

Structure and Stability of Boron Nitrides: Isomers of B₁₂N₁₂

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A number of recent studies have explored the energetics of intermediate-sized clusters, such as small fullerenes. For example, the isomer energies of C₂₀ have proven difficult to ascertain as different theoretical methods give widely varying results. For cluster sizes around 20–30 atoms, it is not immediately clear whether a monocyclic, graphitic, or fullerene structure is energetically preferred. In the present work, the isomers of B₁₂N₁₂, a ring, a “graphitic” sheet, and a fullerene-like cage of four- and six-membered rings, are examined by theoretical means. The energies of the three isomers are calculated using Hartree–Fock theory and density functional theory (DFT) in local and gradient-corrected forms. The Dunning correlation-consistent basis sets are used, with geometries optimized up to the triple- ζ level and energies calculated at the quadruple- ζ level. The effects of the basis set, as well as the effects of local versus nonlocal DFT, are discussed. The results are compared to those of similar studies of C₂₄, which is isoelectronic with B₁₂N₁₂.

Introduction

The smaller cousins of buckminsterfullerene (C₆₀) have received much attention as experimental and theoretical studies have been conducted to elucidate the nature of the intermediate-sized carbon clusters. Ion mobility studies¹ of the fullerene formation process have revealed only cyclic structures for the clusters with 20–28 atoms. However, those results do not necessarily mean that rings are more stable than other structures thermodynamically. The other isomers are perhaps more stable than rings but kinetically forbidden in some phase of the clustering process.

Numerous theoretical calculations have been performed in this area, especially regarding C₂₀. Almlof and co-workers showed^{2,3} that Hartree–Fock (HF) theory favors the ring isomers whereas second-order perturbation theory (MP2) predicts that the cage is the most stable isomer. Raghavachari et al. demonstrated⁴ the variance among the different density functional theory (DFT) methods. Local density approximation (LDA) calculations favor the cage isomer, but the gradient-corrected Becke–Lee–Yang–Parr (BLYP) method yields the ring as the most stable. Using the highly accurate coupled-cluster method (as CCSD(T)), Taylor et al. predicted⁵ that the cage is the most stable isomer, but that study only employed double- ζ (DZ) quality basis sets. Murphy and Friesner employed⁶ their J1 theory based on localized MP2, and that result indicated that the ring is the most stable.

Raghavachari et al. applied⁷ the same techniques from the C₂₀ study to C₂₄. That study considered monocyclic, bicyclic, graphitic, and cage isomers. With the HF, LDA, and BLYP methods, as well as a hybrid HF/BLYP method, the results differed from method to method. LDA calculations resulted in the 6-fold-symmetric cage having the lowest energy. HF/BLYP predicted the coronene-like sheet is lowest in energy, and BLYP showed the sheet and 24-membered ring to be degenerate and much lower than the cage. HF theory favored the ring. Just as in the C₂₀ case, DFT methods strongly disagree on the relative energies of the cluster isomers.

Boron nitrides (BN)_x are isoelectronic to the fullerenes and have themselves been subject to extensive investigation. Jensen

used⁸ MP2 to compare cyclic and cubic isomers of B₄N₄ to isomers of the isoelectronic C₈. Silaghi-Dumitrescu et al. used⁹ the Hartree–Fock method and the semiempirical AM1 method to characterize boron nitride cages. Boron nitride nanotubes^{10–12} have been synthesized and shown to be capped by four-membered rings in the boron nitride networks. Boron nitride nanotubes have also been generated¹³ with pentagons and heptagons in the network.

In the present work, a theoretical investigation is carried out to determine the relative stability of three isomers of the boron nitride B₁₂N₁₂, which is isoelectronic with C₂₄. The ring isomer considered in this work is a 24-membered ring with alternating boron and nitrogen atoms. The cage isomer consists of a three-coordinate network of four- and six-membered rings, with alternating atoms such that the entire cage consists of B–N bonds. The graphitic isomer is a boron nitride analogue to the planar coronene-like C₂₄. The graphitic isomer also has only B–N bonds. These three isomers are computationally characterized using Hartree–Fock theory and density functional theory, and the boron nitrides are compared to their all-carbon counterparts.

Computational Methods

Geometry optimizations and energy calculations on the B₁₂N₁₂ isomers are carried out using the HF method, the B3LYP density functional method,^{14,15} and the LDA^{16,17} employing the Slater exchange and Vosko–Wilk–Nusair correlation functionals. The correlation-consistent basis sets¹⁸ of Dunning are used for boron and nitrogen. Geometry optimizations are carried out with the cc-pVDZ [3s2p1d] and cc-pVTZ [4s3p2d1f] basis sets, and energies are calculated at the triple- ζ (TZ) geometries with the cc-pVQZ [5s4p3d2f1g] basis set. The Gaussian 98 quantum chemistry package¹⁹ is used for all calculations in this study.

Results and Discussion

The ring, graphitic, and cage isomers of B₁₂N₁₂ considered in this study are shown in Figures 1, 2, and 3, respectively. The ring isomer has *D*_{12h} symmetry with equal bond lengths

TABLE 1: Geometric Parameters for the Ring, Graphitic, and Cage Isomers of $B_{12}N_{12}^a$

	HF		LDA		B3LYP	
	DZ	TZ	DZ	TZ	DZ	TZ
	Ring Isomer					
B–N	1.307	1.303	1.313	1.308	1.315	1.311
N–B–N	181.800	180.115	180.179	178.760	181.227	179.565
B–N–B	148.200	149.885	149.821	151.240	148.773	150.435
	Graphitic Isomer					
B1–N1	1.437	1.434	1.439	1.436	1.444	1.442
B1–N4	1.523	1.523	1.520	1.520	1.536	1.536
N1–B4	1.571	1.571	1.553	1.557	1.572	1.576
N4–B7	1.378	1.373	1.375	1.371	1.382	1.378
B4–N7	1.440	1.435	1.434	1.427	1.442	1.437
N7–B10	1.270	1.266	1.283	1.277	1.282	1.277
N1–B1–N3	125.300	125.303	125.045	125.148	125.063	125.136
B1–N4–B7	104.000	104.053	104.583	104.594	104.418	104.380
N1–B4–N7	117.450	117.191	118.033	117.599	117.498	117.072
	Cage Isomer					
B1–N1	1.480	1.476	1.481	1.475	1.490	1.486
B1–N9	1.435	1.433	1.433	1.429	1.441	1.438

^a Bond lengths are given in angstroms and angles in degrees.

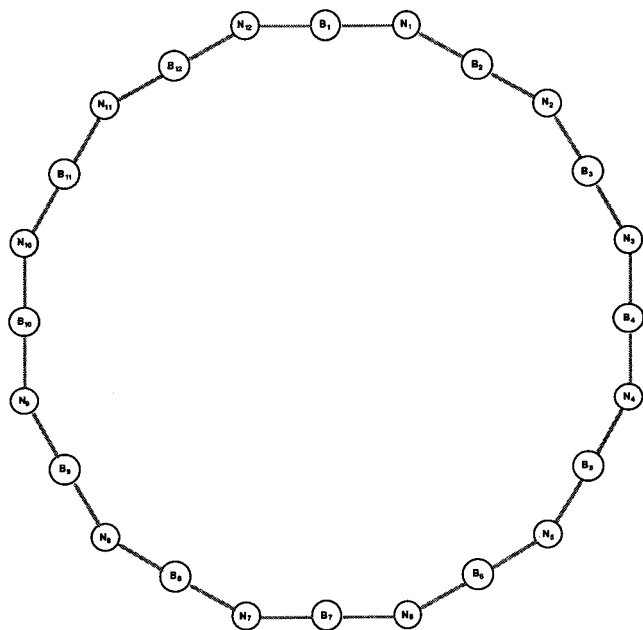


Figure 1.

but unequal bond angles. The D_{12h} symmetry is a result of optimizations begun in the lower C_{12h} symmetry. The graphitic isomer has D_{3h} symmetry, to which the geometries converged from the lower C_{3h} symmetry. The cage isomer consists of four- and six-membered rings and has T_h symmetry with two independent bond lengths. Table 1 is a tabulation of the symmetry-independent geometric parameters of the ring, graphitic, and cage isomers calculated with the three theoretical methods and the DZ and TZ correlation-consistent basis sets. The geometry results in Table 1 show bond length changes of less than 0.01 Å between DZ and TZ, with angle changes of 1–2°. Since TZ–QZ (QZ = quadruple- ζ) geometry changes would be expected to be smaller than DZ–TZ geometry changes, triple- ζ geometries can be considered converged enough for accurate single-point energies with larger basis sets.

Table 2 shows the relative energies of the ring, graphitic, and cage isomers with the HF, LDA, and B3LYP methods, using each of the three basis sets (DZ, TZ, and QZ). The energy results converge well with respect to the basis sets, with the energy change from TZ to QZ//TZ being much smaller than the change

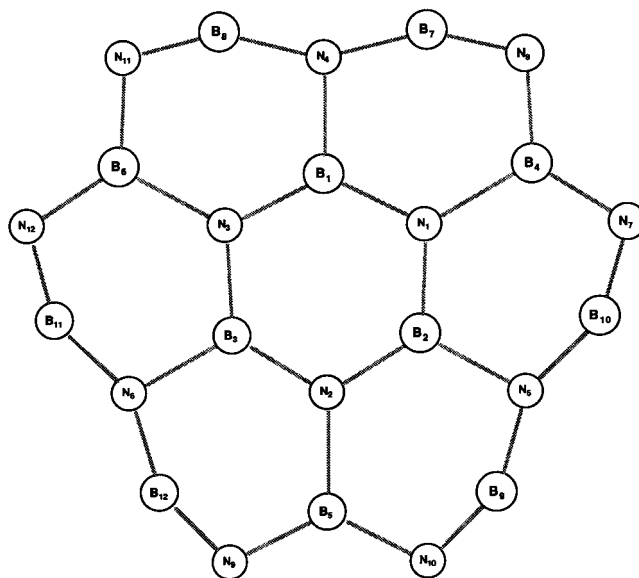


Figure 2.

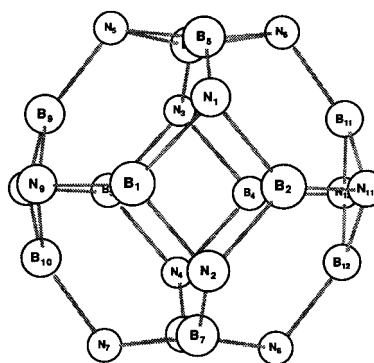


Figure 3.

from DZ to TZ. Further, the energy changes from TZ to QZ//TZ are less than 0.20 eV in all cases and less than 0.10 eV in many cases. Therefore, the energies are converged enough to give a qualitatively accurate picture of the stability of these three isomers.

The variation of the results among the HF, LDA, and B3LYP methods resembles the results from the previous carbon cluster

TABLE 2: Relative Energies of the Ring, Graphitic, and Cage Isomers of B₁₂N₁₂^a

method	basis set	ring	graphitic	cage
HF	DZ	0.00	+1.98	-1.58
	TZ	0.00	+2.46	-1.06
	QZ//TZ	0.00	+2.53	-0.88
LDA	DZ	0.00	-2.18	-8.21
	TZ	0.00	-1.61	-7.46
	QZ//TZ	0.00	-1.51	-7.35
B3LYP	DZ	0.00	+1.40	-1.93
	TZ	0.00	+2.02	-1.10
	QZ//TZ	0.00	+2.07	-1.00

^a Energies in electronvolts.

studies. The HF and B3LYP methods roughly agree with each other on the magnitude of the energy differences, whereas LDA favors the graphitic and cage isomers to a much greater degree. This is another example of the bond energy effect previously cited for LDA.^{4,7} More than the other methods in this work, LDA tends toward very high bond energies. Since the cage has more bonds than the graphitic isomer, which in turn has more bonds than the ring, LDA drastically favors the cage by a tremendous amount of energy.

However, an important contrast exists between the B₁₂N₁₂ results and the carbon studies. Specifically, the three theoretical methods are unanimous in predicting that the cage is the most stable isomer. In the corresponding carbon study,⁷ a controversy regarding the relative stability of the isomers arises. That is why the isomer stability of carbon clusters cannot be conclusively judged on the basis of density functional calculations. For the boron nitrides, though, it can be safely concluded from the present work that the cage is the most stable. More accurate calculations, such as CCSD(T) with a large basis set, would provide more convincing confirmation that the boron nitride cage is the most stable isomer of B₁₂N₁₂, but such expensive calculations are beyond the scope of this work.

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