



B₈₀ Fullerene: An *Ab Initio* Prediction of Geometry, Stability, and Electronic Structure

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The geometry, electronic, and structural properties of an unusually stable boron cage made of 80 boron atoms are studied, using *ab initio* calculations. The shape of this cluster is very similar to that of the well-known C₆₀ fullerene, but in the B₈₀ case, there is an additional atom in the center of each hexagon. **The resulting cage preserves the I_h symmetry, has a relatively large highest occupied and lowest unoccupied energy gap (~ 1 eV) and, most importantly, is energetically more stable than boron double rings, which were detected in experiments and considered as building blocks of boron nanotubes. To our knowledge, this is the most stable boron cage studied so far.**

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Daedalus' early musings on hollow carbon molecules [1], Osawa's carbon soccer ball structure [2], and the first Hückel calculation of stability of carbon fullerenes [3], all remained unsupported by experiment for almost two decades, until the discovery of the carbon buckyball, C₆₀ [4]. Here we describe the structure and stability, and predict the existence of a round boron molecule, B₈₀, which is very similar in shape and symmetry to the carbon fullerene C₆₀. In addition to direct computations, the outstanding stability of the B₈₀ buckyball is explained in terms of its particular construction, which consists of six double-ring clusters interwoven such that they form a round hollow basket. B₈₀ can also be viewed as a B₆₀ (metastable in our calculations) polyhedron reinforced by extra atoms placed in the centers of all hexagons, to satisfy the Aufbau principle for boron-clusters composition [5].

There is a growing interest in exploring the structure and energetics of pure boron clusters and boron containing molecules because they have a wide variety of applications [6]. Because of *sp*² hybridization of the valence electrons, large coordination number and short covalent radius, boron prefers to form strong directional bonds with various elements. These characteristics lead to a large diversity of boron nanostructures: clusters, nanowires, and nanotubes, which have already been observed [5,7–9].

Many experimental and theoretical studies on small boron clusters have been performed [5,10], most important of which appear to be the compact icosahedral B₁₂, and the family of boron double-rings (DRs) with various diameters. It is useful to view the B₁₂ as a tight knot of six overlapping B₁₀ DRs [see Fig. 1(a) (right)]. There is little information in the literature about boron clusters containing more than 36 atoms. In this study, we went beyond this to larger assemblies in order to explore if the reduction in the curvature might further lower the total energy and lead to yet more stable clusters. Of course the tremendous combinatorics of possible arrangements makes any exhaustive comparison almost impossible. Instead, we pri-

marily sought the structures which combine several DRs of larger size (and lower strain) and yet remain not too sparse so that inter-ring bonding serves as an additional stabilizing factor. Indeed, the B₈₀ emerged as a winner, with the largest cohesive energy compared to all others. The connection between the B₈₀ cage and DR tubular clusters (some of which were already synthesized experimentally [8]) motivated us also to include here details of the DRs' energetics.

The calculations were performed within the density functional theory framework, using local-spin-density approximation and generalized gradient corrected exchange and correlation functional PBE [11]. Computations were done using the plane-wave based Quantum-ESPRESSO package [12] and ultrasoft Vanderbilt pseudopotentials [13]. The optimized geometries of the clusters were found by allowing the full relaxation of all the atoms. Molecular

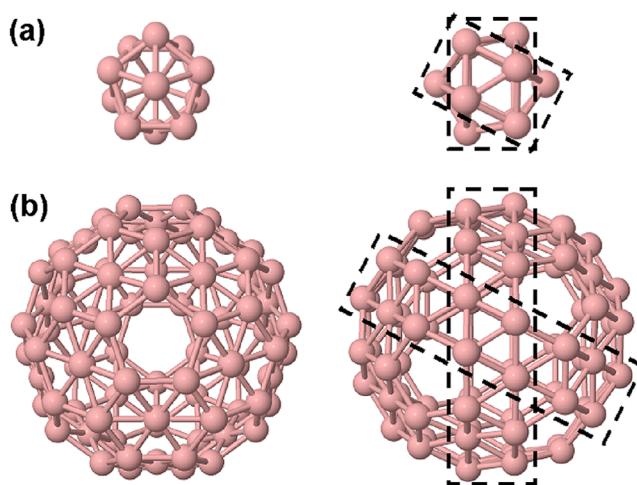


FIG. 1 (color online). Optimized structures of B₁₂ (a) and B₈₀ (b) cages. Both structures are shown in front and side views. For the side views, the subgroup of atoms which form B₁₀ and B₃₀ DRs in B₁₂ and B₈₀ cages, respectively, are outlined.

dynamics simulations were performed using the same package and method, with the choice of 1 fs for the time step. The Γ point was used for the Brillouin zone integrations in the case of the finite structures, and $1 \times 1 \times 16$ ($4 \times 4 \times 4$) k -point sampling was used for the one (three) dimensional infinite structures. To study properties of finite structures, the supercell geometry was taken to be a cubic cell with lattice constant sufficiently large to avoid interactions between the clusters (allowing at least 12 Å between clusters). In order to gain better insight into the electronic properties of the boron cages, most of the structures were recalculated using GAUSSIAN03 package [14]. For the calculations with GAUSSIAN03, we have used the PBE-PBE density functional and all-electron 6-31G(d, p) basis set [15], including polarization functions for all atoms. It should be pointed out that the agreement between the results obtained from both codes is remarkably good.

The properties of small boron clusters are better understood [5,10]. Perhaps the central place among them belongs to B_{12} icosahedron which appears to be the building block of several known crystalline phases of bulk boron [5,16]. In those phases, the B_{12} clusters are held together by directed bonds, either between atoms in adjacent clusters or via intermediate atoms. The most stable bulk structure containing B_{12} units is the α -rhombohedral boron [16]. (The second in stability is the β -rhombohedral boron with the unit cell containing 105 atoms and the structure made up of a B_{84} supercluster with I_h symmetry [16]. The B_{84} cluster alone, however, is not stable and collapses if not supported in the lattice of the bulk, according to our calculations.) Despite its importance, the B_{12} cage is not the most stable boron cluster composed of 12 atoms, since the most stable members of the B_n families with $n < 20$ are known to be planar [17].

Based on the structural similarities among larger boron clusters, a so-called Aufbau principle for boron clusters was conjectured by Boustani [5]. According to this principle, the most stable clusters can be constructed using two basic units: pentagonal pyramid B_6 and hexagonal pyramid B_7 . In Fig. 1(a) we have shown the optimized B_{12} cage. As one can see from the figure, the B_{12} icosahedron is an example of a structure built from pentagonal B_6 units. In this study, however, we look at the B_{12} cage from a different perspective, namely, we consider its structure as built from staggered B_{10} DRs. In the right part of Fig. 1(a), the side view of the icosahedron shows clearly that B_{12} is built from crossing tubular B_{10} structures. The B_{10} structure consists of two pentagonal chains with a staggered arrangement of boron atoms. Each ring is rotated by an angle of $\pi/5$ with respect to the other in order to form the staggered configuration. Because B_{10} is the smallest DR made of boron atoms, B_{12} is the smallest cage built completely from DR clusters.

In our previous studies of the silicon cage clusters and tubes, we observed their remarkable stabilization by insertion of transition metal atoms [18]. Based on this expe-

rience, we tried to similarly stabilize the B_{60} fullerene cage by “reinforcing” each of its hexagonal facets by a transition metal atom, which appeared to be too big. When instead of transition metal, an extra boron atom was placed in each hexagon, the result was surprising. We found a structure, shown in Fig. 1(b), which is built up from 80 atoms, possesses unusually large cohesive energy (E_c), preserves I_h symmetry, and is very stable according to our calculations. In addition, B_{80} has similar characteristics to B_{12} because it is built from DRs. In Fig. 1(b) (right), we mark two crossing B_{30} DRs that are constituents of the cage. The whole cage is made up of 3 such pairs (6 DRs in total). The staggered configuration of each DR is formed by two rings with 15 atoms and each ring is rotated by an angle of $\pi/15$ with respect to the other.

The B_{80} cage is symmetrically similar to the C_{60} structure. The only difference is the presence of an additional atom at the center of each hexagon. These facets of the B_{80} follow the Aufbau principle mentioned before although the hexagonal pyramid units here are rather planar.

In order to evaluate whether or not reinforcing pentagons (instead of or in addition to hexagons) would help with stability of the structure, we investigated two other cages, B_{72} and B_{92} , formed by placing extra boron atoms on top of pentagons (B_{72}) and on pentagons and hexagons (B_{92}) of the B_{60} . The structures are shown in Fig. 2(b) after optimization. The B_{72} cage is round and preserves I_h symmetry but is less stable than the B_{80} . The B_{92} is completely built with triangular bonding units which are generally favorable in boron clusters [10]; however, this cage is also less stable than the B_{80} cage.

This opens up the possibility of a completely new family of boron clusters, which may have similar shapes to carbon fullerenes but have an additional atom at the center of each hexagon. We studied this type of cages with sizes smaller than 80 atoms (derived from fullerenes with less than 60 atoms), as well as one bigger cage, B_{110} . More precisely, we applied reinforcement of hexagons to boron isomorphs of C_{24} , C_{26} , C_{28} , C_{32} , C_{36} , C_{50} , and C_{80} fullerenes (specified by D_6 , D_{3h} , D_3 , D_3 , D_{6h} , D_{5h} , and I_h symmetries, respectively) and then optimized the obtained structures. Four of them were stable (for which, Wolfe conditions for convergence [19] were satisfied) and their relaxed structures are shown in Fig. 2(a). It is worth noting that none of these structures consist of DRs and perhaps for this reason, they do not have the exceptional cohesive energy that we observe for B_{80} . In Table I we summarized the values of E_c .

In order to further verify the stability of B_{80} , we performed quantum molecular dynamics (MD) simulations at different temperatures (each run was 1.7 ps long). At temperature 700 K, the cage maintains its structure during the MD run and no significant deformations occur. At temperature 1000 K, it deforms but retains its hollow construction.

Since we established the link between B_{12} and B_{80} cages on the one hand, and tubular DR clusters on the other, it is useful to compare their relative stability. In Fig. 3 we have

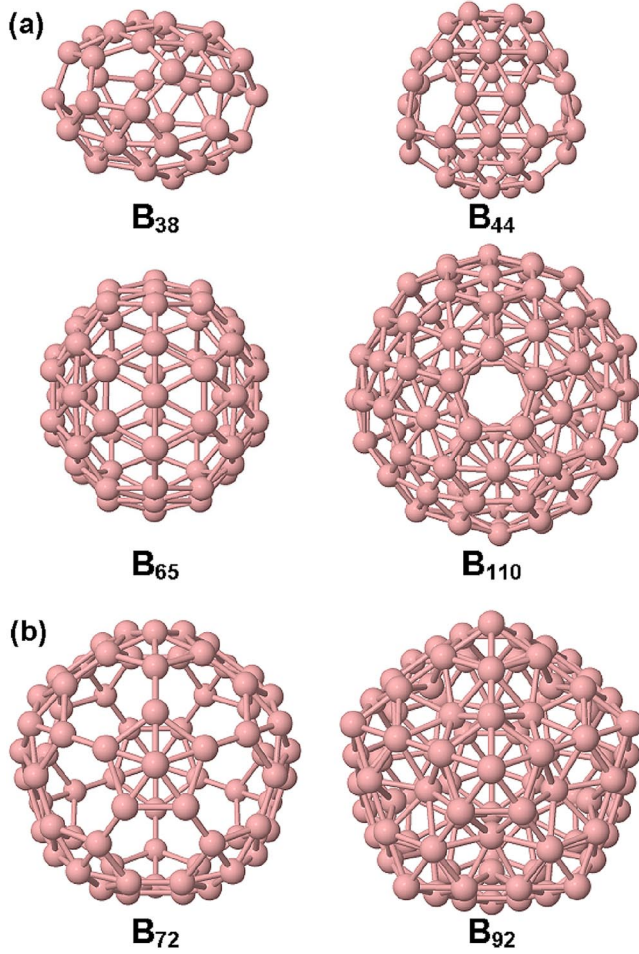


FIG. 2 (color online). (a) Relaxed structures of other members of the family of boron cages with an additional atom at the center of each hexagon, which were found to be stable in our calculations. (b) B₇₂ (left, with atoms at the centers of pentagons) and B₉₂ (right, with atoms at the centers of hexagons and pentagons).

plotted the cohesive energy of several DR structures versus the number of boron atoms (n). In the same figure we have also included the E_c values of all the cages mentioned above, as well as two fullerenes B₂₀ and B₆₀. From Fig. 3 we can see that the E_c values of DRs monotonically increase from the value of 4.72 eV/atom for B₁₀ to the value of 5.69 eV/atom for infinite DR (or strip, which is shown by the blue horizontal line), with the exemption of B₃₂ and B₃₄ DRs, which slightly break the monotonical behavior. Consequently, the most stable structure among all DRs is the strip. The red curve shows the $1/n^2$ behavior, based on the expected dependence of elastic strain energy on the DR diameter (which is proportional to n) [20].

Apart from the fact that DRs appear in the structure of B₈₀, we investigate their energies for yet another reason. Recent calculations show that DR B _{n} clusters with $n = 20, 24, 32$, and 36 are the most stable structures among all clusters with the same number of atoms [8,17,21–23]. Our results show that this is not the case for $n = 80$. B₈₀ ($E_c = 5.76$ eV/atom) is not only more stable than the DR with 80

TABLE I. Symmetries, cohesive energies, and HOMO-LUMO gaps of studied boron cages. The first values (for E_c and energy gap) correspond to results obtained with Quantum-ESPRESSO, whereas the values in brackets were obtained using GAUSSIAN03.

	Symmetry	E_c (eV/atom)	HOMO-LUMO (eV)
B ₁₂	I_h	5.01 (5.00)	0.737 (0.810)
B ₂₀	I_h	4.74 (4.69)	1.253 (0.008)
B ₃₈	D_{3h} , <i>distorted</i>	5.47 (5.48)	0.935 (0.923)
B ₄₄	D_{2h} , <i>distorted</i>	5.55 (5.56)	0.980 (0.965)
B ₆₀	I_h	4.93 (4.91)	0.049 (0.050)
B ₆₅	D_{5h}	5.69 (5.70)	0.095 (0.014)
B ₇₂	I_h	5.60 (5.58)	0.269 (0.001)
B ₈₀	I_h	5.76 (5.77)	1.006 (0.993)
B ₉₂	I_h	5.72 (5.75)	1.129 (1.161)
B ₁₁₀	I_h	5.73 (5.74)	0.119 (0.097)

atoms ($E_c = 5.66$ eV/atom) but is also more stable than the strip ($E_c = 5.69$ eV/atom). The limit for the stability of all boron structures is the α -rhombohedral bulk with $E_c = 6.33$ eV/atom (computed with the same method).

To complete the description of the studied boron cages, it is important to analyze their structural and electronic properties. In the case of B₆₀, all nearest neighbor distances (l_{BB}) are the same (within 5×10^{-3} Å), with an average value of $l_{BB} = 1.689$ Å. The picture for B₈₀ is, however, similar to that of the well-known C₆₀: there are 60 longer ($l_{ph} = 1.727$ Å) and 30 shorter ($l_{hh} = 1.677$ Å) bonds. In

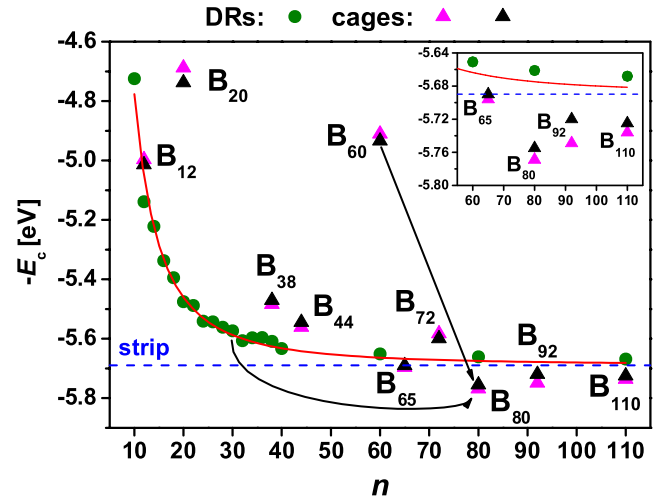


FIG. 3 (color online). Cohesive energy per atom as a function of the number of atoms n in the B _{n} clusters. The circles correspond to double rings, whereas the black (magenta) triangles correspond to cages calculated with Quantum-ESPRESSO (GAUSSIAN03). The blue horizontal line corresponds to the cohesive energy of the infinite double-ring (strip). The arrows show the increase in cohesive energy by reinforcement of hexagons (from B₆₀ to B₈₀) and by appropriate crossing of the double rings to form the icosahedral structure (from B₃₀ DR to B₈₀). The inset shows relative E_c values for four cages B₆₅, B₈₀, B₉₂, and B₁₁₀, more pronouncedly.

addition, there is a third group of 120 bonds (not present in C_{60}) between each atom at the center of each hexagon and its 6 nearest neighbors ($I_{BB} = 1.703 \text{ \AA}$). The B_{60} and B_{80} cages have approximately the same diameter $d = 8.17 \text{ \AA}$, which is much larger than the diameter for C_{60} ($d = 6.83 \text{ \AA}$).

The highest occupied molecular orbital-lowest unoccupied molecular orbital (HOMO-LUMO) energy separation serves as a simple measure of chemical stability [24,25]. Its values for all clusters studied here are listed in Table I. The observation that can be made here is that the gaps exhibit alternations as a function of the number of boron atoms, similar to that known for metallic clusters [26]. When the (nearly) degenerate states (states belonging to the same irreducible representation of the point group) are partially occupied, the gap is small (B_{65} is an example of this case). But when they are fully occupied, the cluster exhibits relatively large HOMO-LUMO gap (which is the case for B_{80}). For B_{80} , the HOMO and LUMO are triply degenerate, forming the bases for T_{2u} and T_{1u} representations of I_h group, respectively (both are odd under parity).

There are no experimental reports about the existence of free boron clusters with exactly 80 atoms. However, there are some facts related to this topic that should be mentioned. In the context of an investigation of the crystal structure of YB_{66} -type boron-rich solids, Higashi *et al.* [27] proposed that YB_{66} contain nonicosahedral B_{80} units with about 50% of the boron sites randomly occupied; however, the structure of those units has not been well established. There are also mass spectroscopy studies of boron-rich glasses [28,29], which clearly display peaks in the mass spectrum at the value 865 amu. These peaks could potentially correspond to clusters with 80 boron atoms, but the authors did not suggest such an interpretation. Although the largest pure-boron clusters experimentally identified so far contain no more than 20 atoms [8,10], it is likely that with proper choice of conditions the larger cages should form. Analysis and comparison of a number of boron structures presented in this work convincingly singles out the spheroid molecule B_{80} as an energetically favorable cage and therefore suggests that it is likely to appear as a result of self-assembly of boron atoms. Of course, self-assembly of 80 atoms even into most stable structure may need to overcome kinetic limitations and only occurs at rather particular conditions which cannot be derived from the present work. Still we believe that the above consideration will act as stimulation in offering a road map for the experimental work in this direction. If the inorganic B_{80} cage is confirmed experimentally, it would be the second example in nature after C_{60} , with a round, monoelemental, and distinct hollow structure.

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