Rationalisation of the Most Stable Isomer of a Fullerene C_n

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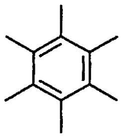
It is proposed that if each isomeric carbon cage for a given fullerene C_n is constructed such that no five-membered ring contains a double bond, then the most stable isomer is that containing the highest number of benzenoid rings (*i.e.* those with alternating double and single bonds). Fullerenes in which a high proportion of the hexagonal rings are benzenoid are very stable, *e.g.* C_{60}, C_{70}, C_{78}, C_{84} and C_{90}; the method correctly predicts the most stable isomer of C_{76}.

Recently we proposed that the factor governing electron distribution in fullerene cages C_n [which consist of twelve pentagonal rings and $(n - 20)/2$ hexagonal ones] is the need to minimise the π-bond order in the pentagonal rings.[1] This dictates the bond distribution in the hexagonal rings, and it turns out to be of critical importance as to whether or not the hexagonal rings are 'benzenoid' *i.e.* do they have an alternating double and single bond structure (with all exocyclic bonds single, **1**) and are thus ideally aromatic. Only C_{60} has this perfect bond alternation in each of its twenty hexagonal rings and is thus the most stable fullerene.



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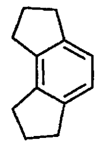

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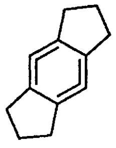

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A key factor in establishing the required bond alternation is the relationship of the pentagonal rings. If they are in a '*meta*' relationship (**2**) this allows for the ideal bond distribution in the adjacent hexagonal ring. In contrast if they are in a '*para*' relationship (**3**), the ideal bond distribution cannot be achieved. This latter arrangement is found throughout icosahedral C_{80} which, like C_{60}, is perfectly symmetrical (and less strained), but lacks its stability. If the pentagonal rings are in an '*ortho*' relationship, not only does this disallow the ideal bond relationship in an adjacent hexagonal ring, but also introduces antiaromaticity;[1,2] structures with adjacent pentagonal rings will therefore be especially unfavourable.

There are three consequences of the pentagonal ring bond-minimisation requirement. First, substantial bond fixation in the fullerenes is predicted. For C_{60} this was indicated by calculations,[3] and confirmed by ^{13}C NMR studies.[4] This feature accounts for the packing configuration of C_{60} at low temperature (whereby the electron-rich bond connecting two pentagonal rings lies over the centre of the π-deficient pentagonal ring).[5]

Secondly, it appears possible to account for the stabilities of the fullerenes by applying the method hitherto applied to planar aromatics, *viz.* those that can be drawn with the highest proportion of benzenoid (*i.e.* Kekulé) rings are the most stable. In a given fullerene, we divide the hexagonal rings into those that are truly benzenoid, those which are benzenoid but have exocyclic double bonds (resulting of course in some pentavalent carbons), and those which are non-benzenoid. Examples in the fragment (Fig. 1) of C_{70} (Fig. 2) are labelled A, B and C, respectively, and this molecule has ten rings of type A and another ten of type B.

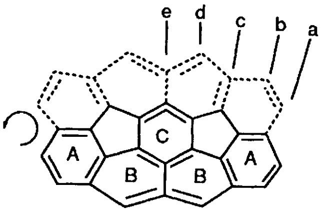

Fig. 1 One of the five aromatic sub-units which comprise C_{70}, showing the predicted bond localisation. Dotted lines are part of an adjacent unit.

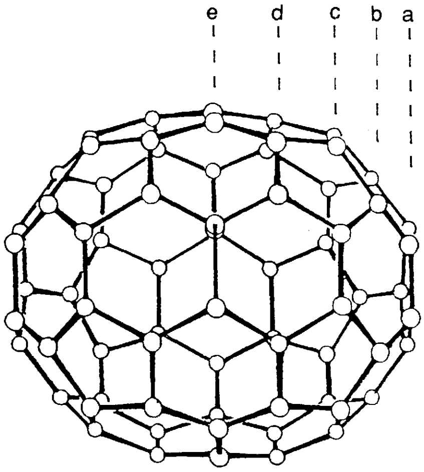

Fig. 2 C_{70}, falmerene

The most stable *isomer* of a fullerene is predicted irrespective of whether one counts only rings A, or A together with B. For C_{76}, a recent proposal was that this existed as the C_{3v} isomer.[6] However, only four of the twenty-eight hexagonal rings in this isomer are benzenoid (and there are also a number of adjacent pentagonal rings, unfavourable for the reasons given above). This isomer is most unlikely to be isolable, and indeed the structure has recently been shown to be D_2.[7] There are only two structures for C_{76} with isolated pentagonal rings, *viz.* T_d and D_2.[8] Application of our procedure shows the number of benzenoid rings in these isomers to be four and twelve respectively; our method therefore correctly predicts the observed result.

C_{78} has twenty-nine hexagonal rings and there are five structures with isolated pentagons: D_{3h}, C_{2v} (containing a coronene fragment), D_3, C_{2v} and D_{3h} (six equatorial pentagons).[9] The number of benzenoid rings in these isomers are, respectively, 26, 14, 14, 5 and 2 so that this sequence is our predicted order of stability. This is precisely the same as that given by Hückel calculations.[9]

Mass spectrometric evidence indicates that C_{80} is somewhat less stable than other fullerenes in this mass region.[10] It is significant therefore that *none* of the thirty hexagonal rings are benzenoid in either the I_h or D_{5h} isomers. In the tube-like D_{5d} isomer twenty rings are benzenoid, so this isomer should be reasonably stable and is likely to be the one eventually isolated.

For C_{84} there are many possible structures with isolated pentagonal rings, of which the D_2, D_{6h} and T_d isomers have closed shells. Hückel calculations predict the order of stabilities as either $D_2 > T_d > D_{6h}$ (delocalisation energy per atom) or $T_d > D_2 > D_{6h}$ (HOMO–LUMO gap).[11] Applying our procedure gives the number of benzenoid rings as 28 (D_2), 28 (T_d) and 12(D_{6h}) so that C_{84} is likely to consist of the former two isomers, which should give twenty-one and four ^{13}C NMR lines respectively. Certainly the former (chiral) isomer must be a substantial component since there are many lines in the spectrum which is thus difficult to resolve from background.[12,13] The high proportion of benzenoid rings (87.5%) nicely accounts for the high stability of this fullerene, though of course these percentages can only be used in a semi-quantitative sense because the ease of formation is likely to diminish with fullerene size as a result of entropy factors. We note that isomers of C_{84} with non-closed shells have a low proportion of benzenoid rings, *e.g.* the D_{3d} isomer has only eight.

C_{90} has been detected but not yet characterised.[13] Significantly, therefore, for the D_{5h} (isolated pentagon) isomer some thirty out of thirty-five hexagonal rings are benzenoid. High stability for this carbon allotrope is thus predicted (see also ref. 8), and it should give six lines in the ^{13}C NMR spectra with intensity ratios 1:1:2:2:2:1 (polar cap to equator).

Lastly, calculations indicate that the high and low bond order regions are fairly accurately predicted by the method proposed in this paper. Thus for C_{70} both STO-3G[14] and Hückel[15] calculations indicate that bonds exocyclic to the pentagonal rings have a high bond order. Only the order of the d–d bond (Fig. 2) is higher than expected and it will be interesting to see if this is confirmed by crystallographic studies.

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