



Stoichiometric boron nitride fullerenes with homopolar B–B and N–N bonds

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ABSTRACT

A new class of boron nitride fullerenes, which are stoichiometric and presents homopolar bonds, is proposed in this work. A combined first-principles/elastic-model approach predicts that stoichiometric fullerenes with more than 1000 atoms which present homopolar bonds are energetically more stable than those without homopolar bonds. The HOMO–LUMO gap of stoichiometric fullerenes with homopolar bonds is 1.7 eV smaller than that of fullerenes without homopolar bonds, which may lead to distinct optical and electrochemical properties. The distribution of B–B and N–N in those new fullerenes gives rise to an electric dipole moment which could make possible to separate them from apolar fullerenes.

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Since carbon fullerenes were first synthesized in 1985 [1], the scientific community searches for fullerene-like structures made of other materials, such as BN [2–7], gold [8–10] and boron element [11]. The BN fullerenes were first synthesized in 1998 by means of a laser ablation process [2,3]. In a subsequent set of experiments, BN fullerenes were produced in larger amounts by means of arc-voltaic technique and characterized by means of mass spectrometry [4–7]. An important goal, then, is to determine the real structure of such fullerenes. High resolution electron spectroscopy (HREM) images [2,3] show that BN fullerenes can adopt square-like shapes which gave strong evidence in favor of the octahedral morphology predicted in theoretical studies [12–14]. Unlike carbon fullerenes, BN fullerenes composed of odd membered rings (i.e., pentagons at C_{60}) presents homopolar B–B or N–N bonds. Such kind of bonds have a high energy cost associated with them [15], therefore, the geometries proposed for the stoichiometric BN fullerenes up to now are composed of even membered rings [3–7,12–14,16]. Some theoretical studies suggest that fullerenes with homopolar N–N bonds may stable in nitrogen rich environments [17,18], however, such fullerenes are non-stoichiometric.

In this work, it is investigated the stability of stoichiometric BN fullerenes with homopolar bonds composed of six-membered rings and side-sharing pentagonal rings, namely, $B_{38}N_{38}$, $B_{62}N_{62}$ and $B_{94}N_{94}$. It was found that such fullerenes present values of formation energy per atom similar to those of octahedral fullerenes with similar sizes ($B_{36}N_{36}$, $B_{64}N_{64}$ and $B_{100}N_{100}$) in which homopolar bonds are absent. Moreover, the differences between the values of formation energies per atom of the two kinds of fullerenes decreases with increasing size. The features regarding the stability of the fullerenes can be understood in terms of a simple elastic model [17,18], which predicts that fullerenes with homopolar

bonds with more than a thousand of atoms are energetically more stable than the fullerenes in which the homopolar bonds are absent. The presence of homopolar B–B and N–N bonds introduce electron states in the large gap of BN fullerenes. The HOMO–LUMO gap of fullerenes with side-sharing pentagonal rings is about 3.1 eV which is roughly 1.7 eV smaller than the HOMO–LUMO gap of octahedral fullerenes composed of even membered rings. It is also observed that the distribution of B–B and N–N bonds on the BN fullerenes give rise to electric dipole moments ranging from 0.14 up to 1.3 Debye. Since the stoichiometric fullerenes without homopolar bonds and non-stoichiometric fullerenes [18] are apolar molecules, it may be possible to separate them from the stoichiometric fullerenes with homopolar bonds.

The used methodology is based on the density-functional theory [19,20] as implemented in the SIESTA code [21]. Norm-conserving Troullier–Martins pseudopotentials were used to represent the ionic core potentials [22] and generalized gradient approximation (GGA) for the exchange–correlation functional [23]. A double- ζ basis function plus polarization orbitals was employed to expand the solutions of the Kohn–Sham equations [24]. The integrals were made in a grid defined by a minimal energy cutoff of 150 Ry [25]. The geometries of the fullerenes were fully optimized until all the forces components were smaller than 0.05 eV/Å. Such methodology produces accurate results compared with those of all electron calculations of Zope et al. [16], as it is described in a previous study [26]. In order test the reliability of the calculations, I have compared the obtained results for the $B_{36}N_{36}$ with results of Zope et al., in addition, I performed calculations on cubic boron nitride which allows comparison with other theoretical and experimental results. Regarding the properties of the $B_{36}N_{36}$, the mean distance of each atom to the center of the cage obtained by Zope et al. [16] by means of all electron density-functional calculations with large polarized GAUSSIAN basis set is 3.94 Å, which is in excellent agreement with the value obtained in this work (3.944 Å). The

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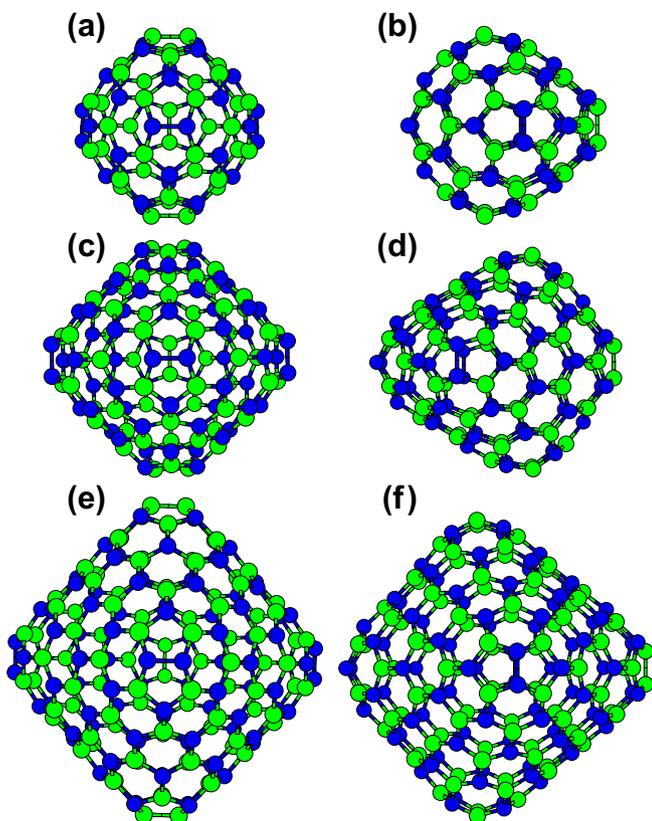


Fig. 1. Geometries of stoichiometric BN fullerenes with homopolar bonds. Panel (a) shows one view of the $B_{38}N_{38}$ fullerene and panel (b) shows a rotation by 90° about the vertical axis of the view shown in (a). Panels (c) and (d) show, respectively, one view of the $B_{62}N_{62}$ fullerene and a rotation by 90° about the vertical axis of the view shown in (c). Panel (e) shows one view of the $B_{94}N_{94}$ fullerene and panel (f) shows a rotation by 90° about the vertical axis of the view shown in (e).

HOMO–LUMO gap obtained in this work (5.0 eV) is also in excellent agreement with the value obtained by Zope et al. (5.0 eV). Regarding the properties cubic boron nitride, I have obtained a value of lattice parameter, 3.619 Å, which is in excellent agreement with the experimental value, 3.6157 Å [27], and with other DFT–GGA calculations, 3.625 Å [28]. The applied methodology predicts a wide band gap for the cubic boron nitride, 4.45 eV, which is in excellent agreement with other DFT–GGA calculations, 4.43 eV [28], and which is consistent with the experimental result, 6.4 eV [29].

Alike octahedral BN fullerenes, which presents six square rings, stoichiometric fullerenes with homopolar bonds presents six topological defects, six pairs of side-sharing pentagonal rings (see Fig. 1). Three pairs of side-sharing pentagonal rings present B–B bonds and the others three pairs of side-sharing pentagonal rings present N–N bonds, in total each fullerene have six homopolar bonds. As it is possible to see in Fig. 1, the stoichiometric fullerenes with homopolar bonds are not perfect octahedrons, the shape of such fullerenes become more similar to the octahedral one with increasing size. All the stoichiometric fullerenes with homopolar bonds can be built by putting together two halves which have the same geometry but differ in stoichiometry (one half can be turned into another by exchange of chemical species). Fig. 2 shows that the $B_{38}N_{38}$ can be built by putting together the halves shown in panels (b) and (c). As it is possible to see, one half contains all the B–B bonds ($B_{20}N_{18}$) and the other one all the N–N bonds ($B_{18}N_{20}$). The geometries of the $B_{62}N_{62}$ and the $B_{94}N_{94}$ fullerenes are depicted in Fig. 3.

In order to compare the stability of the BN fullerenes, it was calculated their formation energy per atom according to following expression:

$$\frac{E_f}{n} = \frac{E_{\text{Total}}}{n} - \frac{\mu_{\text{BN}}}{2}, \quad (1)$$

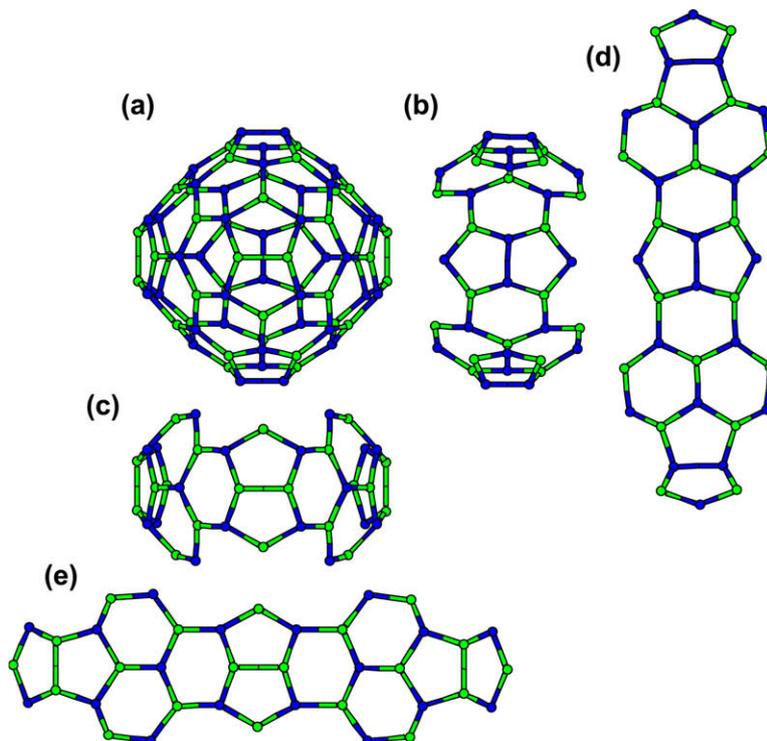


Fig. 2. (a) A view of $B_{38}N_{38}$ fullerene. (b) The geometry of one half of the $B_{38}N_{38}$ which contains all B–B bonds. (c) The geometry of one half of the $B_{38}N_{38}$ which contains all N–N bonds. (d) The structure shown in (b) with some distorted bonds for visualization purposes. (e) The structure shown in (c) with some distorted bonds for better visualization.

where E_{Total} is the total energy of the fullerene obtained from first-principles calculations. n is the total number of atoms of the fullerene and μ_{BN} is the chemical potential of a reservoir of BN pairs. In fact, the relative stability of stoichiometric fullerenes does not depend on the choice of μ_{BN} , for all stoichiometric fullerenes the last term of Eq. (1) is the same. In the present study, the value of μ_{BN} was defined as the first-principles total energy per BN pair of a sheet of hexagonal BN. Therefore, according to Eq. (1), the sheet of hexagonal BN have null value of formation energy.

Fig. 4 shows the values of formation energy per atom as a function of the inverse of the square root of total number of atoms of the fullerene, $1/\sqrt{n}$. The circles represent the fullerenes with side-sharing pentagonal rings and the stars octahedral fullerenes

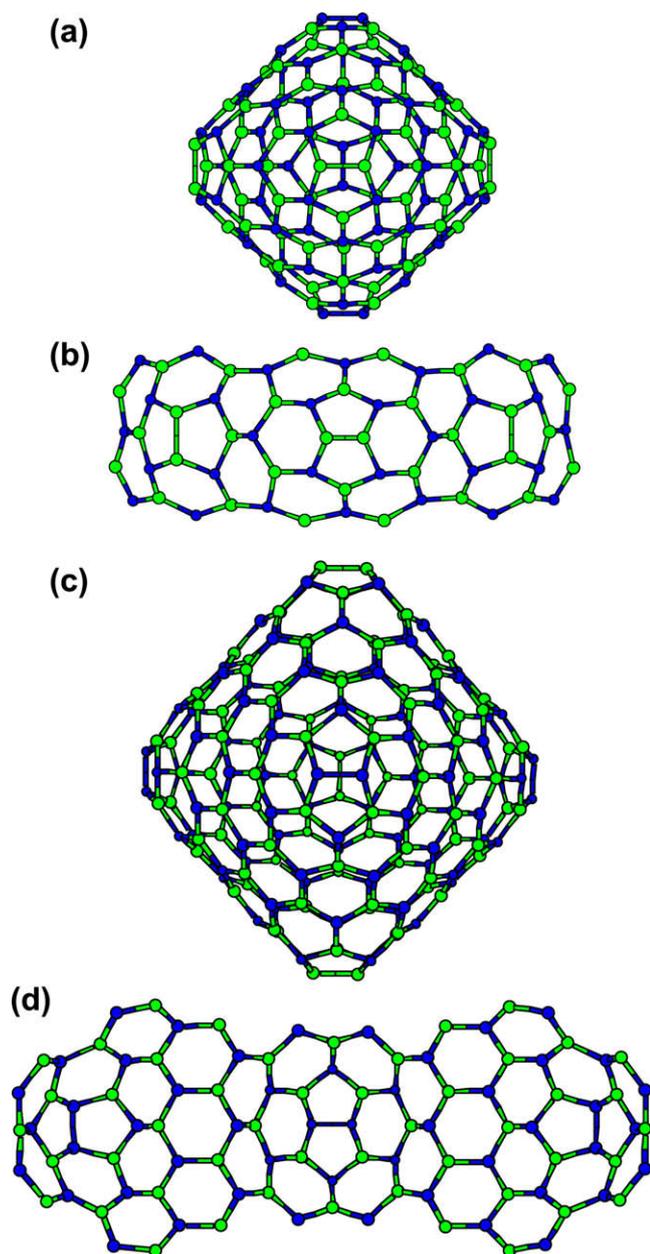


Fig. 3. Fully optimized geometries of the $B_{62}N_{62}$ and $B_{94}N_{94}$ fullerenes. Panel (a) shows a view of the $B_{62}N_{62}$ and panel (b) the half of the $B_{62}N_{62}$ which contains the B–B bonds. Panel (c) shows a view of the $B_{94}N_{94}$ and panel (d) the half of the $B_{94}N_{94}$ which contains the N–N bonds. Some bonds of the geometries shown in (b) and (d) were distorted for visualization purposes. The others halves of the $B_{62}N_{62}$ and $B_{94}N_{94}$ can be obtained by replacing the boron atom by nitrogen and vice versa.

with square rings at the tip. The continuous lines are fittings of an elastic model [17,18] in which the formation energy of the fullerenes is describe in terms of the energy required to wrap a BN sheet into closed structures. According to such a model the formation energy of polyhedral BN fullerenes is given by:

$$\frac{E_f}{n} = A + \frac{B}{n} + \frac{C}{\sqrt{n}}, \quad (2)$$

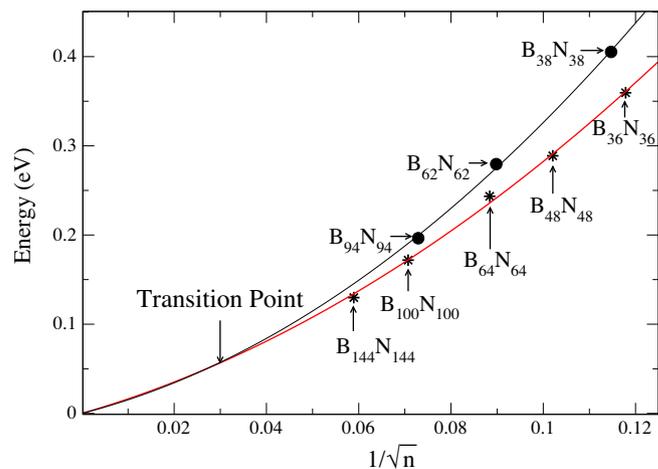


Fig. 4. Formation energy per atom as a function of inverse of the square root of total number of atoms of the fullerene.

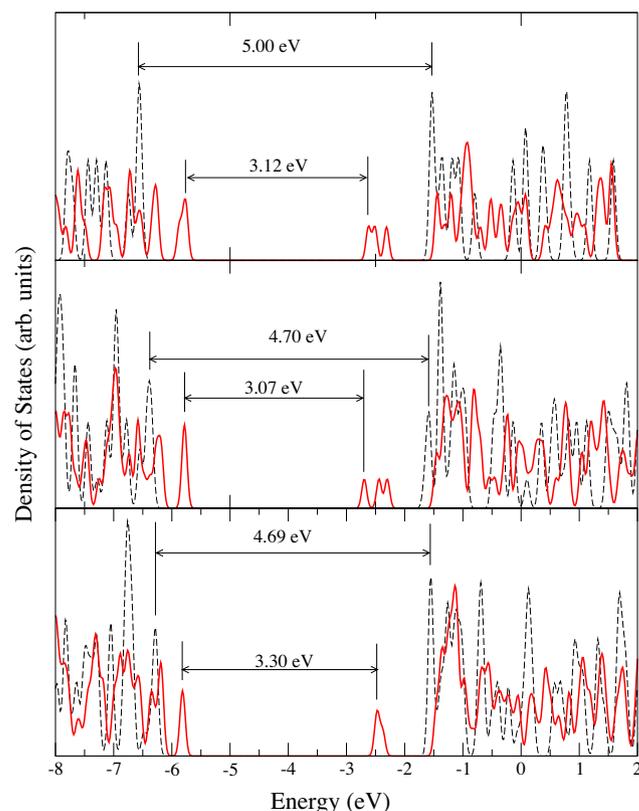


Fig. 5. Density of states of the BN fullerenes. Top panel: $B_{36}N_{36}$ (dashed black line) and $B_{38}N_{38}$ (continuous red line). Middle panel: $B_{64}N_{64}$ (dashed black line) and $B_{62}N_{62}$ (continuous red line). Cotton panel: $B_{100}N_{100}$ (dashed black line) and $B_{94}N_{94}$ (continuous red line).

where A is the formation energy per atom of the structure when $n \rightarrow \infty$, or, equivalently, the formation energy per atom of the BN plane. Since the BN plane is the reference system for the calculation of the formation energy, Eq. (1), $A = 0$. $\frac{B}{n}$ is the contribution due to the strain at the tips of the polyhedron, which is weakly dependent on the system size. The term $\frac{C}{\sqrt{n}}$ is related to the formation of edges of the polyhedron. As it is possible to see in Fig. 4, such model fits very well the data obtained from first-principles. In a previous work [17] it was shown that elastic models also fits very well data from first-principles calculations on BN fullerenes of others symmetries. From the adjust of the model, it was obtained the following values for the constants: $A = 19.35$ eV and $B = 1.33$ eV/atom^{1/2} for fullerenes with side-sharing rings; and $A = 13.33$ eV and $B = 1.49$ eV/atom^{1/2} for fullerenes with square rings at the tips. The values of A shows that tips with side-sharing pentagonal rings have in average ($A/6$) a value of formation energy 1.0 eV higher than tips with square rings, which is expected since the homopolar bonds have a high energy cost in comparison to the B–N bonds. Nevertheless, the tips with side-sharing pentagonal rings are more rounded than tips with square rings (see Fig. 1), therefore, fullerenes with side-sharing pentagonal rings presents smother edges in comparison to those of octahedral fullerenes with square rings at the tips. Indeed, the values of B obtained from the adjust of the model show that the edges of fullerenes with side-sharing rings have a lower energy cost in comparison to those of octahedral fullerenes. Since the energy cost due the edges grows with increasing size, large fullerenes with side-sharing rings (with more than 1000 atoms, see Fig. 3) are energetically more stable than fullerenes with square rings. This result suggests that the tips of nanocones with disclination of 120° may present side-sharing pentagonal rings instead of square rings.

The difference between the values of formation energy per atom of the two kinds of fullerenes is small. The maximum difference is 0.05 eV/atom, which is the difference between the values of formation energy per atom of the $B_{38}N_{38}$ and $B_{36}N_{36}$, respectively. Such an energy difference has the same order of magnitude as the thermal energy ($k_B T$) at 580 K. That temperature is small compared with the values of temperature reached in an arc-voltaic experiment, which is of the order of thousand Kelvin's. Therefore, the formation of fullerenes with side-sharing or square rings should be determined by the kinetic factors.

The fullerenes with side-sharing pentagonal rings presents structures similar to those of fullerenes with square rings. Therefore, it may be difficult to distinguish between the two kinds of fullerenes from electron microscopy images such as those obtained by Goldberg et al. [2]. Nevertheless, the presence of homopolar bonds at tips affects the electronic structure and the chemical properties of the fullerenes which would make possible to separate among them. Fig. 5 shows the density of states of fullerenes with side-sharing and square rings with similar sizes. It is possible that the all fullerenes with square rings have similar HOMO–LUMO gap, roughly 4.7 eV. The HOMO–LUMO gap of the fullerenes with side-sharing pentagonal rings is significantly smaller, roughly 3.1 eV, which may leads to different optical and electrochemical properties compared with those of fullerenes with square rings. As it is possible to see in Fig. 1, the fullerenes with homopolar bonds can

be divided in two halves one with B–B bonds and another with N–N bonds. Such distribution of bonds gives rise to an electric dipole of 0.36, 1.3 and 0.14 Debye for the $B_{38}N_{38}$, $B_{62}N_{62}$ and $B_{94}N_{94}$, respectively. Since the stoichiometric fullerenes without homopolar bonds and non-stoichiometric fullerenes [18] are apolar molecules, it may be possible to separate them from the stoichiometric fullerenes with homopolar bonds.

In summary, new BN fullerenes with homopolar bonds, $B_{38}N_{38}$, $B_{62}N_{62}$ and $B_{94}N_{94}$, are proposed in this study. Such fullerenes present values of formation energy per atom similar to those of octahedral fullerenes without homopolar bonds with similar size, $B_{36}N_{36}$, $B_{64}N_{64}$ and $B_{100}N_{100}$. An elastic model predicts that fullerenes with homopolar bonds with more than 1000 atoms are energetically more stable than the octahedral fullerenes in which the homopolar bonds are absent. The presence of homopolar bonds changes the HOMO–LUMO gap significantly and gives rise to electric dipole which can make possible to separate, experimentally, such fullerenes from the stoichiometric without homopolar bonds and from the non-stoichiometric.

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