

Filled Pentagons and Electron Counting Rule for Boron Fullerenes

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 Supporting Information

ABSTRACT: We have revisited the general constructing schemes for a large family of stable hollow boron fullerenes with $80 + 8n$ ($n = 0, 2, 3, \dots$) atoms. In contrast to the hollow pentagon boron fullerenes with 12 hollow pentagons, the stable boron fullerenes constitute 12 filled pentagons and 12 additional hollow hexagons, which are more stable than the empty pentagon boron fullerenes including the “magic” B_{80} buckyball. On the basis of results from first-principles density-functional calculations, an empirical rule for filled pentagons is proposed along with a revised electron counting scheme to account for the improved stability and the associated electronic bonding feature.

Since the discovery of C_{60} buckyball 25 years ago, the fascinating properties and promising applications of the synthetic carbon allotropes—fullerenes, nanotubes, and graphene—overwhelmingly illustrate their unique scientific and technological importance.^{1,2} As boron and carbon share an abundance of bonding similarities,^{3–10} there has been a tremendous amount of interest in the search for nanostructured counterparts of carbon allotropes. Among efforts in exploiting hollow inorganic cage-like structures, the theoretical prediction of a highly stable “magic” B_{80} buckyball³ by the groups of Szwacki, Sadzadeh, and Yakobson has received a great deal of attention.^{11–20} The boron buckyball B_{80} is structurally analogous to the eminent C_{60} ,¹ with 60 boron atoms placed at the corners of a truncated icosahedron that constitutes 12 pentagons and 20 hexagons, along with an extra 20 boron atoms in the center of each hexagon.³ The 20 capping atoms stabilize the cage of the identical icosahedral (I_h) symmetry as the C_{60} buckyball.

The novel chemical bonding pattern of B_{80} provides crucial insights into the nature of boron nanomaterials and has prompted considerable efforts in designing associated nanostructures such as endohedral complexes,⁹ solids,^{10,11} and hydrogen storage media.¹² Inspired by the B_{80} buckyball configuration, construction rules for a family of stable boron fullerenes were proposed.¹³ Moreover, careful examination of the chemical bonding of B_{80} buckyball with triangular and hexagonal motifs led to re-evaluation of boron sheets and nanotubes composed of purely puckered triangular structures, revealing more stable α -boron sheet (α -BS).⁵

Baruah and co-workers reported that the “magic” I_h - B_{80} buckyball was vibrationally unstable and further showed that a relaxation of the I_h - B_{80} buckyball leads to a vibrationally stable T_h structure.¹⁶ In the present paper, an alternative means for constructing a structurally inequivalent vibrationally stable T_h structure is demonstrated, and a transition state geometry between the two T_h structures is also presented. On the other hand, recent *ab initio* simulation studies have unveiled a few lower energy structures built by an icosahedral B_{12} core along with a shell of pentagonal and hexagonal pyramidal units.^{18,19} These new developments raise questions regarding the relative stability of boron cages.

In accordance with the “Aufbau principle”,²³ stable boron conformations can be constructed from two basic building blocks: the pentagonal pyramid B_6 and the hexagonal pyramid B_7 . The hexagonal B_7 is the precursor for convex and quasi-planar boron clusters and thus closely correlates to the α -BS and the associated boron nanotubes.⁵ On the other hand, the pentagonal B_6 unit is an aromatic component that has attracted revived interest in planar boron clusters such as B_{19} .⁴ In this regard, we have studied a volleyball-shaped B_{80} fullerene that is lower in energy than the previously assumed B_{80} buckyball.²⁰ Contrary to the core-shell structured $B_{12}@B_{68}$, it preserves the desired electronic properties as the boron counterpart of C_{60} .²⁰

A natural question arises as to whether there exists a “magic” boron fullerene in lieu of the latest developments.^{18–22} An important consequence of the stability for the B_{80} volleyball is that, in addition to the hollow pentagon, hollow hexagon, and filled hexagon,¹³ it is necessary to add the pentagon pyramid in the building blocks.²⁰ Herein, we present a revised constructing scheme and demonstrate that the migration of capping atoms from hexagonal pyramids to pentagonal rings leads to highly stable boron fullerenes. Consequently, the electron counting rule is revisited by taking into account the effect of enhanced stability related to the B_6 pentagonal pyramids.

We have employed first-principles calculations based on local and semilocal density-functional approaches. For selecting structural conformations and geometry optimizations, gradient-corrected Becke–Lee–Yang–Parr (BLYP) parametrization^{24,25} of the exchange–correlation was used along with a double numerical (DN) basis set as implemented in the DMol3 package.²⁶ The local density-functional calculation results were subsequently rectified through a semilocal approach using Becke–3–Lee–Yang–Parr (B3LYP) for the exchange–correlation functional,^{24,25} with the 6-311G basis set as implemented in the TeraChem package.²⁸ The optimization of atomic positions was performed for local and semilocal calculations, which proceeded until the

Published: June 01, 2011

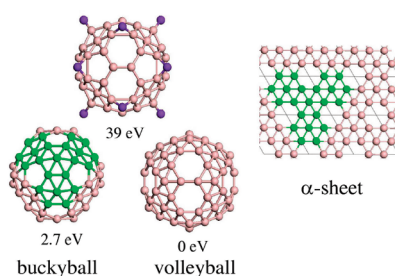


Figure 1. Ball-and-stick representation of the optimized T_h -A B_{80} buckyball and volleyball, along with the transition state between the two conformations and the α -boron sheet. Highlighted with green and purple are the snowdrop pattern and the migrating capping atoms, respectively.

forces were less than 0.01 eV/\AA and the change in energy was less than $5 \times 10^{-4} \text{ eV}$.

It is instructive to examine the buckyball and volleyball structures of B_{80} , as shown in Figure 1. The structure of the vibrational stable T_h - B_{80} (T_h -A)¹⁶ consists of 20 filled hexagons and 12 empty pentagons.³ The filled hexagons are arranged in a snowdrop-like pattern, as highlighted in Figure 1.¹³ The snowdrop constitutes a central hexagonal pyramid surrounded by three hexagonal pyramids and three “hollows” (hollow pentagons or hexagons). By contrast, the B_{80} volleyball can be viewed as the 12 outward capping atoms migrating from hexagonal pyramids to the centers of 12 empty pentagons.²⁰ We illustrate in Figure 1 the transition state between the buckyball and volleyball of B_{80} with an energy barrier of $\sim 39 \text{ eV}$ and the 12 capping atoms highlighted (see the Supporting Information for details of the transition state calculation, along with discussions of models of migrating capping atoms). The exchange between B_6 and B_7 pyramids leads to yet another route of generating a family boron fullerenes.

Carbon fullerenes consist of hexagons and 12 pentagons in conformity with Euler's formula $F - E + V = 2$, where F , E , and V stand for the number of faces, edges, and vertices of the fullerene, respectively. The exactness of 12 pentagons is attributed to the fact that each edge is shared by two faces, each pentagon (hexagon) has five (six) edges, and each vertex is adjacent to three polygons. Let n_p (n_H) denote the number of pentagons (hexagons); one has $F = n_p + n_H$, $E = (5n_p + 6n_H)/2$, and $V = (5n_p + 6n_H)/3$. Therefore, $n_p = 12$.

The isoelectronic requirement for carbon and boron fullerenes implies that the addition of more than 60 carbon atoms needs to be a multiple of 6 for the even number of carbon fullerenes and the trivalent boron, respectively. As a result, the counterpart of C_{60+6n} isolated-pentagon fullerenes is B_{80+8n} . The isoelectronic requirement is important for a closed-shelled electronic structure in that typical high-symmetry boron fullerenes are open-shelled in the absence of such a constraint. For snowdrop B_{80+8n} fullerenes that constitute hexagonal pyramids in addition to pentagonal and hexagonal rings, it is straightforward to conclude that $n_p = 12$, $n_H = n$, and the number of filled hexagons (FHs) $n_{FH} = 20 + 2n$, since each filled hexagon has 12 edges and six triangular faces. For snowdrop-generated boron nanostructures, the total number of valence electrons, $240 + 24n$, is twice that of $120 + 12n$ triangles.¹³ It is worth noting that the snowdrop electron counting rule is applicable to α -BS as well.

Encouraged by the improved stability of the B_{80} volleyball over the B_{80} buckyball,²⁰ herein we propose a filled pentagon model

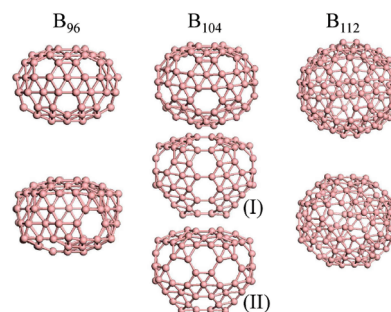


Figure 2. Optimized structures of snowdrop (top panel) and filled-pentagon (bottom panel) fullerenes of B_{96} , B_{104} , and B_{112} .

for boron fullerenes. Specifically, the filled-pentagon (FP) scheme amounts to moving 12 capping atoms from filled hexagons to pentagons, resulting in $n_p = 0$, $n_H = 12 + n$, $n_{FH} = 8 + 2n$, and $n_{FP} = 12$. Consequently, the revised electron counting rule yields more than two electrons per triangle, which is dependent on n but still converged to an α -BS value of 2 as $n \rightarrow \infty$.

Following the nomenclature, hereafter, we refer the filled-hexagon fullerenes as snowdrop fullerenes.^{13,27} In contrast to the snowdrop model where the constructed boron fullerenes are of the same symmetry as the carbon fullerene counterpart, the filled-pentagon fullerenes typically have lower symmetry. The lack of a unique migration path adds another wrinkle to the search for global minimum conformations of boron fullerenes. Owing to the large number of boron atoms involved and the complicated two- and three-center bonding patterns, the associated first-principles density-functional calculations are computationally demanding. Furthermore, owing to the extremely sensitive dependence upon the basis set and the exchange-correlation functional employed, it is necessary to carefully evaluate the local and nonlocal effects in *ab initio* calculations.

Shown in Figure 2 are the optimized structures of B_{96} , B_{104} , and B_{112} , which are the isoelectronic counterparts of C_{72} , C_{78} , and C_{84} , respectively. The snowdrop B_{96} fullerene has a round pillow shape with two hexagonal rings located at the D_{6d} axis. The filled-pentagon B_{96} structure is formed by moving 12 of the 24 capping atoms to fill the 12 pentagons, leaving 14 hollow hexagons. On the equator of D_{6d} - B_{96} , three alternating pairs of hexagons move the capping atoms to the centers of nearest-neighbor pentagons, while the two snowdrop structures near the D_{6d} axis rotate to fill three empty pentagons each. The B_{104} counterpart of C_{78} has five isomers,²⁷ and the snowdrop B_{104} is of D_{3h} symmetry. Among various ways of migrating 12 capping atoms, we show in Figure 2 two low-energy C_{2v} conformations: one has empty hexagons around the equator, while the other has more isolated hexagonal rings. The construction of both conformations involves rotating two snowdrops and hexagonal pair migrations. The B_{112} fullerene consists of 32 hexagons and 12 pentagons.²⁷ Among 24 isomers, we consider the counterpart of C_{84} ground-state structure with D_2 symmetry and an elliptical pillow shape.²⁷ The D_2 snowdrop B_{112} can be transformed to a C_2 filled-pentagon B_{112} through successful rotation of four snowdrops.

An important criterion for structural stability is that vibrational modes are all real. We have performed vibrational analysis for all of the above conformations. While the vibrational stability of filled-pentagon B_{80} , B_{96} , and B_{104} is confirmed, there exist two imaginary modes for snowdrop D_{6d} - B_{96} , analogous to that in

Table 1. Calculated Binding Energies (E_B in eV Relative to Atomic Boron), HOMO–LUMO Gap (E_g in eV), the Energy Difference (ΔE in eV), and Symmetries (S) of Optimization for B_{80+8n} Fullerene Structures Using Local (BLYP) and Semilocal (B3LYP) Approaches, Respectively

n	method	structure	S	E_B (eV)	E_g (eV)	S	E_B (eV)	E_g (eV)	ΔE (eV)
0	BLYP	B_{80}	T_h -A	−406.82	0.94	T_h	−409.53	0.18	2.73
2	BLYP	B_{96}	C_2	−490.48	0.64	D_3	−494.86	0.27	4.38
3	BLYP	B_{104}	D_{3h}	−532.83	0.59	C_{2v} (I)	−534.44	0.27	1.61
3	BLYP					C_{2v} (II)	−536.05	0.20	3.22
0	B3LYP	B_{80}	T_h -A	−453.85	1.87	T_h	−458.13	0.86	4.29
2	B3LYP	B_{96}	C_2	−548.08	1.36	D_3	−553.48	0.93	5.40
3	B3LYP	B_{104}	D_{3h}	−595.81	1.22	C_{2v} (I)	−598.73	0.79	2.93
3	B3LYP					C_{2v} (II)	−598.93	0.91	3.12

I_h - B_{80} .¹⁶ The existence of imaginary frequency modes is attributed to the symmetry constraint of the calculation. A subsequent eigenmode following analysis leads to a lower energy (~ 0.03 eV) and lower symmetry C_2 - B_{96} conformation that has all real vibrational frequencies. We list in Table 1 the calculated binding energies, the gap between the highest-occupied molecular orbital (HOMO) and the lowest-unoccupied molecular orbital (LUMO), the symmetry of the fullerene, and the energy differences between the snowdrop and filled-pentagon models. As is readily observable from Table 1, the filled-pentagon fullerene is systematically lower in energy than the snowdrop counterpart. Furthermore, in contrast to the monotonic decrease of the snowdrop B_{80+8n} with the increase of n , the filled-pentagon B_{80+8n} shows a “magic” number of $n = 2$, corresponding to a filled-pentagon B_{96} . Closer scrutiny of the structure of the filled-pentagon B_{96} reveals that the enhanced stability of B_{96} correlates to the “isolated” empty hexagons or hexagon pairs.

Whereas the snowdrop B_{80+8n} gives rise to a large class of stable boron fullerenes, the filled-pentagon B_{80+8n} leads to structures with improved stability. For $n = 0$, the buckyball and volleyball B_{80} are the first members of the corresponding family. The α -BS is the $n \rightarrow \infty$ analogue for both models. The construction of filled-pentagon cages amounts to transforming a pair of neighboring pentagon rings to filled pentagons, accompanied by the generation of a pair of adjacent hollow hexagons. An optimal arrangement of those building blocks allows for the tuning of the charge transfer, which gives rise to an attractive fluxional behavior and improves the stability. In all of the cases, the improvement of energy is remarkable, ranging from 3.1 eV for B_{104} to 5.4 eV for B_{96} . The semilocal results are in good accordance with those of local results regarding the binding energy, while the correction to the HOMO–LUMO gap is substantial. As seen in Table 1, the rectified gap is about 0.7–0.9 eV for filled-pentagon fullerenes.

In conformity with the donor–acceptor hypothesis on α -BS,⁵ electron transfers in the snowdrop B_{80+8n} can be classified as the capping atoms in the center of hexagonal pyramids as electron donors, while other atoms can be classified as acceptors.¹³ For the filled-pentagon model, the capping atoms of hexagonal and hexagonal pyramids stand for electron donors, while others stand for acceptors.²⁰ As such, it is expected that uniformly distributed hollow hexagons are desired.²⁰ Shown in Figure 3 are the extracted charge-density distributions of HOMO and LUMO for the snowdrop and filled-pentagon B_{96} , respectively. A distinctive feature of the charge density distribution of HOMO (LUMO) is an evident increase in the π (π^*) bonding in the filled-pentagon B_{96} , as compared to that for snowdrop B_{96} . This

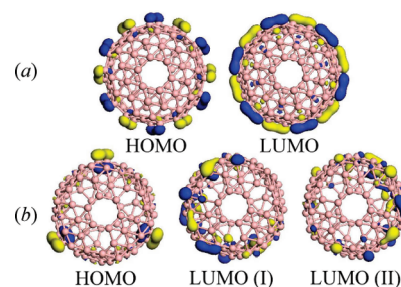


Figure 3. Isodensity surfaces (with an isovalue of 0.02 au) of HOMO and LUMO for (a) the snowdrop and (b) filled-pentagon models of B_{96} , respectively. The positive and negative components are colored with blue and yellow, respectively.

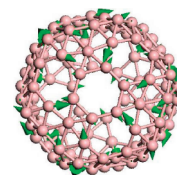


Figure 4. The motions of the infrared-active vibrational mode of 1972 cm^{-1} .

is attributed to the redistribution of the bonding and antibonding patterns related to the capping of pentagon rings.²⁰

A few remarks are immediately in order. (i) Our results demonstrate that the filled pentagon model yields improvement in energy for a family of boron fullerenes not limited to B_{80} . The energy improvement is primarily attributed to the migration of the capping atoms from filled hexagons to pentagons (see Figure S1, Supporting Information) and bonding arrangements associated with changes in aromaticity.^{18,20} (ii) The filled-pentagon fullerenes prefer evenly distributed hollow hexagons in connection to the donor–acceptor charge transfers. (iii) The stability of the filled-pentagon fullerenes is also manifested in the vibrational frequencies. We depict in Figure 4 the motions of the highest vibrational mode for B_{96} . The rest of the vibrational frequencies is in the range of $81\text{--}1411\text{ cm}^{-1}$ (see the Supporting Information). The lowest vibrational modes are significantly softer than the counterparts of carbon fullerenes.^{13,16} (iv) In contrast to the snowdrop building block, for filled-pentagon fullerenes, the basic unit is the adjacent pentagon-hexagon pyramids. (v) The main thrust of the present work is to assert that the filled-pentagon model is energetically preferred. To this end, we have

systematically investigated a large set of snowdrop fullerenes and revealed the existence of a “magic” filled-pentagon B₉₆. Notwithstanding this, there are still a variety of boron fullerenes that remain unexplored. Our results, nevertheless, illustrate that the intriguing bonding pattern of boron keeps bringing surprises.

In summary, we have described a filled-pentagon constructing scheme for a large family of stable boron fullerenes. The improved stability of the filled-pentagon fullerenes over the snowdrop ones is confirmed by intensive first-principles simulations. A revised empirical electron counting rule indicates that a slightly increased electron counting per triangle is energetically preferred, which is useful for seeking for stable boron nanostructures. These results shed important light on the improved stability of boron fullerenes in connection to the aromaticity. We hope that these results can promote revived experimental synthesis of boron fullerenes along with future applications.

■ ASSOCIATED CONTENT

S Supporting Information. The optimized atomic coordinates and vibrational frequencies of B₉₆. This information is available free of charge via the Internet at <http://pubs.acs.org/>.

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■ ACKNOWLEDGMENT

This work was supported by the National Science Foundation (Grant No. DMR-0934142), Army Research Office (Grant No. W911NF-10-1-0302), and Air Force Office of Scientific Research (Grant No. FA9550-10-1-0254).

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