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Hui Li

University of Nebraska-Lincoln, hli4@unl.edu

Nan Shao

University of Nebraska-Lincoln

Bo Shang

University of Science and Technology of China

Lan-Feng Yuan


University of Science and Technology of China, yuanlf@ustc.edu.cn

Jinlong Yang

University of Science and Technology of China

See next page for additional authors

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Authors

Hui Li, Nan Shao, Bo Shang, Lan-Feng Yuan, Jinlong Yang, and Xiao Cheng Zeng

Icosahedral B₁₂-containing core–shell structures of B₈₀†

Hui Li,^a Nan Shao,^a Bo Shang,^b Lan-Feng Yuan,^{*b} Jinlong Yang^b and Xiao Cheng Zeng^{*a}

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Low-lying icosahedral (*I_h*) B₁₂-containing structures of B₈₀ are explored, and a number of core–shell isomers are found to have lower energy than the previous predicted B₈₀ fullerene. The structural transformation of boron clusters from tubular structure to core–shell structure may occur at a critical size less than B₈₀.

Structures of bulk boron have received much attention owing to their intriguing and complex polymorphic behavior.¹ To date, more than 17 polymorphs of boron have been revealed in nature but the most stable crystalline form of boron in ambient conditions is yet to be determined.^{2–4} It is known that chemical properties of boron are between those of metals and insulators because the three valence electrons of boron can form either metallic-like or covalent bonds, which renders determination of structures of boron challenging.⁴ Nevertheless, it has been established that nearly all polymorphs of boron contain linked B₁₂ icosahedra with metallic-like three-centre bonds within the icosahedra and covalent two- and three-centre bonds between the icosahedra. A recent study of high-pressure solid boron further affirmed that the icosahedral (*I_h*) B₁₂-containing structures are quite universal.⁴ On the other hand, previous experimental and theoretical studies of free-standing boron clusters have shown that the *I_h*-B₁₂ structure is unstable in the gas phase and the global minima of small-sized boron clusters exhibit quasi-planar structures.^{5,6} A structural transformation from quasi-planar to double-ring tubular structures^{5,6d,7,8} occurs in the size range of B₁₆ to B₂₄, depending on the charge state of the clusters. In 2007, Szwacki *et al.* reported a highly stable spherical hollow-cage structure of B₈₀, named as boron fullerene (Fig. 1A) because it can be built from the carbon fullerene C₆₀.⁹ Density-functional theory (DFT) calculations show that the fullerene B₈₀ has a point-group symmetry *T_h*, a large HOMO–LUMO gap (~1 eV), and a cohesive energy even greater than that of an infinite double-ring (strip).^{9,10} These intriguing properties of the fullerene B₈₀ have stimulated subsequent explorations of chemical stabilities of boron fullerenes¹¹ as well as novel properties of endohedral and exohedral metallofullerene B₈₀.¹²

The prediction of B₈₀ fullerene is remarkable, not only because it reveals a highly stable hollow-cage structure of boron, but also it implies that the structural evolution of boron from small-sized clusters towards bulk may go through

a series of structural transformations, possibly from (single-sheath) tubular to convex or to spherical hollow-cage at certain cluster sizes,¹³ before eventually to *I_h*-B₁₂-containing bulk-like structures. The high stability of fullerene B₈₀ suggests that the transition from hollow-cage to bulk-like *I_h*-B₁₂ containing structures may take place beyond B₈₀. Indeed, Prasad and Jemmis showed that *I_h*-B₁₂ containing structures (stuffed fullerene) become highly stable in the size range of B₉₈–B₁₀₂ since these clusters have greater cohesive energy per atom than fullerene B₈₀.¹⁴ Recently, we found that the bulk-like *I_h*-B₁₂ containing structures may emerge as early as B₈₄.¹⁵

Can the bulk-like *I_h*-B₁₂ containing structures emerge at sizes even smaller than B₈₄? Due to the lack of experimental evidence of fullerene B₈₀,¹⁶ we attempted to answer this question by using global search methods^{6c,d,17} to seek bulk-like structural family of low-lying isomers of B₈₀.

We performed motif-based searches¹⁸ to seek low-lying *I_h*-B₁₂-containing structures of B₈₀ using the basin-hopping Monte Carlo algorithm.¹⁷ Here the motif is an *I_h*-B₁₂ core. The core is initially flanked by 68 boron atoms located randomly on an irregular shell. To optimize B₈₀ structures during the basin-hopping runs, we employed the QUICKSTEP program in the CP2K density-functional theory (DFT) software package.¹⁹ More specifically, the Perdew–Burke–Ernzerhof (PBE) functional²⁰ was selected, and the core electrons of boron were described by the Goedecker–Teter–Hutter (GTH) norm-conserving pseudopotential.²¹ The basis sets are a combination of the polarized double- ζ quality Gaussian basis, GTH-DZVP²² and a plane-wave basis set (with an energy cutoff of 280 Ry). The basin-hopping searches generated more

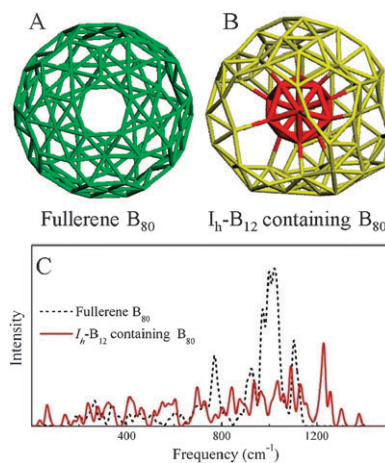


Fig. 1 (A) The structure of fullerene B₈₀, and (B) the structure of *I_h*-B₁₂ containing B₈₀ (A1 isomer), where the icosahedral inner core is highlighted in red. (C) Computed infrared spectra of fullerene B₈₀ and A1 isomer.

^a Department of Chemistry, University of Nebraska-Lincoln, Lincoln, Nebraska 68588, USA. E-mail: xczeng@phase2.unl.edu

^b Hefei National Laboratory for Physical Sciences at the Microscale, University of Science and Technology of China, Hefei, Anhui, China 230026. E-mail: yuanlf@ustc.edu.cn

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than 150 isomer structures, among them the lowest-lying isomer is named as **A1** (Fig. 1B). We then computed relative energy between **A1** and the fullerene B_{80} using the Tao–Perdew–Staroverov–Scuseria (TPSS)²³ functional which was proven by Oger *et al.* to give reasonably accurate energetic properties of small boron clusters,^{8b} and an all-electron 6-311G(2d) basis set, implemented in the *Gaussian 09* package.²⁴ In addition, we computed the relative energy between **A1** and the B_{80} fullerene using a popular B3LYP functional²⁵ based on the B3LYP/6-31G(d) optimized geometries, as well as using the second Møller–Plesset perturbation theory method, MP2/6-31G(d), based on the PBE/GTH-DZVP optimized geometries.

Computed relative energies, HOMO–LUMO gaps, and ionization potentials (IPs) for the fullerene B_{80} and **A1** isomer are listed in Table 1. All levels of theory indicate that the **A1** isomer is much lower in energy than the fullerene B_{80} , although the energy differences are sensitive to *ab initio* methods. Compared to the B3LYP functional, the TPSS functional appears to give closer energy difference to the MP2 method, consistent with a previous conclusion.^{8b} Hence, the TPSS/6-311G(2d) relative energies likely provide a credible measure of relative stability between **A1** and the fullerene B_{80} . All DFT methods show that the HOMO–LUMO gap of the fullerene B_{80} is larger than that of the **A1** isomer, suggesting that the I_h - B_{12} -containing structures of B_{80} are possibly more chemically active than the fullerene B_{80} , even though the latter is energetically metastable.

Harmonic vibrational frequency calculation was performed for the fullerene B_{80} and the **A1** isomer, based on the PBE/GTH-DZVP level of theory. No imaginary frequencies were found, confirming both structures are local minima. The computed infrared (IR) spectra are shown in Fig. 1C. A notable difference between the IR spectrum of the fullerene B_{80} and that of the **A1** isomer is that the highest vibrational frequency of fullerene B_{80} is 1134 cm^{-1} , whereas that of the **A1** isomer amounts to 1379 cm^{-1} . We found that the high-frequency peaks beyond 1200 cm^{-1} for the **A1** isomer are mainly due to vibration modes of the outer shell, suggesting that the outer shell possesses a number of stronger boron–boron bonds. Furthermore, the lowest frequency (33 cm^{-1}) of the **A1** isomer is also higher than that (12 cm^{-1}) of the fullerene B_{80} , suggesting that I_h - B_{12} -containing structures of B_{80} should be mechanically robust. The signature peaks within 1200 – 1400 cm^{-1} therefore may be used to identify I_h - B_{12} -containing structures in large-sized clusters in general and the **A1**-like structure of B_{80} in particular in future experiments.

To gain insights into the thermal stability of I_h - B_{12} containing B_{80} , *ab initio* Born–Oppenheimer molecular dynamics

(BOMD) simulations with the **A1** isomer as the initial structure were performed at five temperatures, *i.e.* 500, 1000, 1500, 2000 and 2500 K, respectively. To this end, a constant-volume and constant-temperature ensemble was chosen in which the Nose–Hoover-chain method²⁶ was used to control the temperature of the system. Again, the PBE/GTH-DZVP level of theory, implemented in the CP2K package, was employed for the five BOMD simulations. Each simulation lasted 2.0 picoseconds, with MD time step setting at 1.0 fs.

The snapshots at four time stages and 1000, 1500, and 2000 K are shown in Fig. SI-1A–SI-1C, respectively.† At 1000 K, the structure of the **A1** isomer was little changed during the simulation. Only a tiny vibration can be discerned; both the inner core and the outer shell maintained their shape like a solid cluster. At 1500 K, the boron atoms in the outer shell diffuse around the inner core, behaving like a liquid layer. However, the I_h - B_{12} core remains intact during the simulation, indicating that the B_{12} core is thermodynamically more stable than the outer shell. At 2000 K, the core–shell structure collapses, and the cluster becomes liquid-like. Note that the melting point of bulk boron is in the range of 2350–2600 K, much higher than the “melting” point of B_{80} cluster in the MD simulations. The melting process can also be characterized by the root mean squared distances (RMSDs) shown in Fig. SI-2A.† The RMSDs of I_h - B_{12} containing B_{80} are smaller than 0.3 Å at 500 and 1000 K, but increase rapidly at 1500–2500 K. The RMSD at 1500 K is significantly larger than that at 1000 K, but much less than that at 2000 K. The RMSDs of the inner core and the outer shell of the core–shell structure at 1500 K are shown in Fig. SI-2B,† where the large values of RMSD of the outer shell are in stark contrast to the small values of RMSD of the inner core, indicating that the icosahedral B_{12} core is more thermally stable than the outer shell. The radial distribution functions (RDFs) and the boron–boron pair distribution functions (PDFs) are displayed in Fig. SI-2C and SI-2D, respectively.† The three main peaks of RDFs at 1.7, 3.5 and 4.5 Å are due to the I_h - B_{12} inner core, the outer shell, and the bridging atoms that connect the inner core and outer shell. The latter two peaks are notably broadened as the temperature increases and eventually disappear at 2000 K or higher temperature. The three main peaks in Fig. SI-2D† are due to three prevailing boron to boron distances. The first peak at $\sim 1.7\text{ Å}$ simply corresponds to the boron–boron bond length. The second peak at $\sim 3.0\text{ Å}$ corresponds to the long diagonal length of the prismatic D_{2d} - B_4 motif (*i.e.*, α - χ distance in Fig. SI-2D†), a basic structure unit in the boron clusters. The third peak at $\sim 4.5\text{ Å}$ corresponds to the length of the summation of the diagonal and a B–B bond (α - δ distance in Fig. SI-2D†). The second and

Table 1 Calculated properties of the fullerene B_{80} and the **A1** isomer, all in units of eV

	Fullerene B_{80}	A1 Isomer of B_{80}
Relative energy	1.578 ^a /1.593 ^b /0.507 ^c /2.498 ^d	0
HOMO–LUMO gap	1.099 ^a /1.022 ^b /1.835 ^c	0.416 ^a /0.429 ^b /1.087 ^c
Ionic potential	6.724 ^e	6.533 ^e

^a Results from TPSS/6-311G(2d)//PBE/GTH-DZVP calculation. ^b Results from TPSS/6-311G(2d)//TPSS/6-31G(d) calculation. ^c Results from B3LYP/6-311G(2d)//B3LYP/6-31G(d) calculation. ^d Results from MP2/6-31G(d)//PBE/GTH-DZVP calculation. ^e Results from PBE/GTH-DZVP optimization.

third peaks in PDFs suggest that the prismatic B_4 motif is a popular structural unit in the core-shell B_{80} cluster.

Finally, structures of the cluster taken from the MD trajectories at 2000 K, with the interval of every 20 fs step, were optimized to local minima. More than 100 additional isomers were collected but none is lower in energy than **A1**. Structures of six lowest-lying isomers (**A1–A6**) obtained from either the basin-hopping or MD simulations are shown in Fig. SI-3A.† All **A1–A6** isomers exhibit the I_h - B_{12} -containing core-shell structure, where the I_h - B_{12} core is highlighted in red (Fig. SI-3A†). Note that the outer shells of the **A1–A6** isomers exhibit some “holes”. This is because the outer shells still favor quasi-planar structures and thus adopt a triangle-web-like pattern as in small-sized quasi-planar boron clusters. As such, the total number of 68 boron atoms is not enough to form a fully closed shell to cover the I_h - B_{12} core. There are significant differences in the distributions of boron–boron bond lengths of **A1–A6** isomers and the fullerene B_{80} , as shown in Fig. SI-3B.† The B–B bond lengths in the fullerene B_{80} are in a narrow range of 1.65–1.75 Å, indicating that the B–B bonds are more or less the same in the fullerene B_{80} . However, in the I_h - B_{12} containing B_{80} , the B–B bond lengths are more broadly distributed, from 1.5 to 2.0 Å. For each of **A1–A6** isomers two higher peaks can be seen in the range 1.65–1.70 Å and 1.75–1.80 Å, respectively, corresponding to two groups of prevailing bond lengths as observed in crystalline boron.^{2,4} Furthermore, both the inner core and the outer shell possess numerous small boron motifs, such as C_{2v} - B_3 , D_{2d} - B_4 , C_{2v} - B_5 , D_{2h} - B_6 , C_{5v} - B_6 , and C_{2v} - B_7 .^{5,6}

Relative energies between **A1** and **A2–A6** were computed using the TPSS/6-311G(2d)//PBE/GTH-DZVP method (Fig. SI-3A†). All **A2–A6** isomers are lower in energy than the fullerene B_{80} (see Table 1). Hence, the highly symmetric and highly stable fullerene B_{80} may be viewed as a deep local minimum on the potential energy surface (PES), whereas the I_h - B_{12} -containing core-shell structures of B_{80} may correspond to a “basin” on the PES, which itself entails a large number of local minima. Some of these local minima (those corresponding to **A1–A6** isomers) are very deep. Hence, we expect that the I_h - B_{12} -containing structures of B_{80} are entropically more favorable at finite temperatures than the sole fullerene structure B_{80} . In closing, we note that because it is impossible to explore entire landscapes of the PES of B_{80} , the obtained **A1** isomer should not be considered as the global minimum of B_{80} . Nevertheless, our aim here is to seek a generic structural family of low-energy B_{80} isomers, rather than to attain a single global minimum. In view of the existence of a large number of low-lying I_h - B_{12} -containing structures of B_{80} , we expect that the structural transformation for boron clusters from tubular to bulk-like I_h - B_{12} -containing structures may occur at a critical size less than B_{80} .

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