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Structure and Stability of BN Microclusters: Ab Initio Calculations for $(BN)_n$ ($n = 2$–4)

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Abstract

Unrestricted Hartree–Fock calculations coupled with second-order Møller–Plesset correlation correction were performed to study the structures and energetics of microclusters. For $(BN)_2$, linear and rhombus forms are almost isoenergetic, whereas cyclic forms are preferable for $(BN)_3$ and $(BN)_4$ clusters. As a general trend, linear isomers prefer the triplet spin state, whereas cyclic isomers prefer the singlet spin state. Total charge density plots show a strong dominance of the B—N bond, indicating that the extent of its polar character becomes stronger with the increase in the cluster size. The loss of a BN monomer is shown to be the most likely fragmentation channel for both neutral and single-ionized clusters. We find that neutral $(BN)_n$ clusters have the same structural configurations as those of their corresponding C_{2n} counterparts. This similarity follows the *isoelectronic principle* and is of importance due to recent interest in the investigations of BN fullerene analogs. © 1994 John Wiley & Sons, Inc.

I. Introduction

Clusters of boron nitride (BN) have been the subject of both experimental and theoretical studies as a way to understand the mechanism of the progressive formation of aggregates and the emergence of condensed-phase properties. Becker and Dietze [1] studied the formation of $B_nN_m^+$ clusters for various combinations of n and m, emerging from a plasma produced by laser irradiation of boron nitride. They found that the dominant series of clusters were the ions $(B_nN_{n-1})^+$ for $n = 2$–9. Recently, BN equivalents of the vapor–phase allotropic modifications of carbon have been conjectured [2] and the existence of closed fullerene structures (i.e., $B_{30}N_{30}$) synthesized from borazine have been reported [3]. Resemblances between BN and C isoelectronic clusters in the vapor-phase state are less known that they are in their corresponding phases, even though the isoelectronic principle suggests the existence of similar geometrical skeletons. The similarities can be expected on the basis of the analogous role that B–N and C=C bonds may play in many compounds.

On the theoretical front, thermodynamic properties of boron, nitrogen, and boron–nitrogen clusters have been reported in the Hartree–Fock framework where the detailed description of stoichiometric BN clusters is restricted to the monomer [4–7]. In this work, we performed electronic structure calculations of several isomers of the $(BN)_n$ ($n = 2$–4) clusters with a threefold purpose: (i) to determine their configurational parameters, (ii) to explore the nature of chemical bonding, and (iii) to analyze cluster stability through the evaporative decay of neutral and ionized BN molecule. Furthermore, a theoretical study on C_m ($m = 2$–10) clusters

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[8] will provide the reference point to explore the linkage between these isoelectronic [$(BN)_n$ and C_{2n}] clusters. The presentation of this article is organized as follows: In Section II, we briefly describe computational details. Results and discussion of the geometrical features, cluster stability, and cluster fragmentation will be presented in Section III. In Section IV, conclusions are given.

II. Computational Details

Calculations have been performed using GAUSSIAN 90 [9] and GAMESS [11] in the unrestricted Hartree–Fock (UHF) approximation coupled with second-order Møller-Plesset (UMP2) correction. The standard 6-31G* Gaussian-type basis set is used to describe both boron and nitrogen atoms. This choice of the basis set is based on the extensive study of Martin et al. [4] on BN, BN_2, and B_2N clusters. It is also supported by our work on MgO clusters, where we found that the use of the 6-311G* basis set does not introduce any appreciable changes in the geometrical parameters obtained using the 6-31G* basis set [10].

We initiate the geometrical optimization of $(BN)_n$ clusters with $n = 2, 3$, and 4 for linear, cyclic, and cubelike configurations in both the singlet and triplet spin states at the UHF/6-31G* level. Table I shows the symmetry group of these configurations. At the optimized geometries, we calculate the UMP2 energy of these isomers to assess their relative stabilities. Binding energies are then obtained for the most stable structures with respect to atomic constituents. For ionized clusters, we use the vertical approximation. Here, the optimized configurations of the most stable (neutral) clusters are kept frozen to compute the UMP2 energy of single-ionized $(BN)_n$ clusters in the double spin state. This approximation has been shown to give satisfactory descriptions of relevant physical properties in MgO microclusters [10].

III. Results and Discussion

A. Structure and Bonding

A complete list of structural parameters of the optimized configurations, such as the equilibrium B—N bond lengths and bond angles, along with their related UHF and UMP2 total energies in both singlet and triplet spin states are presented in Table I. The most stable configurations are shown in Figure 1(a)—(c).

(i) $(BN)_2$: There are several possible arrangements of B and N that can be considered for the linear configuration, such as B—N—B—N, B—N—N—B, N—B—B—N, and N—N—B—B. Among these arrangements, the configurations containing B—N and N—N bonds are likely to be more favorable than those containing B—B bonds (due to differences in binding energies of B—B, N—N, and B—N pairs) (Fig. 2). Our calculations do indeed show that B—N—B—N is the most favorable arrangement with the B—N separation of about 1.3 Å, as in the monomer BN. Among the closed structures, the rhombus is found to be more favorable than the square. In the rhombus configuration, we notice that the N—N separation (2.339 Å) is larger than the B—N separation (1.418 Å), indicating a preference of B—N bond over the N—N bond. This is further confirmed by total (UHF) charge density plots shown in Figure 3. For all the configurations considered here, singlet spin states are found to

TABLE I. Structural parameters of neutral BN clusters at the UHF/6-31G* level and their corresponding UHF and UMP2 energies.

Cluster, Point group	Spin	$\langle S^2 \rangle$	B–N bond length (Å)	Bond angles (°)	UHF (Hartrees)	UMP2 (Hartrees)
$(BN)_2$						
Linear, $C_{\infty v}$	0	0.000	1.2710	—	−158.0577	−158.4617
	1	2.063	1.2994	—	−158.1784	−158.5808
Square, D_{2h}	0	0.000	1.4394	B—N—B = 90.0	−157.9491	−158.5194
	1	2.092	1.4131		−158.0320	−158.4893
Rhombus, D_{2h}	0	0.000	1.3850	B—N—B = 65.1	−158.0922	−158.5603
	1	2.149	1.4180	B—N—B = 68.0	−158.1564	−158.5873
$(BN)_3$						
Linear, $C_{\infty v}$	0	0.000	1.3180	—	−237.2699	−237.9060
	1	2.059	1.2998	—	−237.3760	−238.0005
Two adjacent squares, C_{2v}	0	0.000	1.4333	B—N—B = 90.0	−237.0950	−237.8548
	1	2.214	1.4344		−237.1344	−237.8578
Hexagon, D_{3h}	0	0.000	1.3453	B—N—B = 90.8	−237.4545	−238.1482
	1	2.085	1.3420	B—N—B = 98.7	−237.3500	−238.0158
$(BN)_4$						
Linear, $C_{\infty v}$	0	0.000	1.3120	—	−316.4710	−317.3281
	1	2.054	1.2998	—	−316.5786	−317.4238
Cube, D_{2d}	0	0.000	1.3214	B—N—B = 90.0	−315.9986	−317.0634
	1	2.082	1.3073		−316.0189	−317.0318
Octagon, D_{4h}	0	0.000	1.3163	B—N—B = 135.0	−316.5822	−317.4951
	1	2.054	1.3417		−316.4331	−317.4039

be at much higher energy (3 eV) than are triplets. Corrections for the spin contamination in the triplet states (shown in Table I) are not expected to change this order.

The calculations predict that the linear and rhombus configurations of the $(BN)_2$ cluster are almost isoenergetic. At the UMP2 level, the rhombus configuration is stable by 0.18 eV with respect to the linear one. Recent work of Andrews et al. used the quadratic configuration interaction method [QCISD(T)/6-31G*], yielding the stability of the rhombus over the linear by 0.14 eV [7].

It is interesting to compare the results of $(BN)_2$ clusters with the corresponding carbon clusters. For C_4, the rhombus and linear forms are reported to be isoenergetic [8]. The geometrical parameters of the $(BN)_2$ ground state (rhombus) are very close to those of C_4; the bond length is only 7 mÅ shorter and its acute bond angle is about 7° larger than those in the C_4 cluster. These are the results expected from the isoelectronic principle.

(ii) $(BN)_3$: For linear configuration, we consider either the alternating arrangement, (i.e., B—N—B—N—B—N) or the arrangement with adjacent nitrogen atoms (i.e.,

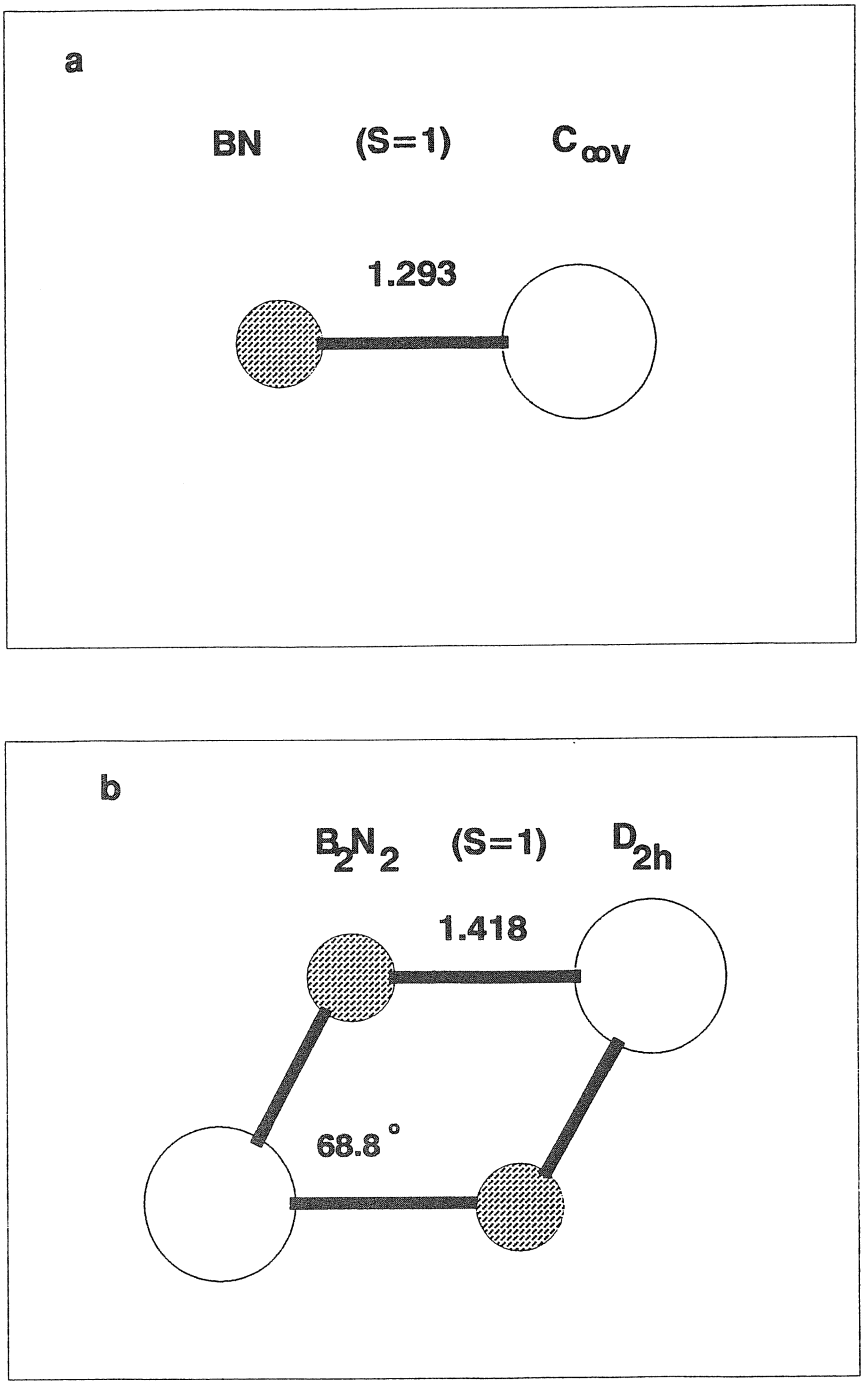
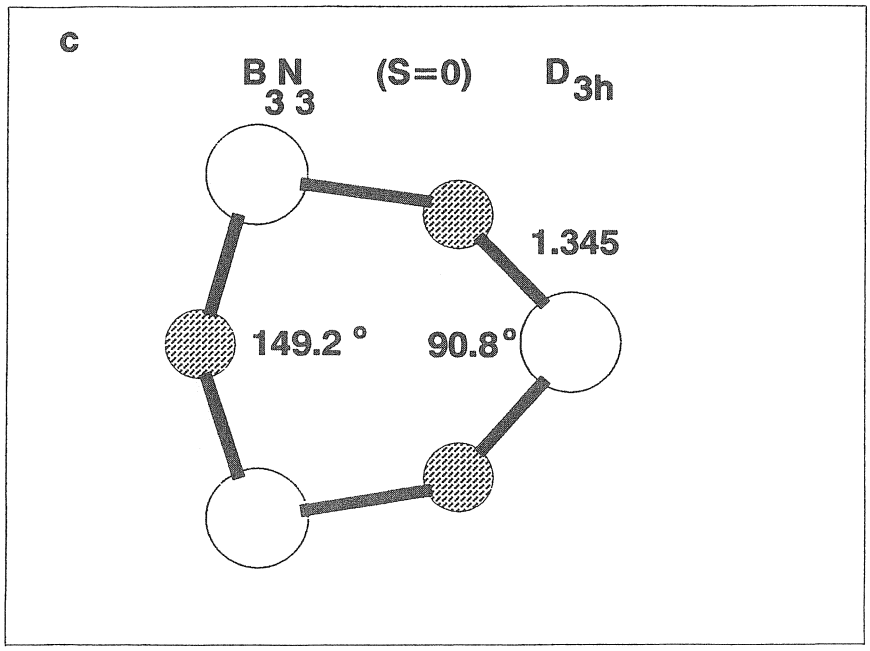


Figure 1. The calculated configurations of BN microclusters at the UHF/6-31G* level.



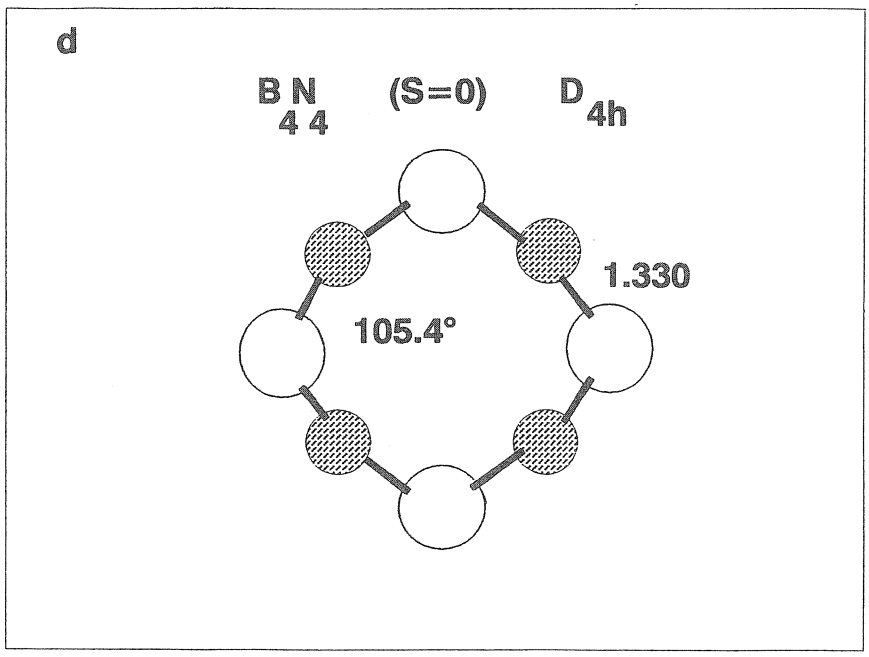


Figure 1. (Continued)

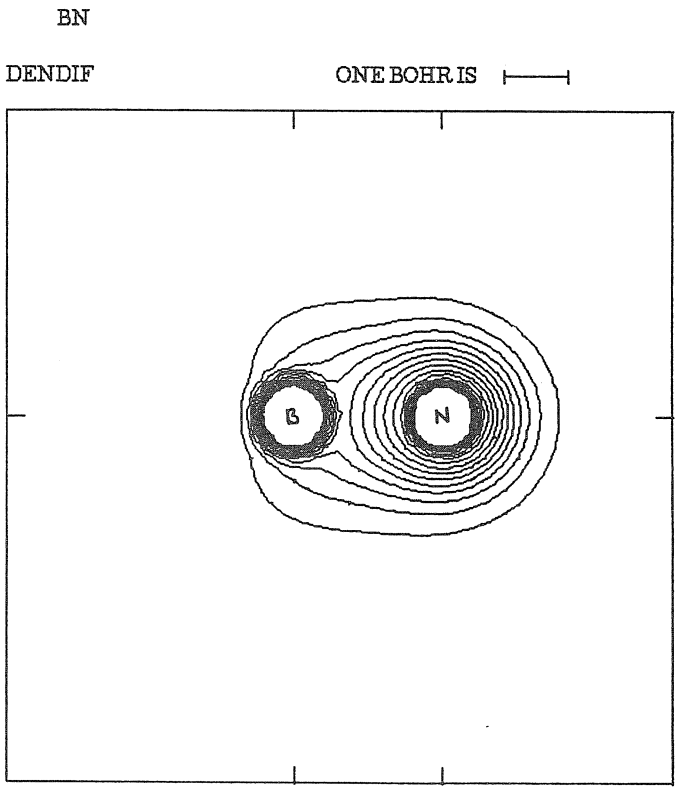


Figure 2. Total (UHF) charge density plots of the predicted ground states of BN microclusters.

B—N—N—B—N—B). At the UHF level, the former one is found to be more stable (by 4 eV) than the latter. This is what we expected on the basis of arguments given for the linear $(BN)_2$. Furthermore, the B—N separation remains about the same as it was in the linear $(BN)_2$.

For the hexagon, the optimized structure has resonant forms analogous to those proposed for benzene, with the B—N separation of about 1.345 Å and the acute bond angle of 90.8°. For comparison, the C—C separation in the C_6 cluster is reported to be 1.316 Å with the angle of 90.4°. Once again, isoelectronic structures are accompanied by isostructural skeletons. We do also consider two-adjacent square form for the $(BN)_3$ cluster. Its optimized structure is found to have much higher total energy than that of the corresponding linear or cyclic form.

In the cyclic configuration, B and N atoms are in the corners of two equivalent triangles having different sizes but the same center. In the triangles, the B—B separation is 1.915 Å and the N—N separation is 2.594 Å. Martin et al. reported that the equilibrium structure of the B_3 cluster is an equilateral triangle with the B—B separation of 1.574 Å. For the N_3 cluster, the linear arrangement is preferred with the N—N separation of 1.159 Å [4]. In the case of the $(BN)_3$ cluster, we may therefore conclude that the bonding between B and N mainly determines the most stable structure. Neither N and N or B and B bonding plays any significant role in stabilizing the cylic structure of the $(BN)_3$ cluster (Fig. 4).

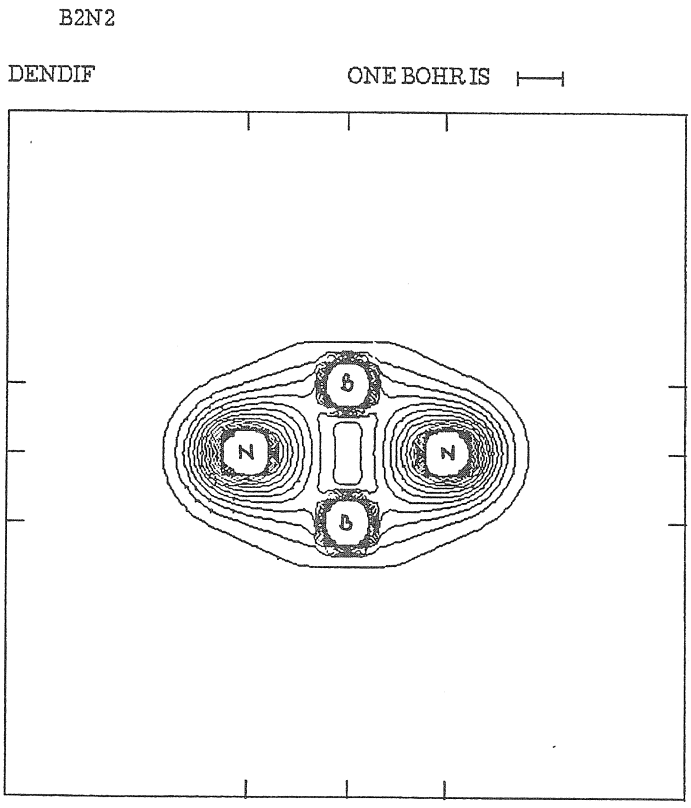


Figure 3. See Figure 2.

(iii) $(BN)_4$: For the eight-atom cluster, we expect to find the highest stability for the three-dimensional configuration for the ground state. But the calculations reveal a different scenario where the ordering (in terms of total energy) comes out to be cyclic(octagon) < linear < cube (Table I).

For the octagon structure, the angles were frozen (BNB) to 135°. When we allow the angles to vary (keeping the D_{4h} symmetry), the resulting structure [Fig. 1(d)] is more stable, with the total energy of −317.6325 Hartrees in the singlet state. This has also been the case with the C_8 cluster where the calculated minimum energy cyclic structure is not a regular octagon [8]. To illustrate the nature of chemical bonding, we show total (UHF) charge density plots of the predicted ground state in Figure 5, where a strong dominance of the B—N bond is clearly visible.

B. Stability

The variation of the atomization energy (total energy with respect to atomic constituents) with the cluster-size reveals information about the energetics of the nucleation process. For the most stable isomers of $(BN)_2$, $(BN)_3$, and $(BN)_4$ clusters, the atomization energy at the UMP2 level is

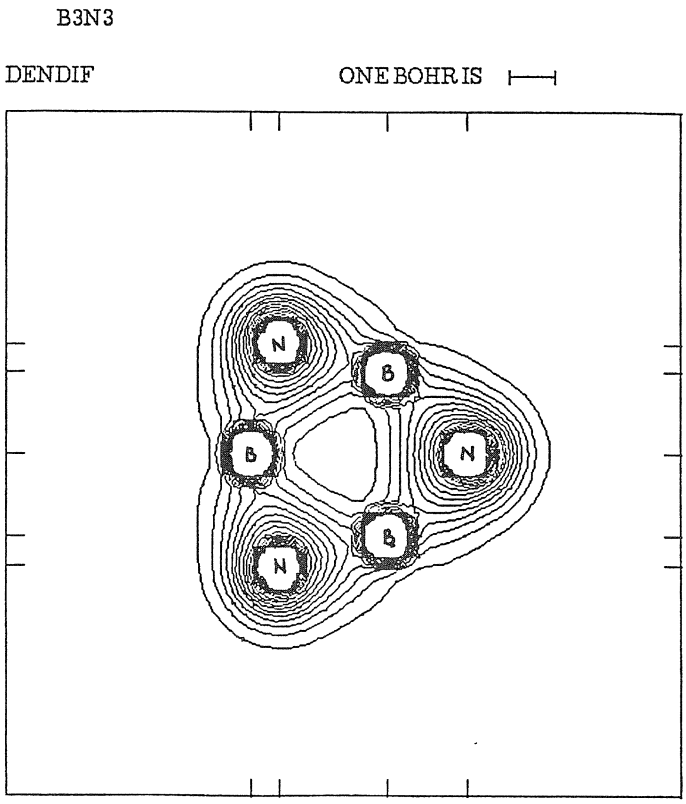


Figure 4. See Figure 2.

15.1, 30.0, and 42.2 eV, respectively. This trend shows that the cluster growth is favorable at least by the addition of one BN molecule. On the other hand, the binding energy (atomization energy per molecule) provides qualitative information concerning the cluster stability. For neutral clusters, our computed values exhibit a similar trend (Table II) as shown by carbon microclusters. (The binding energies of C_2, C_4, C_6, and C_8 are 4.1, 9.3, 10.5, and 10.8 eV, respectively, at the MP2/6-31G* level.) It is to be noted here that we use the results of Martin et al. [4] for the monomer BN.

TABLE II. Binding energy (atomization energy per molecule) and ionization potential of the BN microclusters at the UMP2 level.

Cluster	Binding energy (eV)	Ionization potential (eV)
BN	4.1	12.5
$(BN)_2$	7.6	9.9
$(BN)_3$	10.0	11.7
$(BN)_4$	10.6	8.3

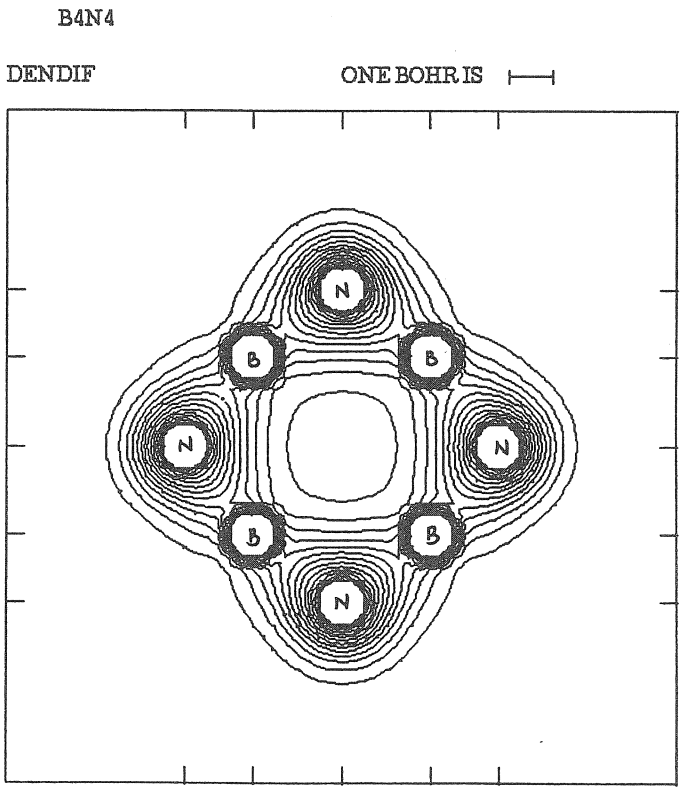


Figure 5. See Figure 2.

For the fragmentation process, the calculations (using the UMP2 energies of the most stable configurations) indicate that the most likely channel to fragment is the loss of the BN molecule (Table III). We define the fragmentation energy as the difference between products and reactives of the fragmentation process, considering only the stoichiometric fragments as products. For example, we consider BN, $(BN)_2$, and $(BN)_3$ clusters as fragmentation products for the $(BN)_4$ cluster. To gain more insight in the fragmentation process of these clusters, boron-excess and boron-deficient isomers should be taken into account. There are also kinetic factors relevant for the fragmentation process. Consideration of all these aspects would involve the computation of potential energy surfaces that are beyond the objectives of the present work.

An indication of the configurational stability of a given cluster can be obtained from the energy splitting between the ground and first metastable states. At the UMP2 level, this energy splitting is 0.04, 0.67, and 0.71 eV/atom for $(BN)_2$, $(BN)_3$, and $(BN)_4$ clusters, respectively. In carbon microclusters, the cyclic structure is more stable than is the linear by about 0.1 eV/atom for C_6, whereas cyclic and linear structures of C_4 and C_8 are found to be almost isoenergetic. This enhanced stability of the C_6 cluster (over C_4 and C_8) for the cyclic form can be understood in terms of complete filling of π orbitals, analogous to the aromatic $4n + 2$ π-electron stabilization [8]. However, this is no longer true for the $(BN)_n$ clusters with polar bonds. The

TABLE III. Fragmentation energetics of neutral and ionized BN microclusters.[a]

Fragmentation	UMP2 (eV)
Neutral	
1. $(BN)_2 \rightarrow 2BN$	6.8
2. $(BN)_3 \rightarrow 3BN$	17.5
$(BN)_3 \rightarrow (BN)_2 + BN$	10.7
3. $(BN)_4 \rightarrow 4(BN)$	26.1
$\rightarrow (BN)_3 + BN$	8.6
$\rightarrow 2(BN)_2$	12.5
Ionized	
1. $(BN)_2^+ \rightarrow BN + BN^+$	9.4
2. $(BN)_3^+ \rightarrow (BN)_2 + BN^+$	11.5
$\rightarrow (BN)_2^+ + BN$	8.9
3. $(BN)_4^+ \rightarrow (BN)_3 + BN^+$	11.3
$\rightarrow (BN)_3^+ + BN$	10.5
$\rightarrow (BN)_2 + (BN)_2^+$	12.6

[a]For BN, the UMP2 energy is taken from Martin et al. [4].

cyclic forms of both $(BN)_3$ and $(BN)_4$ show a much higher stability than that of corresponding linear forms.

C. *Single-ionized Clusters*

For the singly ionized clusters, we used the vertical approximation that consists of a single-point UMP2 calculation at the most stable configuration of the corresponding neutral clusters. The calculations were performed in the doublet spin state of the $(BN)_n^+$ clusters. The results are shown in Table IV.

At the UMP2 level, the ionization potential for BN, $(BN)_2$, $(BN)_3$, and $(BN)_4$ clusters is 12.5, 9.9, 11.7, and 9.8 eV, respectively. This trend does not agree with the one shown by C clusters where the ionization potential decreases with the increase in the cluster size. (The values for C_2, C_4, C_6, and C_8 clusters are reported to be 12.1, 10.5, 9.8, and 9.2 eV, respectively.)

TABLE IV. Total energies for singly ionized clusters (in the doublet spin state) within the vertical approximation.

Cluster	UHF (Hartrees)	UMP2 (Hartrees)
BN^+	−78.5876	−78.7090
$(BN)_2^+$	−157.8149	−158.2221
$(BN)_3^+$	−237.0611	−237.7171
$(BN)_4^+$	−316.3862	−317.2709

Our recent study [10] on $(MgO)_n^+$ clusters have shown that ionization-induced effects introduce about 10% error in the calculated properties. In the present work, we also explore the ionization-induced effects at the single-point MP2 level for BN^+ and $(BN)_2^+$ clusters. The geometry-relaxation step lowers the total energy by 1.0 eV for BN^+ and by 0.5 eV for $(BN)_2^+$ clusters with a very small change in both bond length and bond angle. The resultant effect on the ionization potential of neutral clusters comes out to be within 8% of the corresponding values in the vertical approximation.

In the fragmentation process, the ionized clusters prefer the loss of a neutral BN molecule as opposed to the loss of an ionized BN molecule (Table IV). The fragmentation energy is 9.4, 8.9, and 10.5 eV for $(BN)_2^+$, $(BN)_3^+$, and $(BN)_4^+$ clusters, respectively.

IV. Summary

Our calculations at the UHF/6-31G* level reveal that the strong bonding between B and N plays a significant role in determining the configurational parameters of $(BN)_n$ clusters. The most stable configurations are found to have the same features as those predicted for isoelectronic C_{2n} clusters. However, this similarity is not reflected in the configurational stability due to the polar character of the B—N bond. The cylic forms of $(BN)_3$ and $(BN)_4$ clusters show a much higher stability over the linear forms than that of corresponding C_6 and C_8 clusters, respectively.

In the cyclic forms, the singlet states are found to be more stable than the triplet states. It appears that the presence of π electrons that move around the ring causes the cluster to be more stable in the singlet spin state. A similar prediction has been made for the corresponding C_{2m} clusters. As discussed by Raghavachari and Brinkley [8], the linear isomers have $2m-2\pi$ electrons in the triplet spin state, whereas the cyclic isomers have $m-2\pi$ out-of-plane electrons and m in-plane pseudo 2π electrons. We therefore expect the bond length in the triplet state (linear) to be shorter than that in the singlet state (cyclic). Furthermore, with the increase in the cluster size, the pseudo-π electrons in the singlet state become (true) π electrons, resulting in the decrease of the bond length in cyclic isomers. Our calculations do confirm this expectation as shown in Table I. The (B—N) bond length of about 1.299 Å remains almost constant in the linear isomers, whereas it decreases in cyclic isomers from 1.385 to 1.316 Å as we increase the cluster size from $(BN)_2$ to $(BN)_4$.

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