

Unprecedented Prediction of a B₁₆₀ Cluster Stuffed by Dual-Icosahedron B₁₂

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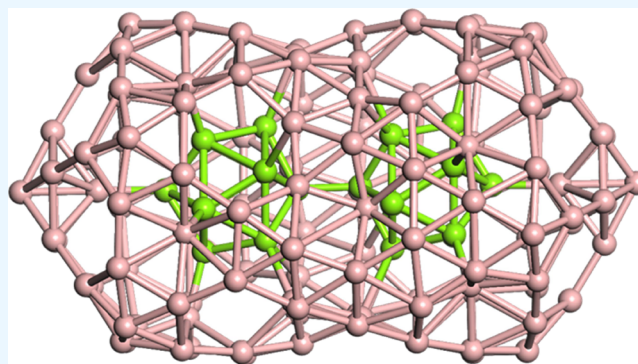


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ABSTRACT: Serving as the premise to understand bulk allotropes, boron clusters have been intriguing experimentalists and theoreticians to study their geometries and chemical bonding. Here, we designed a complete core–shell B₁₆₀ cluster stuffed by two B₁₂ cores, which is energetically preferable over the bilayer structure of the same size. The unprecedented peanutlike structure with C_i symmetry has superior stability and exhibits superatomic electronic configuration and spherical aromaticity. Our theoretical work not only proposed the core–shell structure of dual icosahedrons for the first time but also indicated the multi-B₁₂ core–shell structural pattern in boron particles, bridging to boron crystalline structures.



1. INTRODUCTION

The nature of electron deficiency in boron leads to unique structures and unusual bonding in boron compounds and related nanomaterials.^{1–3} Boron can form fascinating multi-center two-electron bonds (mc–2e). Serving as the premise to understand bulk allotropes, boron clusters have been intriguing experimentalists and theoreticians to study their geometries and chemical bonding.^{4–8} Particular attention was paid to the structural evolution of boron clusters as their size increases: small boron clusters within 19 atoms were characterized to be planar or quasi-planar, and the structural transition from two dimension to three dimension was found to occur at B₂₀ tubes;^{4,5,9} B_n clusters of $n \leq 62$ were extensively studied both experimentally and theoretically, including the plane, irregular cage, tube, and bilayer configurations.^{4–20} For large sizes, Yakobson's research group proposed a perfect B₈₀ buckyball based on the famous C₆₀ fullerene in 2007.²¹ However, this eye-catching structure with high symmetry (T_h) has poor stability, as demonstrated by later studies. For example, two independent works revealed in 2010 that the core–shell B₈₀ structure is more energetically favorable than the buckyball cage, which were obtained using simulated annealing incorporated with first principles molecular dynamics (FPMD-SA)²² and the basin-hopping Monte Carlo algorithm,²³ respectively. Back in 2008, Prasad and Jemmis constructed a few B_{98–102} clusters by stuffing icosahedral B₁₂ in boron fullerenes,²⁴ and these core–shell structures exhibit higher binding energies than the B₈₀ buckyball. The validated density functionals also established that the core–shell structural pattern is energy-preferred for B₈₀.^{25,26} Note that the B₁₂ core of core–shell B_n is not fully covered for $68 \leq n \leq$

84,^{22,23,25–27} and the B₁₂ stuffed boron fullerenes around B₁₀₀ were predicted to have complete core–shell configuration.^{24,25}

Recently, Li's group reported even larger clusters of B_{106–130} core–shell structures:²⁸ B_{108–114} and B_{120–130} were built based on the C₇₀ fullerene cage with D_{5h} symmetry and C₈₀ with I_h symmetry, respectively, and among them, B₁₁₂ with C_s symmetry has the highest binding energy. Beyond the core–shell motif, the quasi-planar/tubular structure, bilayer, and unit of boron crystals were also proposed for large boron clusters,^{29,30} and the core–shell pattern is also prevailing for the boron clusters sized in $n = 92 \sim 124$.³¹ As the size increases, B atoms will be overloaded to the shell for the core–shell (icosahedral-B₁₂ stuffed) structures; what will the stuffing be?

In this work, we successfully designed an unprecedented dual-B₁₂-stuffed B₁₆₀ with C_i symmetry, in which dual B₁₂ are connected by a B–B bond. Note that for large sized boron clusters, it is very challenging to locate the lowest structure; however, the first prediction of the peanutlike geometric feature is of great importance for the structural evolution from boron clusters to boron crystalline structures.

2. COMPUTATIONAL METHODS

The structure optimization and frequency calculation were performed using the combination of the TPSSh functional³²

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and 6-311G(d) basis set as implemented in the Gaussian09 program,³³ since such level of theory is capable of reproducing the energy sequence of B₂₀ isomers at high-level CCSD(T) calculations.²⁵ FPMD simulations were carried out in the NVT ensemble at 300, 500, and 1000 K for 5 ps with a time step of 1 fs, respectively, using the DMol³ code,³⁴ to assess the thermal stability. Chemical bonding was characterized by the natural bond orbital (NBO)³⁵ and adaptive natural density partitioning (AdNDP) methods.³⁶

3. RESULTS AND DISCUSSION

3.1. Structure and Stability. B₁₆₀ was originated from the D_{5h} C₁₀₀ fullerene (consisting of 12 pentagons and 34 hexagons) by replacing all C atoms to B atoms, two B₁₂ icosahedrons connected by a B–B bond (highlighted in green in Figure 1) were stuffed inside the D_{5h} B₁₀₀ cage, 22 B atoms

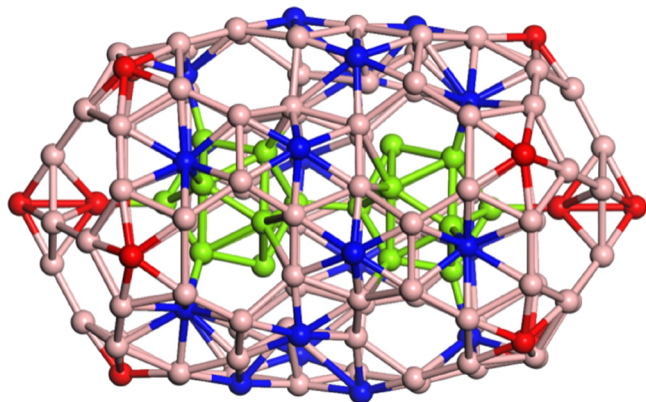


Figure 1. Structure of B₁₆₀. Atoms highlighted in red, blue, and green balls are pentagon capped B, hexagon capped B, and core B, respectively.

were added to the centers of the 22 hexagons in the middle region (highlighted in blue in Figure 1), each of the 12 pentagons was individually capped by one B atom, and one more B atom was added to each of the two end pentagons (highlighted in red in Figure 1), forming two bipyramids. The constructed B₁₆₀ has C_i symmetry and a peanutlike shape (Figure 1). Alternatively, C_i B₁₆₀ can be regarded as the joint of two trunked T_h B₉₆, which was obtained by substituting C₆₀ fullerene to B₆₀ cage and adding 12 B atoms to each pentagon center and another 12 B atoms to the center of the 12 hexagons out of the 20 hexagons and then encapsulating the icosahedron B₁₂.³¹ The optimized coordinates of C_i B₁₆₀ are provided in Table S1 of the Supporting Information.

Our designed B₁₆₀ with C_i symmetry is a local minimum as demonstrated by all positive frequencies (Figure S1 of the Supporting Information). The binding energy (E_b) in this work was defined as $E_b = (nE_1 - E_n)/n$, where E_1 and E_n are the energy of a single B atom and the total energy of the cluster, respectively, and n is the number of B atoms within the cluster. The E_b of B₁₆₀ was calculated to be 5.415 eV/atom. Noting that the proposed bilayer B_{124–828} containing one or multiple conjoined B₇₂ bilayer hexagonal prisms can be viewed as embryos of the newly reported most stable freestanding BL- α^+ bilayer borophenes,^{37,38} we constructed a bilayer B₁₆₀ (Figure 2), whose binding energy (5.366 eV/atom) is lower than the value of our B₁₆₀ at the same level of theory. Therefore, the

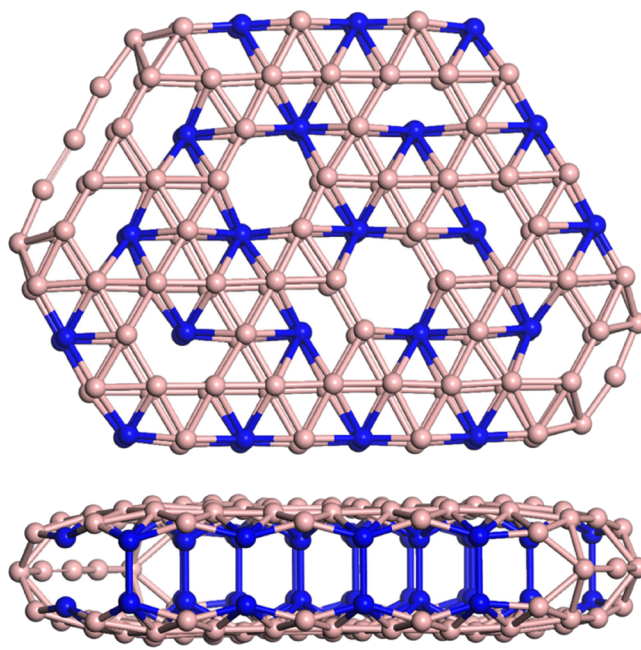


Figure 2. Top and side views of the bilayer B₁₆₀ cluster. The inward-buckled B atoms are highlighted in blue.

dual-icosahedron stuffed B₁₆₀ is energetically favored than the bilayer configuration.

Meanwhile, the FPMD simulations were carried out for our constructed C_i B₁₆₀ to further evaluate its thermal stability. Through 5 ps FPMD simulations, the peanutlike structure was well maintained at both 300 and 500 K (Figure 3); when the temperature was increased to 1000 K, the heated structure was almost identical to the initial one. Thus, B₁₆₀ has very high thermal stability.

3.2. Chemical Bonding Analysis. To gain further insight into the high stability, detailed AdNDP bonding analysis was explored for dual-icosahedral-B₁₂-stuffed B₁₆₀. The AdNDP analysis revealed that each icosahedral-B₁₂ core in C_i B₁₆₀ possesses 13 completely delocalized σ bonds (Figure 4), thus exhibiting obvious superatomic characteristic with the electronic configuration of 1s²1p⁶1d¹⁰1f⁸, which agrees well with the results of B₉₆,³¹ B₁₁₁⁺, and B₁₁₂ clusters.²⁸

In addition, the AdNDP bonding pattern of B₁₆₀ depicted a symmetry of C_i. It possesses 16 localized 2c–2e σ bonds in radial directions of cores, one 2c–2e σ bond connecting the dual-icosahedral B₁₂ cores, 40 2c–2e σ bonds located on outer-shell B₁₃₆, 6 3c–2e σ bonds in radial directions of cores, 60 3c–2e σ bonds on the 12 B₆ pentagonal pyramids, 52 3c–2e σ bonds on the waist of peanut-shaped structure, 10 4c–2e σ bonds on the two ends, 20 4c–2e σ bonds on 10 hexagonal pyramids, 2 and 6 5c–2e σ bonds with C_i symmetry on the waist and hexagonal pyramids, respectively, and one completely delocalized 136c–2e bond on the outer shell. All the bonds have ON of ~ 2 lel, and thus such bonding patterns present spherical aromaticity to their high stability, which were further demonstrated by the negative NICS (nucleus-independent chemical shifts) value of -43.7 ppm at the center of C_i B₁₆₀.

Accordingly, a pronounced feature of a delocalized σ bond can be seen in the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) of this peanutlike cluster (Figure 5a,b). The electron

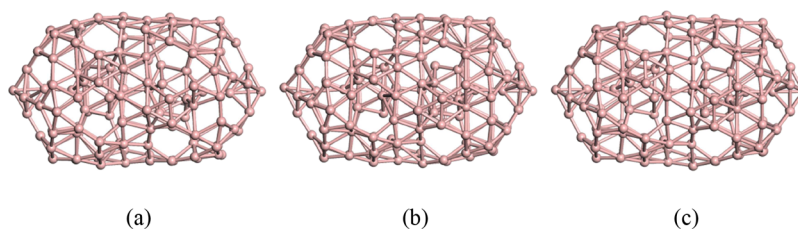


Figure 3. Final structures of $C_i B_{160}$ through 5 ps FPMD simulations at temperature 300 (a), 500 (b), and 1000 K (c), respectively.

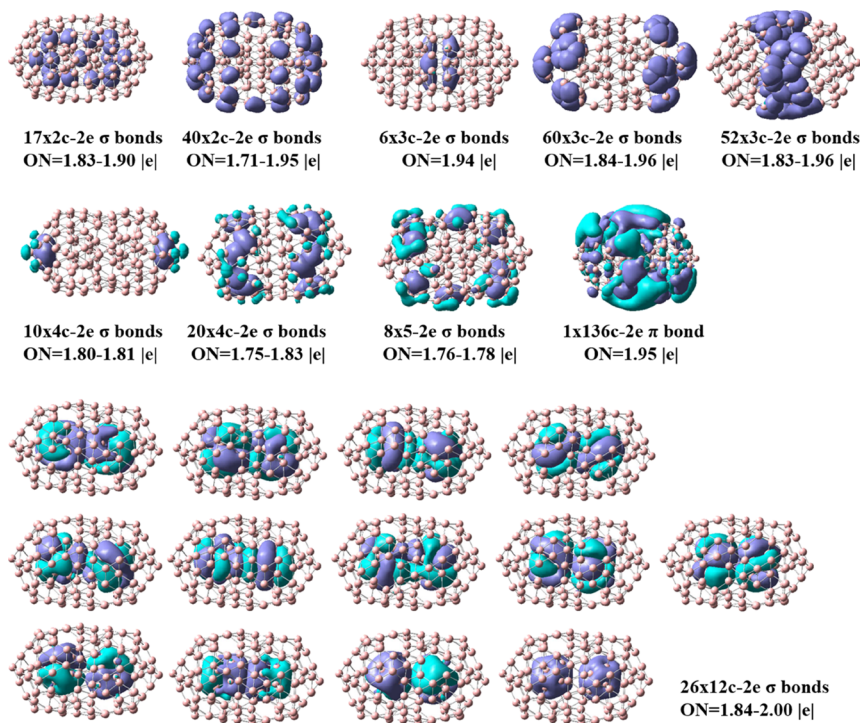


Figure 4. AdNDP chemical bonding patterns of $C_i B_{160}$ with the occupation numbers (ON) indicated.

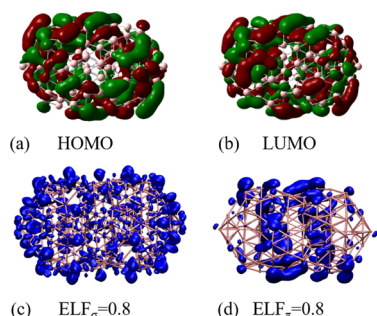


Figure 5. HOMO (a), LUMO (b), and ELF (c,d) of the $C_i B_{160}$ cluster. The isovalue of the ELF was set as 0.8.

localization function (ELF) results (Figure 5c,d) suggest the existence of localized B–B and delocalized σ bonds among the whole structure, while the ELF_π pattern shows the π -system on the outer shell. The bonding picture provided by the frontier MOs and the ELF is consistent with the AdNDP bonding analysis, as displayed in Figure 5.

4. CONCLUDING REMARKS

To sum up, a highly stable B_{160} with a peanutlike structure was constructed, as verified by its all positive frequencies, high binding energy, and structural integrity during FPMD

simulations at high temperatures. B_{160} structurally stuffed by two B_{12} icosahedron cores has higher binding energy than the bilayer counterpart of the same size. The extraordinary stability of dual- B_{12} -stuffed B_{160} can be assigned to its superatomic characteristic and spherical aromaticity. The dual-icosahedral- B_{12} stuffing feature was unprecedentedly and successfully proposed, indicating that larger boron clusters with multi- B_{12} cores are accessible as the embryo to form bulk boron allotropes.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acsomega.2c05918>.

The computed frequencies of $C_i B_{160}$ and the optimized coordinates of $C_i B_{160}$ at the TPSSh/6-311G(d) level (PDF)

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Notes

The authors declare no competing financial interest.

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