Stuffing Improves the Stability of Fullerenelike Boron Clusters

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First-principles electronic structure calculations show that boron clusters B_{98}, B_{99}, B_{100}, B_{101}, and B_{102} based on icosahedral-B_{12} stuffed fullerenes are more stable than the fullerenelike boron clusters. These more stable structures are envisaged as an icosahedral B_{12} each vertex of which is connected to the apex of a pentagonal pyramid (B_6) via radial $2c$-$2e$ $\boldsymbol{\sigma}$ bonds. The resulting B_{84} ($B_{12}@B_{12}@B_{60}$) retains the same symmetry as C_{60}, and the B_n ($n = 84$–116) clusters are generated around it. We further project the possibility of producing such B_{12} based giant clusters.

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Dramatic developments in the chemistry and physics of fullerenes, carbon nanotubes, and graphene have triggered experimental and theoretical investigations towards their boron and other-atom analogues [1–10]. The preference of two dimensional (2D) structures for small boron clusters [1,2], synthesis of boron nanotubes [3], and prediction of 1D boron rings [4] are all the results of this thrust. Recently, Szwacki and co-workers proposed B_{80} as the most stable fullerenelike boron cluster in comparison to a variety of smaller and larger ones [5]. This appeared logical as B_{80} is "isoelectronic" and "isostructural" to C_{60} with the missing 60 electrons of B_{60} provided by the 20 B atoms, each B atom giving three valence electrons. Recent studies of Tang and co-workers [6] on the stability of planar boron structures involving triangles and hexagons imply that with a similar surface B_{80} might indeed be the most stable boron fullerene (Fig. 1). Despite these observations, we present here chemical reasoning based on the electronic structure of boranes, elemental boron, and boron-rich solids for the existence of boron clusters built on an icosahedral base which are more stable than B_{80}. We deduce the electronic structure and energetics of such clusters using first-principles density functional theory (DFT) calculations and the reasons for their stability based on molecular orbital method. We also use density of states (DOS) to understand the bonding in these clusters.

Ab initio DFT calculations are performed using DMOL3 module in Materials Studio [11]. The boron clusters are fully optimized in the given symmetry and also starting from slightly distorted geometries using generalized gradient approximation treated by Perdew-Burke-Ernzerhof exchange-correlation potential [12]. An all electron double numerical atomic orbital augmented by d-polarization functions (DNP) as basis set is used. The self-consistent field (SCF) procedure was used with a convergence threshold of 10^{-6} a.u. on energy and electron density. The direct inversion of the iterative subspace technique developed by Pulay is used with a subspace size 6 to speed up SCF convergence on these large clusters [13]. In order to achieve the SCF convergence when the gap between the highest occupied molecular orbital and the lowest unoccu-

pied molecular orbital (HOMO-LUMO) is small, thermal smearing using finite-temperature Fermi function of 0.005 a.u. is used. Geometry optimizations were performed with a convergence threshold of 0.002 a.u./Å on the gradient, 0.005 Å on displacements, and 10^{-5} a.u. on the energy. In order to compare with the reported B_{80} results we have optimized the lowest energy boron clusters using the GAUSSIAN 03 program [14] within PBEPBE/6-31G(d, p) level of approximation. The harmonic vibrational frequencies for the lowest energy boron clusters has also been calculated. In Table I we summarize the cohesive energy per atom (E_c) and HOMO-LUMO gaps in electron volts for the boron clusters.

Compared to carbon ($1s^2\,2s^2\,2p^2$), boron ($1s^2\,2s^2\,2p^1$) is just one electron deficient. This innate electron deficiency forces boron to form three-center two-electron or multicenter two-electron bonds ($3c$-$2e$ or mc-$2e$). This leads to a wide range of boron structures beginning from its conventional three dimensional (3D) trigonal polyhedral geometries to the recently uncovered quasi-2D and tubular 1D geometries (Figs. 1 and 2). But, whenever boron
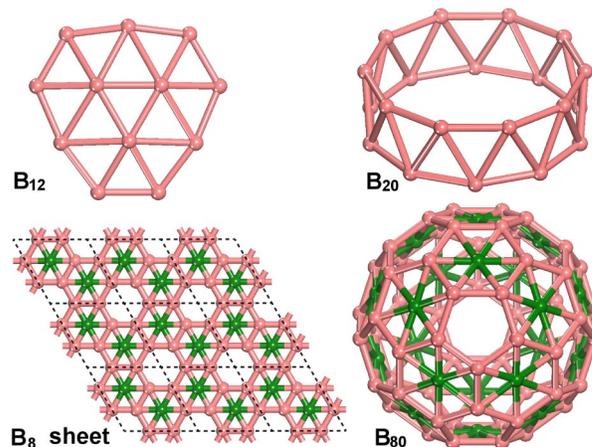
FIG. 1 (color online). Optimized boron clusters based on triangle and hexagon motifs: quasi-2D B_{12} [2], 1D B_{20} ring [4]. The 2D B_8 sheet [6] and 3D B_{80} fullerene [5]. The central hexagonal boron atoms are shown in green (dark areas).

TABLE I. Cohesive energies (eV/atom) and HOMO-LUMO (*H-L*) gaps (eV) for different boron cluster (B_n) along with symmetry labels.

B_n	$-E_c$	H-L	B_n	$-E_c$	H-L
B_{60} (I_h)	4.848	0.385	B_{72} (I_h)	5.494	0.336
B_{80} (I_h)	5.640	0.987	B_{84} (I_h)	5.346	0.910
B_{96}(I_h)	5.62	0.03	B_{98} (D_{3d})	5.67	0.062
B_{99} (C_{3v})	5.678	0.368	B_{100} (C_{2h})	5.689	0.356
B_{101} (C_s)	5.721	0.419	B_{102} (D_{3d})	5.715	0.632
B_{104} (D_{3d})	5.626	0.314	B_{106} (D_{5d})	5.547	0.613

gains an electron, boron may adapt structures preferred by their neighbor in the periodic table, because boron acquires carbon electronic configuration ($B^- \sim C$). For example, the high temperature superconductor MgB_2 ($Mg^{+2}(B^{-1})_2 \sim C_2$) and the LiB ($Li^+B^- \sim C$) 1D chain are analogous to graphite and polycarbyne, respectively [15]. There are also boron nitride analogues of diamond, graphite, fullerenes, and nanotubes ($B^+N^- \sim C_2$) [16]. All of them are known experimentally. The modeled B_{80} fullerene ($B_{60}^{-60} \sim B_{80} \sim C_{60}$) and the B_8 sheet ($B_6^{-6} \sim B_8$) mentioned above are the new additions to the list.
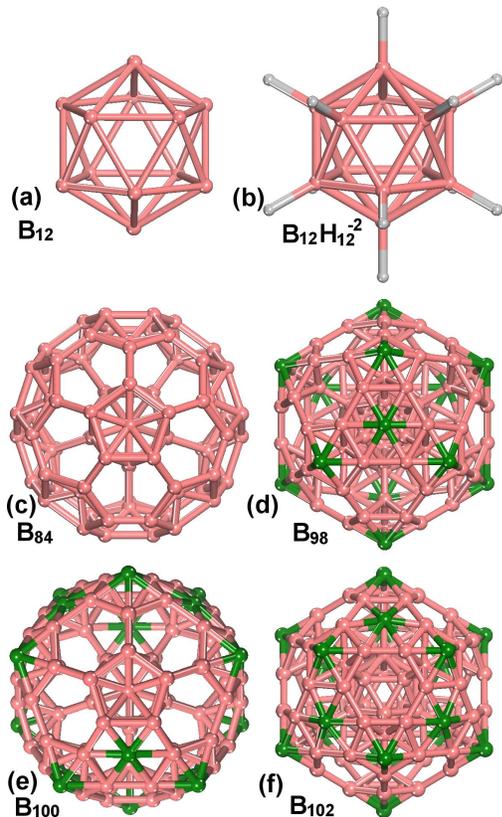
FIG. 2 (color online). Optimized boron clusters based on icosahedron units: (a) B_{12}, (b) $B_{12}H_{12}^{-2}$. (c) B_{84} is extracted from β-boron [17]. In B_{98} (d), B_{100} (e), and B_{102} (f) the added boron atoms are on top of the B_{84} at respective positions shown in green (dark areas). B_{99} and B_{101} are generated by removal of three and one central hexagonal boron atoms from B_{102}.

However, elemental boron never formed carbon analogues experimentally. They are predominantly constructed by the 3D icosahedral B_{12} networks with electron deficient *mc*-2*e* bonds [17–21]. The stand-alone B_{12} cluster [Fig. 2(a)], where the dangling valence is saturated by radial 2*c*-2*e* $\boldsymbol{\sigma}$ bonds, is a dianion according to the Wades $n + 1$ skeletal electron counting rule [Fig. 2(b)] [22,23]. The electron deficiency of these B_{12} clusters in boron and boron-rich icosahedral cluster solids (BRICS) can be annihilated by the formation of electron-saving intercluster *mc*-2*e* bonds and various possible condensations of B_{12} units. This process creates vacancies and partial occupancies (intrinsic defects) [17–21,24]. Such crystal packing with B_{12} unit is found to be stable. In fact β-rhombohedral boron (β-boron) is the thermodynamically most stable boron allotrope with such crystal packing [21,25]. Not surprisingly the dominant polyhedral borane in the series $B_nH_n^{-2}$ is the icosahedral $B_{12}H_{12}^{-2}$ [19]. However, when we knock out the radial 2*c*-2*e* $\boldsymbol{\sigma}$ B-H bond the resulting pure boron clusters turn out to be stable in quasiplanar or tubular geometries. If the missed radial electrons are provided by 2*c*-2*e* $\boldsymbol{\sigma}$ bonds, the resultant clusters would be more stable in the conventional polyhedral skeleton rather than in the quasi-2D geometry. This is because of the better utilization of radial electrons in the formation of the strong 2*c*-2*e* $\boldsymbol{\sigma}$ bond. The peripheral orbitals of the flat structures otherwise would be participating in quasi-$\boldsymbol{\pi}$ bonding or remain as nonbonding [2]. Here, we formulate reaction enthalpies (electron volts) to understand the efficacy to produce 3D boron clusters from the 2D clusters as shown in the set of chemical reactions:

$$B_{12}(C_{3v}) + 3H_2 \rightarrow B_{12}H_6(C_{2v})\Delta H = -7.700$$

$$B_{12}(C_{3v}) + 4\frac{1}{2}H_2 \rightarrow B_{12}H_9(C_s)\Delta H = -11.863$$

$$B_{12}(C_{3v}) + 6H_2 \rightarrow B_{12}H_{12}(C_{2v})\Delta H = -14.210$$

$$B_{12}^{-2}(C_1) + 6H_2 \rightarrow B_{12}H_{12}^{-2}(I_h)\Delta H = -19.469.$$
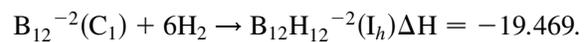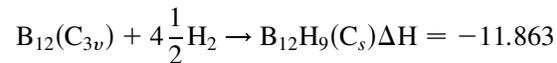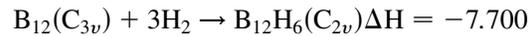
The consistent increment in the large heat of formation towards B_{12} icosahedron suggests strongly that the structures based on icosahedral B_{12} units with precise electron requirements would be more stable. Is there a way to design C_{60} like boron structures when we introduce the additional radial 2*c*-2*e* $\boldsymbol{\sigma}$ bonds with right electron count into the clusters?

The tight-binding calculations of Ivanovskaya and co-workers and *ab initio* DFT calculations of the present authors on MgB_2 and boron analogues of fullerene showed that structures based on B_{60} and B_{84} clusters are stable [9,10]. B_{60}, which is generated by substituting all carbons of C_{60} by boron, is unstable. The finite icosahedral B_{84} cluster is extracted from β-boron. This is a stellation of B_{12} icosahedron and 12 B_6 pentagonal pyramids [$B_{12}@(B_6)_{12}$ or $B_{12}@B_{12}@B_{60}$] found in β-boron allotrope where it is situated at the lattice vertices and connects nearest B_{84} units by the formation of slightly distorted B_{12} units along the lattice direction [17]. All the 12 vertices of the inner

B_{12} unit are connected to the 12 pyramidal apex atoms of the B_6 units by the radial $2c$-$2e$ $\boldsymbol{\sigma}$ bonds, as shown in Fig. 2(c). The 12 pentagons of B_6 units, in turn, extend the crystal lattice by complex condensation within the rhombohedral symmetry. Ideally $B_{12}@12B_{12}$ should be formed, but the perfect fivefold symmetry does not allow the formation of a periodic crystal. If $B_{12}@12B_{12}$ competes towards crystallization there will be complex intrinsic defects along with the termination of intercluster B-B bonds as in YB_{66} [26,27]. Unfortunately, the finite B_{84} cluster is deficient by 50 electrons according to the Wades $n + 1$ and $n + 2$ skeletal electron counting rules [22,23]. So the 50 electron deficient B_{84} should not be expected as a stable finite cluster. If the 50 electrons can be given to B_{84} by excess boron atoms in suitable arrangements, it would be stable. The outer surface of B_{60} of B_{84} has the same symmetry as C_{60} and hence B_{84} is formally a stuffed fullerene based on boron [28].

The 50 electron deficient B_{84} cluster can be made electron sufficient by adding 16.66 boron atoms. So the $B_{100.66}$ would be the right candidate. But fractional boron atoms are not possible. B_{84} can approach near electron sufficiency by adding 14–18 boron atoms on the surface of the cluster systematically. This would generate B_{98} (D_{3d}), B_{99} (C_{3v}), B_{100} (C_{2h}), B_{101} (C_s), and B_{102} (D_{3d}) boron clusters [Figs. 2(d)–2(f)]. Out of the several combinations possible, we have restricted to the ones built from the previous structure of high symmetry. The cohesive energy per atom E_c of these clusters suggests that the "B_{84}" gets increasingly more stabilized while nearing electron sufficient structures (Table I). B_{98} already overcomes E_c of B_{80} by 0.030 eV, though it is 8 electrons deficient. The B_{99}, B_{100}, and B_{101} are 0.038, 0.049, and 0.081 eV more stable than B_{80}, which are close to $B_{100.66}$. The B_{102} which has four electrons more than needed is still 0.075 eV more stable than B_{80}, but less stable than B_{101} by 0.006 eV. Clusters B_{104} (I_h) and B_{106} (D_{5d}) are 0.014 and 0.093 eV less stable than B_{80}. The HOMO-LUMO gap in B_{98} is only 0.062 eV and the gap increases in B_{99} (0.368), B_{100} (0.356 eV), B_{101} (0.419 eV), and B_{102} (0.632 eV) (Table I). The Gaussian basis set based calculations also corroborate the stability of B_{101} and B_{102} over B_{80} by 0.075 and 0.068 eV, respectively. The harmonic vibrational frequencies for B_{100}, B_{101}, and B_{102} are all positive and hence they are local minima. This is to be contrasted with B_{80} (I_h) with 7 low imaginary frequencies; however, the B_{80} (T_h) is a minimum [29] (refer to the auxiliary information [30]). When compared to B_{84} the radial $2c$-$2e$ $\boldsymbol{\sigma}$ bonds are shortened from 1.844 to 1.579 Å in B_{98} to B_{102} clusters. The average B-B cluster bond distance is about 1.780 Å. The average radius (from center of the cluster to the central boron of the hexagon) of the nearly electron sufficient clusters is 4.20 Å, whereas the radius of B_{84} and B_{80} clusters is about 4.01 and 3.83 Å, respectively.

Why is there a range of stable clusters (B_{98} to B_{102}) around $B_{100.66}$? We have to look at the energy of the added electrons in the molecular orbital energy spectrum. For

that, the site projected DOS (PDOS) [31] for B_{102} and for comparison B_{80} fullerene has been generated as shown in Fig. 3. Since the required electrons are provided in terms of boron atoms one should not expect large charge variations from boron to boron. Indeed, the extra 18 boron PDOS of B_{102} and 20 boron PDOS of B_{80} are mixing largely with the B_{84} and B_{60} MO electronic states in the entire energy spectra as shown in Fig. 3. In B_{102} there is a large energy gap (1.348 eV) between HOMO (nearly double degenerate) and HOMO-2 (see Fig. 3, MO energies bar code), which essentially indicates stability of the $B_{100.66}$ cluster ($\sim B_{101}$). The geometry of the spherical clusters did not change much with the excess of electrons as in Li_xC_{60} ($6 \leq x \leq 24$) fullerides [32]. The central hexagonal boron atoms on the surface of the clusters larger than B_{102} are in fact above the surface. The highest unoccupied energy levels in B_{60} and B_{84} are anyway determined by their geometries. If the addition of the required boron atoms retains nearly the same shape of the parent cluster, the added electrons will occupy energy levels which are largely localized on the parent cluster as in B_{80}, and B_{98}-B_{102}.

In order to have a complete energy profile of this B_{84} cluster with respect to the electron count, the B_{108} (D_{2h}), B_{110} (D_{3d}), and B_{116} (I_h) have been generated. For comparison the C_{60} based clusters such as B_{82} (D_{5d}), B_{84} (D_{2h}), B_{86} (D_{3d}), B_{88} (D_{2h}), B_{92} (I_h), and B_{80} tube (four B_{20} rings) are also studied (Fig. 4). The cohesive energy profile of the clusters shows lowering of energy while reaching the required electron count and raising with excess electrons in both B_{84} and B_{60} series (Fig. 4). This strongly suggests that the key to the stability of a given cluster is the ability to provide the required number of electrons as closely as possible. In addition, the B_{12} stuffed fullerenes gains extra stability via the strong radial $2c$-$2e$ $\boldsymbol{\sigma}$ bonds. Therefore the icosahedral B_{12} bonding scenario helps to construct more stable clusters. However, this is not the complete picture. Since several possible isomers can be generated for a given cluster size, the E_c may vary depending on the effectiveness of filling the unoccupied bonding orbitals of B_{60} (in the case of B_{80}) and B_{84} (in the case of $B_{100.66}$). We have
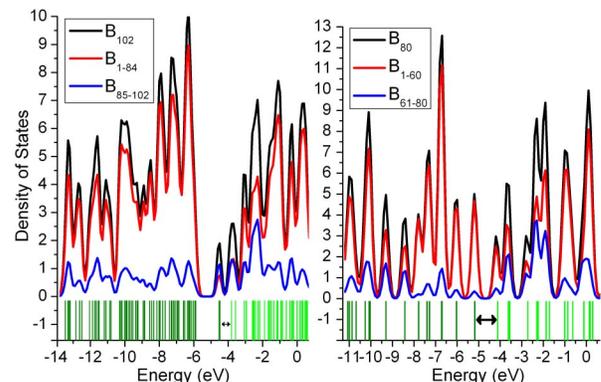
FIG. 3 (color online). PDOS of B_{102} and B_{80} fullerene. The $\leftrightarrow$ between the MO energy bar code indicates the gap between HOMO and LUMO.
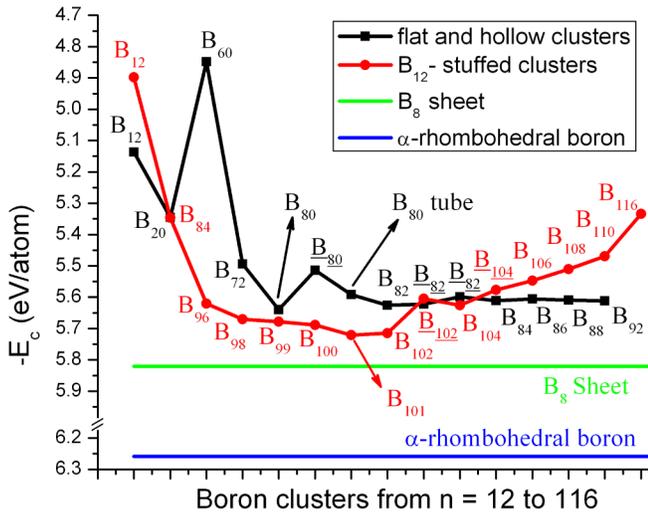
FIG. 4 (color online). Cohesive energy versus number of atoms for the optimized boron clusters. The cohesive energies of the B_8 sheet and α-boron are shown as a guide.

calculated a few isomers B_{80} (D_{5d}), B_{82} (D_{5d}), B_{102} (D_{3d}), and B_{104} (I_h) which are higher in energy (clusters shown with underline in Fig. 4). The B_{80} tubular structure is 0.048 and 0.129 eV higher in energy than B_{80} fullerene and B_{101}. The clusters larger than B_{80} would prefer icosahedral B_{12} based stuffed fullerenes. The new 2D boron sheet is 0.438 eV less favorable than α-rhombohedral boron (α-boron).

In conclusion, the trigonal polyhedron based boron clusters are preferentially stabilized by the combination of radial $2c$-$2e$ σ bonds and mc-$2e$ cluster bonding with the stipulated electronic requirements. The B_{12} stuffed fullerenes, B_{98}-B_{102} are thermodynamically more stable than B_{80} fullerene. Existence of giant B_{84} and $B_{12}@(B_{12})_{12}$ in boron and BRICS prompt us towards a search for B_{12} stuffed fullerenes. There could be a possibility to trace the giant B_{84} based clusters in the melt of β-boron or BRICS [33]. The icosahedral B_6O and B_4C crystals are characterized within the micron size which hints at their nano counterparts [34,35]. The stuffed fullerenelike boron clusters are expected to be less compressible than the hollow ones and would be useful as nanolubricants. If the stable extended 2D boron sheets were synthesized, there would be a kinetic and thermodynamic competition between the hollow and stuffed fullerenes.

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