

Constricted boron nanotubes

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Abstract

The recent discovery of pure boron nanotubes raises questions about their detailed atomic structure. Previous simulations predicted tubular structures with smooth or puckered surfaces. Here, we present some novel results based on ab initio simulations of bundled single-wall zigzag boron nanotubes (ropes). Besides the known smooth and puckered modifications, we found new forms that are radially constricted, and which seem to be energetically superior to the known isomers. Furthermore, those structures might be interpreted as intermediate states between ideal tubular phases and the known bulk phases based on boron icosahedra.

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1. Introduction

Besides the well known carbon nanotubes (CNTs) [1] there are various other inorganic materials forming nanotubular compounds [2,3]. A material that was originally predicted by theory [4,5] are nanotubes made of pure boron. The stability and the mechanical properties of boron nanotubes (BNTs) should be quite similar to C- and BN-nanotubes [6]. But from an electronic point of view, BNTs should always be metallic, independent of their structure [6], in contrast to CNTs, which are either semiconducting or metallic, depending on their radius and chirality [7]. Another difference between CNTs and BNTs is the potential of the latter to form covalent intertubular bonds [8], whereas the CNTs may only bind to each other via van der Waals types of interactions [7]. Very recently Ciuparu et al. [9] successfully synthesized BNTs and thus confirmed the suggested existence of BNTs, after similar efforts had already lead to the discovery of novel types of boron nanorods by various other groups [10–13].

Among other nanotubular materials which have already been synthesized in the past, we just mention some of the most prominent materials, which are BN [14] or MoS₂ [15] nanotubes. Beyond that, some recent theoretical studies point out the possible existence of a large family of metal-boron nanotubes [8,16], or the structurally related CaSi₂ nanotubes [17], which are still waiting for their experimental verification.

Nanotubes are geometrically constructed by rolling up a rectangular sheet that has been cut from a (quasi)-planar structure. For CNTs this planar structure will be the honeycomb lattice (Fig. 1a) [7], while for BNTs the reference structure is a quasiplanar sheet, where the boron atoms form a puckered hexagonal lattice (Fig. 1b) [6]. Due to differences in the bond lengths ($a_{C-C} = 1.44 \text{ \AA}$ and $a_{B-B} \approx 1.65\text{--}1.85 \text{ \AA}$) the boron and carbon sheets have different sizes. All BNTs discussed in this paper are closely related to the structure of CNTs, as they may be classified in a standard fashion employing a pair of integers (N, M). The latter determine the so-called wrapping vector $\mathbf{W} = N\mathbf{a}_1 + M\mathbf{a}_2$, where \mathbf{a}_1 and \mathbf{a}_2 are basis vectors for a honeycomb lattice. It should be mentioned that BNTs may as well be classified using the hexagonal basis vectors \mathbf{b}_1 and \mathbf{b}_2 (see Fig. 1b), but we certainly prefer the use of the

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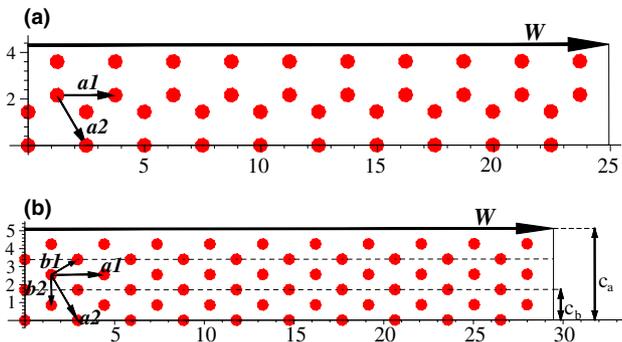


Fig. 1. Constructing the supercells for the simulation of various nanotubes: (10, 0) sheets for (a) a carbon nanotube and (b) a boron nanotube. Also shown are the wrapping vector W , the basis vectors a_1 and a_2 of a honeycomb lattice and b_1 and b_2 of a hexagonal lattice, and c_a , c_b , which are the different heights of the supercells. The dashed lines indicate that for zigzag systems $c_a = 3c_b$. Units are Å.

well-established classification scheme known from CNTs. For a detailed discussion of the geometrical construction of nanotubes see [7].

The existence of BNTs may be looked upon as special case of a more general *Aufbau principle* for boron clusters and bulk materials proposed by Boustani [18]. According to this principle, stable *boron clusters* can be constructed from two basic units: a pentagonal B_6 and a hexagonal B_7 pyramid. One structural paradigm is α -boron, one of the well-known bulk phases of pure boron, which is ‘built’ from pentagonal pyramids forming B_{12} icosahedra. In the bulk phase, the icosahedral clusters occupy the vertices of a rhombohedral unit cell, and the resulting structure is further stabilized by complex multi-center bonds between the icosahedra. As for the hexagonal pyramidal units, the *Aufbau principle* suggests that they may be combined to form convex or quasiplanar clusters, which give rise to more complex modifications, like spheres [19], sheets [20], or the above mentioned nanotubular forms of boron.

In summary, the boron atoms in α -boron have an inverse umbrella sixfold coordination, while the tubular modifications mainly exhibit a distinctive quasiplanar sixfold coordination. In the following, we will report about new modifications of zigzag boron nanotubes, which might be interpreted as intermediate structures between ideal nanotubular forms and the known bulk phases of pure boron, emphasizing the general validity of the *Aufbau principle*.

2. Theoretical methods

In order to simulate nanotube bundles (ropes), we have to construct a solid composed of suitable supercells. Each supercell contains a single small boron ring. By piling up the supercells in the z -direction (with lattice constant c) we build up an infinite nanotubular struc-

ture. Within the xy -plane, we arrange the nanotubes side by side on a hexagonal lattice with lattice constant a .

The lattice constant c depends on the chirality and the lattice type of the nanotube [7], and it is particular small for zigzag¹ systems. Fig. 1 illustrates that $c = c_a$ derived from the honeycomb lattice (basis vectors a_1 and a_2) leads to a supercell that is three times bigger than one constructed from the basis vectors b_1 and b_2 ($c_a = 3c_b$). After a few simulations it turned out that the results obtained from these two models are identical, and that all known properties of BNTs can be well reproduced with the help of the smaller supercells. Therefore, most of the calculations were performed with $c = c_b$ (see Table 1).

Due to its electron deficient character [21] boron has a complicated and versatile chemistry, as indicated above. The only theoretical tools that allow to describe its chemistry properly are first principles calculations [18].

To this end, we used the VASP ab initio package, version 4.4.5 [22,23]. The latter is a density functional theory [24] based ab initio code using plane wave basis sets and a supercell approach to model solid materials. During all simulations, the electronic correlations were treated within the local-density approximation using the Perdew–Zunger–Ceperley–Alder exchange-correlation functional [25,26], and the ionic cores of the system were represented by ultrasoft pseudopotentials [27] as supplied by Kresse and Hafner [28].

With the help of the VASP program, one can determine interatomic forces and relax the different degrees of freedom for a given decorated unit cell, and eventually detect atomic configurations which correspond to (local) minima on the total energy hypersurfaces. In order to carry out those structure optimizations effectively, we employed a preconditioned conjugate gradient algorithm [29] and allowed all degrees of freedom to relax (i.e., the complete set of atomic configurations as well as the supercell parameters). The total energy and the k -point sampling were converged such that changes in the total energies were less than 10^{-3} eV and interatomic forces were less than 0.04 eV/Å.

The versatile chemistry of boron is reflected in a complicated energy hypersurface, which is full of local minima. This is a particular problem for structure optimizations that aim at detecting structures corresponding to global minima on those energy hypersurfaces, because the standard techniques like the conjugate gradients method used in this study are only able to find local minima. In order to approach the most stable structures, we developed a procedure where the starting configurations were pre-relaxed with lower numerical precision until a (local) minimum was found,

¹ Zigzag means $(N, M) = (N, 0)$.

Table 1
Structural data and stabilities

System	Isomer	C_n	n	$(a, b, c)_{h/m}$	a_{B-B}^{intra}	a_{B-B}^{inter}	E_{coh}	ΔE_{coh}
(6, 0)	A	C_6	12	$(8.18, 8.18, 1.65)_h$	1.65–1.78	–	6.87	–
(9, 0)	A	C_3	54	$(11.3, 11.3, 4.89)_h$	1.63–1.80	–	6.81	0.19
	B	C_3	18	$(10.65, 10.65, 1.62)_h$	1.62–1.81	–	6.95	0.05
	C	C_3	54	$(10.15, 10.15, 4.85)_h$	1.62–1.86	1.95	7.00	–
(10, 0)	B	C_2	20	$(10.45, 11.81, 1.68)_m$	1.68–1.90	1.71, 1.96	6.91	0.06
	C	C_2	20	$(11.46, 10.46, 1.64)_m$	1.64–1.82	1.84, 2.00	6.97	–

C_n : rotational symmetry, n : number of atoms per supercell, $(a, b, c)_{h/m}$: lattice constants a, b, c of the hexagonal or monoclinic (index h or m) supercell in Å, a_{B-B}^{intra} , a_{B-B}^{inter} : range of bond lengths in Å of intratubular and intertubular bonds, respectively, E_{coh} : cohesive energies in eV/atom, ΔE_{coh} : energies relative to the most stable isomer of each system in eV/atom.

and afterwards we continued the relaxations with optimal precision. A reduced precision leads to somewhat imprecise interatomic forces, but we found that such a procedure would result in the scanning of the energy hypersurface over a wider range. This technique significantly improves the optimizations, but the results still depend on the starting configurations. Therefore, we carefully examined each system using different relaxation procedures and a number of distinct initial structures, with smooth or puckered surfaces.

We studied (6, 0), (9, 0), and (10, 0) zigzag systems, and obtained different isomers, which also vary in their cohesive energies². Depending on the structure of the surface we discriminate between smooth (A), puckered (B) and constricted (C) isomers. The related structural data, the parameters of the supercells, the range of bond lengths and the cohesive energies of all relaxed structures are given in Table 1. A top view of all isomers placed around the center of their supercells can be found in Figs. 2–4. In these figures the big spheres stand for the upper boron atoms and the small ones for the lower boron atoms (with respect to the z -direction). The various lines between the boron atoms point in the direction of the nearest neighbors³: a thin line symbolizes a single neighbor, and a thick line two nearest neighbors. According to the structures considered here and our experience with other boron systems we found that it is chemically reasonable to interpret distances ≤ 1.9 Å as bonds of mainly covalent character.

The structure dubbed (6,0)A was preredaxed with the Brillouin zone being sampled by a $3 \times 3 \times 5$ grid, and finished with a $5 \times 5 \times 11$ grid. Structure (9, 0)A was completely relaxed on a $4 \times 4 \times 4$ grid. Isomer (9, 0)B was preredaxed on a $2 \times 2 \times 9$ mesh and completed on a $3 \times 3 \times 17$ mesh. For structure (9, 0)C a $2 \times 2 \times 2$ sampling was used for the preredaxation, and a $5 \times 5 \times 5$ mesh to finish this simulation. A $5 \times 5 \times 11$ grid was used

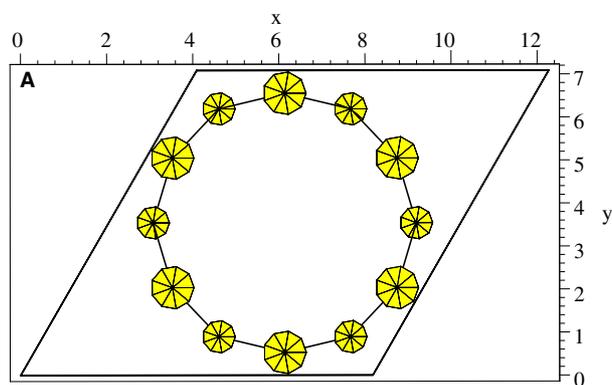


Fig. 2. Top view of the only isomer of the (6, 0) zigzag system in its supercell. The big spheres stand for the upper atoms and the small ones for the lower atoms (with respect to the z -direction).

to finish structure (10, 0)B, with a $5 \times 5 \times 5$ mesh used to carry out the preredaxation. Finally (10, 0)C was preredaxed with $3 \times 3 \times 5$, and finished with a $5 \times 5 \times 11$ grid. The cutoff energy for the expansion of single electron wave function in terms of plane waves was 257.1 eV for structures (9, 0)B, and (10, 0)C, and 321.4 eV for all the other BNTs.

3. Results

A general feature of all nanotubes considered in this Letter is the sixfold intratubular coordination with rather typical B–B bond lengths (see Table 1, column a_{B-B}^{intra}). Furthermore, all BNTs showed a metallic density of states, confirming the results in [6]. The rotational C_n -symmetry of the tubes follows from a simple rule: n is the greatest common divisor of the sixfold symmetry imposed through the arrangement on a hexagonal superlattice and the N -fold symmetry of the BNT itself given by the $(N, 0)$ structure type.

For the relaxation of the (6, 0) system, we used different relaxation schemes, and smooth or puckered initial structures, as well as different supercell heights (see above). All structural optimizations led to the same final structure, which is displayed in Fig. 2. It has a smooth

² The cohesive energy was calculated by dividing the binding energy per supercell by the number of atoms contained within that supercell.

³ Only nearest neighbor distances up to 2 Å were taken into account.

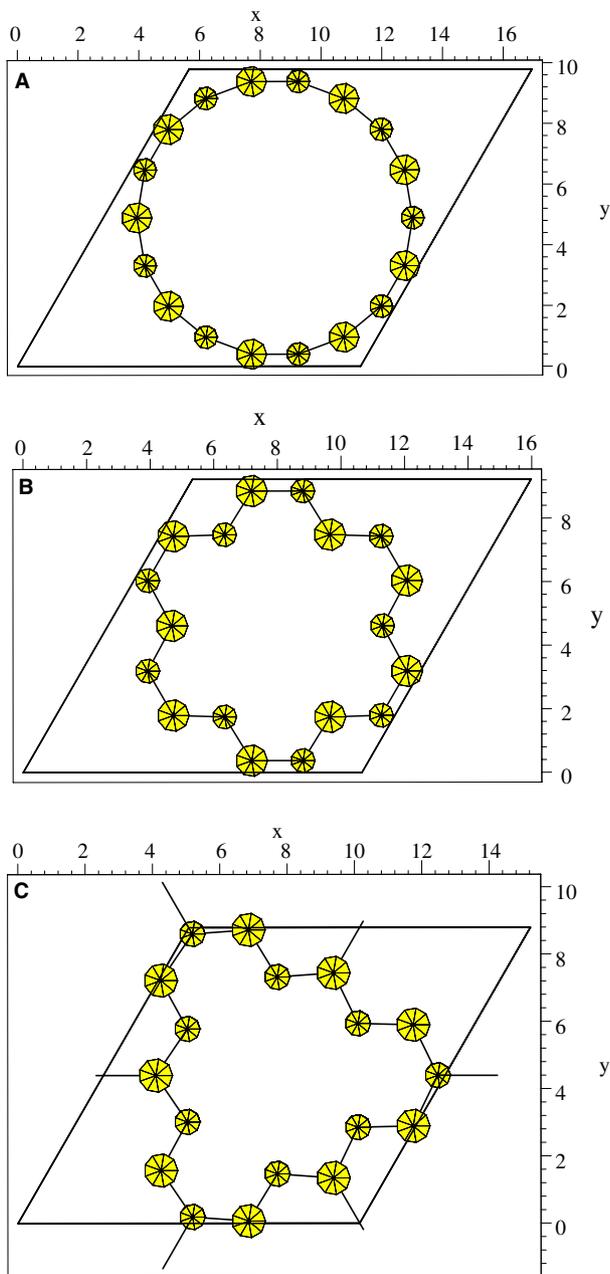


Fig. 3. Top view of three isomers of the (9, 0) system placed around the center of their supercells. In isomer (C), each of the six additional thick lines point towards *two* atoms in the adjacent supercells within a distance of 1.95 Å.

surface and no intertubular bonds. The radius of (6, 0)A is 3.03 Å and the intertubular distance is 2.12 Å.

The energy surface of the (9, 0) system seems to be more complex, and we found three distinct isomers, which are displayed in Fig. 3. Similar to (6, 0)A, structure (9, 0)A has a smooth surface and no intertubular bonds. The radius is 4.57 Å and the intertubular distance is 2.16 Å. The second isomer (9, 0)B has a puckered structure described in [6], which results from rolling up a regular quasiplanar surface on a cylinder.

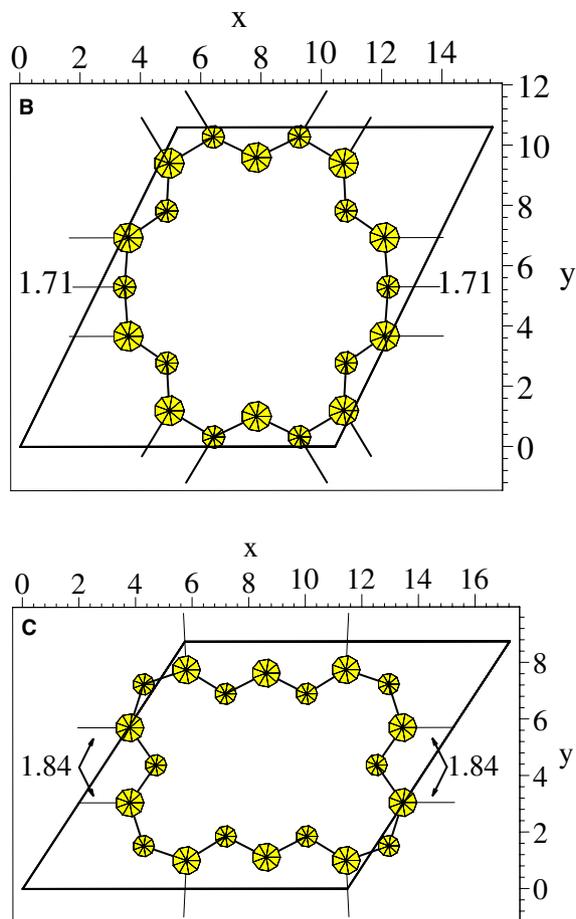


Fig. 4. Two isomers of the (10, 0) system in top view located around the center of their monoclinic supercells. The additional lines point in the direction of nearest neighbors: a thin line symbolizes a single neighbor, a thick line two nearest neighbors. Isomer (B) has two intertubular bonds with $a_{B-B} = 1.71$ Å, whereas the remaining outward pointing lines indicate atoms within a distance of 1.96 Å. Isomer (C) has four intertubular bonds ($a_{B-B} = 1.84$ Å) and there are four atoms in neighboring supercells, which are 2.00 Å apart.

There are no intertubular bonds; the closest distance of apex atoms to an adjacent BNT is 2.63 Å. The new modification (9, 0)C is qualitatively different from the previous ones, because it is radially constricted, and cannot be generated by simply rolling up a quasiplanar reference structure. The constriction generates three bumps, each of them formed by five atoms. Furthermore there are six atoms per supercell that have two neighbors in adjacent supercells, which are 1.95 Å apart (indicated by thick lines pointing outwards in Fig. 3, (isomer (C))).

For the (10, 0) system we only found two isomers. It was not possible to locate an A-type structure. During the relaxation procedure the hexagonal symmetry of the supercells was broken, and the lattice systems changed to monoclinic. The smaller angle of the (10, 0)B supercell is 63.8°, and the one for (10, 0)C is 56.7° (for a hexagonal supercell this angle would be 60°). Structure

(10, 0)B is puckered, but its cross-section is elliptical and not circular as for the other BNTs considered so far; it has two intertubular bonds per supercell, which raise the coordination number of those atoms to seven. Furthermore, each BNT is surrounded by 20 atoms per supercell, which belong to adjacent nanotubes that are 1.96 Å apart (see the outward pointing lines in Fig. 4, isomer (B)). The cross-section of the constricted isomer (10, 0)C deviates significantly from circular or elliptical shapes. The structure has four bumps, each formed by five atoms. Furthermore, it has four intertubular bonds per supercell and four nearest neighbors in adjacent supercells in a distance of 2.00 Å.

The bumps found within the (9, 0)C and (10, 0)C structures are formed by five boron atoms per supercell, which are sitting on the corners of an imaginary zigzag 6-ring, similar to the six apex atoms of a B₁₂ icosahedra seen along each of its 3-fold axes. Therefore, the constricted nanotubes might be interpreted as intermediate structures between the ideal (puckered) nanotubular structures reported before and the well-known bulk phases of boron based on B₁₂ icosahedra. The more as previous ab initio studies [30] showed that in principle, B₁₂ icosahedra may be fused to form extended nanotubular 6-ring systems similar to the columnar wings of the (9, 0)C and (10, 0)C structures.

4. Conclusions

We explored the geometry, energetics and basic chemical properties of boron nanotube bundles (ropes) of zigzag type.

Our results confirm that zigzag BNTs tend to have puckered surfaces [6]. The (9, 0)B isomer is clearly more stable than the smooth A-type isomer. For the (6, 0) system we were unable to find a puckered isomer, while for the (10, 0) system we were unable to find a smooth BNT. From this one could certainly conjecture that for small radii the surface tension is smoothening the BNT, while for bigger radii there will be a strong tendency to puckered modifications. In that context it might be surprising that the (9, 0)A isomer is somewhat lower in binding energy than (6, 0)A, which seems, at first sight, to be in conflict with the strain energy studies in [4,6] (for a general discussion about strain energy see [7]). But these studies generally referred to isolated BNTs, whereas in the present Letter, we are dealing with ropes made from BNTs, which show some complex intertubular bonding that is very likely to alter the cohesive energies in a less predictable fashion. Furthermore, by applying numerical optimization methods to complex materials, one can never guarantee that the algorithm will really succeed in locating the proper local minimum corresponding to a smooth (9, 0)A isomer.

Apart from that, the A- and B-type isomers basically confirm previous results known for (nanotubular) cluster systems [4,31,6]. For periodic systems containing (9, 0) and (10, 0) zigzag boron nanotubes, we found new types of radially constricted BNTs (C-type isomers). These isomers seem to be energetically favored over the previously known BNT modifications (see column ΔE_{coh} in Table 1), and their structures are qualitatively different from all BNTs reported so far, because it cannot be derived from simply rolling up a quasiplanar reference sheet on a cylinder. The C_n symmetry of these structures looks like a compromise between the symmetry of the zigzag BNTs and the symmetry constraints imposed by their arrangement within a hexagonal tubular network (see above). Therefore we conjecture that the constriction of the C-type isomers are most likely due to the special boundary conditions imposed during the formation of nanoropes, which lead to novel structures, quite different from structures predicted for isolated BNTs.

Furthermore, the constriction of zigzag BNTs produces bumps formed by five atoms per supercell sitting at the corners of a imaginary 6-ring, similar to structural motives found within B₁₂ icosahedra. Therefore, these structures may be looked upon as intermediate structures between ideal nanotubular boron systems and the known bulk phases of boron based on B₁₂-icosahedra, confirming a general *Aufbau principle* for boron structures suggested by Boustani [18].

We hope that our results will inspire further experimental work on BNTs going beyond the pioneering work of Ciuparu et al. [9]. In particular a metallic nanotubular materials with versatile structural and chemical properties may allow for many interesting applications within nanotechnology.

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