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Structure and Stability of Boron Nitrides: The Crossover between Rings and Cages

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A previous study on $B_{12}N_{12}$ showed that the Hartree−Fock (HF) method, local density approximation (LDA), and gradient-corrected density functional theory (specifically B3LYP) all agree in predicting that the cage isomer of $B_{12}N_{12}$ is the most stable. If the cage is the most stable $(BN)_x$ for $x = 12$, then the energetic crossover between rings and cages must take place at some $x < 12$. Rings would be most stable for small molecules, and cages would be most stable for larger molecules. The current study explores the question of whether rings or cages are more stable at sizes smaller than $B_{12}N_{12}$, with the goal of defining a crossover point between rings and cages. These issues are examined by theoretical calculations using the HF, LDA, and B3LYP methods, along with second-order perturbation theory (MP2). In particular, an energetic comparison is carried out between the ring and cage isomers of $(BN)_x$ for $x = 8-11$. The major result is that boron nitride cages are more stable than rings if at least two of the six four-membered rings are isolated by hexagons, an arrangement that is first seen for the $B_{11}N_{11}$ cage.

Introduction

Carbon clusters and fullerenes have been the subject of extensive experimental and theoretical investigation. Boron nitrides, the isoelectronic cousins to the fullerenes, have received attention as various studies are undertaken to synthesize and/or characterize boron nitride cages[1,2] and nanotubes.[3−6] A recent study[7] of $B_{12}N_{12}$ involves theoretical calculations on three isomers: a 24-membered ring, a graphitic sheet of six-membered rings, and a cage of four- and six-membered rings. In that study, the Hartree−Fock (HF) method, the local density approximation (LDA), and a gradient-corrected density functional (DFT) method (specifically B3LYP) unanimously predict that the cage is the most stable isomer. That unanimity is unusual because HF, LDA, and gradient-corrected DFT have been shown to conflict with each other in the cases of C_{20} (ref 8) and C_{24} (ref 9). This leaves open the question of which cluster isomer is the most stable for those carbon clusters.

However, the $B_{12}N_{12}$ cage is the most stable $B_{12}N_{12}$ isomer according to a diverse set of theoretical methods. It is reasonable to suppose that $(BN)_x$ clusters smaller than $B_{12}N_{12}$ may show the same isomer ambiguities as those of C_{20} and C_{24}. Rings are more stable than cages at small cluster sizes, and the reverse is true for large clusters. Therefore, there should exist a cluster size range where an energetic crossover occurs between rings and cages. In the current study, boron nitride clusters $(BN)_x$ will be examined by theoretical calculations for $x = 8-11$, with the goal of defining a crossover point between the stability of rings and the stability of cages.

Computational Methods

Geometry optimizations and energy calculations on the boron nitrides B_8N_8, B_9N_9, $B_{10}N_{10}$, and $B_{11}N_{11}$ are carried out using the HF method, the B3LYP density functional method,[10,11] and the LDA employing the Slater exchange and Vosko−Wilk−Nusair correlation functionals.[12,13] Second-order perturbation theory (MP2) energy calculations are carried out on Hartree−Fock optimized geometries. The use of single-reference MP2 is reasonable for these molecules in this study because they have singlet ground states with large HOMO−LUMO gaps, making near-degeneracies unlikely. The basis sets are the correlation-consistent double-ζ (cc-PVDZ) and triple-ζ (cc-PVTZ) sets of Dunning.[14] All calculations in this study are carried out on the Cray SV1 supercomputer operated in Huntsville, Alabama, by the Alabama Supercomputer Authority. The Gaussian 98 quantum chemistry software package[15] is used for all calculations in this study.

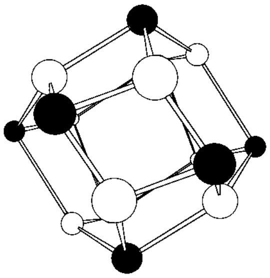

Figure 1. B_8N_8 cage isomer (S_4 point group symmetry). The six four-membered rings are arranged in two ribbons of three edge-sharing four-membered rings.

Results and Discussion

All the ring isomers in this study consist of alternating boron and nitrogen atoms with equal bond lengths and alternating bond angles such that the bond angles at the boron vertexes are approximately 180°. All the $(BN)_x$ rings have D_{xh} symmetry ($x = 8-11$). All the cage isomers have six four-membered rings. Since the previously studied $B_{12}N_{12}$ cage[7] is the smallest cage that can have all the four-membered rings isolated from each other, the cages in this study must include four-membered rings that share edges.

1. B_8N_8. The cage isomer of B_8N_8 in this study has S_4 point group symmetry and is shown in Figure 1. The six four-membered rings are arranged in two “ribbons” of three consecutive edge-sharing four-membered rings. The data in Table 1 show that all the theoretical methods in this study agree that

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TABLE 1: Relative Energies for the Cage and Ring Isomers of B_8N_8[a]

method	basis set	ring	cage
HF	cc-PVDZ	0.00	+5.36
	cc-PVTZ	0.00	+5.79
LDA	cc-PVDZ	0.00	+0.27
	cc-PVTZ	0.00	+0.63
B3LYP	cc-PVDZ	0.00	+4.58
	cc-PVTZ	0.00	+4.99
MP2//HF	cc-PVDZ	0.00	+2.45
	cc-PVTZ	0.00	+1.97

[a] Energies in eV.

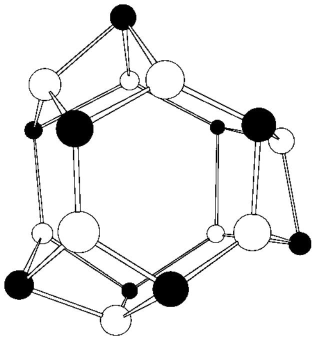

Figure 2. B_9N_9 cage isomer (C_{3v} point group symmetry). The six four-membered rings are arranged in three edge-sharing pairs.

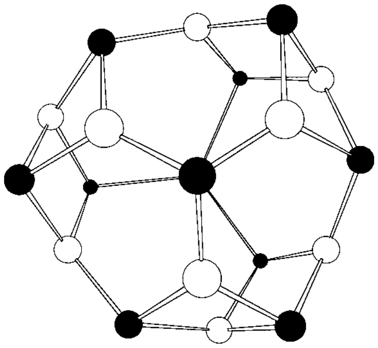

Figure 3. $B_{10}N_{10}$ cage isomer (C_3 point group symmetry). The six four-membered rings are arranged in three edge-sharing pairs.

TABLE 2: Relative Energies for the Cage and Ring Isomers of B_9N_9[a]

method	basis set	ring	cage
HF	cc-PVDZ	0.00	+3.95
	cc-PVTZ	0.00	+4.21
LDA	cc-PVDZ	0.00	−1.83
	cc-PVTZ	0.00	−1.40
B3LYP	cc-PVDZ	0.00	+3.02
	cc-PVTZ	0.00	+3.52
MP2//HF	cc-PVDZ	0.00	+0.50
	cc-PVTZ	0.00	+0.05

[a] Energies in eV.

the ring is more stable than the cage. Since these methods have disagreed in the prior carbon studies[8,9] of C_{20} and C_{24}, the fact that they are unanimous in regard to B_8N_8 means that the ring can be safely concluded to be the most stable isomer.

TABLE 3: Relative Energies of the Cage and Ring Isomers of $B_{10}N_{10}$[a]

method	basis set	ring	cage
HF	cc-PVDZ	0.00	+4.23
	cc-PVTZ	0.00	+4.58
LDA	cc-PVDZ	0.00	−2.21
	cc-PVTZ	0.00	−1.70
B3LYP	cc-PVDZ	0.00	+3.27
	cc-PVTZ	0.00	+3.87
MP2//HF	cc-PVDZ	0.00	+0.31
	cc-PVTZ	0.00	−0.13

[a] Energies in eV.

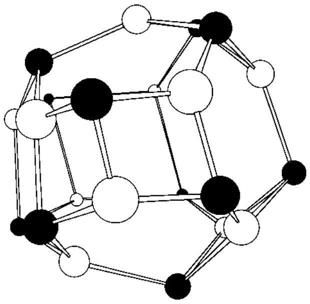

Figure 4. $B_{11}N_{11}$ cage isomer (C_s point group symmetry). The six four-membered rings are arranged as two edge-sharing pairs and two isolated squares.

TABLE 4: Relative Energies for the Cage and Ring Isomers of $B_{11}N_{11}$[a]

method	basis set	ring	cage
HF	cc-PVDZ	0.00	+1.94
	cc-PVTZ	0.00	+2.38
LDA	cc-PVDZ	0.00	−4.78
	cc-PVTZ	0.00	−4.15
B3LYP	cc-PVDZ	0.00	+1.18
	cc-PVTZ	0.00	+1.89
MP2//HF	cc-PVDZ	0.00	−2.17
	cc-PVTZ	0.00	−2.57

[a] Energies in eV.

2. B_9N_9 and $B_{10}N_{10}$. The cage isomers for B_9N_9 and $B_{10}N_{10}$ in this study are shown in Figures 2 and 3, respectively. Both cages have a 3-fold point group symmetry (C_{3v} for B_9N_9 and C_3 for $B_{10}N_{10}$), and the six four-membered rings in each cage appear as three pairs of edge-sharing rings. The theoretical data on B_9N_9 and $B_{10}N_{10}$ are shown in Tables 2 and 3, respectively. The theoretical methods disagree as to which isomer is the most stable. HF and B3LYP strongly favor the ring, LDA strongly favors the cage, and the MP2 results predict that cages and rings are approximately isoenergetic. It is not immediately clear from these results whether rings or cages are the most stable isomer.

3. $B_{11}N_{11}$. The $B_{11}N_{11}$ cage has C_S point group symmetry and is shown in Figure 4. The $B_{11}N_{11}$ cage has two pairs of edge-sharing four-membered rings and two isolated squares. Table 4 shows the theoretical results for $B_{11}N_{11}$. HF and B3LYP favor the ring, and LDA favors the cage. Since MP2 strongly (more than 2 eV) favors the cage and LDA favors the cage by more than 4 eV, it seems likely that the cage is the most stable isomer.

4. Approximate Coupled-Cluster Results. Results from more accurate methods, such as coupled-cluster theory, would lend stronger support to a definitive judgment regarding the stability of cages and rings. However, full coupled-cluster calculations on the molecules in this study are beyond the scope of the present work. The results of coupled-cluster theory (CCSD and CCSD(T)) will be approximated using benchmark calculations on B_4N_4, whose cage isomer is a cube of alternating boron and nitrogen atoms. HF geometry optimizations have been carried out on the ring and cube isomers of B_4N_4, and MP2 and CCSD(T) calculations have been performed at the HF geometries.

The results are shown in Table 5. The objective of the B_4N_4 calculations is to obtain a correction term that shows how MP2

TABLE 5: Relative Energies of the Ring and Cage Isomers of B_4N_4[a]

method	basis set	ring	cage	correction[b]
MP2//HF	cc-PVDZ	0.00	+5.66	
	cc-PVTZ	0.00	+5.31	
CCSD//HF	cc-PVDZ	0.00	+5.90	+0.030 eV/atom
	cc-PVTZ	0.00	+5.66	+0.044 eV/atom
CCSD(T)//HF	cc-PVDZ	0.00	+5.72	+0.008 eV/atom
	cc-PVTZ	0.00	+5.45	+0.018 eV/atom

[a] Energies in eV. [b] Correction to the MP2 ring−cage energy difference to obtain the coupled-cluster result (divided by 8 to obtain the per atom correction).

TABLE 6: Approximate Coupled-Cluster Energies for B_8N_8 through $B_{11}N_{11}$[a]

	basis set	MP2//HF	CCSD//HF	CCSD(T)//HF
B_8N_8	cc-PVDZ	+2.45	+2.93	+2.58
	cc-PVTZ	+1.97	+2.67	+2.26
B_9N_9	cc-PVDZ	+0.50	+1.04	+0.64
	cc-PVTZ	+0.05	+0.84	+0.37
$B_{10}N_{10}$	cc-PVDZ	+0.31	+0.91	+0.47
	cc-PVTZ	−0.13	+0.75	+0.23
$B_{11}N_{11}$	cc-PVDZ	−2.17	−1.51	−1.99
	cc-PVTZ	−2.57	−1.60	−2.17

[a] Energies in eV for the cage isomer relative to the corresponding ring.

results and coupled-cluster results differ. The difference between MP2 and coupled-cluster results for B_4N_4 divided the eight atoms in B_4N_4 to derive a correction that will then be used to approximate the results of coupled-cluster calculations on the larger molecules. For example, Table 5 shows that CCSD(T)/cc-PVTZ differs from MP2/cc-PVTZ by +0.018 eV/atom. This correction is added to the MP2 results for the larger molecules to approximate CCSD(T) results for the larger molecules. Table 6 shows the approximate coupled-cluster results for B_8N_8 through $B_{11}N_{11}$.

5. Defining the Crossover Between Cages and Rings. The results show that B_9N_9 and $B_{10}N_{10}$ cages are roughly isoenergetic with the corresponding rings, and the $B_{11}N_{11}$ cage is clearly more stable than the ring. In terms of molecular architecture, cages with ribbons of three consecutive edge-sharing squares (B_8N_8) are unstable compared to rings. Doing away with these ribbons and having only pairs of edge-sharing squares requires at least 18 atoms, and the cage isomers of B_9N_9 and $B_{10}N_{10}$ each have three pairs of edge-sharing squares. These cages have a stability comparable to that of rings.

Introducing isolated squares to the cage requires at least 20 atoms (two isolated squares and two edge-sharing pairs), but no cage isomer of $B_{10}N_{10}$ was found with isolated squares. However, the $B_{11}N_{11}$ cage has two isolated squares, and that cage is more stable than the ring. It is therefore not required to isolate all the squares to have a cage that is more stable than the rings. Isolating some of the squares is sufficient. Any boron nitride cage $(BN)_x$ with at least two isolated squares should be more stable than the corresponding boron nitride ring.

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