Localised Models and Leapfrog Structures of Fullerenes

Patrick W. Fowler
Department of Chemistry, University of Exeter, Exeter EX4 4QD, UK

It is shown that fullerene structures C_n ($n = 60 + 6k$, $k \neq 1$) generated by the leapfrog construction, in addition to having closed electronic shells, have the maximum proportion of benzenoid hexagons and satisfy the stability criteria of a recently proposed localised model.

The family of experimentally characterised fullerenes is growing,[1–4] and with it interest in the general factors governing their stability.[5–13] Qualitative molecular orbital theory predicts three infinite series of 'magic numbers' for clusters C_n with closed shells: $n = 60 + 6k$ ($k \neq 1$) and a leapfrog[7,8] structure, $n = 70 + 30k$ (all k) and a five-fold cylindrical structure, $n = 84 + 36k$ (all k) and a six-fold cylindrical structure.[9] Some fullerenes outside these series (*e.g.* C_{76}) are stable, though not properly closed-shell within the Hückel approximation, and have been identified by exhaustive computer search using the ring-spiral algorithm.[11] An alternative, localised model has been suggested in which the criteria for stability of a fullerene isomer are (i) minimisation of π-bond order in the pentagons[14] and (ii) maximisation of the number of benzenoid hexagons.[15] The present note shows that for the 'leapfrog numbers' $60 + 6k$ the localised model predicts maximum (and equal) stability for all leapfrog isomers. This agrees with the general stability order found by use of the spiral algorithm in conjunction with molecular orbital theory *i.e.* leapfrogs < cylinders < isolates < others.[16] This order is based on electronic factors alone (π-bonding) and may be subject to some rearrangement when steric factors (*e.g.* σ-strain) are taken into account.

The leapfrog construction is a geometrically based method of generating structures for large fullerenes from those of smaller ones.[7,8] A fullerene polyhedron with n vertices, 12 pentagonal and $(\frac{1}{2}n - 10)$ hexagonal faces, and $(3n/2)$ edges is first capped on every face and then the dual is taken. The final polyhedron is also a fullerene but with $3n$ atoms. Most importantly from a chemical point of view, the leapfrog fullerene always has a closed electronic shell,[7] regardless of the electronic configuration of the starting fullerene. Since pentagon + hexagon polyhedra exist for all even values of $n \geq 20$ (except 22), at least one closed-shell structure can be found for $n = 60 + 6k$ ($k \neq 1$). Truncated icosahedral C_{60} is the leapfrog of dodecahedral C_{20} and repetition of the process yields C_{180}, C_{540}, C_{1620}, *etc.* The number of closed-shell leapfrog isomers of C_{3n} is equal to the total isomer count for C_n; thus whilst C_{60}, C_{72} and C_{78} have a single closed-shell isomer apiece, C_{84} has two leapfrog (and one cyclindrical) closed shells[12] and C_{90} has three.[11] The effect of the leapfrog operation on the various structural components is shown in Fig. 1. Briefly, each atom of the parent molecule is replaced by a hexagon, each edge by a transverse edge in the leapfrog, and each face by a similar polygon rotated through 180°. All pentagons in the leapfrog are isolated.

Taylor has proposed a simple way of estimating the stability of a fullerene isomer.[14,15] A Kekulé structural diagram is drawn in which as many pentagonal edges as possible are single bonds. The number of simultaneous benzenoid hexagons (*i.e.* hexagons with alternating formal single and double bonds) that can then be drawn is an index of stability. Ideally each pentagon will have five double bonds radiating from it and will be isolated from all other pentagons. If two pentagons are linked to a common hexagon they must be in a '*meta*' relationship.[14]

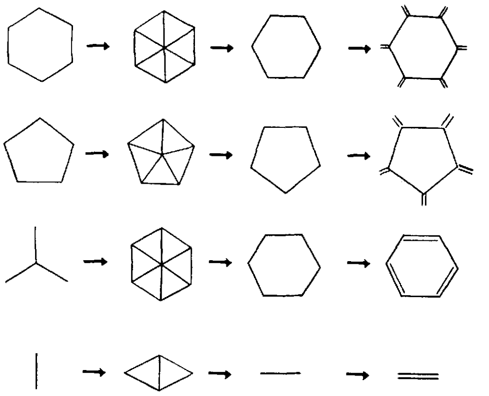

Fig. 1 Effect of the leapfrog operation on structural components of a fullerene. The final column shows the arrangement of double bonds in the best Kekulé structure for the leapfrog.

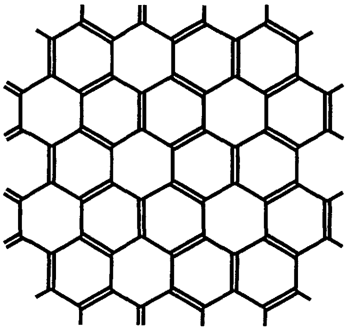

Fig. 2 Kekulé structure of the graphite sheet. One of three equivalent arrangements of formal single and double bonds is shown. For each atom in the sheet there are $2 \times \frac{1}{6} = \frac{1}{3}$ benzenoid hexagons, $\frac{1}{6}$ non-benzenoid hexagons, $2 \times \frac{1}{2} = 1$ single bonds and $\frac{1}{2}$ double bonds.

To make the connection between localised and delocalised models, we first note that the maximum number of benzenoid hexagons in a localised Kekulé structure of a fullerene with n atoms is $n/3$. This is easily seen from the following argument: in the limit where each hexagon of a given patch is isolated three double bonds per hexagon are needed to give benzenoid character, but in the opposite limit of a graphite patch (Fig. 2), where each hexagon is surrounded by six others, each double bond does duty in two hexagons and only (3/2) double bonds per hexagon are needed. The $(3n/2)$ edges of a fullerene split into n single and $(n/2)$ double bonds, so at most $\frac{2}{3} \times \frac{n}{2} = \frac{n}{3}$ benzenoid hexagons can be built on the cluster surface.

A Kekulé structure for a leapfrog fullerene can always be found that attains this maximum number of hexagons and, in addition, has no double bond inside a pentagon. The recipe for drawing it is simple: draw a double bond on each edge that derives from one in the parent. Put another way: draw a double bond at right angles to each edge of the parent and join all the ends with single bonds. As the final column of Fig. 1 shows, this recipe produces $(n/3)$ benzenoid hexagons, $(n/6 - 10)$ non-

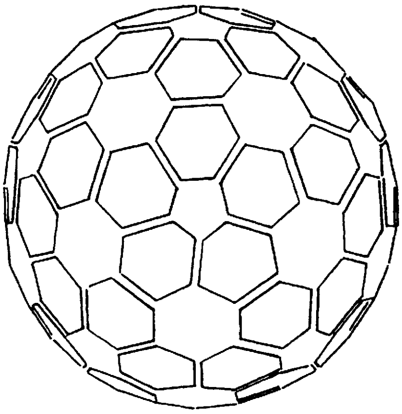

Fig. 3 Best localised bonding scheme for the hypothetical leapfrog fullerene C_{180}

benzenoid hexagons and 12 pentagons with interior single and exterior double bonds. Thus, every leapfrog satisfies the Taylor criteria, and all leapfrog isomers at a given *n* appear equally (and maximally) stable on the localised model. Fig. 3 shows the best localised structure for icosahedral C_{180}, a leapfrog structure with 60 benzenoid hexagons.

The numbers of 20, 26, 28, 28 and 30 benzenoid hexagons found in ref. 15 for C_{60}, C_{78}, both leapfrog forms of C_{84} and one of the leapfrog isomers of C_{90}, respectively, are thus explained. C_{60} has particular stability on this model because *all* its hexagons are benzenoid ($\frac{1}{2}n - 10 = \frac{1}{3}n$), a feature it shares with the infinite graphite sheet. Graphite is itself a leapfrog structure, since capping and taking the dual of the hexagonal tesselation of the plane simply amounts to a scaling and rotation of the original pattern. All leapfrogs have maximum benzenoid character, and in this respect are the finite three-dimensional analogues of graphite.

For the most stable fullerenes with closed electronic shells—the leapfrogs—the predictions of qualitative molecular orbital and localised bond models have been shown to be equivalent. Molecular orbital theory has however the advantage that it lends itself to automated searching of non-leapfrog or charged fullerene isomers, and can be used to predict their electronic configurations. A target for future work is the marrying of this qualitative discussion of electron factors with steric factors to give uniformly reliable predictions of relative stability.

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