

New Boron Barrelenes and Tubulenes

L. A. Chernozatonskii^a, P. B. Sorokin^{a-c}, and B. I. Yakobson^d

^a Emanuel Institute of Biochemical Physics, Russian Academy of Sciences, ul. Kosygina 4, Moscow, 119334 Russia

e-mail: cherno@sky.chph.ras.ru

^b Siberian Federal University, Krasnoyarsk, 660041 Russia

^c Kirensky Institute of Physics, Siberian Branch, Russian Academy of Sciences, Akademgorodok, Krasnoyarsk, 660049 Russia

^d Department of Mechanical Engineering & Material Science and Department of Chemistry,
Rice University 7751, Houston, Texas, USA

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The structure of a new class of boron nanostructures—barrelenes and tubulenes—based on a boron atomic lattice constructed by the alternating *B*-atomic polygons with central atoms and without them has been proposed and their properties have been described. Ab initio density functional calculations have been performed for the energy and electronic structure of the fullerene–barrelene–nanotube series based on the lowest energy fullerene B₈₀. It has been shown that the energy and band gap of a barrelene are lower than the respective quantities of the corresponding fullerene and tend to the respective values for nanotubes in the infinite limit. It has been shown that there are isomers of nanotubes of the same type that are significantly different in symmetry and electronic properties: a semiconductor (*C*_{5v} symmetry) and a metal (*D*_{5h} symmetry).

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INTRODUCTION

In view of the possible nanotechnological applications, interest has been recently increased not only in a carbon nanostructure, but also in boron nanostructures, which are clusters, nanopetals, nanotubes, and fullerenes [1–6]. Attention in those works was focused on the structure based on the triangular network of atoms each covalently bonded with the six nearest neighbors (for nanotubes) or some with the five nearest neighbors (for polyhedral clusters), which correspond to the construction rule for boron clusters, called the Aufbau principle [2]. A similar triangular lattice with a hexagonal structure of the normal carbon nanotubes, but fastened by atoms at the centers of each six-term cycle, was used to construct other hollow structures based on diborides [7–9] and aluminum [10]. Note that an increase in the stability of such polyhedrons MB₂ when removing some metal atoms M from the centers of polygons was pointed out previously using the example of M_{1–x}B₂ fullerenes [9]. Recently, this idea was supported by the prediction of the B₈₀ fullerene, where the skeleton of the truncated icosahedron B₆₀ contains additional boron atoms only at the centers of 20 hexagons. This appeared to be the most energetically favorable among a number of skeleton fullerene structures with a larger or smaller number of boron atoms. According to the calculations performed by the same authors, the B₆₀ fullerene appeared to be metastable.

A layer similar to the boron structure was shown to be stable and to have metal properties [6], whereas nanotubes are semiconductors [11].

In this work, we call attention to the possibility of the existence of a class of polyhedral structures similar to B₈₀ in construction, which are also energy stable with energies lower than those of B₈₀, and stable metallic nanotubes differing in symmetry from previously considered semiconducting nanotubes.

METHOD AND DETAILS OF THE CALCULATION

All calculations were performed within the framework of the density functional theory [12] with the use of the VASP program [13–15], which allows ab initio quantum-mechanical calculations in the generalized gradient approximation with the Perdew–Burke–Ernzerhof parameterization [16]. A set of plane waves was used as the basis. A cutoff energy of 318 eV was taken in the calculations. The atomic structure was optimized until the interatomic forces became smaller than 0.04 eV/Å. The structures under investigation were placed in a “periodic box,” so that the distance between them and their periodic images was no less than 12 Å.

RESULTS AND DISCUSSION

A number of boron clusters B_{*n*} with *n* = 12, 20, 38, 44, 60, 65, 72, 80, 92, and 110 were investigated in [1].

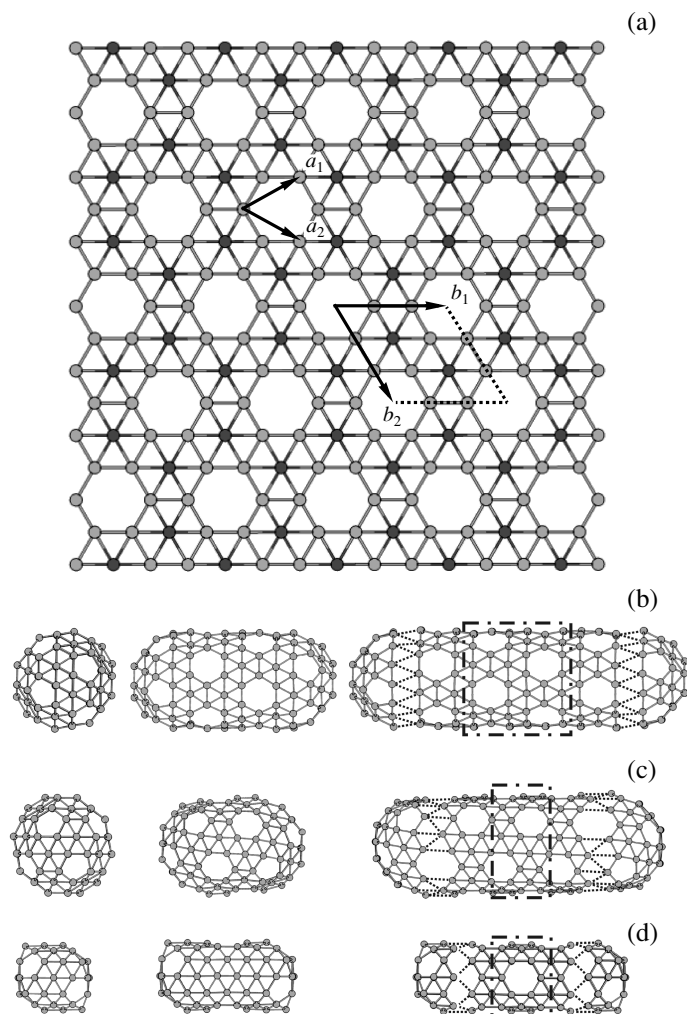


Fig. 1. (a) “Light” hexagonal boron layer with eight atoms in the unit cell with one “empty” center that consists of three unit cells of the MB_2 layer structure occupied over the centers of the B hexagons [9]. The central atoms are shown in dark. The structures of (b) armchair and (c) zigzag boron fullerenes and B_{80} -based barrelenes corresponding to the $\{5, 0\}$ and $\{3, 3\}$ nanotubes, respectively; and (d) the structure of zigzag boron fullerenes and B_{50} -based barrelenes corresponding to the $\{2, 2\}$ nanotube. The dash-dotted frame denotes the unit cells of the corresponding nanotubes.

In particular, the cohesion energy of the structures B_{65} , B_{80} , B_{92} , and B_{110} appeared to be lower than the energy of the ring with an infinite radius (boron belt), which can be treated as the measure of the stability of the boron structures. We consider a new class of boron clusters based on an atomic lattice constructed according to the same principle as B_{80} , i.e., by the alternating B -atomic polygons with and without central atoms (see Fig. 1a). In the B_8 cell consisting of three MB_2 unit cells [9], eight sites are occupied by boron atoms and one site is empty. The relation between the unit vectors of the unit cell of the planar structure, which is the basis for the nanotubes, and of the simple hexagonal lattice (normal graphite or MB_2 layer [9]) has the form

$$\mathbf{b}_1 = \mathbf{a}_1 + \mathbf{a}_2, \quad \mathbf{b}_2 = 2\mathbf{a}_2 - \mathbf{a}_1.$$

Owing to the different orientations of the vectors \mathbf{b}_i and \mathbf{a}_i , the classification of $\{N, M\}$ boron nanotubes is different from the classification of nanotubes based on the simple hexagonal lattice [11]. In particular, they are also divided into two classes, chiral and achiral (depending on the presence or absence of the screw symmetry axis in their symmetry group); however, the latter class is divided into (i) zigzag nanotubes with the same indices $N = M$ (in contrast to $n = 0$ for normal zigzag nanotubes [17]) and (ii) armchair nanotubes with one zero index $M = 0$ and $N \neq 0$ (in contrast to equal indices $n = m$ for normal armchair nanotubes [17]). Note that a similar layer (see Fig. 1a) and stable structures based on this layer can be organized by changing the central boron atoms to atoms of another element, e.g., metal atoms M , the MB_3 lattice.

In contrast to sphere-like polyhedrons [1], the polyhedrons under investigation contain a cylindrical fragment incorporated between the hemisphere hats (see Figs. 1b–1d). Such barrel-like and tubular carbon structures were previously called barrelenes (where the cylinder length is comparable with the hat diameter) [18] and tubulenes (where the length is much larger than their diameter) [19]. More recently, these cylindrical structures were called nanotubes [17].

Now, we discuss in detail the structure and properties of fullerene–barrelene–nanotube series based on the B_{80} fullerene (see Figs. 1b and 1c), and a similar series based on a new small barrel-like fullerene B_{50} (see Fig. 1d).

Fullerene B_{80} . The distances between neighboring atoms in the B_{60} skeleton are $d_{B-B} = 1.68 \text{ \AA}$ and $d_{B-B} = 1.73 \text{ \AA}$, and the distance between the skeleton atoms and atoms at the centers of hexagons is $d_{B-B} = 1.70 \text{ \AA}$ in complete agreement with the results of previous work [1]. The fullerene diameter is $D = 8.28 \text{ \AA}$.

Barrelenes. Let us consider the structures with cylindrical fragments of an armchair nanotube, which is denoted as $\{5, 0\}$ [11], with hats that are halves of B_{80} . The number of atoms in the cluster series under investigation begins with 80 (fullerene), then, it is 120, 160, 200, and 240. Their extended structures are more compact in the waist: the average cylinder diameters are 8.11, 8.04, 7.93, and 8.00 \AA , respectively. The stability of barrelenes increases with the length: the energy of the armchair barrelenes is lower than the energy of the initial fullerene B_{80} owing to the quantum size effect. The energy of the barrelenes containing n atoms decreases as $an + b$ ($a = 10.2$ and $b = -0.2 \text{ eV}$) and, in the limit, is transformed to the energy of the corresponding nanotubes: the energy of the tubulene B_{240} is close to the energy of the $\{5, 0\}$ nanotube (see Fig. 2a and the table).

The electron structure of nanotubes and barrelenes, which depends on the position of the central atoms with respect to the surface of the hexagonal-skeleton cylinder, is interesting. Let us consider this using the example of the $\{5, 0\}$ nanotube corresponding to the B_{80}

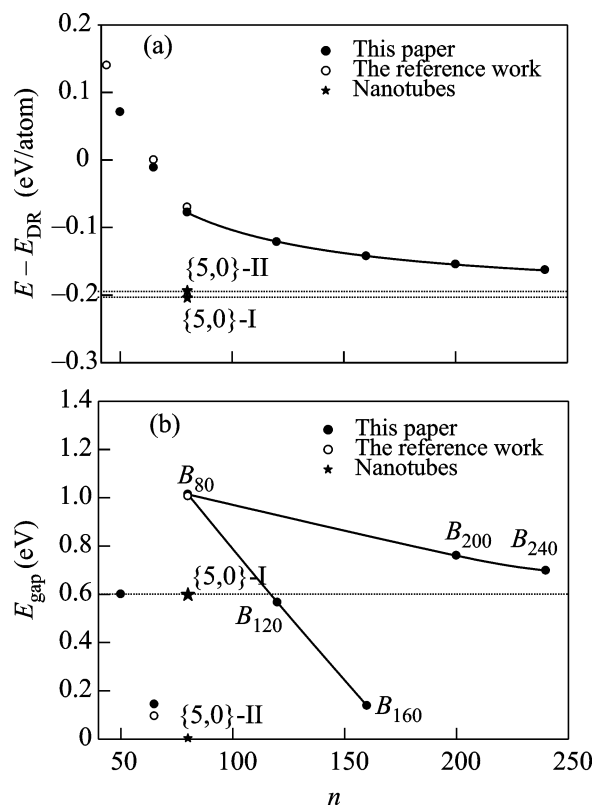


Fig. 2. Energy of boron structures versus (a) the number of atoms and (b) the band gap of the boron clusters under investigation. The open circles are the results from [1]. The asterisks and dotted line are the calculations of the infinite boron structures—tubulenes (nanotubes, see notation in the main text). The energies are measured from the energy E_{DR} of the boron belt (ring with infinite radius).

fullerene. Two of its isomers with close energies are observed: a semiconducting nanotube (I), where the locations of the central atoms inside and outside the cylinder surface alternate in a chessboard order (the corresponding shifts in radius are -0.4 and 0.2 \AA) and a metallic nanotube (II), where atoms are located inside the skeleton cylinder. As an example, Fig. 3 shows the

Electron, geometric, and energy characteristics of the structures under investigation

Structure	Energy $E - E_{DR}$, eV	Band gap width, eV	Minimum bond length, \AA	Maximum bond length, \AA	Diameter D , \AA
50	0.07	0.60	1.63	1.87	5.94
80	-0.08	1.01	1.68	1.73	8.28
120	-0.12	0.57	1.68	1.73	8.11
160	-0.14	0.14	1.67	1.74	8.04
200	-0.15	0.76	1.67	1.74	7.93
240	-0.16	0.70	1.67	1.74	8.00
Nanotube $\{5, 0\}$ -I	-0.20	0.60	1.64	1.76	8.24
Nanotube $\{5, 0\}$ -II	-0.19	0.00	1.67	1.75	8.11

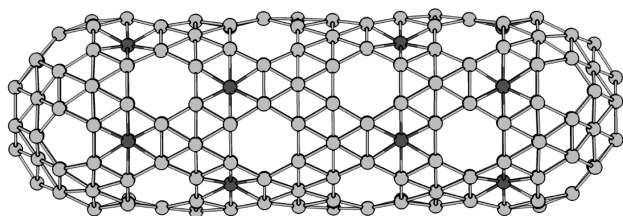


Fig. 3. Barrelene B_{240} . The atoms inside the surface of the skeleton cylinder of the barrelene are shown in dark.

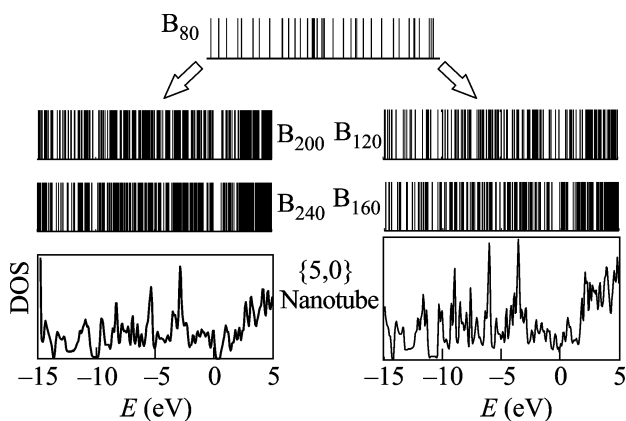


Fig. 4. Evolution of the electron structure of a fullerene (B_{80})–barrelene– $\{5, 0\}$ nanotube. The energies are measured from the energy of the highest occupied orbital of the structures.

structure of the barrelene B_{240} with alternating atoms inside and outside the surface. The difference between the isomer energies of the $\{5, 0\}$ nanotube is 0.01 eV (isomer I is slightly more favorable than isomer II). It is important to note that this fact was not pointed out in [11].

In view of the effect of the closing fullerene hemispheres, the difference in the geometric structure between semiconducting and metal barrelenes is not obvious. However, as seen in Fig. 2b, the band gap width of some barrelenes (B_{200} and B_{240}) tends to the bandwidth of the semiconducting nanotube, whereas the band gap width of the B_{120} and B_{140} barrelenes, to the zero gap of the metal nanotube. The evolution of the electron structure of the fullerene–barrelene–nanotube structures I and II is shown in Fig. 4, where the left and right panels show the energy spectra of the semiconducting series B_{80} – B_{200} , B_{240} – $\{5, 0\}$ -I nanotube and metal series B_{80} – B_{200} , B_{240} – $\{5, 0\}$ -II nanotube.

Note that the geometry of the atoms on the hemisphere hats differs by the shift of the central atoms along the radius (see Fig. 3), which indicates the possibility of the existing structure isomers of the fullerene B_{80} , barrelenes, and tubulenes with various sizes.

The table presents the calculated parameters of the structures under consideration.

Thus, it can be assumed that the synthesis of such boron nanotubes at high temperatures is accompanied by the formation of metal nanotubes, which should be transformed to semiconducting nanotubes at low temperatures; this transition is an analog of the known Mott transition in crystals.

Fullerene B_{50} . We also observed a new stable fullerene B_{50} with a small diameter; owing to the small diameter, its structure is more stressed than that of the B_{80} fullerene. The spread in the bond lengths is larger: the minimum and maximum bond lengths between the neighboring boron atoms are 1.63 and 1.87 Å, respectively. The structure of this fullerene has the D_{3d} point symmetry group. The energy of this structure lies in the gradually decreasing series of the energies of the B_{48} , B_{50} , B_{65} , and B_{80} fullerenes. The other considered modification of the B_{50} structure with the D_{3h} symmetry is less stable.

The fullerene–barrelene– $\{2, 2\}$ series nanotube can also be constructed on the basis of the B_{50} fullerene (Fig. 1d). Such structures from a similar “light” lattice of boron atoms are also stable, but the curve of the dependence of the energy on the number of atoms in the cluster is higher than the corresponding curve of the considered B_{80} -based structure. For this reason, they will be considered later.

The structures whose hats are halves of the fullerenes with a larger diameter can be constructed similarly. How these structures can be synthesized? They can most likely be prepared by using carbon nanotubes. A carbon nanotube can serve, first, as a nanoreactor during the process of the “pumping” of a boron atom vapor inside and subsequent fast cooling similar to the growth of small-diameter carbon nanotubes inside a larger-diameter nanotube and, second, as the surface on which this vapor is deposited, as in the production of BN nanotubes on carbon nanotubes [20].

Note that similar stable structures can be formed from other atoms, e.g., MB_2 whose lattice is similar to that shown in Fig. 1a, but with metal atoms ($M = Be, Mg, Zr$, etc.) inserted into the centers of the hexagons. Their structure and properties will be considered in our next work.

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