition in both of these further sets is identical to the first, proceeding *via* allyl and cyclopentadienyl intermediates. However, isomers are possible owing to the number of possible locations of the addends in the central pentagons. Addition
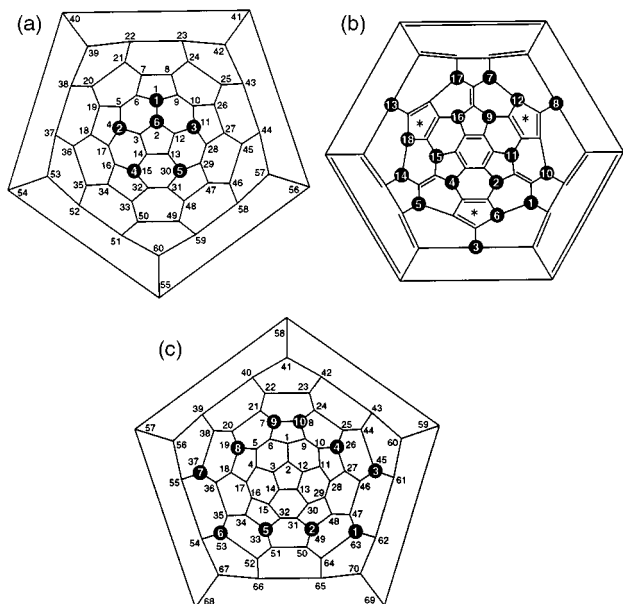
Fig. 1 Sequence of attack on C_{60} and C_{70} (in the IUPAC numbering scheme).[17] (a) The first six addends on C_{60} give the experimental structure $C_{60}X_6$ (X = Cl, Br).[2,3] (b) After 18 additions, the remaining six available sp^2 sites (outer hexagon of the Schlegel diagram) are part of an 18-atom aromatic π system. Isomers are possible since addends 6, 12 and 18 could be attached to any of the five sites in the pentagons marked with an asterisk. (c) The first ten addends on C_{70} give the experimental structure of $C_{70}Cl_{10}$.[4,18]

beyond 18 addends may be less favourable as the six remaining available (non-adjacent) sp^2 sites are part of a stable aromatic π system. The predicted order of attack by addends 7–12 and 13–18, leading to $C_{60}X_{12}$ and $C_{60}X_{18}$ respectively, is summarised in Fig. 1(*b*). Although not found for Br, these structures are plausible candidates for addition of, for example, X = Cl.

Addition to C_{70}: for C_{70} it is not necessary to invoke the bulk of the addend, as 1,4 addition is favoured electronically at every spin-quenching stage. Addition according to rules (i) and (ii) proceeds around the equator, forming a belt of 1,4 links across hexagons, which after the ninth addition can be spin-quenched by forming an sp^3–sp^3 adjacency. Addition at this position (8 in the IUPAC labelling[17]), which is the centre of maximum spin density, splits the π system into 28- and 32-atom components, each with a significant HOMO–LUMO gap. (The site that would be occupied under strict non-adjacent attack has a much lower spin density, 0.097 *cf.* 0.270.) Again, the result of alternate quenching of free valence and spin [Fig. 1(*c*)] is a known pattern, the experimental structure of $C_{70}Cl_{10}$.[4] At least within the small number of structures compatible with the ^{13}C NMR spectrum of the compound, this structure is also the one that is thermodynamically favoured over its competitors.[18]

The model presented here can be seen as essentially a kinetic one, since the rules choose the site most directly reactive towards an approaching radical, rather than necessarily the thermodynamically most stable product. The practice of predicting addition patterns by following sequences of thermodynamically stable species is common,[19] and has correctly predicted the structures of experimentally characterised derivatives. As the degree of addition to the cage increases, a combinatorially exploding number of thermodynamic calculations is needed to cover all possible patterns at each step. The model developed here is based on simple rules that lead directly

from one pattern to the next in a deterministic sequence. Examples exist where semi-empirical thermodynamic energies predict no clear candidate for the most stable isomer, a case in point being $C_{60}Br_8$.[20] It is certain that in $C_{60}Br_6$ itself, some rearrangement must occur on further bromination, as its six bromine positions do not form a subset of those in either $C_{60}Br_8$ or $C_{60}Br_{24}$.[3] The present Br$_6$ pattern *may* in fact also be the thermodynamic result for $C_{60}Br_6$, but this is not established. A theoretical test would be a calculation of energies for all $C_{60}Br_6$ isomers. In this connection, it is worth noting that the experimental isomers of $C_{60}Br_6$ and $C_{70}Cl_{10}$ are selected uniquely from 418 470 and 19 835 545 518 possibilities[21] by the present, purely graph-theoretical model.

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