From Two- to Three-Dimensional Structures of a Supertetrahedral Boran Using Density Functional Calculations

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Dedicated to Professor Roald Hoffmann on the occasion of his 80th birthday

Abstract: With help of the DFT calculations and imposing of periodic boundary conditions the geometrical and electronic structures were investigated of two- and three-dimensional boron systems designed on the basis of graphane and diamond lattices in which carbons were replaced with boron tetrahedrons. The consequent studies of two- and three-layer systems resulted in the construction of a three-dimensional supertetrahedral borane crystal structure. The two-dimensional supertetrahedral borane structures with less than seven layers are dynamically unstable. At the same time the three-dimensional superborane systems were found to be dynamically stable. Lack of the forbidden electronic zone for the studied boron systems testifies that these structures can behave as good conductors. The low density of the supertetrahedral borane crystal structures (0.9 g cm^{-3}) is close to that of water, which offers the perspective for their application as aerospace and cosmic materials.

The rapid development of science and technology constantly increases the needs in creating new one- (1D), two- (2D) and three-dimensional (3D) materials with properly adjustable features predictable on the basis of the properties of the individual molecules (0D) or structural units of the material components. The concept of transformation of the molecular (0D) electronic structure into the electronic band structure of one- (1D), two- (2D), and three-dimensional (3D) infinite systems was developed by R. Hoffmann and his collaborators,[1] convincingly demonstrated that the principal properties of solids can be reliably predicted based on the properties of the constituent molecules. Among the most important properties to be found in new advanced materials are the light

weight (low density) at the sufficiently high strength and hardness. For this reason, special attention is currently drawn to various boron compounds[2] and boron two-dimensional systems: fullerenes,[3] tubulenes,[4] and boron layers.[5] The existence of boron fullerenes was predicted in 2007,[3a] and in 2014 the first representative of this class of compounds, a cluster B_{40}^{-}, was obtained[3b] to become the first example of the non-carbon spherical structure formed by light elements. The stable boron-containing nanotubular species were theoretically predicted in 1997,[4a] and in 2004, a pure boron single-layer nanotube representing a new type of the boron topological structure with unique physical, chemical, and electronic characteristics and opening up tremendous prospects for the use in nano- and microelectronics was synthesized.[4b] In recent years, much attention has also been paid to the search for new allotropic modifications of boron 2D structures, such as borophen,[5a] alpha boron,[5b] and other boron forms.[5c–i] An expedient approach to design new stable closo boranes has been developed.[5j–l] Based on the concept of an electronic confined space analogy method that clarifies equivalence of the ($4n+2$) Wade–Mingos and Hückel rules for three- and two-dimensional molecular systems. As shown by theoretical calculations,[5m] properties of thin boron films are determined by the nature of the substrate on which they are grown that can be adjusted by forming specific boron–metal interactions. In contrast to graphene forming a hexagonal grid, regardless of the substrate, boron is the first 2D material, the structure of which is regulated by the interaction with the substrate. One of the unsolved problems of 2D boron is the difficulty of separating a boron film from the substrate, but this fact has also a positive effect. As shown by calculations,[5j] boron films on nickel or gold substrates can compete with platinum as catalysts in hydrogen fuel cells. Other predicted[2,6,7] technically useful properties of two-dimensional boron films include their superconductivity[6a,7a,b] and high firmness.[7b–e]

The design of new three-dimensional boron compounds is another area of structural boron chemistry which shows high activity. Earlier Burdett and Li[8] noted that a tetrahedral carbon atom in a diamond crystal lattice can be replaced with a C_4 tetrahedron, which leads to the formation of a new allotropic form of carbon—supertetrahedral carbon. Another new allotropic form of carbon—supercubane can be obtained by replacement of carbon atoms

1, T_d
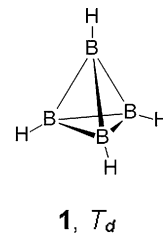
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in a diamond lattice by cubane C_8.[9] Similarly, supertetrahedral boron forms can be derived by substitution of carbon atoms in the diamond lattice by tetrahedrane B_4 fragments. The possibility of such replacement is justified by the fact that in agreement with experimental[10] and theoretical data[11–13] the electron-deficient tetrahedral B_4H_4 structure **1** of T_d symmetry is kinetically stable, even though it does not conform to the global minimum on the corresponding potential energy surface (PES).[13]

The goal of the present work is to computationally (by density functional theory (DFT) calculations)[14–24] study the geometrical and electronic structures of two- and three-dimensional boron-containing systems constructed on the basis of graphane and diamond lattices in which carbon atoms are replaced with boron tetrahedrons **1**. In the first step, we studied one layer **3** of the supertetrahedral borane. Then in the same way, we consequently studied two and three layers and accomplished the study with a three-dimensional supertetrahedral borane crystal structure (Figure 1).
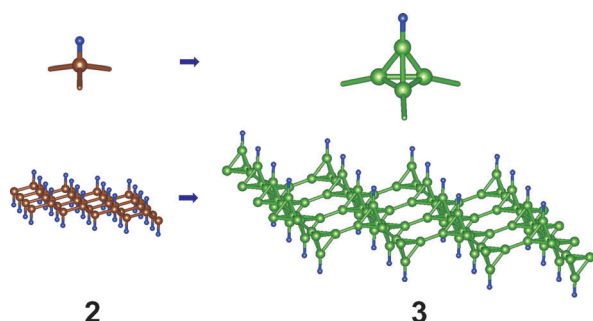

Figure 1. Transformation from a 1D one- to two-, and three-layer structures and finally to the 3D crystal structure.

A scheme of a supertetrahedral monolayer structure and the corresponding unit cell are depicted in Figure 2 and Figure S1 in the Supporting Information. The unit cell for such structure is hexagonal and contains eight boron and two hydrogen atoms (Figure S1). Three neighboring elementary cells form a cycle in which the boron tetrahedranes have a chair conformation. In this case the hydrogen atoms bonded to the adjacent tetrahedranes directed to opposite side from the plane of the entire system. The calculated geometric parameters have the following values $R_1 = 1.626$ Å, $R_2 = 1.682$ Å, $R_3 = 1.708$ Å, which do not differ much from the values calculated in the supermolecular approximation ($R_1 = 1.637$ Å, $R_2 = 1.678$ Å, $R_3 = 1.704$ Å).[25] Calculations of electronic band structure indicate that this system is a direct-gap semiconductor with a band gap of 0.49 eV (Figure S2). The calculated phonon dispersion (Figure S2c) shows that the structure is dynamically unstable.
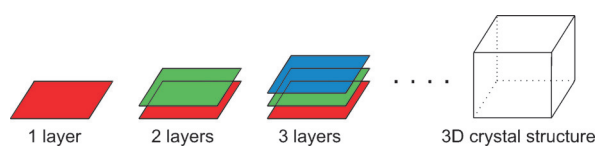
A scheme of a two-layer supertetrahedral structure and the unit cell are presented in Figures S3 and S4. The calculations of the electronic band structure indicate that as well as the monolayer structure the bilayer system represents a direct-gap conductor with a band gap of 0.07 eV (Figure S5a). The calculated phonon dispersion (Figure S5b) shows that the system, as well as the previous one, is dynamically unstable.

The unit cell for the three-layer supertetrahedral structure is given in Figure S6. The electronic band structure calculations indicate that this structure has the property of a direct-gap conductor with a band gap of 0.00 eV (Figure S7). The calculation of the phonon dispersion (Figure S7c) shows that the system is also dynamically unstable. Approximation of change (see Figure S8) of the length of the piece which is cutting off on an abscissa axis, when the phonon acoustic curves going to the negative area, from number of layers says that the multilayer system becomes dynamically stable at number of layers not less than seven.

The geometrical characteristics of the solid found by the calculations with imposition of periodic boundary conditions and comparison to previous results of the corresponding supermolecular calculations[26] are given in Table 1. These data well coincide with each other (Figure 3).

The calculation of the electronic band structure of the supertetrahedral borane (Figure 4) points to the absence of the forbidden electronic gap, which indicates metallic properties of this system.

The calculation of the phonon dispersion (see Figure S9) showed the absence of branches in the negative area that

Table 1: Geometrical and physical parameters of the 2D and 3D crystalline supertetrahedral structures obtained by the DFT calculations.[a]

n	Method	a [Å]	R_1 [Å]	R_2 [Å]	R_3 [Å]	E_g [eV]	ρ [g cm^{-3}]	H_v [GPa]
1	PBEsol	6.057	1.626	1.682	1.708	0.49	0.57	
2	PBEsol	6.050	1.623	1.682	1.709	0.07	0.70	
3	PBEsol	6.047	1.622	1.682	1.709	0.00	0.76	
3D	PBEsol	8.548	1.618	1.701	1.701	−0.53	0.92	15.2
	PBE	8.584	1.623	1.710	1.710	−0.14	0.91	
	HSE06	8.581	1.636	1.698	1.698	0.25	0.90	
	B3LYP	–	1.638	1.705	1.705	2.02	–	

[a] n = number of layers; R_1–R_4 = bond lengths, E_g = electronic gap; ρ = density of material; H_v = hardness of the materials. [b] Refs. [26a].

Figure 2. Scheme of the two-dimensional structure of graphane **2** and the corresponding 2D supertetrahedral borane structure **3**.
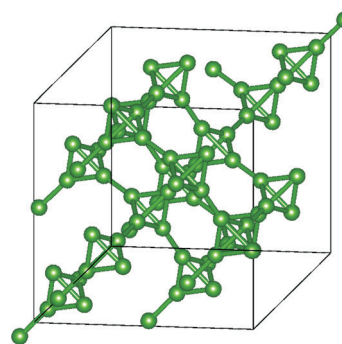

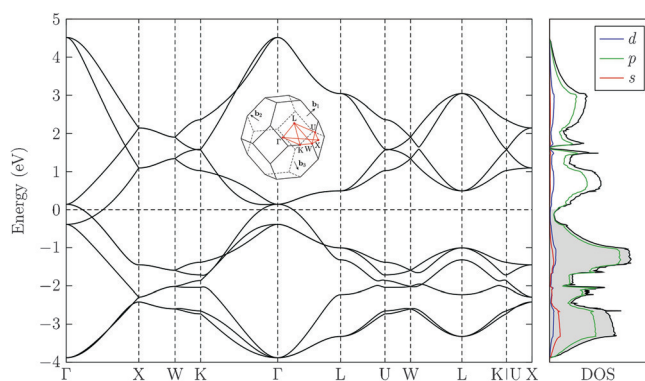***Figure 3.*** Scheme of the supertetrahedral crystal structure.

Figure 4. Calculated electronic band structure along high-symmetry lines in the first Brillouin zone (left panel), total and orbital-projected electronic density of states (right panel) for the solid-state structure (cF-B_8). The Fermi level is shifted to 0 eV. The first Brillouin zone (in the center), the reciprocal lattice vectors, high-symmetry k-points and the k-path for the face-centered cubic lattice in solid state (cF-B_8).

testifies to dynamic stability of this crystalline structure. The predicted intertetrahedral BB bonds are shorter than the intratetrahedral BB bonds. This fact can be explained by the former ones that are formed as ordinary two-center two-electron (2c-2e) covalent bonds while the latter BB bonds are electron-deficient three-center two-electron (3c-2e) bonds similar to the nature of BB bonds in supertetrahedral borane systems.[26b] At present no experimental data are available on boron solid-state supertetrahedral structures. So the results of the calculations are possible to compare only with the known polyhedral structures,[27–30] in which BB bonds are in the limits (1.65–1.98 Å),[30,31] that not much differs from data obtained in the present work.

The Vickers hardness (15.2 GPa) calculated by the empiric formula of Šimůnek and Vackář[32] for covalent and ionic solid states (see Table 1) is substantially lower than that of diamond (96.0 GPa) and is comparable with the hardness of silicon (Si 11.3 GPa) and germanium (Ge 8.8 GPa).

The density of the studied supertetrahedron borane structure equal to 0.93 g cm^{-3} is surprisingly close to and even lower than the density of water. This fact is explained by the presence of large cavities between the nearby tetrahedrane units of the crystalline structure.

The calculated values of the cohesive energy are collected in Table 2. With the increase in the number of layers and the subsequent transition to the 3D crystalline structure the cohesive energy decreases which points to the gradual strengthening of the systems. The calculated cohesive energy of the monolayer system is lower than that of various boron hydride monolayers: -5.037 eVatom^{-1},[33a] -5.016 eVatom^{-1},[33a] -4.901 eVatom^{-1},[33a] and borophene -4.898 eVatom^{-1}.[33a]

The calculated elastic constants c_{11}, c_{12}, c_{66}, in-plane Young's modulus (in-plane stiffness) Y_s, and Poisson's ratio ν are given in Table 2. Due to the crystal symmetry, the elastic properties of all

structures are isotropic. The calculated in-plane Young's modulus of a monolayer is much lower than that of boron hydride monolayers *Pbcm* (108–113 N m^{-1}),[33a] *C2/m* (62–100 N m^{-1}),[33a] *Cmmm* (66–91 N m^{-1}),[33a] borophane (120–190 N m^{-1},[33b] 111–172 N m^{-1}),[33c] graphane (243 N m^{-1}),[33d] graphene (340 N m^{-1}),[33e] silicene (62 N m^{-1}),[33f] and germanene (48 N m^{-1}).[33f]

The dependence of the real and imaginary parts of the dielectric constants on the photon energy for the four structures is illustrated in Figure S10. The calculated values of the static dielectric constants in direction of wavelengths of layers (ε_{xx}) and perpendicular to them (ε_{zz}) for all the structures are given in Table 2. The energies of photons corresponding to the absorption edge are equal to 0.39 eV for one, 0.09 eV for two, 0.02 eV for three layers, and 0 eV for the solid-state structure and correlate well with the calculated width values of the forbidden region E_g for these structures. For all structures the longest wavelength absorption is to be found in the visible spectral region with band maxima at 460–490 nm.

To sum up, we have presented the first computational analysis of one-, two-, and three-layer supertetrahedral borane systems as well as a three-dimensional supertetrahedral borane crystal structure. The calculations showed that up to six layers supertetrahedral two-dimensional borane systems are dynamically unstable. Stability of the multilayer supertetraborane system can be achieved when the number of the layers exceeds six and the system acquires principal characteristics and properties of the three-dimensional supertetrahedral structure. Lack of the forbidden electronic zone of the boron systems testifies to their good conductive properties. The low density of the borane crystal structures equal to

Table 2: The calculated cohesive energy (E_c, in eVatom^{-1}), elastic constants (c_{ij}, in N m^{-1} for 2D materials and in GPa for cF-B_8), in-plane (Y_s, in N m^{-1}, for 2D materials) and isotropic (Y_s, in GPa, for cF-B_8) Young's modulus, Poisson's ratio (ν), and static dielectric constants (ε_{xx} and ε_{zz}) for all structures.

n	Structure	E_c[a]	c_{11}	c_{12}	c_{66}	Y_s[b]	ν	ε_{xx}	ε_{zz}
1	h-B_8H_2	-5.057	36.05	15.87	10.09	29.06	0.4402	4.30	1.23
2	h-$B_{16}H_2$	-5.371	68.67	32.93	17.88	52.88	0.4795	133.31	1.90
3	h-$B_{24}H_2$	-5.492	99.48	52.04	19.14	72.26	0.5231	160.71	3.00
3D	cF-B_8	-5.766	78.13	63.00	26.04	44.20	0.3917	41.31	41.31

[a] The cohesive energy E_c for h-B_8H_2, h-$B_{16}H_2$, h-$B_{24}H_2$, and cF-B_8 can be calculated by the following equations, respectively:

$$E_c = \frac{E_{str} - 8E_B - 2E_H}{10}$$

$$E_c = \frac{E_{str} - 16E_B - 2E_H}{18}$$

$$E_c = \frac{E_{str} - 24E_B - 2E_H}{26}$$

$$E_c = \frac{E_{str} - 8E_B}{8}$$

where E_{str} ($str = h$-B_8H_2, h-$B_{16}H_2$, h-$B_{24}H_2$, cF-B_8), E_B, E_H, are the total energy of h-B_8H_2, h-$B_{16}H_2$, h-$B_{24}H_2$, cF-B_8 and the energy of isolated B and H atoms, respectively. [b] The in-plane Young's modulus and Poison's ratio were calculated using the following relationships:

$$Y_s = \frac{c_{11}^2 - c_{12}^2}{c_{11}}$$

$$\nu = c_{12}/c_{11}$$

0.9 g cm^{-3} is close to the density of water. The calculated cohesive energy, elastic constants, Young's modulus, and Poisson's ratio are very close to those of traditional constructive materials (aluminum, silicon, and others) and render these systems suitable candidates for building materials of aerospace and cosmic facilities.

Acknowledgements

Conflict of interest

The authors declare no conflict of interest.

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[14] Computational details: The study of two- and three-dimensional supertetrahedral systems constructed on the basis of the diamond crystal in which carbon atoms are replaced by tetrahedrons B$_4$ has been performed using two program suits: Vienna ab initio simulations package[15–17] and Gaussian 09[23] with imposing periodic boundary conditions. The calculations were carried out using the Vienna ab initio simulations package[15–17] with PAW pseudopotentials[18, 19] and the PBEsol density functional.[20] A plane-wave cutoff energy of 750 eV for the associated pseudopotentials was used. The Brillouin zone has been sampled by the Monkhorst–Pack method[21] with an automatically generated grid $15 \times 15 \times 15$. The calculated geometric characteristics of the studied systems were visualized using the Vesta program.[22] Calculations using the Gaussian 09[23] program were carried out by density functional theory (DFT) with PBE/6-311G(d) and HSE06/6-311G(d) functionals. Geometry optimization was carried out with "tight" keyword. The graphics of molecular structures shown in drawings were obtained by using the ChemCraft[24] program, for which input parameters of the corresponding Cartesian coordinates of atoms found in the calculations were used.

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