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Quantum-chemistry calculation of B_nN_n-rings (n = 1–6) and fulborenes, the fullerene-like molecules B_nN_n (n = 12, 24, 60)

D.M. Sheichenko, A.V. Pokropivny, V.V. Pokropivny
Institute for Problems of Materials Science, National Academy of Sciences of Ukraine, Krzhyzhanovsky str.3, Kiev 03142, Ukraine. E-mail: pokr@ipms.kiev.ua

Abstract: Electronic structure of the boron nitride rings and fullerene-like BN-molecules (the fulborenes) are calculated using MNDO, AM1, Extended Huckel, INDO and *ab initio* (STO-3G) methods. The fulborene $B_{60}N_{60}$ is confirmed as the boron nitride analogue of buckminsterfullerene C_{60}. Comparisons with other calculations are presented and possible applications as nanoporous materials and photonic crystals are discussed.

Keywords: boron nitride, fullerenes, fulborenes, MNDO, AM1, Extended Huckel methods.

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1. Introduction

Discovery of carbon fullerenes, nanotubes and fullerites have opened a new research and technological avenue in a materials science, nanotechnology and optoelectronic [1] at 21 Century. Similarity between a graphite and a graphene boron nitride make possible to predict and to synthesize the boron nitride analogous of nanotubes [2,3] fullerenes [4] and fullerites (the fulborenites) [5,6]. In particular, the following BN-nanostructures have been studied theoretically by a quantum-chemistry calculation and by a molecular dynamics simulation, namely: the molecules $B_{12}N_{12}$ [7], the $B_{12+3n}N_{12+3n}$ (n = 0–3) and $B_{22}N_{22}$ [8], the $B_{12}N_{12}$ and $B_{16}N_{16}$ [9,10], the $B_{36}N_{36}$ [11], the $B_{12}N_{12}$, $B_{24}N_{24}$ and $B_{60}N_{60}$ [12], the B_xN_{x+4} (x = 8–33) [13] the $B_{30}N_{30}$ as a formal analogue of buckminsterfullerene [14], the rings B_3N_3 and B_4N_4 [15], the boron nitride nanotubes [16], the polymers [17] and the heteroconnectors as quantum dots [18]. In contrast to carbon cages the boron nitride fullerene-like molecules and multiwalled nanocages are suggested to posses unique spectroscopic properties due to Jahn-Teller and piezoelectric effect. Formerly we proposed to applicate zeolite-like crystals built from covalently bonded BN-molecules as nanosieves and nanomembranes [5,6,12].

The aim of this work is to study the electronic properties of novel $B_{24}N_{24}$ and $B_{60}N_{60}$ molecules predicted by us [12] in comparison with calculations of other accompanied molecules and rings.

2. Calculation methods

All calculations presented here were performed using HyperChem 5.0 program with semi-empirical MNDO, AM1, INDO, Extended Huckel (EH) and *ab initio* (STO-3G) methods. After building of structure, the special starting algorithm attempts to lower the energy of a molecular system by adjusting its geometry (not used in EH and INDO methods). The methods make the limited changes in a molecular structure that is useful for correcting of a draft starting geometry, and these is most effective when the system is far from minimum. After the structure correction the calculation method mentioned above is chosen to compute the total and binding energies, the heats of formations, the bond lengths, the angles between bonds, the molecular point groups, the distributions of electrons, the effective charges, the electrostatic potentials, the molecular orbitals, etc. For convenience of comparisons and analysis the total and binding energies are devided on the sum of all atoms in rings or molecules. $\Delta\varepsilon$ is a gap between LUMO (the lowest unoccupied molecular orbital) and HOMO (the highest occupied molecular orbital).

3. Results and discussion

First of all let us consider the results for the simplest boron nitride rings which are regarded as the precursors and structural elements of fulborenes or nanotubes and next the fulborenes themselves.

Resulting optimized atomic structures for B_nN_n-rings (n = 1–6) are shown in Fig.1, while a quantitative parameters are summarized in tables 1-5 obtained by different methods and authors. Optimized atomic structure of B_nN_n-molecules (n = 12, 24, 60) predicted in [5,6,12] are shown in Fig. 2, while a quantitative parameters are summarized in tables 6-8. According to the stability rule of polyhedra [19] the near spherical polyhedra is more stable. For this reason the $B_{12}N_{12}$, the $B_{24}N_{24}$ and the $B_{60}N_{60}$ is more stable than the B_xN_{x+4} with near ellipsoid form [13] In addition a formation of [5,6]-fullerenes [7,13] results to existence of B-B or N-N bonds, which is less stable then B-N. The distribution of electron densities for the 5-membered B_5N_5 ring and the $B_{12}N_{12}$ molecule are demonstrated in Fig. 3. One unexpected feature of this atomic structures stands out at once, namely: the started symmetrical skeleton structure transforms in such a manner that the BNB angle between two double bonds of N atoms with neighboring B atoms becomes obtuse. It must be regarded as the general rule, rather then the error, because it is a common feature for all of the rings considered.

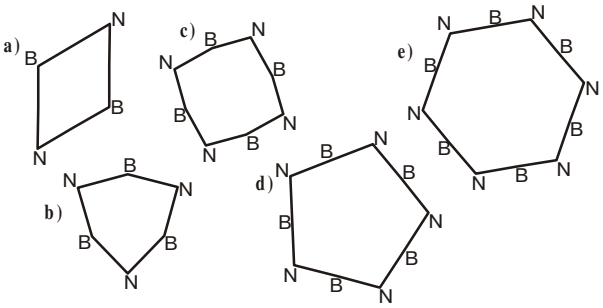

Fig. 1. Configuration of the boron nitride rings B_2N_2 (a), B_3N_3 (b), B_4N_4 (c), B_5N_5 (d) and B_6N_6 (e) after optimization.

The second feature is the charge transfer from the boron to the nitrogen atom. For example, MNDO-calculation shows that an eight membered B_4N_4-ring transforms into square, the atoms B and N of which become the ions with charges + 0.26 and – 0.26, respectively. Also the starting BNB and NBN angles transform after geometry optimization into the BNB angle 100.09°, the NBN-an-

Table 1. Parameters calculated for the BN chain

Method	Total energy per atom, eV	Binding energy per atom, eV	Heat of formation, eV	Net charges per atom B (+) and N (–)
AM1	–131.73	–1.33	–13.448	0.03
MNDO	–131.84	–1.59	–13.974	0.07
MINDO3	–128.17	–3.57	3.643	0.04

Table 2. Parameters calculated for the D_{2H} symmetry 4-membered rings B_2N_2

Method	Total energy per atom, eV	Binding energy per atom, eV	Heat of formation, eV	$\Delta\varepsilon$, eV	Bond lengths, Å	Bond angles, deg.
AM1	–136.5	–5.82	7.708	6.74	1.429	BNB=72.9, NBN=107.8
MNDO	–136.7	–3.236	8.625	4.84	1.457	BNB=64.8, NBN=115.2
Ext. Huckel	–	–	–	3.65	–	–
Ab initio	–1061	–	–	–	–	–
INDO	–198.3	–14.05	–34.69	9.80	–	–
AM1 [8]					1.53 and 1.34	BNB=65.2
3-21G [8]					1.68 and 1.28	BNB=61.9

Table 3. Parameters calculated for the D_{3H} symmetry 6-membered rings B_3N_3

Method	Total energy per atom, eV	Binding energy per atom, eV	Heat of formation, eV	$\Delta\varepsilon$, eV	Bond lengths, Å	Bond angles, deg.
AM1	–137.97	–4.91	4.46	8.31	1.360	BNB=87.9, NBN=152.1
MNDO	–138.09	–4.65	2.92	7.77	1.386	BNB=89.2, NBN=150.8
Ext. Huckel	–	–	–	5.57	–	–
Ab initio	–1062.7	–	–	12.68	1.352	–
ROHF [15]	–1076.5	–	–	–	1.3468	NBN=149.22
CCSD (T) [15]	–1079.8	–5.04	–	–	1.3763	NBN=147.87

Table 4. Parameters calculated for the D_{4H} symmetry 8-membered rings B_4N_4

Method	Total energy per atom, eV	Binding energy per atom, eV	Heat of formation, eV	$\Delta\varepsilon$, eV	Bond lengths, Å	Bond angles, deg.
AM1	–138.50	–5.44	–0.37	8.30	1.32	BNB=97.62, NBN=172.37
MNDO	–138.62	–5.18	1.69	7.62	1.35	BNB=100.09, NBN=169.89
Ext. Huckel	–	–	–	4.95	–	–
Ab initio	–1063.2	–	–	–	–	–
ROHF [15]	–	–	–	–	1.333	BNB=104.81, NBN=156.19
CCSD (T) [15]	–	–5.40	–	–	1.359	NBN=142.9

Table 5. Parameters calculated for the D_{5H} symmetry 10-membered rings B_5N_5

Method	Total energy per atom, eV	Binding energy per atom, eV	Heat of formation, eV	$\Delta\varepsilon$, eV	Bond lengths, Å	Bond angles, deg.
AM1	–138.71	–5.64	–2.51	9.78	1.30	BNB=106.2, NBN=178.6
MNDO	–138.88	–5.44	–0.47	9.24	1.33	BNB=109.8, NBN=178.0
Ext. Huckel	–	–	–	4.93	–	–
Ab initio	–1063.4	–	–	14.96	–	–

gle 169.89°, while BN-bond lengths decrease from 1.64Å to 1.35Å.

All rings and molecules considered are stable because of its calculated binding energies per atom ranges from — 3.24 eV (for the less stable B_2N_2 ring) to –5.63 eV and — 5.95 eV (for the most stable $B_{24}N_{24}$ and $B_{60}N_{60}$ molecules). It was known that the 8-membered ring was energetically favourable then 6-membered ring [7] We confirm this and conclude, that 10-membered rings is energetically favourable than both 6-membered by 0.60 eV and 8-membered rings by 0.24 eV, respectively. The last conclusion is important, because of B_5N_5 rings are the structural elements of the $B_{60}N_{60}$ fulborene, providing its stability.

The large LUMO-HOMO gap is often regarded as a molecule stability condition. The same values for $\Delta\varepsilon$ equal to 7.98, 8.34 and 8.73 (in eV) were obtained by MNDO method [12] for the $B_{12}N_{12}$, the $B_{24}N_{24}$ and the $B_{60}N_{60}$ molecules, respectively. This indicate that the $B_{24}N_{24}$ and the $B_{60}N_{60}$ is the more stable then $B_{12}N_{12}$. Nearly the values $\Delta\varepsilon$ equal to 4.84, 7.77, 7.62 and 9.24 (in eV) obtained by MNDO method (see tables 2-8) for the B_2N_2, B_3N_3, B_4N_4 and B_5N_5, respectively, confirm a favoured stability of 10-membered rings.

It is a reason to believe that one of the stability condition of molecules is a little deviation of the valent angles sum on 360°. This values equal to 32.7° for the $B_{12}N_{12}$ fulborene and 17.8° for the $B_{24}N_{24}$ fulborene. That is the $B_{24}N_{24}$ is more stable than the $B_{12}N_{12}$.

Spectroscopically speaking, rings and molecules have several infrared-active bands. For example, B_3N_3 and B_4N_4 rings have only one band in the 1550-1650 cm^{-1} and in the 1700-1800 cm^{-1} range, respectively [15] The $B_{12}N_{12}$ fulborene has two dominant IR active vibrations [7] at 909cm^{-1} and 1649 cm^{-1}. Furthermore the leading line for the $B_{12}N_{12}$ fulborene had been observed in a synthetic amorphous boron nitride, but the reproducibility of the experiments was poor [7].

The electron structure of the BN-cages and its crystals make possible to predict them in the capacity of microporous optic materials and photonic crystals.

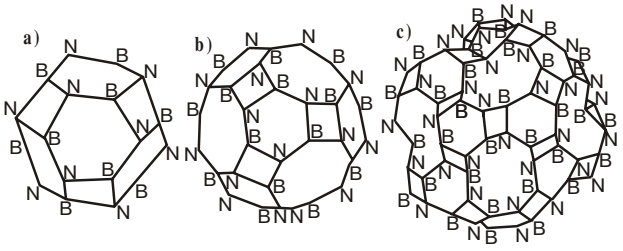

Fig. 2. Configuration of the fulborenes [4,6]-$B_{12}N_{12}$ (a), [4,6,8]-$B_{24}N_{24}$ (b) and [4,6,10]-$B_{60}N_{60}$ after optimization.

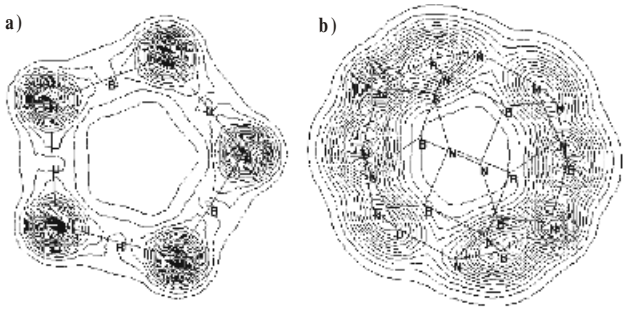

Fig. 3. Isodensity contours (a) for the B_5N_5 ring and (b) for the $B_{12}N_{12}$ molecule in a cross section of a figures.

Table 6. Parameters calculated for the [4,6]-fulborene $B_{12}N_{12}$

Method	Total energy per atom, eV	Binding energy per atom, eV	Heat of formation, eV	$\Delta\varepsilon$, eV	Bond lengths, Å	Bond angles in 4- and 6-membered rings, deg.
AM1	–138.89	–5.82	–10.355	8.85	1.570	4 : BNB=81.4, NBN=97.7
						6 : BNB=113.4, NBN=124.4
MNDO	–139.07	–5.63	–5.648	8.39	1.516	4 : BNB=81.4, NBN=97.7
						6 : BNB=113.4, NBN=124.4
Ext. Huckel	–	–	–	5.90	–	–
MNDO [12]	–	–5.13	–6.357	7.98	d=4.96	–
Ab initio [7]	–	–	–	14.42	(4,6)=1.483	4 : BNB=81, NBN=97.2
					(6,6)=1.408	6 : not reported
MNDO [9]	–	–	–5.568	8.4	(4,6)=1.516	4 : NBBN=162.7
					(6,6)=1.456	
AM1 [8]	–	–	–10.359	8.85	(4,6)=1.504	4 : BNB=79.92, NBN=97.29
					(6,6)=1.418	6 : BNB=106.43,NBN=128.49
Ab initio [8]	–945.27	–3.78	–	13.49	(4,6)=1.508	4 : BNB=84.08, NBN=95.39
					(6,6)=1.438	6 : BNB=114.49,NBN=124.19

Table 7. Parameters calculated for the [4,6,8]-fulborene $B_{24}N_{24}$

Method	Total energy per atom, eV	Binding energy per atom, eV	Heat of formation, eV	$\Delta\varepsilon$, eV	Bond lengths, Å	Bond angles in 4-, 6- and 8-membered rings, deg.
AM1	–139.12	–6.06	–31.879	8.81	(4,6)=1.50	4 : BNB=83.0, NBN=95.4
					(4,8)=1.45	6 : BNB=111.0, NBN=125.6
					(8,6)=1.38	8 : BNB=127.9, NBN=136.7
MNDO	–139.39	–5.95	–26.699	8.73	(4,6)=1.51	4 : BNB=84.6, NBN=94.57
					(4,8)=1.48	6 : BNB=115.1, NBN=123.1
					(8,6)=1.41	8 : BNB=129.5, NBN=137.6
Ext. Huckel	–	–	–	5.24	–	–
MNDO [12]	–	–5.56	–8.098	8.34	d=6.88	–

Table 8. Parameters for the [4,6,10]-fulborene $B_{60}N_{60}$ and for the [5,6]-fullerene $B_{30}N_{30}$

Molecule – method	Total energy per atom, eV	Binding energy per atom, eV	Heat of formation, eV	$\Delta\varepsilon$, eV	diameter d, Å	Net charges per atom B (+) and N (–)
$B_{60}N_{60}$ –MNDO [12]	–	–5.63	–29.28	8.73	4.95	0.30
$B_{30}N_{30}$ –MNDO [14]	–139.3		–29.54	–	–	0.23

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