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FROM MATERIALS OF ALL-RUSSIAN CONFERENCE "CHEMISTRY OF SURFACE AND NANOTECHNOLOGY"

Adsorption of Atomic Hydrogen on the Surface of the Boron–Carbon Nanotubes

S. V. Boroznin, I. V. Zaporotskova, E. V. Boroznina, and D. I. Polikarpov

Volgograd State University, ul. Bogdanova 32, Volgograd, 400062 Russia
e-mail: sboroznin@mail.ru

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Abstract—Results of theoretic studies of geometrical, electronic, and energy composition of monolayer boron–carbon BC_3 nanotubes of the zig-zag type (n, 0) and the cylindrical symmetry are presented. The mechanism of adsorption of atomic hydrogen on the outer surface of the boron-containing BC_3-nanotubes of the (6, 0) type is studied. The calculations are carried out on the basis of models of the ion-incorporated covalent-cyclic cluster using the semiempiric MNDO scheme and density functional (DFT) methods.

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Surprising properties of carbon nanotubes made them the source of ideas for hundreds of their applications in science and technique. They also inspired the researches to look for new nanotubular structures among the other classes of inorganic compounds [1]. In 2003 the monolayer boron–carbon nanotubes were synthesized [2]. These compounds may be regarded as a new class of nanotube systems exhibiting unique physicochemical properties and opening wide opportunities for their use in nanotechnology [3]. It is expected that the boron–carbon nanotube systems may become functional blocks for the next generation of nanodimension devices. Therefore the investigation of their structure, electronic and energy composition and adsorption properties is very important. In this paper the results of the study of structure and properties of the boron-containing BC_3 nanotubes of the (n, 0) type using quantum-chemical methods like MNDO [4] and DFT with the chosen B3LYB potential [5] are presented. The mechanism of adsorption of atomic hydrogen on the outer surface of the boron-containing BC_3 nanotubes of (6, 0) type is considered.

It was noted in [6–8] that one of the possibilities of structural development of the boron carbide BC_3 might be the formation of its stabile quasiplanar form analogous to the graphite structure. In Fig. 1 extended unit cells of quasiplanar hexagonal boron carbide differing in reciprocal orientation of the boron and carbon atoms, the so-called **A** and **B** types of atom ordering, are presented.

It is presumable that nanotube systems on the basis of hexagonal boron carbide are formed by twisting of corresponding quasiplanar BC_3 monolayers. Therefore we studied the boron-containing BC_3 nanotubes of **A** and **B** type and theoretically investigated their geometrical and electron-energy structure. In Fig. 2 clusters of the boron–carbon (6, 0) nanotubes of **A** and **B** type are presented.

The monolayer BC_3 tubes (n, 0) where n = 4, 6, 7, 10, 12 are studied. Interatomic distances between the neighboring atoms of boron and carbon obtained after optimization occurred to be 1.4 Å for all the nanotubes under consideration. The so-called deformation energies E_d as the difference between the specific energies of quasiplanar extended unit cell of the boron carbide and extended unit cell of the corresponding nanotube obtained by twisting the hexagonal BC_3 monolayer (Fig. 3) were evaluated. While calculation by means of MNDO method it was found that minimum values of deformation energies correspond to the nanotube diameter of 4–7 Å. The calculations by means of DFT

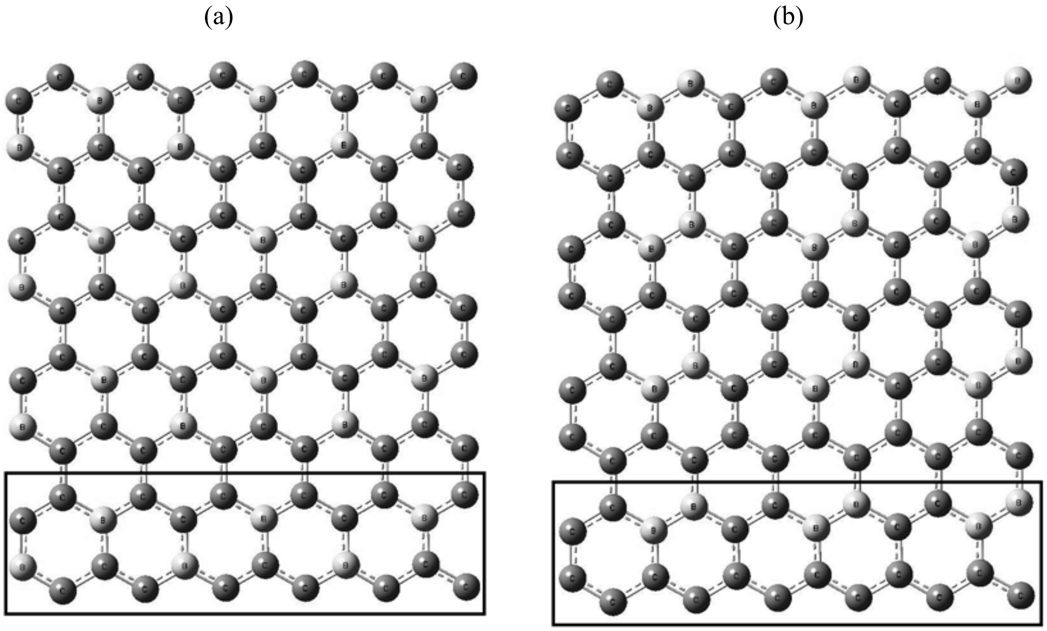


Fig. 1. Extended unit cell of quasiplanar hexagonal boron carbide: (a) **A** type of mutual orientation of C and B atoms and (b) **B** type of mutual orientation of C and B atoms. Unit cell is marked by a rectangle.

method in this range of nanotube diameters give monotonous decrease in deformation energy with the increase in *d*. So it can be suggested that the most stable structures are nanotubes with the diameter varying from 4 to 7 Å. Hence, the formation of such nanotubes by means of twisting of quasiplanar boron carbide is most favorable by energy, and therefore most probable. The results of calculation of main characteristics of BC_3 (n, 0) nanotubes are presented in Table 1.

Analysis of width of the forbidden zone ΔE_g for the nanotubes of **A** type showed that by the character of conductivity these structures belong to semiconductors, and at the increase in the diameter of the tube the decrease in the width of the forbidden zone takes place. Tubes of **B** type proved to be the narrow-slot semiconductors. In this case the contribution to the conductivity zone is made by *s*- and *p*-orbitals of carbon and boron atoms, and in the valence zone, by *s*- and *p*-orbitals of carbon and *p*-orbitals of the boron atom.

We have also studied the possibility of adsorption of hydrogen atom on the outer surface of monolayer (6, 0) boron–carbon BC_3 nanotubes of **A** and **B** types. Four kinds of location of hydrogen atom in relation to the surface of nanotubes under study were considered: I, above the boron or carbon atom; II, above the center of bond between the atoms forming the angle with the longitudinal axis of nanotube, the so-called C–B^1 or B–B bond; III, above the center of bond parallel to the longitudinal axis of nanotube (C–B^2 and C–C bonds); IV, above the center of hexagon of the tube surface. Due to specific features of spatial orientation of the boron and carbon atoms on the surface of BC_3 nanotubes there exist the boron–carbon bonds corresponding to several versions of location of hydrogen atom above the surface of nanotube (II and III).

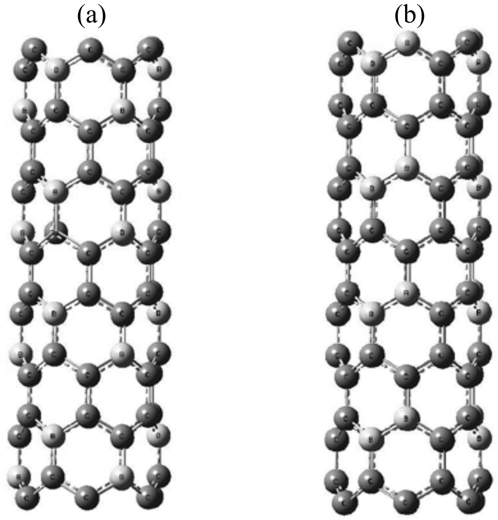


Fig. 2. Extended unit cell of BC_3 (6, 0) nanotubes: (a) **A** type of mutual orientation of C and B atoms and (b) **B** type of mutual orientation of C and B atoms.

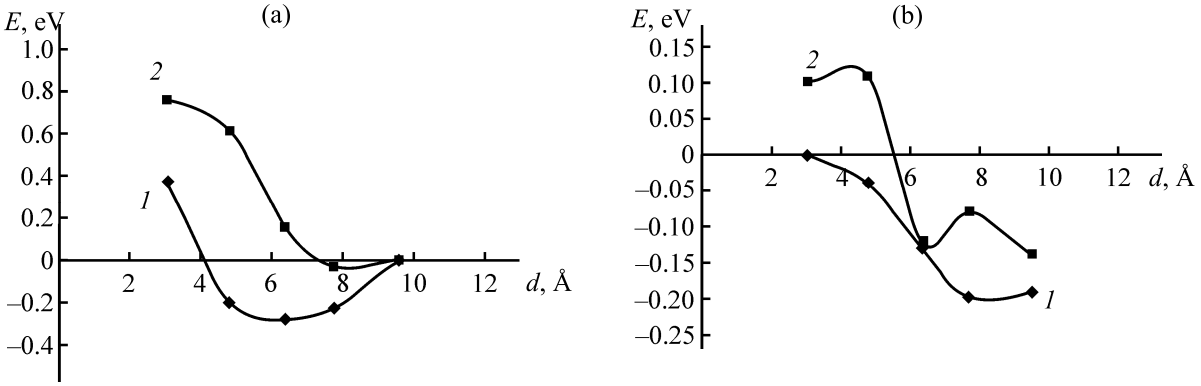
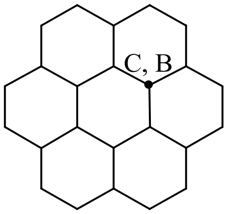
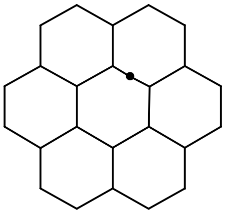


Fig. 3. Dependence of deformation energy E_d on the diameter D of BC_3 tubes of the type **A** and **B** calculated by means of: (a) MNDO and (b) DFT.



I



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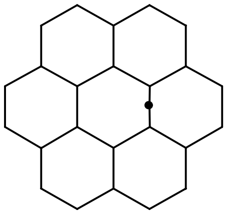

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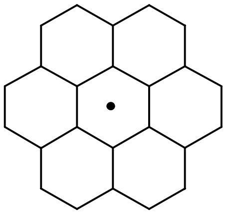

IV

Therefore for the kind II we have accepted C–B^1 bond designation, and for the case III, C–B^2 designation. Results of calculations showed that the adsorption process of the atomic hydrogen is invariant to orientation of C–C bond in relation to the longitudinal axis of nanotube [10]. Thus at in this article the case is considered when C–C bond is parallel to the longitudinal axis of BC_3 nanotube.

Table 1. Main characteristics of the boron–carbon nanotubes (n, 0) of **A** and **B** type[a]

(n, 0)	d, Å	ΔE_g, eV	E_d, eV	
			MNDO	DFT
Boron–carbon nanotubes of **A** type				
(4, 0)	3.03	2.54	0.37	0.01
(6, 0)	4.77	1.21	–0.20	0.04
(8, 0)	6.35	1.07	–0.28	0.13
(10, 0)	7.72	0.77	–0.23	0.20
(12, 0)	9.57	0.12	0	0.19
Boron–carbon nanotubes of **B** type				
(4, 0)	3.03	0.27	0.76	0.10
(6, 0)	4.77	0.07	0.61	0.11
(8, 0)	6.35	0.35	0.16	–0.12
(10, 0)	7.72	0.03	–0.03	–0.08
(12, 0)	9.57	0.29	0	–0.14

[a] (d) Diameter of nanotube, (ΔE_g) width of the forbidden zone calculated by means of MNDO method within the frame of ion-incorporated covalent cluster model [9], (E_d) deformation energy calculated by means of MNDO and DFT methods.

For all the considered kinds of the location of hydrogen atom the process of adsorption was simulated by gradual approaching (0.1 Å step) of the adsorbing atom to the nanotube surface along the perpendicular to the longitudinal axis of the tube. The calculations performed permitted obtaining the profiles of potential energy of these processes (Fig. 4). Analysis of energy curves showed that the adsorption of hydrogen atom on the surface of both types of the boron–carbon (6, 0) nanotubes is possible for all the considered versions. But the adsorption complex formed by the boron–carbon nanotube of **B** type and hydrogen atom located above the carbon atom of surface occurred to be metastable (Fig. 4b). The analysis of charge distribution in the system showed that in the course of adsorption the electron density transfer from the hydrogen atom to the carbon or boron atom of the tube surface takes place except for the approaching of hydrogen to the boron atom of BC_3 nanotube of **B** type. Consequently in this process together with weak van der Waals interactions an important role is played by the appearing Coulomb interaction.

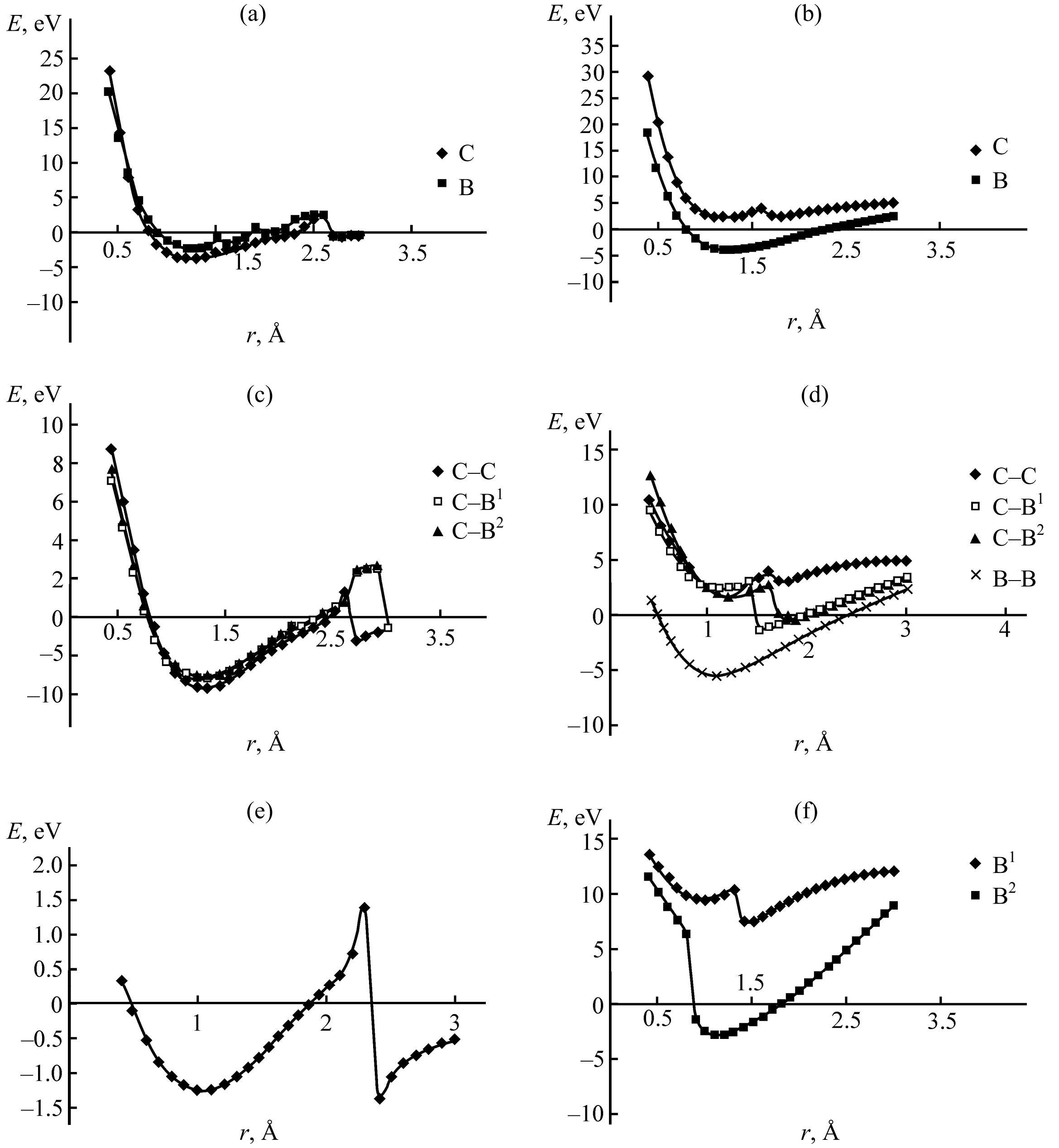

Fig. 4. Profiles of potential energy of the adsorption of hydrogen atom on the outer surface of BC_3 nanotubes: (a) over the boron/carbon atom of the type **A** nanotube; (b) over the boron/carbon atom of the type **B** nanotube; (c) over the centers of C–C, C–B^1, C–B^2 bonds of the type **A** nanotube; (d) over the centers of C–C, B–B, C–B^1 and C–B^2 bonds of the type **B** nanotube; (e) over the center of surface hexagon; and (f) over the centers of surface hexagons of BC_3 nanotube of **B** type containing one (B^1) and two (B^2) boron atoms.

The analysis of interaction of hydrogen atom with the surface of BC_3 nanotube of the type **A** for the case IV shows that hydrogen atom is adsorbed above the center of hexagon to form the stable adsorption complex, but for achievement of energy minimum point corresponding to this complex the hydrogen atom must overcome a potential barrier of 2.71 eV (Fig. 4e). The analysis of energy curves permitted establishing some differences in the mechanisms of adsorption of hydrogen atoms above the centers of surface hexagons containing different number of boron atoms. For example, adsorption complex “hydrogen atom–BC_3 nanotube” in the case of orientation of hydrogen atom above the hexagon containing one

Table 2. Main characteristics of adsorption of atomic hydrogen on the surface of the boron–carbon nanotubes of **A** type for the considered kinds of orientation of H atom with respect to the surface of the tube[a]

Kinds of location of hydrogen atom	Method	r_{ad}, Å	E_{ad}, eV	Q
I, above B atom	MNDO	1.3	2.37	0.11
	DFT	1.3	1.09	0.20
I, above C atom	MNDO	1.2	3.77	0.17
	DFT	1.2	2.45	0.22
II, above the center of C–C bond	MNDO	1.2	3.59	0.24
	DFT	1.3	1.09	0.30
II, above the center of C–B^1 bond	MNDO	1.3	3.06	0.22
	DFT	1.3	0.80	0.26
III, above the center of C–B^2 bond	MNDO	1.2	3.2	0.19
	DFT	1.2	1.63	0.23
IV, above the center of hexagon containing one boron atom	MNDO	1.0	1.26	0.51
	DFT	1.0	1.02	0.61

[a] (E_{ad}) adsorption energy, (r_{ad}) adsorption distance, (Q) effective charges on the adsorbing hydrogen atom.

boron atom is metastable because the minimum on the energy curve has a positive value. When hydrogen atom is located above the center of hexagon containing two boron atoms a stable adsorption complex is formed (Fig. 4f). Main calculated energy characteristics and geometrical parameters of adsorption processes are compiled in Tables 2 and 3. The adsorption energy was calculated as the difference between the total energy $E(r)$ of the system "nanotube–adsorbed H" at the corresponding distance r and the total energy of the system at $r = \infty$.

$$E_i = E(r_i) - E(\infty),$$
$$i = \text{a, c}.$$

Analysis of values of adsorption energy and the shape of energy curves of the described processes showed that for the nanotubes of **A** type the presence of boron atoms near the adsorption centers does not affect the values of adsorption energy and the proceeding of adsorption on the whole. In the case of BC_3 nanotubes of **B** type the adsorption process becomes energetically favorable, and hence more probable, when the adsorption centers are localized near two boron atoms on nanotube surface (see Table 3).

Hence, it can be stated that boron atoms of the boron–carbon nanotube surface positively affect the process of adsorption of atomic hydrogen and improve the sorption activity of BC_3 tubes with respect to H atoms.

Table 3. Main characteristics of adsorption of atomic hydrogen on the surface of the boron–carbon nanotubes of **B** type for the considered kinds of orientation of H atom with respect to the surface of the tube[a]

Kinds of location of hydrogen atom	Method	r_{ad}, Å	E_{ad}, eV	Q
I, above B atom	MNDO	1.2	4.12	–0.09
	DFT	1.2	1.90	–0.14
I, above C atom	MNDO	1.2	2.09	0.16
	DFT	1.2	0.04	0.21
III, above the center of C–C bond	MNDO	1.0	2.59	0.16
	DFT	1.0	0.04	0.20
II, above the center of C–B^1 bond	MNDO	1.5	1.40	0.05
	DFT	1.5	0.06	0.08
III, above the center of C–B^2 bond	MNDO	1.8	0.07	0.15
	DFT	1.8	0.11	0.12
II, above the center of B–B bond	MNDO	1.1	5.40	0.02
	DFT	1.1	0.16	0.05
IV, above the center of hexagon containing one boron atom	MNDO	1.4	3.06	0.21
	DFT	1.4	0.03	0.23
IV, above the center of hexagon containing two boron atoms	MNDO	1.1	1.18	–0.21
	DFT	1.1	0.05	–0.19

[a] (E_{ad}) adsorption energy, (r_{ad}) adsorption distance, (Q) effective charges on the adsorbing hydrogen atom.

The analysis of one-electron spectra of the adsorption complexes "BC_3 nanotubes–hydrogen atom" showed that *s*-orbitals of H atom contribute to n the valence zone of obtained complex.

The analysis of geometrical parameters of adsorption complexes showed that no significant alterations in geometry of nanotubes in the course of the addition of hydrogen atom to their surface takes place.

It is found that the boron–carbon nanotubes of **A** and **B** type belong to semiconductors. For BC_3 nanotubes of A type clear dependence of width of the forbidden zone on the diameter is found. It has the monotonously decreasing character. The analysis of the dependence of deformation energy on the diameter of the boron–carbon tube showed that the formation of nanotubes of **A** and **B** types by twisting of quasiplanar monolayer of the boron carbide BC_3 is fairly probable. The lowest deformation energy corresponds to BC_3 nanotubes of **A** type with the diameter from 4 to 7 Å.

The performed quantum-chemical study of sorption activity of BC_3 nanotibes in relation to atomic hydrogen showed that adsorption of H is possible on the surface of both types of the boron–carbon (6, 0) nanotubes for all the considered cases of orientation of hydrogen atom with respect to the surface of tube. Boron atoms of surface positively affect the adsorption of atomic hydrogen and improve the sorption activity of BC_3 tubes toward the H atom.

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