Are hemispherical caps of boron-nitride nanotubes possible?

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Abstract

We report all-electron, density-functional calculations with large Gaussian polarization basis set of the recently synthesized octahedral $O \text{B}_{24}\text{N}_{24}$ cage that is perfectly round by symmetry, and boron-nitride (BN) clusters that its existence might suggest. We consider whether it is energetically possible that the two halves of this round cage could cap the BN nanotubes, modeled by $B_{28}\text{N}_{28}$ and $B_{32}\text{N}_{32}$. The energetics show that BN nanotubes with such round caps, are only slightly less favorable than the BN clusters containing six squares as the only defects in the otherwise perfect hexagonal lattice. A larger $B_{96}\text{N}_{96} O$ cage formed from $B_{24}\text{N}_{24}$ by adding sufficient hexagons to isolate all squares is not very favorable energetically.

Key words: boron nitride, fullerides, nanotubes, cages, fullerene, density-functional calculations, $X\alpha$.
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Boron-nitride clusters have been made by vacuum arc melting, dissolved in pyridine, and detected using time-of-flight mass spectroscopy, which shows that the $B_{24}\text{N}_{24}$ cluster is made in abundance [1]. Its structure is likely to be the largest, and thus most round, alternate boron-nitride (BN) cage in which all atom pairs are equivalent by octahedral symmetry, in analogy to the icosahedral $C_{60}$ cluster. The latter cluster is a fullerene, which is a hexagonal graphite sheet made to close into a cage by twelve pentagons as required by Euler’s theorem [2], for which there are no alternate BN cages [3]. Alternate BN cages are made by substituting alternate $sp^{2}$ carbon atoms of certain
fullerene-like cages with boron and nitrogen atoms. These cages contain only squares, hexagons, octagons, etc., and only strong BN nearest-neighbor bonds. The simplest and most stable alternate BN cages contain hexagons that are closed by exactly six isolated squares [4]. However, B_{24}N_{24} is the alternate cage for the perfectly round C_{48} cluster with O_h symmetry [5]. Both are made round by the addition of twelve defects—six octagons and the corresponding six squares required by Euler’s theorem. When made from carbon this cluster is quite unfavorable [6], but apparently not when made from boron nitride. Our calculations show that the B_{24}N_{24} cage containing six squares isolated by hexagons is about 4-5 eV lower than the octahedral B_{24}N_{24} cage[4]. Perhaps BN cages are almost as versatile as fullerene cages; that could be the case if defects in boron nitride cages cost significantly less energy than they do in fullerene cages.

A study of the smaller fullerenes suggests that it is never favorable to replace, in the context of Euler’s theorem, two pentagons with a single square [7]. So in carbon cages squares are likely to be twice as energetically unfavorable as pentagons, which cost, when isolated, at least 2.3 eV each [8]. Heptagons and octagons are less energetically favorable in carbon cages, but are required to bend and twist free-standing nanotubes [8]. The energetics of fullerenes if applied to B_{24}N_{24} would argue strongly against its existence.

The most abundant fullerenes are buckminsterfullerene, C_{60}, and C_{70}. The latter can be viewed as being formed by cutting buckminsterfullerene into hemispheres in a highest-symmetry direction and inserting a ring of ten atoms, and then rotating the top hemisphere half a revolution before reconnecting it. It is natural to think about extending that process to larger capsules [10] and ultimately to the (5,5) carbon nanotube in the infinite limit [12,11]. Contrary to early belief, C_{60} is not the most stable fullerene. The larger icosahedral fullerenes are more stable [13], but C_{60} is the most stable in a wide range of cluster sizes and shapes [14]. Perhaps perfect roundness facilitates making C_{60} and B_{24}N_{24}.

If, on the other hand, extra defects in boron nitride fullerenes are so costly that they never occur except in B_{24}N_{24}, then boron nitride caps have a very special shape. If half a defect-free BN fullerene caps a BN nanotube just as half a defect-free fullerene caps a carbon nanotube [15] then each BN cap has precisely three squares. Furthermore, the three squares must lie on the periphery of the nanotube, and, as three points determine a plane, the BN nanotube cap must be flat. Defect-free flat and triangular BN caps are quite different from hemispherical carbon nanotube caps.

If B_{24}N_{24} is spherical and under some circumstances abundant, it is natural to ask if an additional ring of BN atoms can be added to form a less abundant but still possible cluster that is reminiscent of C_{70}, and if further rings are possible
to make hemispherically capped BN nanotubes. We study the energetics of this possibility using analytic density functional theory.

Our calculations use the Slater-Roothaan method. It uses Gaussian bases to fit the orbitals and Kohn-Sham potential [16] of density-functional theory. The method through robust and variational fitting is analytic and variational in all basis sets [17]. The most general functionals that it can treat so far are certain variants of the X\(\alpha\) functional [18]. In particular, it can handle different \(\alpha\)'s on different elements analytically and variationally so that the atomized energies of any cluster can be recovered exactly, and all energies are accurate through first order in any changes to any basis set. Thus the energy does not change if we choose to constrain any fit, which we do for all fits at no cost to the calculated energetics and negligible cost in computer time. Our work has spawned research efforts that brought both useful fitting techniques and density-functional theory to Gaussian-based ab initio quantum chemistry. Thus there are good basis sets for fitting the Kohn-Sham potential. The best \(s\)-type fitting bases are still those scaled from the \(s\)-part of the orbital basis [19]. A package of basis sets has been optimized [20] for use with DGAuss [21]. We use the valence double-\(\zeta\) orbital basis set DZVP2 and the \(pd\) part of the (4,3;4,3) (A2) charge density fitting basis. Ahlrichs' group has generated a RI-J basis for fitting the charge density of a valence triple-\(\zeta\) orbital basis set used in the Turbomole program [22]. We use its \(pdf\) part with the standard 6311G** basis set downloaded from PNNL (http://www.emsl.pnl.gov:2080/forms/basisform.html). For both sets of calculations the values of \(\alpha\) chosen for B and N are, respectively, 0.786751 and 0.767473, which give the exact atomic energies [23] when used with the triple-\(\zeta\)/RI-J basis. The accuracy of this method using Hartree-Fock values of \(\alpha\) [24] away from the sides of the periodic table is roughly that of Becke’s half-and-half method [25], but as it requires no numerical integration. The method is ideal for use with Gaussian basis sets [17]. Forces are computed nonrecursively using the 4-j generalized Gaunt coefficients [26].

The symmetry restricted optimization of the BN cages was performed using the BFGS computer code [27]. The optimized hemispherically capped BN nanotubes are shown in Fig. 1 while their symmetries are given in the Table I. The (4,4) nanotubes are generated by extending along the four-fold axis [Fig 1(b)]. The caps start off perfectly round by the symmetry of B\(\text{24}\)N\(\text{24}\). They remain quite round after geometry optimization. In the figure they look a little flat at the tops and bottoms because the octagons take up a significant portion of their caps. The (3,3) BN nanotube generated by extending the three-fold direction would have rounder caps, but are probably less likely to be made because they contain significantly more curvature. The binding energy per BN pair (BE), the energy gap between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO), and the vertical ionization potential calculated at the optimized geometries are
Fig. 1. (Color online) The optimized structures for hemispherically-capped BN nanotubes. (a) and (b) are two different views of the \( \text{B}_{24} \text{N}_{24} \) cage: (a) along the \( \text{C}_3 \) axis, (b) along \( \text{C}_4 \) axis. (c) \( \text{B}_{28} \text{N}_{28} \) (\( \text{C}_{4h} \)) cage obtained by adding a ring of eight alternating B and N atoms, (d) tubular \( \text{B}_{32} \text{N}_{32} \) (\( \text{S}_8 \)) cage by inserting two rings of eight alternating B and N atoms (see text for more details).

The coordinates (in Å) of the B and N atoms optimized with 6311G**/RI-J basis set for the recently synthesized octahedral \( \text{B}_{24} \text{N}_{24} \) cage are (0.66, 1.66, 2.59) and (2.74, 1.65, 0.74) respectively for the three-fold axis in the (1,1,1) direction. The positions of all remaining of atoms in the cage can be generated by symmetry operations. The HOMO and LUMO both have \( e \) symmetry and yield a large gap of 4.94 eV that agrees with the value of 4.95 eV \([1]\) obtained using DV-X\( \alpha \) at the PM5 geometry.

The \( \text{C}_{4h} \) \( \text{B}_{28} \text{N}_{28} \) cage [Fig. 1(c)] is generated from the base \( \text{B}_{24} \text{N}_{24} \) cage by cutting the latter into two halves after orienting it along the \( \text{C}_4 \) axis, then inserting a ring of eight alternating B and N atoms perpendicular to the axis,
Table 1
The binding energy per BN pair (BE), the energy gap between the highest occupied molecular orbital and the lowest unoccupied molecular orbital, and the vertical ionization potential (VIP) for the optimized BN cages, all in eV.

| Symmetry | 631G**/RI-J | DZVP2/A2 |
|----------|-------------|----------|
|          | BE          | GAP      | VIP      | BE        |
| B_{24}N_{24} O | 14.63 | 4.94 | 6.66 | 14.64 |
| B_{28}N_{28} C_{4h} | 14.89 | 4.86 | 8.48 | 14.90 |
| B_{28}N_{28} T | 14.95 | 5.38 | 8.64 | 14.95 |
| B_{32}N_{32} S_8 | 14.96 | 4.95 | 8.36 | 14.98 |
| B_{36}N_{36} T_d | 15.06 | 5.33 | 8.42 | 15.11 |
| B_{96}N_{96} O | 14.97 | 4.25 | 7.74 | 15.12 |

Fig. 2. The optimized structures for the favorable B_{28}N_{28} (left) and B_{36}N_{36} (right) cages.

i.e. horizontally, and then rotating the top half by an eighth of a revolution. The resultant cage structure has C_{4h} symmetry with eight inequivalent atoms. If another ring of four BN dimers is inserted in the same manner, then the resultant B_{32}N_{32} cage is a tubular structure with S_8 symmetry [Fig. 1(d)]. Table I shows systematic increase in the binding energy by going from B_{24}N_{24} to the B_{28}N_{28} cage (0.26 eV per BN pair) and from B_{28}N_{28} to B_{32}N_{32} cage (0.06 eV/BN pair). The successive additions of more BN rings will result in further stabilization of the BN tubular cages and will ultimately lead to the (4,4) BN nanotube. Thus our total energy calculations do not rule out the possibility of BN tubes with round caps similar to those observed in case of
carbon nanotubes. A recent molecular dynamics study of the growth mechanism of BN nanotubes has also noted the formation of a cap containing four squares and octagon for this nanotube [28]. Molecular models of caps with four squares, octagons and hexagons were also speculated earlier [30]. All the BN cages studied have rather large HOMO-LUMO gaps of about 4.9-5.5 eV similar to those observed for the infinite BN nanotubes (∼ 5.5 eV) [29]. The vertical ionization potential (VIP) calculated as the energy difference of the two self-consistent calculations for the neutral and singly positively charged cage also show relatively large values.

Fig. 2 shows two examples of the most favorable BN cages that are composed of eight equivalent triangular faces meeting at six isolated squares [4,3]. Their BE, HOMO-LUMO gap and VIP are given in Table 1. The smaller cage, $T_{B_{28}N_{28}}$, Fig. 2(a) has the same stoichiometry as the middle-sized nanotube of Fig. 1. That $C_{4h} B_{28}N_{28}$ hemispherically-capped nanotube is related to this cage by the insertion of twelve defects: six squares and six octagons. Using the triple-ζ basis the energetic cost is 0.14 eV per defect and using the double-ζ basis the cost is 0.12 eV per defect, which is more than an order of magnitude less than the cost of any additional defect in a carbon fullerene. The calculations indicate that these cages are energetically more stable than the $B_{24}N_{24}$ cage. The trend is similar to that observed in case of $C_{60}$ where higher fullerenes have larger binding energy than the $C_{60}[13]$. 

Fig. 3. (Color online) The optimized structures for the (a) $B_{24}N_{24}$ and (b) $B_{96}N_{96}$ cages.
C$_{60}$ does not cap the most important carbon nanotubes. Probably the metallic (10,10) nanotube is most important [31]. It can be capped by halves of round, but not perfectly round like C$_{60}$, icosahedral C$_{240}$ [32]. B$_{24}$N$_{24}$ can be enlarged by adding hexagons. Another such round cage of octahedral symmetry is B$_{96}$N$_{96}$. The two optimized round cages of this study are shown in Fig. 3. The Table shows that B$_{96}$N$_{96}$ is the more stable than the B$_{24}$N$_{24}$. Its halves (Cf. Fig. 4) would cap a round (8,8) BN nanotube. It is clearly different, from B$_{24}$N$_{24}$, in that while being mostly round, its twelve squares stick out significantly, like the detonators of a sea mine. Furthermore, B$_{96}$N$_{96}$ is not substantially more stable than the other cages of Table I, despite the fact that it is at least three times as large. Thus we think it unlikely that hemispherical caps for larger than BN (4,4) nanotubes, if they exist at all, will have isolated squares, but no really attractive possibilities come to mind. For example, six square-octagon-square units could be placed on the two-fold axes.

Fig. 4. (Color online) The possible round cap of the (8,8) nanotube based on the B$_{96}$N$_{96}$ cage.
of the octahedral group, but the Euler overclosure would have to be balanced by two extra octagons inserted elsewhere to form a hemisphere. Of course, BN nanotubes could be capped by hemispheres of carbon fullerenes.

To summarize, all electron analytic density functional based calculations have been performed on selected boron-nitride cage structures including the recently synthesized B$_{24}$N$_{24}$ cage. The energetics of the BN tubular structures with the end caps based on this cage points to possible existence of round capped BN nanotubes. Amongst the BN cages that satisfy the six isolated square rule the higher B$_{28}$N$_{28}$ and B$_{32}$N$_{32}$ cages are found to be energetically more stable than the smallest B$_{24}$N$_{24}$ consistent with earlier calculations [4], but apparently they are not more abundant experimentally [1]. Additional topological defects in the most favorable BN cages seem more energetically favorable than defects in the fullerenes. Probably round caps on BN nanotubes with circular cross section are more likely than flat caps on triangular carbon nanotubes.

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