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Structural, Rotational, and Vibrational Properties of Mixed Ionized Boron−Nitrogen Clusters $B_nN_n^+$ ($n = 3-10$)

M. G. Giuffreda, M. S. Deleuze,* and J-P. François

Department SBG, Institute for Materials Science (IMO), Limburgs Universitair Centrum, Universitaire Campus, B-3590 Diepenbeek, Belgium

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The structural, rotational, and vibrational properties of $B_nN_n^+$ clusters ($n = 3-10$) have been investigated using density functional theory (DFT) and compared with that of their neutral counterparts. The $B_nN_n^+$ species with $n = 4, 6, 8, 10$ are found to possess as lowest energy form a fully regular structure of D_{nh} symmetry, as the neutral species. In both cases, their IR vibrational spectrum invariably contains four lines, relating to one out-of-plane nondegenerate and three in-plane doubly degenerate normal modes. On the other hand, the B_nN_n clusters with $n = 3, 5, 7, 9$ are found to evolve from a fully regular D_{nh} structure to a more alternating one upon an adiabatic ionization process. In this case, ionization is also shown to strongly enhance the infrared activity. Rotational moments and adiabatic ionization potentials are eventually provided to trace the structural variations induced by ionizing these clusters.

1. Introduction

Boron (B_n), nitrogen (N_n), and mixed boron−nitrogen (B_mN_n) clusters have been extensively studied both experimentally and theoretically.[1−19] Large and mixed boron−nitrogen clusters have attracted much attention as precursors in the growth of β-BN thin film using chemical vapor deposition or plasma techniques.[1] Particular effort is made to synthesize the sphalerite-type (or β-crystalline phase) of boron nitride, which is isostructural and isoelectronic to cubic diamond, and displays outstanding physicochemical properties (e.g., mechanical hardness, thermal stability and conductivity, chemical stability with respect to ferrous alloys, the possibility of n or p doping, and the emission of blue light at the p−n junction).[1−3] Investigations on large B_nN_n clusters are also topical in view of the synthesis and characterization of chemical derivatives of fullerenes in which carbon atoms are substituted by boron and nitrogen and other elements like metal atoms. In particular, it is well-known that graphite and diamond allotropes have boron nitride analogues, and the existence of boron−nitrogen clusters with fullerene geometries has been recently postulated.[4−6]

Small boron−nitrogen clusters such as BN, B_2N, BN_2, B_2N_2, B_3N, BN_3, B_3N_2, and B_2N_3 have been subject of high-level theoretical studies with emphasis on their structures, vibrational (BN_4), thermochemical, dissociation, and spectroscopic properties.[7−13] Furthermore, on the experimental side, matrix infrared spectroscopy measurements combined with pulsed vapor evaporation have confirmed earlier theoretical predictions[7] of the structure and reactivity of B_2N and BN_2.[10−14] B_2N has been also experimentally investigated using electron spin resonance.[15]

The structure, stability, and vibrational spectra of neutral boron−nitrogen clusters B_nN_n ($n = 3, 4$) have already been characterized theoretically at the UMP2[16] and CCSD(T)[17] levels (i.e., unrestricted second-order Møller−Plesset[18] perturbation theory and coupled cluster ansatz with all single and double excitations and a quasiperturbative treatment of connected triple excitations,[19] respectively). The geometries and harmonic vibrations of the B_nN_n species with $n = 3-10$ have also been studied[20] with density functional theory (DFT) using the hybrid B3LYP functional[21] (Becke's three-parameter Lee−Yang−Parr functional) in conjunction with Dunning's correlation consistent polarized valence double-ζ (cc-pVDZ) basis set.[22] These studies show that the B_nN_n ($3 \leq n \leq 10$) clusters have D_{nh} cumulenic monocyclic structures with θ_{NBN} the largest and θ_{BNB} the sharpest angle. Experimental studies[23] have been reported on plasmas of $B_nN_m^+$ clusters produced by laser irradiation of boron nitride. On the other hand, no study of structural and spectroscopic properties of the ionized species $B_nN_n^+$ has been reported yet.

In the present contribution, we theoretically investigate the structural, rotational, and vibrational properties of cyclic boron−nitrogen cluster cations, $B_nN_n^+$, with $n = 3-10$, using DFT. Vibrational harmonic frequencies and infrared (IR) activities as well as the vibrational zero-point energies are also evaluated at the same level of theory.

2. Methods

In the present paper, DFT calculations have been performed using the Becke three-parameter Lee−Yang−Parr (B3LYP) functional.[21] This functional consists of the Lee−Yang−Parr[24] correlation functional in conjunction with a hybrid exchange functional which is a linear combination of the LDA (local density approximation) expression, Becke's gradient correction,[25] and the Hartree−Fock exchange energy based on Kohn−Sham[26] orbitals. Geometries and vibrational frequencies have been obtained at the B3LYP level combined with Dunning's correlation consistent polarized valence double-ζ (cc-pVDZ) basis sets[22] for boron and nitrogen which are a [3s2p1d] contraction of a (9s4p1d) primitive basis set.

As already pointed out in a previous study on carbon cluster cations,[27] the B3LYP/cc-pVDZ level provides structures and vibrations of quality comparable to the CCSD(T)/cc-pVDZ level, with the advantage of a much reduced computational cost.

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* Corresponding author. E-mail: deleuze@luc.ac.be.

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TABLE 1: Geometries of the Cyclic $B_nN_n^+$ Cations Compared with Those of the B_nN_n Neutral Systems[a] from Which They Derive (B3LYP/cc-pVDZ Results[b])

$\mathbf{B_3N_2}^+$ ^{2}A′ (C_s)	$r_{12} = 1.3229$, $r_{23} = 1.3749$, $r_{16} = 1.4263$ $\theta_{123} = 91.89$, $\theta_{234} = 150.10$, $\theta_{456} = 146.89$, $\theta_{561} = 92.36$
$\mathbf{B_3N_3}$ ^{1}A$_1$′ (D_{3h})	$r = 1.3601$ $\theta_{123} = 89.00$, $\theta_{234} = 151.00$
$\mathbf{B_4N_4}^+$ ^{2}B$_{1u}$ (D_{4h})	$r = 1.3441$ $\theta_{123} = 107.23$, $\theta_{234} = 162.77$
$\mathbf{BuN_4}$ ^{1}A$_{1g}$ (D_{4h})	$r = 1.3436$ $\theta_{123} = 103.19$, $\theta_{234} = 166.80$
$\mathbf{B_5N_5}^+$ ^{2}A (C_1)	$r_{21} = 1.3367$, $r_{32} = 1.3106$, $r_{43} = 1.3630$, $r_{54} = 1.3158$, $r_{65} = 1.3513$ $\theta_{123} = 117.94$, $\theta_{234} = 169.85$, $\theta_{345} = 118.54$, $\theta_{456} = 169.62$, $\theta_{567} = 118.03$, $\theta_{10,1,2} = 170.07$
$\mathbf{B_5N_5}$ ^{1}A$_1$′ (D_{5h})	$r = 1.3325$ $\theta_{123} = 115.02$, $\theta_{234} = 172.98$
$\mathbf{B_6N_6}^+$ ^{2}B$_{1g}$ (D_{6h})	$r = 1.3269$ $\theta_{123} = 126.32$, $\theta_{234} = 173.68$
$\mathbf{B_6N_6}$ ^{1}A$_{1g}$ (D_{6h})	$r = 1.3273$ $\theta_{123} = 123.38$, $\theta_{234} = 176.62$
$\mathbf{B_7N_7}^+$ ^{2}A$_2$ (C_{2v})	$r_{21} = 1.3227$, $r_{32} = 1.3392$, $r_{43} = 1.3077$, $r_{54} = 1.3448$, $r_{65} = 1.3044$, $r_{76} = 1.3339$, $r_{87} = 1.3156$ $\theta_{123} = 132.29$, $\theta_{234} = 176.11$, $\theta_{345} = 132.74$, $\theta_{456} = 175.86$, $\theta_{567} = 132.83$, $\theta_{678} = 175.74$, $\theta_{789} = 132.63$, $\theta_{2,1,14} = 176.25$
$\mathbf{B_7N_7}$ ^{1}? (D_{7h})	$r = 1.3231$ $\theta_{123} = 130.23$, $\theta_{234} = 178.34$
$\mathbf{B_8N_8}^+$ ^{2}? (D_{8h})	$r = 1.3204$ $\theta_{123} = 137.47$, $\theta_{234} = 177.53$
$\mathbf{B_8N_8}$ ^{1}? (D_{8h})	$r = 1.3204$ $\theta_{123} = 135.46$, $\theta_{234} = 179.54$
$\mathbf{B_9N_9}^+$ ^{2}A″ (C_s)	$r_{21} = 1.3180$, $r_{32} = 1.3271$, $r_{43} = 1.3092$, $r_{54} = 1.3338$, $r_{65} = 1.3035$, $r_{76} = 1.3340$, $r_{87} = 1.3042$, $r_{98} = 1.3256$, $r_{10,9} = 1.3130$ $\theta_{123} = 141.13$, $\theta_{234} = 178.72$, $\theta_{345} = 141.42$, $\theta_{456} = 178.59$, $\theta_{567} = 141.75$, $\theta_{678} = 178.34$, $\theta_{789} = 141.74$, $\theta_{8910} = 178.13$, $\theta_{9,10,11} = 141.60$, $\theta_{2,1,18} = 178.75$
$\mathbf{B_9N_9}$ ^{1}? (D_{9h})	$r = 1.3183$ $\theta_{123} = 139.75$, $\theta_{234} = 179.75$
$\mathbf{B_{10}N_{10}}^+$ ^{2}? (D_{10h})	$r = 1.3167$ $\theta_{123} = 144.77$, $\theta_{234} = 179.23$
$\mathbf{B_{10}N_{10}}$ ^{1}? (D_{10h})	$r = 1.3168$ $\theta_{123} = 143.44$ $\theta_{234} = 180.67$

[a] Martin, J. M. L.; El-Yazal, J.; François, J. P. *Chem. Phys. Lett.* **1996**, *248*, 95. [b] Atoms are systematically labeled starting from a boron atom as number one. Only symmetrically nonredundant parameters are given. Bond lengths in Å and bond angles in deg. (?) indicates that no consistent treatment of symmetry groups containing rotation axis of large but finite orders such as D_{7h}, D_{8h}, D_{9h}, and D_{10h} were possible with the GAUSSIAN98 package.

All the calculations have been carried out using the Gaussian 98 package[28] running on a Alpha Digital workstation (model 533au2) at the Limburgs Universitair Centrum.

3. Results and Discussion

As stated in ref 20, the neutral B_nN_n clusters with $n = 3-10$ adopt clearly as lowest energy form a ring of D_{nh} symmetry, with alternating sharp BNB and flat NBN angles. Since all bond lengths are equal, such form can be somewhat abusively referred to as "cumulenic", in analogy with the nomenclature adopted for pure carbon rings.[27] A comparison (Table 1) between the structure of the neutral B_nN_n species and of their cations clearly shows that an adiabatic ionization process preserves the D_{nh} symmetry and "cumulenic" nature of these clusters, when $n =$ 4, 6, 8, 10. In this case, ionization affects the bond angles rather than the bond lengths. More specifically, the bond lengths remain almost unchanged whereas the angles θ_{BNB} clearly increase and the angles θ_{NBN} decrease with respect to the neutral species. On the other hand, a lowering of symmetry (Table 1) and distortion toward a more alternating structure (Table 2) is observed upon ionization for the B_nN_n clusters with $n = 3$, 5, 7, 9. The effect of ionization on bond lengths clearly decreases within rings of increasing size, reflecting the larger delocalization of the positive charge due to ionization. As in the neutral species, the θ_{NBN} angles remain the largest and tend to approach 180° as n increases, while the angle θ_{BNB} increases monotonically from 91.89° ($B_3N_3^+$) to 144.77° ($B_{10}N_{10}^+$). Interestingly, the behavior of the $B_nN_n^+$ species with $n = 3$, 5, 7, 9 is similar to that of cumulenic carbon clusters C_{4n+2} with $n = 1-4$ where ionization also appears to yield a slight but significant departure from a completely nonalternating pattern.[27] This points out a principle of structural similarity between the cumulenic carbon rings and the isoelectronic mixed boron−nitrogen rings. On the other hand, it must be reminded that, unlike B_nN_n rings with $n = 4$, 6, 8, and 10, C_{4n} clusters with $n = 2-4$ are displaying a clear alternation of bond lengths, and are thus referred to as "polyynic".[27] The principle of structural similarity following the Hückel topological rules for double aromaticity or antiaromaticity is thus only partially followed between the isoelectronic C_{2n} and B_nN_n clusters.

TABLE 2: Bond Length Alternations (in Å) in Boron−Nitrogen Cluster Cations in Their Doublet States

$B_3N_3^+$	0.103	0.051						
$B_4N_4^+$	0.000							
$B_5N_5^+$	0.026	0.052	0.047	0.036				
$B_6N_6^+$	0.000							
$B_7N_7^+$	0.017	0.032	0.037	0.040	0.030	0.018		
$B_8N_8^+$	0.000							
$B_9N_9^+$	0.009	0.018	0.025	0.030	0.031	0.030	0.021	0.013
$B_{10}N_{10}^+$	0.000							

Inspection of the outermost molecular orbitals helps to rationalize the behavior of these systems upon ionization. In doubly aromatic rings, as for instance B_7N_7 (Figure 1), the highest molecular orbital (HOMO) is doubly degenerate and displays a π-symmetry. This set relates to out-of-plane conjugation and provides a fully symmetric and regular electronic distribution along the ring. Clearly, as for the C_{4n+2} ($n = 1-4$) clusters,[27] ionization of one of these two degenerate orbitals yields some asymmetrization of the electron density and hence, alternations of bond lengths. In other words, this behavior can be seen as a consequence of a Jahn−Teller effect[29] due to the double degeneracy of the outermost orbitals. On the other hand, the B_nN_n clusters with n even (e.g., B_6N_6, Figure 2) display as outermost occupied level a nondegenerate orbital of π-symmetry and a clear nonbonding character on the nitrogen atoms. Ionization of this orbital solely yields a fully symmetric decrease of the electronic density in the region around these atoms, without therefore affecting the fully regular character and thus the D_{nh} symmetry of these clusters.

The behavior of the B_nN_n clusters upon ionization could nicely be traced by means of rotational spectroscopy,[30] which is a very sensitive tool even for the weakest structural alterations. Thus, an analysis of the moments of inertia which come from diagonalization of the inertia tensor, i.e., $I_{qq} = \sum_i m_i q_i^2$ with $q = x, y, z$ is displayed in Table 3. In their neutral form, all these species are clearly found to be oblate symmetric rotors. As can be expected from the observations already made, the isotropic rotational characteristics of the B_nN_n clusters with n even remain unchanged upon adiabatic ionization whereas those with n odd become asymmetric tops in their ionized form. For the clusters with n odd, ionization is found to yield an increase of the total circumference of the rings. It can also be noticed that in both

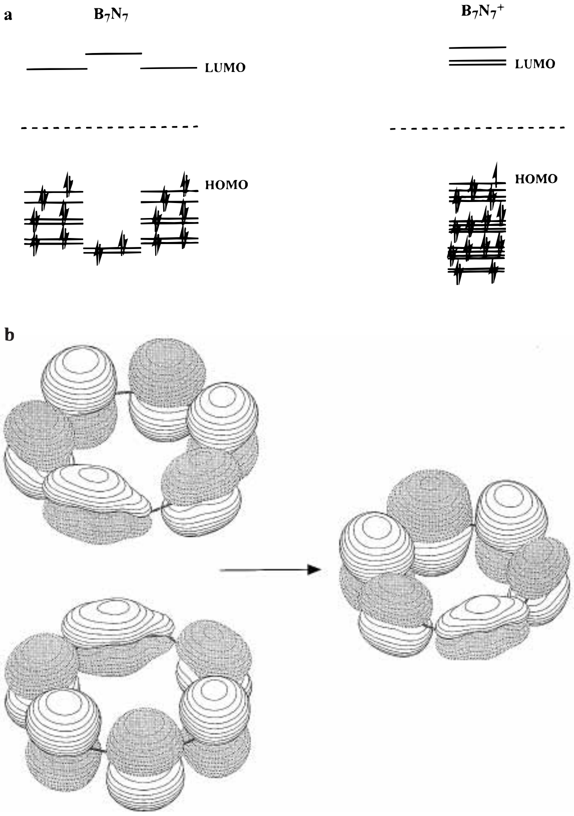

Figure 1. (a) Energy level diagrams of the B_7N_7 and $B_7N_7^+$ clusters; (b) schematic drawings of the highest occupied molecular orbitals (HOMO).

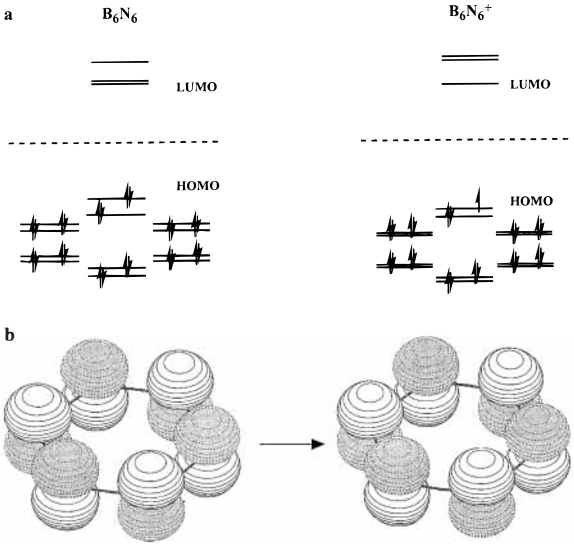

Figure 2. (a) Energy level diagrams of the B_6N_6 and $B_6N_6^+$ clusters; (b) schematic drawings of the highest occupied molecular orbitals (HOMO).

TABLE 3: Total Lengths (Obtained as a Sum of the Bond Lengths, in Å) and Moments of Inertia (kg m^2) of Boron−Nitrogen Clusters in Their Neutral and Ionized Forms (Geometries Optimized at the B3LYP/cc-pVDZ Level)[a]

		moments of inertia		
species	total length	I_{xx} ($\times10^{-46}$)	I_{yy} ($\times10^{-46}$)	I_{zz} ($\times10^{-46}$)
		n Even		
B_4N_4	10.749	24.675	24.675	49.350
$B_4N_4^+$	10.753	24.983	24.983	49.967
B_6N_6	15.928	79.065	79.065	158.131
$B_6N_6^+$	15.923	79.732	79.732	159.464
B_8N_8	21.126	185.291	185.291	370.582
$B_8N_8^+$	21.126	186.279	186.279	372.559
$B_{10}N_{10}$	26.336	360.653	360.653	721.306
$B_{10}N_{10}^+$	26.334	361.832	361.832	723.664
		n Odd		
B_3N_3	8.161	11.385	11.385	22.771
$B_3N_3^+$	8.248	11.323	12.078	23.401
B_5N_5	13.325	46.474	46.474	92.648
$B_5N_5^+$	13.355	46.994	47.292	92.948
B_7N_7	18.523	124.621	124.621	249.241
$B_7N_7^+$	18.537	125.377	125.936	251.313
B_9N_9	23.729	263.209	263.209	526.419
$B_9N_9^+$	23.737	263.699	265.390	529.089

[a] Atomic units have been converted into SI units, using $[L] = a_0 = 5.2917 \times 10^{-11}$ m and $[M] =$ amu $= 1.6605 \times 10^{-27}$ kg.

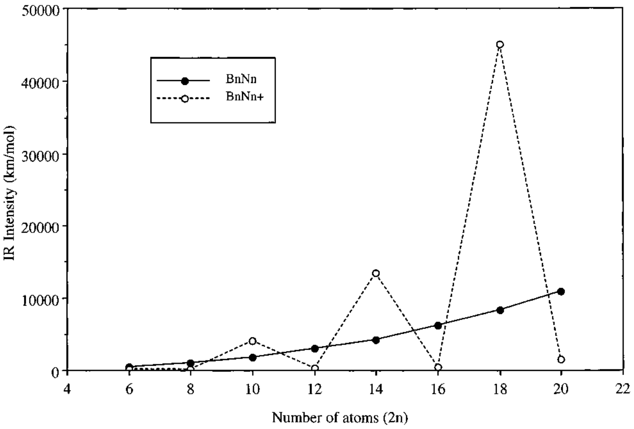

Figure 3. IR activity associated with the most intense line of the cyclic $B_nN_n^+$ clusters as a function of the total number of atoms (2*n*).

cases ionization yields a slight increase of all principal components of the inertia tensor with the exception of I_{xx} for $B_3N_3^+$ which slightly decreases with respect to the neutral counterpart.

Like their neutral counterparts,[20] the cyclic $B_nN_n^+$ clusters with $n = 4$, 6, 8, and 10 have only four infrared active bands, which relate to a nondegenerate out-of-plane wagging vibrational mode of a_{2u} symmetry and three doubly degenerate stretching modes of e_u ($n = 4$) or e_{1u} ($n = 6$, 8, 10) symmetry. Unlike the B_4N_4 and B_6N_6 clusters, the most intense line in the IR spectrum of $B_4N_4^+$ and $B_6N_6^+$ relates to the a_{2u} vibration whereas both the B_nN_n and $B_nN_n^+$ ($n = 8$, 10) forms display as most intense line the e_{1u} normal mode. On the other hand, lowering of symmetry in the ionized $B_nN_n^+$ species ($n = 3$, 5, 7, 9) leads to a spreading of the infrared activity over many more vibrational normal modes, and thus to an IR fingerprint which sharply differs from that of the corresponding neutral forms.[20] From inspection of the most intense lines (Figure 3), it appears furthermore that the IR activity of the $B_nN_n^+$ cations displays a clear 2*n* periodicity, with *n* odd and *n* even corresponding to a rise or a drop of the IR activity, also in sharp contrast with the regular increase observed for the neutral B_nN_n rings.

The calculated IR activity of the ionized $B_nN_n^+$ species with *n* odd increases very rapidly with the size of the ring and, with the exception of B_3N_3, is overall much larger than that of their neutral counterpart. On the other hand, ionization of B_nN_n clusters with *n* even results in a strong decrease of the intensity of the most active mode. These variations in the IR activity can be easily explained from the changes induced by ionization in the dipole and quadrupole moments (Table 5), which in turn provide some insight into the charge delocalization properties of these clusters. All B_nN_n and $B_nN_n^+$ clusters are characterized by nonvanishing quadrupole moments. The reduction of the IR

TABLE 4: Harmonic Frequencies (cm^{-1}) and IR Intensities (km/mol) of the $B_nN_n^+$ Cations at the B3LYP/cc-pVDZ Level[a]

$B_3N_3^+$ C_s cyclic doublet ZPE = 14.31	287(a′, 119), 377(a′, 0), 425(a′, 56), 508(a′, 55), 564(a′, 39), 741(a′, 1), 878(a′, 75), 930(a′, 30), 1018(a′, 34), 1186(a′, 8), 1522(a′, 38), **1572(a′,137)**
$B_4N_4^+$ D_{4h} cyclic doublet ZPE = 21.39	**465(a_{2u}, 166)**, 565(e_u, 113×2), 1005(e_u, 25×2), 1536(e_u, 29×2)
$B_5N_5^+$ C_1 cyclic doublet ZPE = 25.32	97(601), 137(1), 137(0), 168(4), **241(4080)**, 403(0), 424(116), 449(16), 462(0), 465(1), 489(2), 522(86), 558(122), 572(14), 579(60), 763(0), 896(7), 914(112), 1186(16), 1254(53), 1622(22), 1704(57), 1781(52), 1889(812)
$B_6N_6^+$ D_{6h} cyclic doublet ZPE = 33.10	**479(a_{2u}, 228)**, 545(e_{1u}, 168×2), 815(e_{1u}, 0.5×2) 1662(e_{1u}, 24×2)
$B_7N_7^+$ C_{2v} cyclic doublet ZPE = 36.68	41(b_2, 3300), **140(b_2, 13359)**, 155(b_2, 2640), 451(b_2, 3), 454(b_1, 163), 486(b_1, 7), 502(a_1, 2), 505(b_2, 309), 520(b_1, 95), 527(b_2, 11), 527(a_1, 176), 737(a_1, 7), 764(b_2, 1554), 1044(a_1, 14), 1050(b_2, 285), 1325(b_2, 2), 1369(a_1, 3), 1733(a_1, 14), 1734(b_2, 3), 1786(a_1, 1), 1836(b_2, 81), 1848(b_2, 38), 1995(a_1, 1629)
$B_8N_8^+$ D_{8h} cyclic doublet ZPE = 44.57	481(a_{2u}, 298), 506(e_{1u},172×2), 681(e_{1u},14×2), **1678(e_{1u},449×2)**
$B_9N_9^+$ C_s cyclic doublet ZPE = 48.04	40(a′, 351), 100(a′, 2064) **146(a′, 44958)**, 157(a′, 454), 448(a′, 1), 463(a", 221), 470(a", 1), 477(a′, 5), 477(a′, 18), 479(a′, 27), 480(a′, 158), 498(a", 27), 508(a′, 2), 510(a′, 270), 514(a", 86), 638(a′, 62), 664(a′, 5115), 874(a′, 17), 884(a′, 1431), 1172(a′, 3), 1172(a′, 24), 1770(a′, 7), 1774(a′, 76), 1836(a′, 1), 1847(a′, 126), 1894(a′, 59), 1924(a′, 1), 2044(a′, 2652)
$B_{10}N_{10}^+$ D_{10h} cyclic doublet ZPE = 55.83	432(e_{1u}, 134×2), 479(a_{2u}, 371), 607(e_{1u}, 68×2), **1682(e_{1u}, 1546×2)**

[a] Only IR-active modes with intensity ≥1 km/mol are given. The zero-point vibrational energies (ZPE) are expressed in kcal/mol.

TABLE 5: Quadrupole Moments (in D·Å) and Dipole Moments (D) of Boron−Nitrogen Clusters in Their Neutral and Ionized Forms

species	total dipole moment	quadrupole moments XX	YY	ZZ
		n Even		
XX	*YY*	*ZZ*		
B_4N_4	0	−45.7589	−45.7589	−42.1422
$B_4N_4^+$	0	−32.8610	−32.8610	−38.2156
B_6N_6	0	−69.7904	−69.7904	−63.1258
$B_6N_6^+$	0	−47.3364	−47.3635	−59.0154
B_8N_8	0	−93.9812	−93.9812	−83.9313
$B_8N_8^+$	0	−59.1165	−59.1165	−79.7708
$B_{10}N_{10}$	0	−118.2435	−118.2435	−104.6923
$B_{10}N_{10}^+$	0	−67.8366	−67.8366	−100.5041
		n Odd		
B_3N_3	0	−33.6846	−33.6846	−31.8863
$B_3N_3^+$	0.860	−25.2709	−24.4025	−27.9264
B_5N_5	0	−57.5911	−57.5911	−52.7232
$B_5N_5^+$	1.442	−40.6114	−40.3727	−48.6042
B_7N_7	0	−81.8009	−81.8009	−73.5574
$B_7N_7^+$	2.287	−69.3670	−53.6682	−53.5254
B_9N_9	0	−106.1203	−106.1203	−94.3181
$B_9N_9^+$	3.153	−63.9514	−63.6922	−90.1076

activity in the ionized $B_nN_n^+$ ($n = 4, 6, 8, 10$) clusters compared with that of the neutral B_nN_n ones corroborates a reduction of quadrupole moments (Table 5), which relates in turn to a perfect delocalization along the ring of the positive charge due to ionization (see, e.g., $B_{10}N_{10}^+$ (Figure 4)). On the other hand, the symmetry lowering in the $B_nN_n^+$ ($n = 3, 5, 7, 9$) clusters induced by ionization leads to a localization of charge (Figure 5 for $B_9N_9^+$), resulting in turn in a large dipole moment (Table 5). The size-extensivity properties of the dipole and quadrupole moments overall explain the size dependence of the IR activity of these clusters.

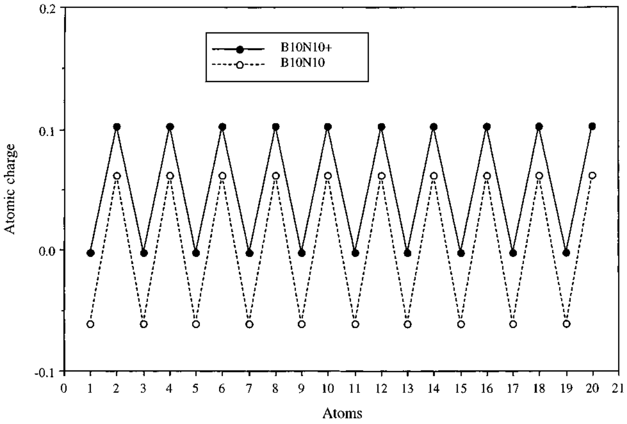

Figure 4. Distribution of atomic charges within the $B_{10}N_{10}^+$ cyclic cluster (results of a Mulliken population analysis of the B3LYP/cc-pVDZ wave function). Odd numbers refer to boron atoms, whereas even numbers correspond to nitrogen atoms.

Finally, some considerations can be made on the adiabatic ionization potentials (AIP) which are calculated as a byproduct of the present work. These are collected in Table 6 including the corrections for zero-point vibrational energies (to be found in Table 4). The contribution of these corrections to the ionization potentials is rather small, in general around 0.1−0.2 eV. Overall, the “2*n*” periodicity of B_nN_n clusters already noticed for the IR activity can also be detected from a periodic modulation in the size dependence of the AIP (Figure 6). The B_nN_n clusters with $n = 3, 5, 7, 9$ are characterized by maxima in the AIP’s, which nicely confirms our cumulenic-like depiction of these species and their doubly aromatic character. In spite of these modulations, which appear to progressively vanish with

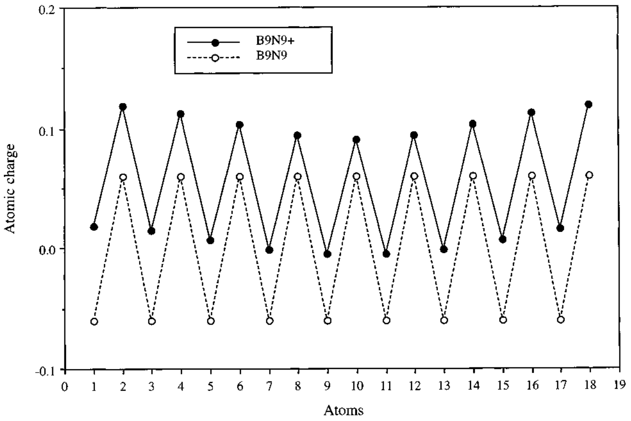

Figure 5. Distribution of atomic charges within the $B_9N_9^+$ cyclic cluster (results of a Mulliken population analysis of the B3LYP/cc-pVDZ wave function). Odd numbers refer to boron atoms, whereas even numbers correspond to nitrogen atoms.

TABLE 6: Adiabatic Ionization Potentials (eV) of Boron−Nitrogen Clusters, at the B3LYP/cc-pVDZ Level [B_nN_n(singlet) → $B_nN_n^+$(doublet) + e^-][a]

species		species	
B_3N_3	10.7 (−0.094)	B_7N_7	9.3 (−0.166)
B_4N_4	9.5 (−0.051)	B_8N_8	8.8 (−0.074)
B_5N_5	9.9 (−0.149)	B_9N_9	8.9 (−0.173)
B_6N_6	9.1 (−0.064)	$B_{10}N_{10}$	8.5 (−0.082)

[a] B3LYP results incorporate the variations of zero-point vibrational energies (in parentheses).

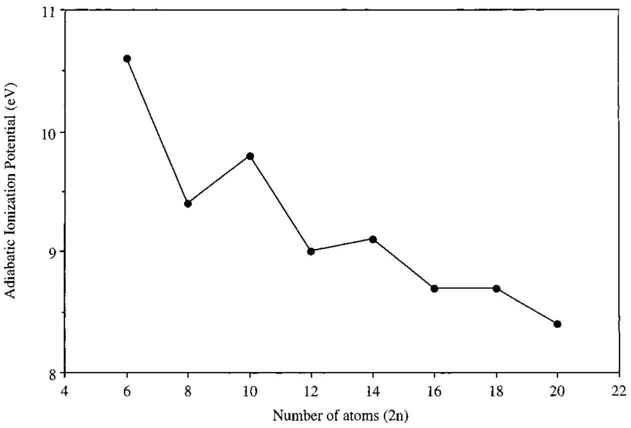

Figure 6. Size dependence of the adiabatic ionization potential of cyclic B_nN_n clusters.

the size of rings, the AIP's of the B_nN_n rings show a faster convergence toward some asymptotic value than that displayed in ref 27 for pure carbon rings. This obviously relates to an intrinsic alternation of the electron density in rings mixing boron and nitrogen atoms.

4. Conclusions

In the present paper, we report an exhaustive and very first study of the structural, rotational, and vibrational properties of mixed boron−nitrogen clusters $B_nN_n^+$ ranging from $n = 3$ to $n = 10$, at the B3LYP/cc-pVDZ level of theory. This work is a natural extension of a similar study[27] on carbon cluster cations C_n^+ with $n = 4-19$.

When investigating the structural variations induced by adiabatic ionization, it has been found that the B_nN_n clusters display different behaviors depending on whether they have an even ($n = 4, 6, 8, 10$) or odd ($n = 3, 5, 7, 9$) number of BN pairs. Like the neutral systems, the $B_nN_n^+$ cations with n even display a D_{nh} symmetry and by analogy with isoelectronic carbon clusters can thus be reported as cumulenic monocyclic structures. On the other hand, the $B_nN_n^+$ clusters with n odd show a lowered symmetry compared to the neutral form from which they derive, reflecting a reduction of their out-of-plane π-aromaticity.

The IR spectrum of the $B_nN_n^+$ clusters with n even is characterized by four active modes of a_{2u} and e_u or e_{1u} symmetry with an intensity smaller than the neutral systems. In these clusters the positive charge due to ionization is perfectly delocalized and significantly lowers the quadrupole moments with respect to the neutral counterparts, resulting in a decrease of the IR activity. On the contrary, the $B_nN_n^+$ cations with n odd ($n = 5, 7, 9$) exhibit a much more pronounced IR activity than the neutral ones. In these systems a localization of charges due to symmetry lowering yields strong dipole moments, which explains in turn the net increase of the IR activity due to ionization.

From their behavior upon adiabatic ionization, due to the nonbonding character of the HOMO in the $B_nN_n^+$ clusters with n even, a structural similarity following the isoelectronic principle is thus found only between the doubly aromatic B_nN_n rings with n odd and the cumulenic carbon clusters C_{4n+2} with $n = 1-4$.

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References and Notes

(1) *Gmelins Handbook of Inorganic Chemistry*, 8th ed.; Springler: Berlin, 1988; Boron compounds, 3rd suppl., Vol. 3. Paine, R. T.; Narula, C. K. *Chem. Rev.* **1990**, *90*, 73.

(2) Demazeau, G. *Diamond Relat. Mater.* **1995**, *4*, 284.

(3) Komatsu, S.; Yarbrough, W.; Moriyoshi, Y. *J. Appl. Phys.* **1997**, *81*, 7798 and references therein.

(4) La Placa, S. J.; Roland, P. A.; Wynne, J. J. *Chem. Phys. Lett.* **1992**, *190*, 163.

(5) Xia, X.; Jelski, D. A.; Bowser, J. R.; George, T. F. *J. Am. Chem. Soc.* **1992**, *114*, 6493.

(6) Jensen, F.; Toftlund, H. *Chem. Phys. Lett.* **1993**, *201*, 89.

(7) Martin, J. M. L.; François, J. P.; Gijbels, R. *J. Chem. Phys.* **1989**, *90*, 6469.

(8) Martin, J. M. L.; Lee, T. J.; Scuseria, G. E.; Taylor, P. R. *J. Chem. Phys.* **1992**, *97*, 6549.

(9) Slanina, Z.; Martin, J. M. L.; François, J. P.; Gijbels, R. *Chem. Phys. Lett.* **1993**, *201*, 54.

(10) Andrews, L.; Hassanzadeh, P.; Burkholder, T. R.; Martin, J. L. M. *J. Chem. Phys.* **1993**, *98*, 922.

(11) Martin, J. M. L.; Taylor, P. R.; François, J. P.; Gijbels, R. *Chem. Phys. Lett.* **1994**, *222*, 517.

(12) Martin, J. M. L.; Slanina, Z.; François, J. P.; Gijbels, R. *Mol. Phys.* **1994**, *82*, 155.

(13) Peterson, K. A. *J. Chem. Phys.* **1995**, *102*, 262.

(14) Hassanzadeh, P.; Andrews, L. *J. Phys. Chem.* **1992**, *96*, 9177.

(15) Knight, L. B.; Hill, D. W.; Kirk, T. J.; Arrington, C. A. *J. Phys. Chem.* **1992**, *96*, 555.

(16) Sutjianto, A.; Pandey, R.; Recio, M. J. *Int. J. Quantum Chem.* **1994**, *52*, 199.

(17) Martin, J. M. L.; El-Yazal, J.; François, J. P.; Gijbels, R. *Chem. Phys. Lett.* **1995**, *232*, 289.

(18) Møller, C.; Plesset, M. S. *Phys. Rev.* **1934**, *46*, 618. Binkley, J. S.; Pople, J. A. *Int. J. Quantum Chem.* **1975**, *9*, 229. Pople, J. A.; Binkley, J. S.; Seeger, R. *Int. J. Quantum Chem.* **1976**, *10*, 1.

(19) (a) Raghavachari, K.; Trucks, G. W.; Head-Gordon, M.; Pople, J. A. *Chem. Phys. Lett.* **1989**, *157*, 479. (b) Hample, C.; Peterson, K.; Werner, H. J. *Chem. Phys. Lett.* **1992**, *190*, 1. (c) Lee, J. T.; Scuseria, E. G. Achieving Chemical Accuracy with Coupled-Cluster Theory. In *Quantum Mechanical*

Electronic Structure Calculations with Chemical Accuracy; Langhoff, S. R., Ed.; Kluwer: Dordrecht, 1995.

(20) Martin, J. M. L.; El-Yazal, J.; François, J. P. *Chem. Phys. Lett.* **1996**, *248*, 95.

(21) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648.

(22) Dunning, T. H. *J. Chem. Phys.* **1989**, *90*, 1007.

(23) Becker, S.; Dietze, H.-J. *Int. J. Mass. Spectrom. Ion Process.* **1986**, *73*, 157.

(24) Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev.* **1988**, *37B*, 785.

(25) Becke, A. D. *J. Chem. Phys.* **1988**, *88*, 1053.

(26) Kohn, W.; Sham L. J. *Phys. Rev.* **1965**, *140*, 1133.

(27) Giuffreda, M. G.; Deleuze, M. S.; François, J.-P. *J. Phys. Chem.* **1999**, *103*, 5137.

(28) *Gaussian 98* (Revision A.6); Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Zakrzewski, V. G.; Montgomery Jr., J. A.; Stratmann, R. E.; Burant, J. C.; Dapprich, S.; Millam, J. M.; Daniels, A. D.; Kudin, K. N.; Strain, M. C.; Farkas, O.; Tomasi, J.; Barone, V.; Cossi, M.; Cammi, R.; Mennucci, B.; Pomelli, C.; Adamo, C.; Clifford, S.; Ochterski, J.; Petersson, G. A.; Ayala, P. Y.; Cui, Q.; Morokuma, K.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Cioslowski, J.; Ortiz, J. V.; Baboul, A. G.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Gonzalez, C.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Andres, J. L.; Gonzalez, C.; Head-Gordon, M.; Replogle, E. S.; Pople, J. A. Gaussian, Inc.: Pittsburgh, PA, 1998.

(29) Jahn, H. A.; Teller, E. *Proc. R. Soc.* **1937**, *A161*, 220.

(30) Herzberg, G. *Molecular Spectra and Molecular Structure. Infrared and Raman Spectra of Polyatomic Molecules*; van Nostrand Reinhold: New York, 1945. Kroto, H. W. *Molecular Rotation Spectra*; Dover Publications: New York, 1992.