

Fullerenes with symmetrically arranged defects: geometry and electronic structure

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Recently, fullerene structures with symmetrically arranged pairs of pentagonal-heptagonal defects have been proposed to explain the round shape of giant multilayer fullerene cages. Even though those proposed cages are defective they belong to the icosahedral point group. Using a Tersoff–Brenner potential we have calculated the shape of these defective fullerenes. It has been found that they present a rounder shape than structures without defects. It has also been calculated the electronic structure of these fullerenes with defects within the Hückel approach. Electronic structures are closed and gaps between bonding and antibonding orbitals are higher in almost all cases than for fullerenes with no defects.

Multilayer fullerene cages (MFC) have been obtained by intense electron–beam irradiation of carbon soot particles [1]. It has been shown in Ref. [2] that these multilayer molecules are more stable than single cage molecules above certain critical number of atoms (about 6000 atoms). This stability is a consequence of van der Waals interactions between different shells. Transmission electron micrographs of MFC show that these molecules present an almost perfect round shape, while it is well-known that large isolated fullerene cages have a polyhedral shape. Fullerene cages prefer a polyhedral shape since planar arrangement of carbon atoms such as in graphite sheets are more stable due to the fact that covalent bonds have less strain. This strain comes from the bending of sp^2 orbitals. Fullerene are possible due to the energy decrease produced when removing dangling bonds. It seems that in order to keep round shapes the strain of the lattice must be reduced.

Some authors proposed that the addition of defects to fullerene structures could help to reduce the strain of covalent bonds [3–5]. In Ref [5], defective fullerene structures belong to the icosahedral point group even though they are defective. These fullerene structures are obtained after dualizing the solutions to the Thomson’s problem, see Ref. [5] for details. Fullerenes with icosahedral symmetry have a number N of carbon atoms given by the expression: $N = 60(k^2 + hk + h^2)$, where k and h are integers. When $h = k$ or $h > k = 0$, the structure belong to the I_h point group. On the other hand, when $h > k > 0$ the structure has chirality and it belongs to the pure rotational point group I . This kind of molecules (no matter if they have chirality or not) have 12 five-membered rings with the rest of the rings having six carbon atoms. Henceforth, we name disclinations to each one of these 12 five-membered rings. We focus in this work on fullerenes with $h = k$, so the number N of carbon atoms is equal to $N = 60k^2$. These structures can be divided into 60 equivalent triangular patches of k^2 carbon atoms. Patches are formed by k zigzag lines. Disclinations are surrounded by five of these triangular patches. Each zigzag line has $2i - 1$ carbon atom, where i is the order number of the zigzag line.

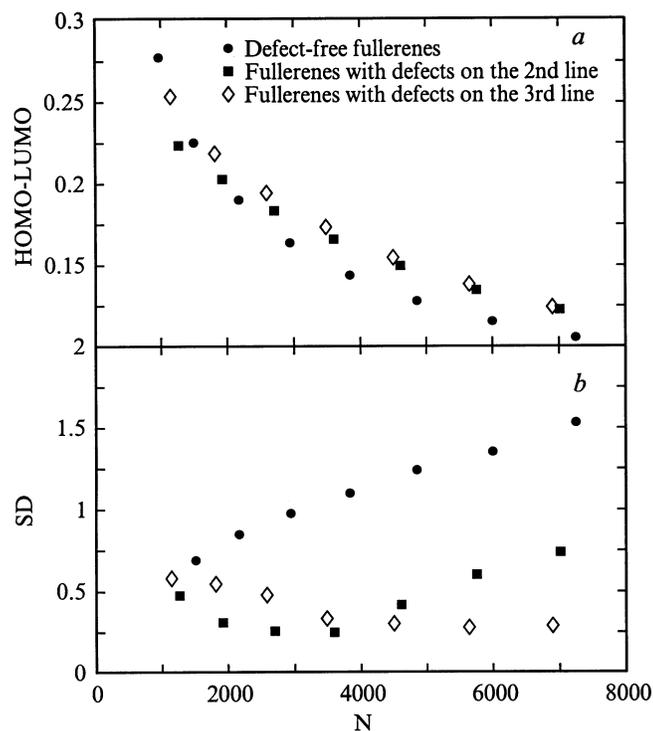
1. Defects in fullerenes

Basically, defects are bounded pairs of seven and five membered rings. Those defects can be symmetrically arranged around each disclination, i. e. one defect per triangular patch so there is five defects around each disclination and at the same distance. We say that we put defects on the i th line if this line is the first one which does not have $2i - 1$ carbon atoms, as corresponds to defect-free fullerenes. We study defects on the second and on the third line. The structures obtained for the former case belong to the pure rotational point group I while for the latter case the structures belong to the point group I_h .

2. Electronic structure

To calculate the electronic structure of fullerenes we use the Hückel approximation with the improvement developed by Tang and Huang [6]. This method allows the calculation of electronic structure of giant fullerenes with I symmetry with low cost of computer time and resources. It consists of solving five secular equations, one for each irreducible representation of the I point group (A, T_1, T_2, G, H).

We find that fullerenes with defects on the second line and in the case of defects on the third line, have closed electronic shells, i. e. equal number of bonding and antibonding orbitals and not any non-bonding orbital. The difference between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) is larger for fullerenes with defects than for defect-free fullerenes for a large enough number of carbon atoms. In Figure (part a), this energy difference, HOMO–LUMO, it is shown versus the number of carbon atoms for defect-free fullerenes (solid circles), fullerenes with defects on the second line (solid squares) and for fullerenes with defects on the third line (empty diamonds). Some authors take this gap as a measure of chemical stability so, using this criteria, defective fullerenes seem to be more stable than defect free fullerenes for a large enough number of carbon atoms.



Energy gap, HOMO–LUMO (*a*), and the standard deviation of the radii as a function of the number of carbon atoms (*b*). Solid circles correspond to defect-free fullerenes, solid squares to fullerenes with defects on the second line and empty diamonds to fullerenes with defects on the third line.

3. Geometry of fullerenes with defects

To carry out a numerical study of shapes of fullerene structures we use a Tersoff–Brenner potential [7,8]. That potential allows the numerical calculation of the energies of covalent bonds of carbon compounds. We minimize the Tersoff–Brenner energy using a conjugated gradient algorithm to obtain stable shapes for each structure. The energy landscape of this potential has many metastable minima so we also use a simulated annealing like method to improve the searching of the lowest minimum for each case.

Pictures of the fullerene structures obtained after energy minimization show that defective fullerenes present a more spherical shape than defect-free fullerenes. The latter adopt a perfect polyhedral shape as many other authors have already calculated. We find that the standard deviation (SD) of the radii is smaller for fullerenes with defects than for isolated defect free fullerenes. Figure (part *b*) shows the standard deviation of the radii as a function of the number of carbon atoms for defect free fullerenes (solid circles), for fullerenes with defects on the 2nd line (solid squares) and for fullerenes with defects on the 3rd line (empty diamonds). In that figure, we can check that the type of defective fullerene with a rounder shape (lower SD) depends on the number *N* of carbon atoms and it is expected that as this number grows new arrangements of defects could appear.

Our numerical results give indications that defective fullerenes could be the explanation of why multilayer fullerene cages show an almost perfect spherical shape while isolated fullerenes have flat faces. We find that electronic structures of defective fullerenes are closed for the cases considered and the gap HOMO–LUMO is larger for defective fullerenes than for defect-free fullerenes for a large enough number of carbon atoms. We also find that the standard deviation of the radii is lower for defective fullerenes indicating that they are rounder than for the defect free case.

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