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New Boron Nitride $B_{24}N_{24}$ Nanotube

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The structure and stability of the $(B_{12}N_{12})_n$ ($n = 1, 2$) cages have been computed at the B3LYP level of density functional theory. The most stable $B_{12}N_{12}$ cage is the T_h symmetrical structure with six isolated squares. The dimerization pattern of $B_{12}N_{12}$ differs strongly from those of C_{60} and C_{20}. The most stable $B_{24}N_{24}$ structure, deduced from two $B_{12}N_{12}$ (T_h) cages, has an unexpected tube form.

Introduction

Heterofullerenes are fullerenes in which one or more cage carbon atoms are replaced by other elements.[1] Among these, one of the most interesting substitution patterns is the coupled boron−nitrogen (BN) replacement because of its isoelectronic relation to the C_2 carbon unit. Therefore, complete substitution of C_{60} by BN gives $(BN)_{30}$, and the most stable structure without direct B−B or N−N bonds in a fullerene structure is $C_{12}(BN)_{24}$.[2] As the isolated pentagon rule in carbon fullerenes,[3] the isolated square rule is found in $(BN)_n$ cages,[4] and the $(BN)_{30}$ cage with six isolated squares avoiding B−B and N−N bonds is found to be more stable than the isomer with twelve isolated pentagons by more than 100 kcal/mol. Due to the special physical and chemical properties, the formation and characterization of small BN clusters,[5] cages,[6,7] and nanotubes[8−10] have received intensive attention both experimentally and theoretically. Among BN cages studied theoretically, the T_h symmetrical $(BN)_{12}$ structure with six isolated squares is found to be more stable than the graphite-like structure or monocyclic ring, and fullerene cages[11−13] and to have enhanced thermodynamic and kinetic stability on the basis of the calculated binding energy and HOMO−LUMO gap.[7]

Recently, the preparation and characterization of fullerene dimers and other all carbon oligomers have attracted considerable attention. For example, the most stable $(C_{60})_2$ structure has a four-membered ring as a formal [2 + 2] addition product as computed by Thiel,[14] and this finding is supported by the experimental studies.[15] The most stable $(C_{60})_2^{2-}$ or its isoelectronic $(C_{59}N)_2$ are computed to have a single bond connection in anti-C_{2h} or gauche-C_2 conformation.[16] In contrast to $(C_{60})_2$, the most stable dimer of the smallest C_{20} fullerene has an unexpected open [2 + 2] connection and the intuitively closed [2 + 2] dimer as $(C_{60})_2$ is higher in energy by 36.6 kcal/mol at B3LYP/6-31G*.[17] It is also found that dimerization of $C_{58}(BN)_1$ through the B−N bonds is more exothermic than C_{60} by 16 kcal/mol, indicating the higher tendency for polymerization or oligomerization of BN-doped fullerenes.[2]

In this paper, we present a B3LYP/6-31G* density functional theory (DFT) investigation on the structure and stability of the $B_{12}N_{12}$ monomer cages obeying both the isolated square and pentagon rules, and the dimeric structures from the most stable $B_{12}N_{12}$ cages. The most stable $B_{12}N_{12}$ monomer is the T_h symmetrical structure with six isolated squares. The dimerization pattern of $B_{12}N_{12}$ (T_h) differs from those of C_{60} and C_{20}. The most stable $B_{24}N_{24}$ structure from the connection of the two six-membered rings has an unexpected tube form rather than the expected formation of a hexagonal cylinder.

Computational Method

All structures were optimized at the B3LYP/6-31G* density functional level of theory and the related frequency calculations at the same level (at the HF level for the C_1 symmetrical $B_{24}N_{24}$ isomers) were used to characterize the optimized structures to be energy minima without imaginary frequencies.[18] For comparison, ab initio Hartree−Fock (HF) and MP2(fc) single-point calculations with the 6-31G* basis set and the B3LYP/6-31G* optimized geometries for the $B_{12}N_{12}$ isomers were carried out. Additional calculations at the B3LYP level with the more flexible 6-311+G* basis set and the B3LYP/6-31G* geometries were used for testing the basis set effect. All calculations were carried out with the Gaussian 98 program.[19] The total electronic energies are summarized in the Supporting Information.

Results and Discussion

$B_{12}N_{12}$ Isomers. Computationally, the T_h symmetrical $B_{12}N_{12}$ cage is found to be more stable than the graphite-like structure with fused six-membered rings and the fullerene cage with pentagons and hexagons containing B−B and N−N bonds.[11−13] Blase et al. found that an alternating B−N hexagon is more stable than a six-membered-ring with two B−B and two N−N bonds by 163.7 kcal/mol.[13] Therefore, structures with B−B and N−N bonds are likely to be significantly less stable than those with fully alternating B−N bonds. However, Rogers et al.[20] found that $B_{36}N_{36}$ cages with twelve isolated pentagons in classical fullerene structures are more stable than the cage composed of six squares and thirty-two hexagons by 98 to 170 kcal/mol. This is in contrast to the structure and stability of $B_{12}N_{12}$ or $B_{30}N_{30}$ cages.[4]

To verify the T_h symmetrical $B_{12}N_{12}$ cage to be the most stable isomer, we computed a set of additional $B_{12}N_{12}$ cages with six squares (F_{46}) and twelve pentagons (F_{56}). The optimized structures are shown in Figure 1 and the computed energetic data are given in Table 1.

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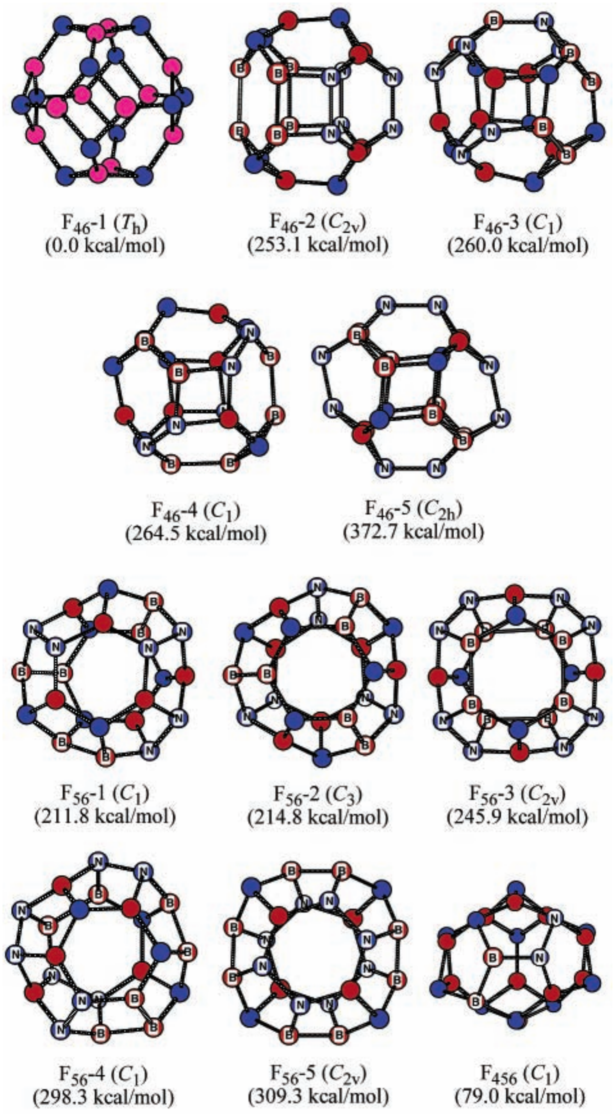


F_{46}-1 (T_h) (0.0 kcal/mol)
F_{46}-2 (C_{2v}) (253.1 kcal/mol)
F_{46}-3 (C_1) (260.0 kcal/mol)
F_{46}-4 (C_1) (264.5 kcal/mol)
F_{46}-5 (C_{2h}) (372.7 kcal/mol)
F_{56}-1 (C_1) (211.8 kcal/mol)
F_{56}-2 (C_3) (214.8 kcal/mol)
F_{56}-3 (C_{2v}) (245.9 kcal/mol)
F_{56}-4 (C_1) (298.3 kcal/mol)
F_{56}-5 (C_{2v}) (309.3 kcal/mol)
F_{456} (C_1) (79.0 kcal/mol)

Figure 1. B3LYP/6-31G* structures of F_{46} and F_{56} $B_{12}N_{12}$ monomers.

TABLE 1: Relative Energies (E_{rel}, kcal/mol), HOMO−LUMO Gap (Gap, eV) of $B_{12}N_{12}$ Monomers

isomer	E_{rel} [a]	Gap [a]	E_{rel} [b]	E_{rel} [c]	E_{rel} [d]
F_{46}-1 (T_h)	0.0	6.83	0.0	0.0	0.0
F_{46}-2 (C_{2v})	253.1	4.27	251.6	287.2	273.5
F_{46}-3 (C_1)	260.0	4.19	258.3	295.8	280.8
F_{46}-4 (C_1)	264.5	3.87	263.7	299.9	283.4
F_{46}-5 (C_{2h})	372.7	3.02	371.5	418.0	394.6
F_{56}-1 (C_1)	211.8	4.63	210.1	240.6	228.1
F_{56}-2 (C_3)	214.8	4.95	213.0	244.2	231.8
F_{56}-3 (C_{2v})	245.9	4.67	244.1	283.9	266.1
F_{56}-4 (C_1)	298.3	3.84	296.2	339.6	320.4
F_{56}-5 (C_{2v})	309.3	4.92	307.2	355.6	329.2
F_{456} (C_1)	79.0	5.38	78.3	90.4	84.2

[a] At B3LYP/6-31G*//Fopt. [b] At B3LYP/6-311+G**//B3LYP/6-31G*. [c] At HF/6-31G*//B3LYP/6-31G*. [d] At MP2(fc)/6-31G*//B3LYP/6-31G*.

As shown in Figure 1, F_{46}-1 is the T_h symmetrical $B_{12}N_{12}$ isomer with fully alternating B−N bonds, while F_{46}-2, F_{46}-3, and F_{46}-4 are isomers with three N−N and three B−B bonds, and they are less stable than F_{46}-1 by 253−265 kcal/mol, respectively. Isomer F_{46}-5, which has four N−N and four B−B bonds, is even higher in energy than F_{46}-1 by 373 kcal/mol. It is interesting to note that each N−N or B−B bond has an average contribution of roughly 45 kcal/mol.

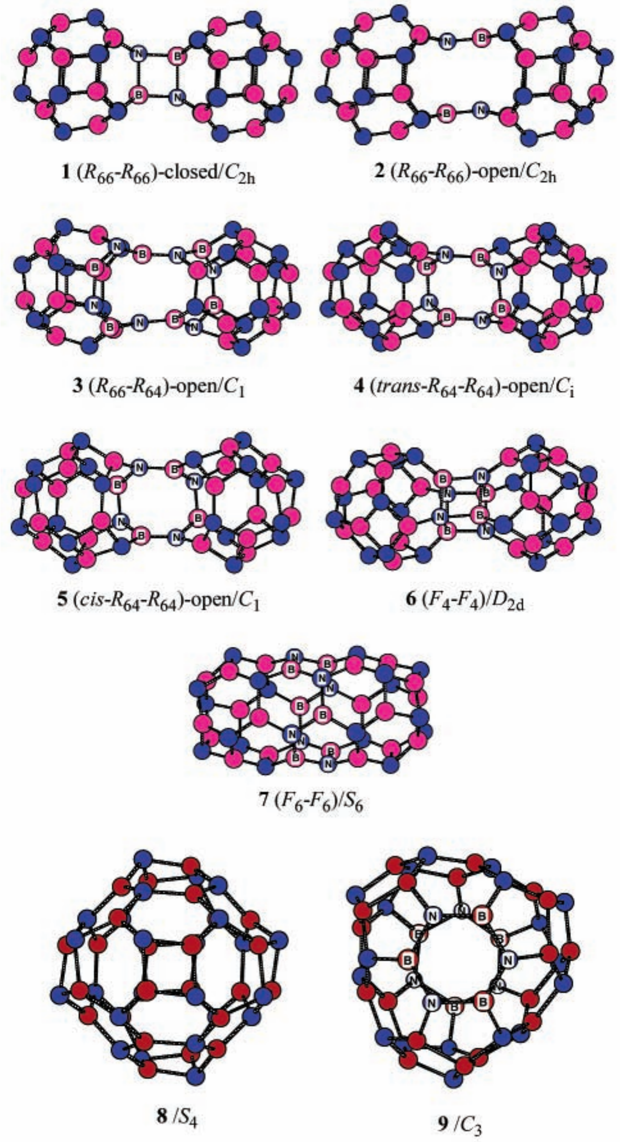
As compared to F_{46}-1, the fullerene-like $B_{12}N_{12}$ isomers (from F_{56}-1 to F_{56}-5) are also higher in energy. Thus, the T_h symmetrical $B_{12}N_{12}$ cage is the most stable isomer, and it also has the largest HOMO−LUMO gap, indicating the high kinetic stability (Table 1). However, F_{56}-1 and F_{56}-2 with three N−N and three B−B bonds are lower in energy than the corresponding F_{46}-2, F_{46}-3, and F_{46}-4. Structures of F_{56} (F_{56}-3, F_{56}-4, and F_{56}-5) with four N−N and B−B bonds are lower in energy than F_{46}-5 by 127 to 83 kcal/mol. This indicates that N−N and B−B bonds in F_{46} structures are higher in energy than in F_{56} isomers, and this difference can be ascribed to the strain strengths of the four- and five-membered rings. On the basis of these results, one might expect that the energetic effects of N−N and B−B bonds can be compensated or overestimated by the reduced strain in five-membered rings with increased cage sizes. This explains the energetic order for the $B_{36}N_{36}$ isomers found by Rogers et al.[20]

Apart from F_{46}-1, the higher energetic F_{46} and F_{56} isomers have more than one pair of B−B and N−N bonds. To check the lower-lying isomers with one pair of B−B and N−N bonds, we have optimized a structure (F_{456}) with four squares, four pentagons, and six hexagons, deduced from a 90-degree rotation of a B−N bond shared by two hexagons in F_{46}-1.[21] In F_{456}, the four pentagons are fused (Figure 1). As expected, F_{456} is higher in energy than F_{46}-1 by 79.0 kcal/mol, and each B−B or N−N bond has a contribution of about 40 kcal/mol, close to that from F_{46} isomers.

As shown in Table 1, the relative energetic order of F_{46} and F_{56} isomers at B3LYP/6-31G* are parallel to those at HF/6-31G* and MP2(fc)/6-31G*, apart from their quantitative differences. In addition, B3LYP/6-311+G* shows the same relative energies (within 2 kcal/mol) as B3LYP/6-31G*. Therefore, B3LYP/6-31G* is sufficient for such large B−N cages.

$B_{24}N_{24}$ Isomers. There are two individual B−N bond types among the 36 B−N bonds in F_{46}-1; one is shared by two six-membered rings (R_{66}), and another by a four- and a six-membered ring (R_{64}). R_{66} (1.486 Å) is longer than R_{64} (1.439 Å). They are both shorter than the single bond in $H_3B{-}NH_3$ (1.668 Å), but longer than the double bond in $H_2B{=}NH_2$ (1.393 Å) at B3LYP/6-31G*. Both boron and nitrogen center in $B_{12}N_{12}$ are pyramidal, indicated by the sum of three NBN or BNB angles (349.8 vs 302.5°). The four-membered ring (F_4) is puckered with a torsion angle of 164.1°, and the B−B and N−N cross-distances of F_4 are 1.920 and 2.247 Å, respectively. The six-membered ring (F_6) has a chair form. On the basis of the structure, one might expect the dimerization of $B_{12}N_{12}$ through not only the B−N bonds (R_{66}−R_{66}, R_{66}−R_{64}, and R_{64}−R_{64}), but also the four-membered rings (F_4−F_4) and the six-membered rings (F_6−F_6), respectively.

The optimized structures and energies for the $(B_{12}N_{12})_2$ isomers are given in Figure 2 and in Table 2. The first isomer bridged by two B−N bonds is the connection of two R_{66} bonds for the formation of a closed [2 + 2] form (**1**), which mimics $(C_{60})_2$.[14,15] The dimerization energy of **1** is exothermic by 38.0 kcal/mol, and the B−N bridge bond length is 1.566 Å and the R_{66} distance is 1.643 Å, and they are longer than those of **1** due to tetra bonding. As in case of $(C_{20})_2$,[17] we also found an open form (**2**) connected by two B=N bonds (1.404 Å) and the R_{66} distance is 2.875 Å. It is very interesting to note that both closed **1** and open **2** forms are very close in energy with a difference of only 0.2 kcal/mol, and this is in sharp contrast to that of $(C_{20})_2$, in which the open form is more stable than the closed one by 36.6 kcal/mol.[17] That **1** and **2** are close in energy despite



1 (R_{66}-R_{66})-closed/C_{2h}　**2** (R_{66}-R_{66})-open/C_{2h}

3 (R_{66}-R_{64})-open/C_1　**4** (*trans*-R_{64}-R_{64})-open/C_i

5 (*cis*-R_{64}-R_{64})-open/C_1　**6** (F_4-F_4)/D_{2d}

7 (F_6-F_6)/S_6

8 /S_4　**9** /C_3

Figure 2. B3LYP/6-31G* structures for $(B_{12}N_{12})_2$ (**1**−**9**).

TABLE 2: Relative Energies (E_{rel}, kcal/mol), HOMO−LUMO Gap (Gap, eV) of $B_{24}N_{24}$ Isomers

isomer	E_{rel} [a]	Gap	E_{rel} [b]
1 (C_{2h})	−38.0	6.28	205.6
2 (C_{2h})	−37.8	6.04	205.8
3 (C_1)	−50.2	5.97	193.4
4 (C_i)	−54.0	5.85	189.6
5 (C_1)	−67.7	6.00	175.9
6 (D_{2d})	−37.4	6.38	206.2
7 (S_6)	−243.6	6.43	0.0
8 (S_4)	−283.8	6.61	−40.2
9 (C_3)	−138.0	4.71	105.6

[a] Relative to two $B_{12}N_{12}$ T_h monomers. [b] Relative to isomer **7**.

their large structural difference can be ascribed to the compensation of the bonding and strain energies.

The next dimer is deduced from the combination of R_{66} and R_{64} bonds. As expected, only the open structure (**3**) is found and no closed form is located. This structure is lower in energy than **1** by 12.2 kcal/mol. In **3**, the two bridging B═N bond lengths are 1.409 Å, and the R_{66} and R_{64} distances are elongated to 2.763 and 2.578 Å, respectively.

For the dimer with two R_{64} bonds, there are two conformations relative to the orientation of the F_4 (or F_6), i.e., trans (**4**) or cis (**5**), in which the two F_4 (or F_6) are at the opposite (trans) or at the same (cis) sides. In both cases, only open structures are found on the potential energy surface. Both **4** and **5** have B═N bridges (1.430 vs 1.425 Å), and the R_{64} distances are elongated (2.519 vs 2.760/2.759 Å). At B3LYP/6-31G*, **5** is the most stable structure bridged by two B═N bonds, and the exothermic dimerization energy of 67.7 kcal/mol is much larger that those of **1**−**4** (Table 2).

In contrast to $(C_{60})_2^{2-}$ or $(C_{59}N)_2$,[16] many attempts to locate a dimer bridged by single B−N bond structures such as H_3B-NH_3 failed, and this is not so very surprising, since the dimerization energies of **1**−**5** are much larger than that for H_3B-NH_3 of 27.0 kcal/mol at the same level.

Apart from the bond connections, we have also investigated the dimerization through the four-membered (F_4) or six-membered (F_6) rings with the formation of four and six additional B−N bonds. As shown in Figure 2, a dimer in D_{2d} symmetry with four additional B−N bonds (**6**) forms a B_4N_4 cube bridging two cages, in which the B−N bridging bond length is 1.575 Å, and the R_{64} distance is 1.635 Å. Despite the formation of four additional B−N bonds, the dimerization energy of 37.4 kcal/mol is comparable with those of **1** and **2**, and much smaller than that of **5** (Table 2), and this is due to the formation of the highly strained cube.

For the dimer with two F_6−F_6 connections, we have found a structure (**7**) in a perfect tube form in S_6 symmetry rather than the expected hexagonal cylinder, which was used as the initial structure for the optimization. At B3LYP/6-31G*, **7** has the largest dimerization energy of 243.6 kcal/mol, which is much larger than those of **5** (67.7 kcal/mol) and open $(C_{20})_2$ (145.2 kcal/mol).[17] This large energetic effect is easily understood, since in **7** there are only six F_4 remaining in the tube, and the other six F_4 originated from two monomers and the additional six F_4 from the expected hexagon are converted into F_6. This reduces the enhanced strain considerably and results in the abnormal dimerization energy. The stability of **7** correlates also with the HOMO−LUMO gap (Table 2). This finding indicates that $B_{12}N_{12}$ can be considered as a building block for the formation of different sized BN nanotubes. Therefore, it should be possible to control the BN nanotube formation.

However, it is necessary to point that this tube structure (**7**) is less stable than the cage isomer (**8**) by 40 kcal/mol. In **8**, the six squares are isolated (obeying the isolated square rule[22]), while the six squares in **7** are located at the tube ends and annelated to the hexagons. Since Roger et al.[20] found that the fullerene-like $B_{36}N_{36}$ is more stable than isomer with six isolated squares, we have also computed the fullerene-like $B_{24}N_{24}$ isomer (**9**, the D_3 symmetrical C_{48} fullerene structure is used as template for optimization[23]). However, it is found that the classic fullerene structure **9** in C_3 symmetry with three B−B and three N−N bonds is higher in energy than **7** and **8** by 105.3 and 145.6 kcal/mol, respectively. This relative stability agrees with that for $B_{30}N_{30}$,[4] but is in contrast to that for $B_{36}N_{36}$.[20]

The tube of **7** has a length of 8.6 Å and a diameter of 3.6 Å, and each end of the tube has a hexagon surrounded by three squares. The high-resolution electron microscope images of BN nanotubes show typical flat ends corresponding to triangular facets and being the result of the hexagonal BN network.[24] They show also sharp inner angular and peculiar structures for the tip because of four-membered rings.[10] Besides the observation of $B_{12}N_{12}$ cage,[25] no such small tubes have been observed yet.

Conclusions

The structure and stability of the $B_{12}N_{12}$ monomeric and dimeric isomers were investigated at the B3LYP/6-31G* level of density functional theory. Among the structures obeying the isolated square and pentagon rules, the most stable $B_{12}N_{12}$ cage is T_h symmetrical and has six isolated squares with fully alternating B−N bonds. Structures with direct B−B and N−N bonds are higher in energy. It is found that the dimerization pattern of two $B_{12}N_{12}$ cages differs strongly from those of C_{60} and C_{20}. The most stable $B_{24}N_{24}$ isomer, deduced from two $B_{12}N_{12}$ cages, has a tube structure, and also the largest exothermic dimerization energy. Therefore, monomeric $B_{12}N_{12}$ can be a building block for BN nanotubes, and this should enable the mechanistic investigation on nanotube formation.

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Supporting Information Available: Total electronic energies are listed. This material is available free of charge via the Internet at http://pubs.acs.org

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