

## Research Article

# Structure and Stability of $B_{10}N_{14}$ : Cages, Sheets, and Rings

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Boron nitride is a material similar to carbon in its ability to adopt numerous molecular forms, including two-dimensional sheets and three-dimensional cages and nanotubes. Boron nitride single molecules, such as  $B_{12}N_{12}$ , have isomeric forms that include rings and sheets, as well as cage forms analogous and isoelectronic to the carbon fullerenes. Such cages tend to be composed of squares and hexagons to allow perfect alternation of boron and nitrogen atoms, which is possible because of the 1:1 ratio of boron-to-nitrogen atoms. What about molecules in which this 1:1 ratio does not apply? In the current study, theoretical calculations are carried out on molecules of  $B_{10}N_{14}$  to determine energetically favorable isomers. Density functional theory is used in conjunction with Dunning basis sets. Cage, sheet, and ring isomers are considered. Energetic trends are calculated and discussed, in comparison to comparable studies on  $B_{12}N_{12}$ .

## 1. Introduction

Boron nitrides have been experimentally produced in a wide variety of forms. Boron nitride “fullerenes” and nanotubes have been produced [1] from boron and iron oxide in the presence of  $N_2$  gas. Boron nitride nanotubes have also been synthesized [2] by heating a boron/catalyst mixture with  $N_2$  and  $NH_3$  atmospheres. Various boron nitride nanostructures have been synthesized [3] by chemical vapor deposition. Single molecules [4] of  $B_{24}N_{24}$ , bulk material [5] of  $B_{12}N_{12}$ , and boron nitride chains [6] have also been observed. Theoretical studies have compared [7]  $B_{12}N_{12}$  to the isoelectronic  $C_{24}$  and demonstrated [8, 9] the stability of molecules including  $B_{12}N_{12}$ ,  $B_{16}N_{16}$ ,  $B_{28}N_{28}$ , and  $B_{36}N_{36}$ . For  $B_{13}N_{13}$ ,  $B_{14}N_{14}$ , and  $B_{16}N_{16}$ , square-hexagon cage structures have been shown [10] to be far more stable than fullerene-like pentagon-hexagon structures. Other theoretical studies have characterized [11, 12] the interactions between  $B_{12}N_{12}$  and other molecules, including other molecules [13] of  $B_{12}N_{12}$ . Carbon doping of hexagonal boron nitride network solids has been explored extensively [14].

A theoretical study [15] on molecules ranging from  $B_8N_8$  to  $B_{11}N_{11}$  compared two isomeric forms: rings and square-hexagon cages. That study concluded that rings are the more stable form at the smaller sizes, but the cages are the favored form provided that at least two of the six squares are isolated by hexagons. This arrangement of polygons first becomes possible for  $B_{11}N_{11}$ , for which the cage is more stable than the ring. For  $B_{12}N_{12}$ , all six squares can be isolated by hexagons, and a theoretical study [16] of  $B_{12}N_{12}$  showed a very large stability advantage for the cage. What about boron nitride molecules with an atom ratio other than 1:1? In the current study, the structures and relative stability of isomers of  $B_{10}N_{14}$  are calculated to determine whether the trends seen for  $B_xN_x$  molecules also apply to non-1:1 boron nitrides. Rings, cages, and two-dimensional “graphitic” sheet structures are considered.

## 2. Computational Details

Geometries and energies in this study are calculated using the PBE1PBE density functional theory method [17–19].

Vibrational frequencies and zero-point energies (ZPE) are also calculated for each molecule. The Dunning cc-pVDZ atomic orbital basis set [20] is used for all calculations. Calculations are carried out using the Gaussian 03W computational chemistry software [21] package.

### 3. Results and Discussion

All molecules in this study have ten boron atoms isolated from one another, hereafter referred to as the isolated boron atom rule (IBAR). As justification for the IBAR, the energy was calculated for the following model reaction:



Since replacement of a boron-boron single bond and nitrogen-nitrogen single bond with two boron-nitrogen single bonds is *greatly* exothermic, it is clear that the number of boron-nitrogen bonds should be maximized, hence IBAR. Cage isomers in this study are further subject to geometric constraints. If cages are limited to squares, pentagons, and hexagons, and the terms  $n_4$ ,  $n_5$ , and  $n_6$  are used to indicate the number of squares, pentagons, and hexagons, respectively, then the following constraints apply:

$$2n_4 + n_5 = 12 \text{ (Euler's theorem for a three - coordinate cage),}$$

$$n_4 + n_5 + n_6 = 14 \left( \text{faces} = 2 + \left( \frac{\text{vertices}}{2} \right) \text{ and vertices} = 24 \right). \quad (2)$$

Each cage isomer in this study is denoted by  $n_4n_5n_6$ , which indicates the distribution of polygons. The combinations 0(12)2 and 527 are excluded from this study because 0(12)2 has no IBAR-compliant isomers and because no cage structures conforming to 527 were found.

**3.1. Cage Isomer Stability.** For  $\text{B}_{12}\text{N}_{12}$ , the 608 cage (six squares, zero pentagons, and eight hexagons) is by far the most stable because it is the only IBAR-compliant cage. By contrast,  $\text{B}_{10}\text{N}_{14}$  has a wide variety of IBAR-compliant cages, several of which are shown in Figure 1. The relative energies of these cages are shown in Table 1, with the major result being the number of isomers that are energetically competitive with, and in some cases more stable than, the 608 cage. Two isomers of  $\text{B}_{10}\text{N}_{14}$  on the 608 framework are considered, and neither one is the most stable  $\text{B}_{10}\text{N}_{14}$  cage. A major difference between  $\text{B}_{10}\text{N}_{14}$  and  $\text{B}_{12}\text{N}_{12}$  cages is that  $\text{B}_{10}\text{N}_{14}$  can incorporate pentagons while remaining IBAR-compliant. Since a regular pentagon has interior angles of  $108^\circ$ , pentagons can more easily accommodate nitrogen's preferred  $\text{sp}^3$  bond angles of about  $105^\circ$  as in ammonia. Therefore, it should be expected that boron nitride cages whose atomic composition is mostly nitrogen should have stable isomers that include pentagons.

**3.2. Ring Isomer Stability.** Ring isomers of  $\text{B}_{10}\text{N}_{14}$  are shown in Figure 2. Each ring is labeled by a four-digit number  $abcd$ , in which each digit indicates how the boron atoms are grouped relative to the nitrogen-nitrogen bonds. A zero

indicates two adjacent N–N bonds without boron atoms in between, the result being an  $\text{N}_3$  bonding group in the ring structure. The relative energies of the ring isomers are shown in Table 2. Only three isomers are shown; other isomers that were considered have at least one imaginary vibrational frequency and are therefore not local minima. Table 2 indicates that the 4141 ring isomer, which has all of its nitrogen-nitrogen bonds isolated from one another by at least one boron atom, is far less stable than isomers incorporating the  $\text{N}_3$  bonding group.

**3.3. Graphitic Sheet Stability.** Graphitic two-dimensional networks of hexagons are shown in Figure 3. These isomers of  $\text{B}_{10}\text{N}_{14}$  have a total of six nitrogen-nitrogen bonds. Stability is maximized if those bonds occur as two N–N single bonds and two N=N double bonds because the bond enthalpy of the double bond is more than twice that of the single bond. (The same argument would suggest sheet isomers with three N=N double bonds, but no IBAR-compliant isomers of that kind were found.) The relative energies of the isomers are shown in Table 3. The results indicate that not only are N=N double bonds favored, but the  $\text{N}_3$  bonding group formed by adjacent N=N and N–N bonds is a stabilizing feature. Sheet S1 in Figure 3 is a representative molecule with two N=N double bonds, along with two N–N single bonds in the interior of the structure. Sheets 2, 3, and 4 all have their two single bonds adjacent to the double bonds along the perimeter of the structure, forming  $\text{N}_3$  bonding groups. As with the rings, the  $\text{N}_3$  bonding groups are a stabilizing feature, as those sheets having them are more than 300 kJ/mole more stable than sheets that do not.

**3.4. Cage vs. Ring vs. Sheet.** The relative energies of the most stable isomers of each kind are shown in Table 4, with the major result being that the graphitic sheets are the most stable isomers of  $\text{B}_{10}\text{N}_{14}$ . The results in Table 4 are consistent with the previous  $\text{B}_{12}\text{N}_{12}$  results [15] inasmuch as the ring isomers are significantly less stable than the cage isomers. As with  $\text{B}_{12}\text{N}_{12}$ , this is likely the result of the greater number of boron-nitrogen single bonds in a cage versus a ring. The unique feature of  $\text{B}_{10}\text{N}_{14}$  that  $\text{B}_{12}\text{N}_{12}$  does not possess is the N=N double bond on the perimeter of a graphitic sheet. The strength of the N=N double bond lowers the total energy of the graphitic sheet to the point that it becomes the lowest energy isomer of all. Therefore, in contrast to  $\text{B}_{12}\text{N}_{12}$ , which has the energy ordering cage < ring < sheet, the  $\text{B}_{10}\text{N}_{14}$  isomers follow the energy ordering sheet < cage < ring.

## 4. Conclusions

$\text{B}_{10}\text{N}_{14}$  has been shown to differ from  $\text{B}_{12}\text{N}_{12}$  in two significant ways: (1) Cages including pentagons can satisfy the isolated boron atom rule (IBAR), thereby avoiding over 400 kJ/mole in energetic penalty, and those pentagon-bearing cages are energetically competitive with square-hexagon cages and (2) graphitic sheets are the dominant isomer for  $\text{B}_{10}\text{N}_{14}$ , as opposed to the  $\text{B}_{12}\text{N}_{12}$  cage. Since the

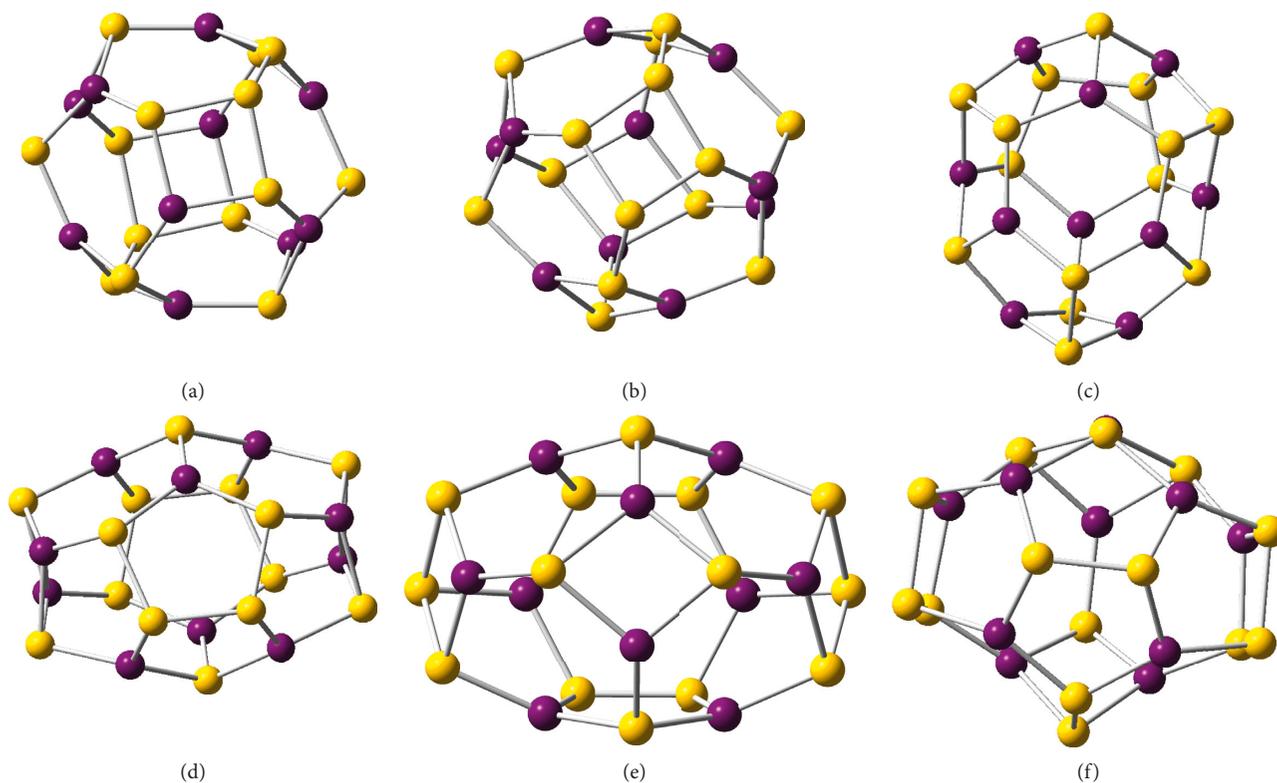


FIGURE 1:  $B_{10}N_{14}$  cages: (a) isomer 608A; (b) isomer 608B; (c) isomer 1-10-3; (d) isomer 284; (e) isomer 365; (f) isomer 446. Boron atoms are shown in purple and nitrogen atoms in yellow.

TABLE 1: Relative energies of the  $B_{10}N_{14}$  cages shown in Figure 1.

Isomer	Energy (kJ/mole)
608A	0.0
608B	+10.7
1-10-3	-8.1
284	+63.8
365	-33.2
446	+17.6

Energies calculated are PBE1PBE/cc-pVDZ energies, including ZPE corrections.

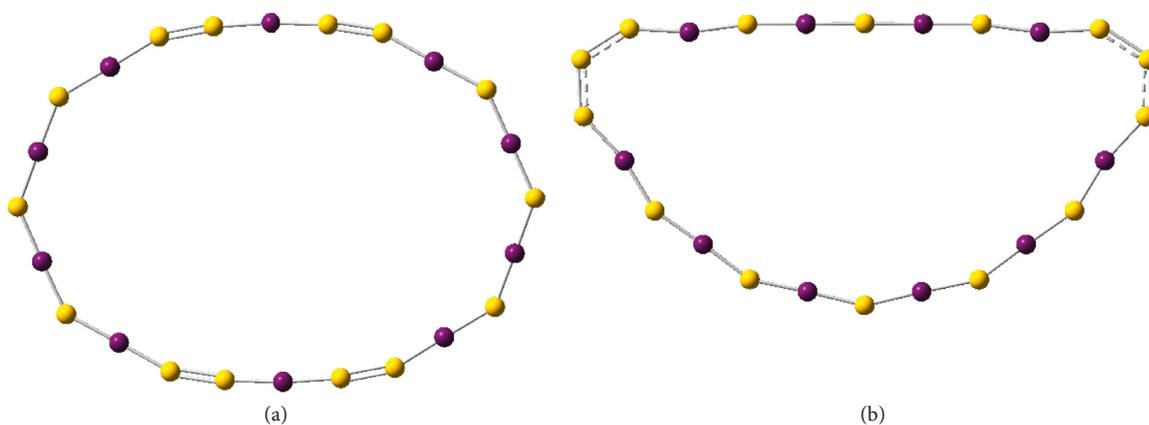


FIGURE 2: Continued.

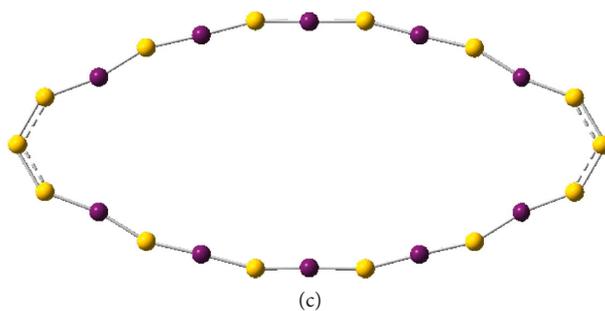


FIGURE 2:  $B_{10}N_{14}$  rings: (a) isomer 4141; (b) isomer 6040; (c) isomer 5050. Boron atoms are shown in purple and nitrogen atoms in yellow.

TABLE 2: Relative energies of the  $B_{10}N_{14}$  rings shown in Figure 2.

Isomer	Energy (kJ/mole)
4141	0.0
5050	-613.7
6040	-609.5

Energies calculated are PBE1PBE/cc-pVDZ energies, including ZPE corrections.

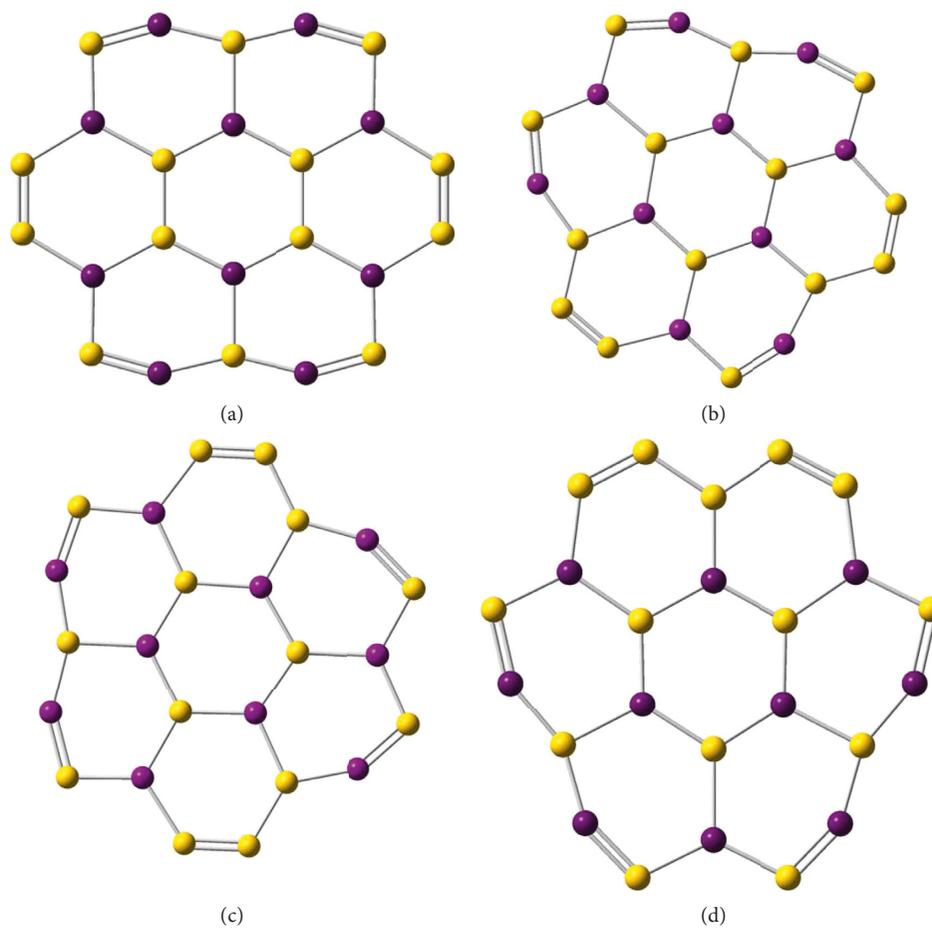


FIGURE 3:  $B_{10}N_{14}$  graphitic sheets: (a) isomer S1; (b) isomer S2; (c) isomer S3; (d) isomer S4. Boron atoms are shown in purple and nitrogen atoms in yellow.

TABLE 3: Relative energies of the  $B_{10}N_{14}$  sheets shown in Figure 3.

Isomer	Energy (kJ/mole)
S1	0.0
S2	-336.6
S3	-326.6
S4	-355.7

Energies calculated are PBE1PBE/cc-pVDZ energies, including ZPE corrections.

TABLE 4: Cage vs. ring vs. graphitic sheet comparison for  $B_{10}N_{14}$ .

Isomer	Energy (kJ/mole)
608A cage	0.0
608B cage	+10.7
365 cage	-33.2
5050 ring	+351.1
6040 ring	+355.3
S2 sheet	-129.2
S3 sheet	-119.2
S4 sheet	-148.3

Relative energies are calculated using PBE1PBE/cc-pVDZ, including ZPE corrections.

likeliest explanation for this is the stabilizing influence of the N=N double bond (409 kJ/mole bond enthalpy [22], more than double the 163 kJ/mole of the single bond), other boron nitrides in which nitrogen is the atomic majority should have graphitic isomers that are energetically favorable.

## Data Availability

Energies and coordinate geometries for each molecule in this study are available from the corresponding author upon request.

## Conflicts of Interest

The authors declare that they have no conflicts of interest.

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