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Why are buckyonions round?

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Abstract. Multi-layered round carbon particles (onions) containing tens to hundreds of thousands of atoms form during electron irradiation of graphite. However, theoretical models of large icosahedral fullerenes predict highly faceted shapes for molecules with more than a few hundred atoms. This discrepancy in shape may be explained by the presence of defects during the formation of carbon onions. Here, we use the semi-empirical tight-binding method for carbon to simulate the incorporation of pentagon-heptagon defects on to the surface of large icosahedral fullerenes. We show a simple mechanism that results in energetically competitive derivative structures and a global change in molecular shape from faceted to round. Our results provide a plausible explanation of the apparent discrepancy between experimental observations of round buckyonions and theoretical predictions of faceted icosahedral fullerenes.

Key words: Fullerenes – Tight-binding

1 Introduction

Spheroidal multi-layered carbon nanoparticles, dubbed buckyonions, have been observed during electron irradiation of graphitic particles [1, 2]. The mechanical and energetic properties of these molecules make them of great experimental and theoretical interest [3–5]. Transmission electron micrographs (TEM) of buckyonions have provided a wealth of knowledge about their shape and structure as well as more detailed information about inter-shell spacings and local areas of non-uniformity (defects) [1, 6, 7].

Local areas of high defect density have been observed on the surface of the individual shells of buckyonions at room temperature. However, at experimental temperatures of 700°C, TEM of buckyonions show highly uniform defect-free round layers extending to radii of 50 nm or more, suggesting removal of defects with increased thermal energy [8]. Radial compression of these buckyonions due to sputtering and carbon loss results in extremely high pressures in the buckyonion interior and significant changes in the inter-shell spacings as a function of proximity to the onion core. Remarkably, pressures inside onions have been shown to exceed that necessary to effect a phase transition from sp^2 carbon to diamond [8]. Inter-shell spacings range from about 0.31 nm at the exterior of buckyonions, near the van der Waals interaction distance between layers of graphite, to as small as 0.22 nm. The observed compression is accredited to radiation-induced interchange of carbon species between shells, resulting in a net flux of carbon out of the buckyonion [8, 9]. Carbon rearrangement and evaporation most likely occur at local areas of high defect density in buckyonion structure during formation. Therefore, radial compression and removal of defects likely occur as two results of the same process.

Each shell of a buckyonion can be modeled as a closed carbon cage, or fullerene. The size of each shell within a buckyonion ranges from the inner-most shell, which is usually smaller than C_{60}, a Buckminsterfullerene (C_{60} BF), to the outer-most shells which contain tens or hundreds of thousands of carbon atoms. Studies on large fullerenes may have interesting implications which apply to each layer within buckyonions, and thus to buckyonions as a whole. In particular, icosahedral (I_h) fullerenes, widely thought to represent the lowest energy fullerene isomers for a given molecular size, have been well-characterized in a series of theoretical studies [10–15]. These molecules are composed solely of five- and six-membered rings. Large I_h fullerenes possess strongly faceted geometries and include 12 vertices and 20 faces, composed of five-membered rings and graphene sheets, respectively. A "divide-and-conquer" implementation of density functional methods has predicted two different geometries for I_h C_{240}, each representing a separate energetic minimum: one corresponding to a spherical shape and the other corresponding to a faceted shape [16]. However, results using the Tersoff-Brenner

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classical potential [10, 17, 18], tight-binding (TB) [13], MNDO [14, 15], Hartree-Fock [11] and density functional methods [12] have clearly shown a unique minimum: that of a highly faceted geometry for I_h fullerenes larger than C_{60} BF. This result is in direct contrast with the observed shape of buckyonions under experimental conditions [1, 2]. The predicted geometry of these fullerenes suggests that the curvature strain is localized at the five-membered rings allowing the I_h faces, composed of graphene sheets, to remain flat.

In order to gain a more cohesive understanding of the connections between the various observed carbon nanostructures, it is important to reconcile the observed shape of buckyonions with theoretical predictions of I_h fullerene shape. Work by others has explored the possible effects of van der Waals forces [19, 20] and axes of observation [10] on the observed appearance of large I_h fullerenes and buckyonions. While van der Waals studies have shown significant distortion of nanotube [19] and buckyonion [20] walls under particular experimental conditions, a cohesive theory by which the overall shape of buckyonions can be explained in terms of van der Waals forces has yet to be developed. It is unlikely that the axis of observation can explain the discrepancy between I_h fullerene and buckyonion shapes because TEM of buckyonions represent time-averaged images of mobile carbon molecules [21]. Alignment of buckyonions along a particular axis of observation has not been conclusively demonstrated under these experimental conditions.

Previous studies have examined the role of non-classical ring structure in determining the topology of graphitic surfaces [10, 22, 23]. These studies have proposed that a balance of positive and negative curvature on the surface of large fullerenes, exerted by five- and seven-membered rings, respectively, may result in an overall spheroidal shape. We have also proposed mechanisms by which seven-membered rings may be introduced on to the surface of large fullerenes via C_2 fragmentation and Stone-Wales rearrangement [24]. The energetics of these processes have been examined in detail [22, 25, 26].

In this study, we propose a mechanism of 5-7-5 defect introduction via repeated C_2 removal from pentagon-hexagon (5-6) bonds on the surface of I_h fullerenes that is consistent with the observed thermal migration of interstitial species during buckyonion formation. This mechanism and the resulting structures are discussed in detail below. Our calculations indicate that this scheme results in a global change of I_h fullerene geometry from faceted to spheroidal with a loss of only 24 atoms and the introduction of only 12 5-7-5 defects. Quantum chemical calculations confirm a geometry for the resulting molecules consistent with observed buckyonion shape. The energetics of this mechanism of C_2 removal and the resulting structures are also discussed in detail.

2 Computational methods

Calculations were initially performed using a linear-scaling implementation [13] of the semi-empirical TB potential for carbon [27]. Properties of the TB potential and functional form are discussed thoroughly elsewhere [27]. For molecules with 60 atoms or less, we performed more rigorous calculations using the 3-21G basis set at the Hartee-Fock (HF) level of theory. All HF calculations were carried out using a development version of the Gaussian suite of programs [28]. All TB energy values quoted in this paper correspond to molecules with geometries fully optimized by a TB conjugate-gradient scheme. HF energy values were obtained at molecular geometries fully optimized at the 3-21G/HF level of theory.

3 Results and discussion

As discussed above, C_2 fragmentation is an important method of introducing defects on to the surface of I_h fullerenes, particularly at high experimental temperatures [29]. Figure 1 depicts two different mechanisms by which C_2 removal may occur on the surface of an I_h fullerene. For illustrative purposes, we perform this C_2 removal from the surface of C_{60} BF. In Fig. 1A, a C_2 fragment is removed from a 5-6 bond resulting in an intermediate structure with four dangling bonds, as shown in the middle entry of Fig. 1A. Rebonding of these dangling bonds results in a seven-membered ring with two five-membered rings, termed a 5-7-5 defect. Details of the C_2 loss mechanism were presented in previous publications [25, 26]. In Fig. 1B, a C_2 fragment is removed from a 6-6 bond of C_{60} BF. Again, we see an intermediate structure with four dangling bonds. Rebonding creates an eight-membered ring with two four-membered rings, a 4-8-4 defect.

The energetics of these two schemes for C_2 removal are shown in Table 1. We calculate the energy of C_2 removal from a 5-6 bond of C_{60} BF as 11.5 eV and 14.0 eV, using TB and 3-21G/HF, respectively. In contrast, we find the reaction energy for C_2 removal from the 6-6 bond of C_{60} BF to be 15.8 eV and 17.9 eV, using TB and 3-21G/HF, respectively. Both levels of theory

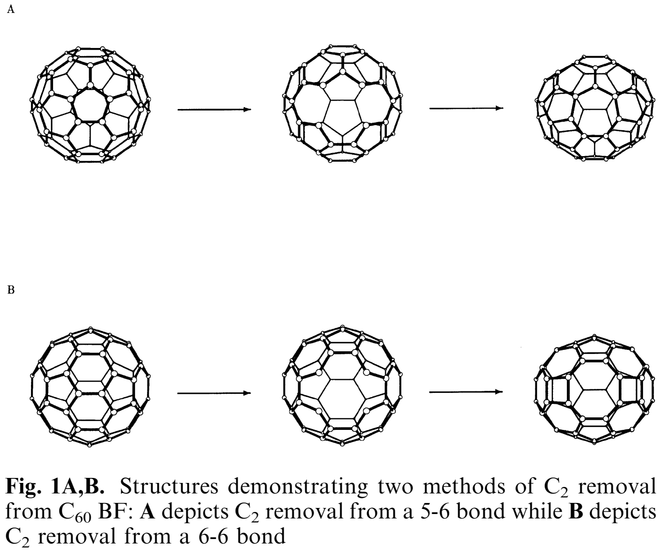

Fig. 1A,B. Structures demonstrating two methods of C_2 removal from C_{60} BF: **A** depicts C_2 removal from a 5-6 bond while **B** depicts C_2 removal from a 6-6 bond predict approximately 4 eV less energy required to introduce a 5-7-5 defect as compared to a 4-8-4 defect. In order to confirm these results for larger fullerenes, we performed an analogous set of calculations for C_2 removal from C_{960}, this time using TB only. In this case, we compare the energy of C_2 removal from a 5-6 bond of C_{960} with C_2 removal from one 6-6 bond located in the center of an icosahedral face. We found an energy of 10.0 eV on introduction of the 5-7-5 defect as compared to an energy of 16.7 eV for the introduction of the 4-8-4 defect. Here, we see that 6.7 eV less energy is required for the removal of C_2 from the 5-6 bond rather than a 6-6 bond. Based on these calculations, we predict that 5-7-5 defects, rather than 4-8-4 defects, may play an important role in buckyonion formation.

In order to investigate a potential connection between I_h fullerenes and buckyonions, we studied the effect of 5-7-5 defects on the shape of I_h fullerenes. For the 5-7-5 cluster, isolated and surrounded by a graphene sheet, our TB and 3-21G/HF results predict a flat surface. In Fig. 2, we compare the shapes of corannulene and a graphene-surrounded 5-7-5 cluster, both fully optimized using 3-21G/HF. While corannulene is decidedly curved, the 5-7-5 cluster is shown to be flat. The difference in shape between these two structures provides a key for understanding the topological effect of 5-7-5 defects on the surface of icosahedral fullerenes. By removing a C_2 fragment from a 5-6 bond on each five-membered ring of an I_h fullerene and allowing full geometry reoptimization, we imposed 12, 5-7-5 defects with a total removal of 24 atoms. The resulting molecule we dub C_{936} DF jor C_{936} with defects. Figure 3 compares the shapes of I_h C_{960} and C_{936} DF along two different axes of observation. Figure 3A and B shows the highly faceted I_h C_{960} as viewed along the C_5 and C_2 axes, respectively. Figure 3C and D shows C_{936} DF along the same axes of observation. These pictures clearly demonstrate a dramatic change of shape from faceted I_h C_{960} to a much more spheroidal C_{936} DF. Figure 4 shows an identical set of pictures for I_h C_{3840} and C_{3816} DF, the largest system that we studied. As in Fig. 3, removal of 12 C_2 fragments drastically changes the shape of I_h C_{3840} from highly faceted to spheroidal. We attribute these results to a more even distribution of curvature strain on the surface of the molecules with 5-7-5 defects. This interpretation is consistent with the flat topology of both graphene sheets, 5-7-5 clusters, and 5-7-5 defects within graphene sheets. The competition between each of these substructures which want to be flat results in a more even distribution of strain and a spheroidal shape.

The previous C_2 removal scheme was performed for a total of nine I_h fullerenes, ranging in size from C_{540} to C_{3840}, resulting in molecules C_{516} DF to C_{3816} DF. The standard deviation (SD) of the radii of these molecules

Table 1. Energetics of C_2 removal from 5-6 and 6-6 bonds

Molecule	TB energy (eV)	HF/3-21G energy
C_{60}	0.0	0.0
$C^{a}_{58} + C_2$	11.5	14.0
$C^{b}_{58}(2) + C_2$	15.8	17.9
C_{960}	0.0	
$C^{a}_{958}(1) + C_2$	10.0	
$C^{b}_{958}(2) + C_2$	16.7	

[a] C_2 removed from 5-6 bond
[b] C_2 removed from 6-6 bond

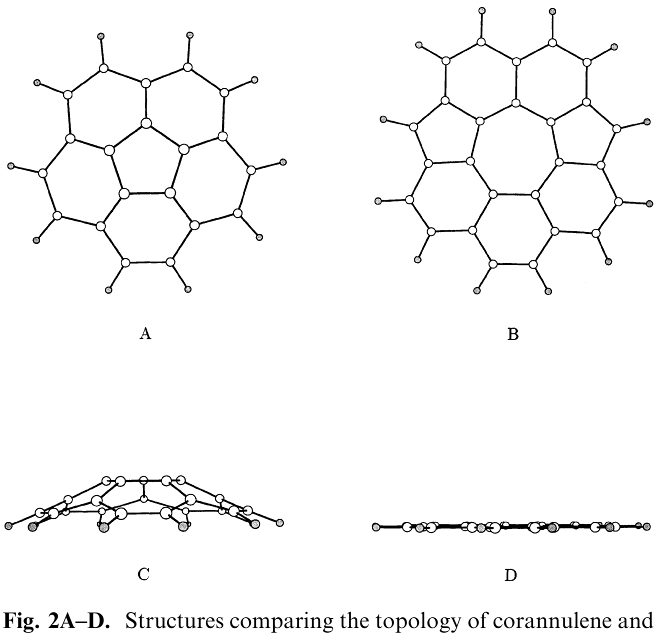

Fig. 2A–D. Structures comparing the topology of corannulene and the graphene-surrounded 5-7-5 cluster, both fully optimized using 3-21G/HF. **A** and **C** depict top and side views of corannulene, respectively. **B** and **D** depict top and side views of the graphene-surrounded 5-7-5 cluster, respectively

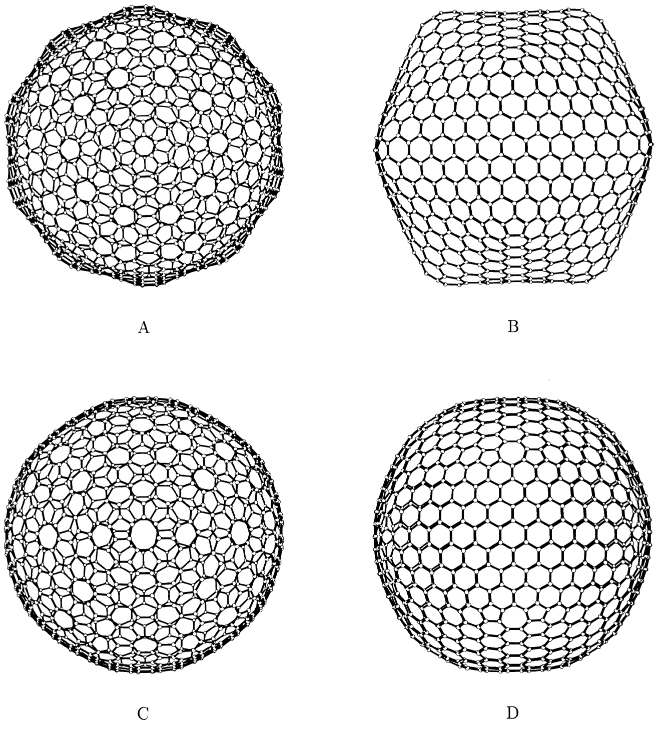

Fig. 3A–D. Structures of C_{960} I_h (**A** and **B**) and C_{936} DF (**C** and **D**) viewed along two separate axes of observation. **A** and **C** are views along the I_h C_5 axis while **B** and **D** are views along the I_h C_2 axis

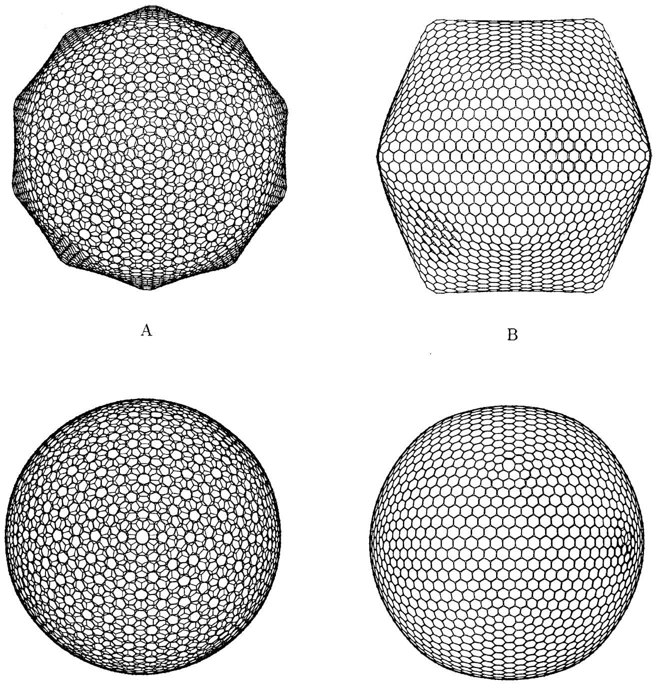

Fig. 4A–D. Structures of C_{3840} I_h (**A** and **B**) and C_{3816} DF (**C** and **D**) viewed along two separate axes of observation. **A** and **C** are views along the I_h C_5 axis while **B** and **D** are views along the I_h C_2 axis

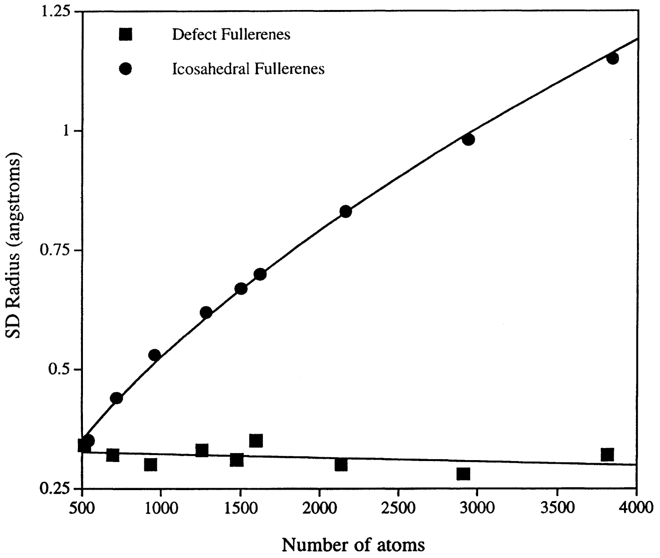

Fig. 5. Graph showing the standard deviation (SD) of the radii for I_h fullerenes and molecules with defects

and those molecules with defects was calculated as a measure of the degree of sphericity of the molecules. A molecule whose radius has an SD of zero, such as C_{60} BF, is deemed spherical while molecules with an increasing SD of their radius are increasingly non-spherical. Figure 5 shows the SD of the radii for all the molecules mentioned above. While the SD of the radius

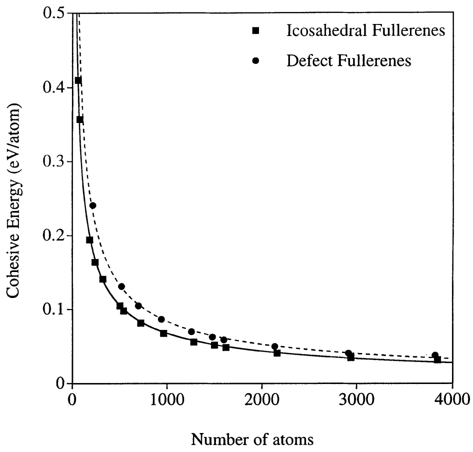

Fig. 6. Graph showing the tight-binding (TB) energy per atom of I_h molecules and molecules with defects as a function of molecule size. All energies are relative to an infinite sheet of graphite

of the I_h fullerenes increases steadily with increasing molecular size, reaching 1.15 Å for I_h C_{3840}, the SD of the radii for the molecules with defects stays at approximately 0.33 Å with increasing molecular size.

Figure 6 shows TB energies on a per atom basis of the fully optimized geometries for the molecules discussed above relative to an infinite sheet of graphite. The energies of these molecules are compared to those of I_h fullerenes of similar size which represent global energetic minima. While the molecules with defects are slightly higher in energy than the I_h molecules, their characteristic energy curve closely follows the I_h energy curve, and approaches it with increasing molecular size. This result demonstrates that the molecules with defects are relatively stable structures that compare favorably with I_h fullerenes for large systems. Initial attempts to find classical isomers of these molecules by carbon rearrangement to remove seven-membered rings were unsuccessful. Therefore, these molecules may or may not represent global energetic minima for their molecular size. Further studies will be required to determine the energetics of these molecules with relation to their isomers.

The results of our study provide a framework by which experimental observations of buckyonions can be understood in terms of I_h fullerenes. Introduction of a minimal number of 5-7-5 defects via serial C_2 removal from 5-6 bonds results in a dramatic change in the shape of large I_h fullerenes from faceted to round. This phenomenon can be attributed to a more even distribution of curvature strain on the surface of large fullerenes containing 5-7-5 defects rather than isolated pentagons. Our scheme of subsequent C_2 removal is energetically feasible and consistent with experimental observation of carbon evaporation during buckyonion formation. As shown in Fig. 7, buckyonions composed of these molecules (Fig. 6B) are much more consistent with experimental images than onions formed of polyhedral fullerenes (Fig. 6A). The dramatic effect achieved by removal of only 24 atoms from the surface of these large I_h fullerenes strongly suggests a very simple explanation

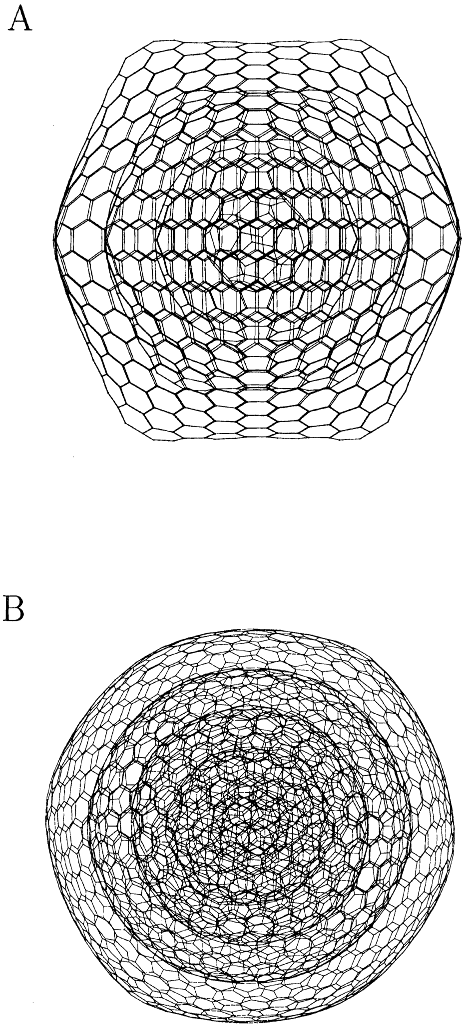

Fig. 7A,B Theoretical buckyonion models: **A** depicts a polyhedral onion composed of $C_{60}@C_{240}@C_{540}@C_{960}@C_{1500}$; **B** depicts a spheroidal onion composed of $C_{60}@C_{216}@C_{516}@C_{936}@C_{1476}$

for the observed sphericity of buckyonions and a closer relationship between the two carbon nanoparticles than previously expected.

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