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## Structures, Bonding, and One-Bond B–N and B–H Spin–Spin Coupling Constants for a Series of Neutral and Anionic Five-Membered Rings Containing BN Bonds

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**Abstract:** The structures and bonding of a series of five-membered rings with BN bonds  $C_xN_yB_zH_5$  ( $x + y + z = 5$ ) and their most stable deprotonated anions  $C_xN_yB_zH_4^-$  as well as anionic rings  $C_xN_yB_zH_5^-$  have been investigated at the MP2/6–311++G(d,p) level of theory. The great majority of these rings present BN bond orders close to that found in borazine, suggesting that there is substantial electron delocalization in these rings. This observation is also supported by both NBO and ELF analyses. Ab initio equation-of-motion coupled-cluster singles and doubles (EOM-CCSD) calculations have also been performed to obtain the  $^{15}\text{N}$ – $^{11}\text{B}$  and  $^1\text{H}$ – $^{11}\text{B}$  spin–spin coupling constants. For neutral systems, the former range from –10 to –35 Hz, thereby bracketing the value of  $^1\text{J}(\text{B–N})$  for borazine, which is –29 Hz.  $^1\text{J}(\text{B–N})$  spans an even greater range in the anions, from –3 to –36 Hz. The absolute value of  $^1\text{J}(\text{B–N})$  decreases upon deprotonation if coupling involves the deprotonated nitrogen or a boron atom bonded to the deprotonated N.  $^1\text{J}(\text{B–H})$  always decreases upon nitrogen deprotonation.

### Introduction

Boron is an element with quite unusual bonding properties<sup>1,2</sup> which arise from its intrinsic electron-deficient character and are reflected in the versatility of its chemistry. Many boron derivatives are widely used in synthesis because they are very good electrophiles. However, a novel synthesis recently produced a diazaborole five-membered ring with BN bonds and B acting as a nucleophilic center.<sup>3</sup> Other five-membered rings containing BN bonds have also been synthesized and characterized as suitable ligands.<sup>4,5</sup> They can replace the usual cyclopentadienyl ligand and form face-on sandwich complexes.<sup>5</sup> However, while the all-carbon ligands display almost exclusively  $\eta^5$  coordination, the BN-containing analogues exhibit variability in their coordination manner, and  $\eta^1$ ,  $\eta^2$ ,  $\eta^3$ , and  $\eta^4$  coordination modes have been

assigned.<sup>5</sup> The variability of the coordination modes appears to be closely related to BN bonding characteristics and electron delocalization due to the presence of BN bonds in the rings. In rings containing a NN bond instead, electron delocalization seems to be restricted to the NBCBN skeleton with no participation of the NN linkage.

We have recently been involved in a systematic study of the BN bond in different environments,<sup>2,6–8</sup> paying particular attention to bonding characteristics and  $^{11}\text{B}$ – $^{15}\text{N}$  coupling constants. In the present paper we present the results of the next logical extension of our studies to five-membered BN-containing rings. For this study we have considered both neutral and anionic rings containing at least one B–N bond and fully saturated valency. Only the most stable anion derived from one of the neutral rings by deprotonation has been included.

### Computational Details

The geometries of the BN rings were optimized at the MP2/6–311++G(d,p) level. Harmonic vibrational frequencies

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were calculated at the same level to confirm that the stationary points found are local minima on the corresponding potential energy surfaces. The bonding in these rings has been analyzed by means of the NBO partitioning technique,<sup>9</sup> the electron localization function (ELF) theory,<sup>10</sup> and the atoms in molecules (AIM) theory.<sup>11</sup> The NBO approach examines the bonding in terms of localized hybrids and lone pairs obtained as local block eigenvectors of the one-particle density matrix as well as in terms of the interactions between occupied and unoccupied MOs through a second-order perturbation analysis of the Fock matrix. These NBO calculations were carried out allowing for the detection of three-center bonding. The Wiberg bond orders were also evaluated in the framework of this approach. By means of the AIM theory we have located for each ring the different bond critical points (BCPs) that together with the bond paths define the molecular graph. At each BCP the electron density was also evaluated since it usually provides information about the nature and relative strengths of the bonds with which the BCP is associated. ELF<sup>10</sup> is a function which becomes large in regions of space where electron pairs, either bonding or lone pairs, are localized. Usually an ELF value around 0.80 defines isosurfaces which provide clear pictures of the regions of electron localization or attraction basins which may be related to key bonding concepts, such as core, valence, and lone-pair regions, while their populations have been related to bond order. ELF grids and basin integrations have been evaluated with the TopMod package.<sup>12</sup>

The one-bond  $^{11}\text{B}-^{15}\text{N}$  and  $^{11}\text{B}-^1\text{H}$  coupling constants were computed using the equation-of-motion coupled-cluster singles and doubles (EOM-CCSD)<sup>13–16</sup> method in the CI(configuration interaction)-like approximation with all electrons correlated. These calculations were carried out using the Ahlrichs<sup>17</sup> qzp basis set on C and N, the qz2p basis on H atoms bonded to B, and the cc-pVDZ basis set on the remaining H atoms.<sup>18,19</sup> Since an Ahlrichs qzp basis is not available for B, a new “hybrid” basis was constructed for this atom from the boron cc-pV5Z basis for s orbitals, the boron cc-pVQZ for p orbitals, and a single set of d polarization functions and used in previous studies<sup>6–8</sup> of systems containing BN bonds. The total coupling constant  $J$  is a sum of four terms: paramagnetic spin-orbit (PSO), diamagnetic spin-orbit (DSO), Fermi-contact (FC), and spin-dipole (SD). For selected molecules and anions, all terms were evaluated. However, because of the size and low-computational symmetry of the BN rings, only the FC term was evaluated and used to approximate total  $J$  for the majority of molecules and ions. That the FC term is a good approximation to total  $J$  for B–N and B–H coupling constants was observed previously in the study of the six-membered borazine rings<sup>6</sup> and is also evident from the data of Table 1. In general, the FC term overestimates the absolute value of  $^1J(\text{B}-\text{N})$  by about 2 Hz, the approximate contribution from the PSO term, and is an excellent approximation to  $^1J(\text{B}-\text{H})$ . Hence, in this paper, the FC term will be used to approximate total  $J$ . The level of theory used for these calculations has been shown to reproduce the experimental one-bond C–N coupling constants in the prototypical six-membered rings pyridine and pyridinium and the C–P

**Table 1.** B–N and B–H Total Coupling Constants ( $J$ , Hz) and Components of  $J$  for Selected Molecules and Ions

species	pair	PSO	DSO	FC	SD	$J$
<b>C2N2B_1</b>	N1–B2	2.34	–0.11	–32.40	–0.27	–30.45
<b>C2NB2_1</b>	N1–B2	2.24	–0.08	–25.75	–0.10	–23.70
<b>C2NB2_1_A</b>	N1–B2	2.80	–0.07	–15.64	–0.09	–13.00
<b>N3B2_2_A</b>	N1–B2	2.43	–0.10	–19.19	–0.37	–17.24
<b>N2B3_1</b>	N1–B2	1.78	–0.09	–29.62	–0.10	–28.03
	N3–B4	2.82	–0.08	–20.49	–0.12	–17.87
<b>C2N2B_1</b>	B2–H7	–0.82	0.99	145.30	0.31	145.77
<b>C2NB2_1</b>	B2–H7	–1.22	0.74	128.89	0.39	128.80
<b>C2NB2_1_A</b>	B2–H6	–1.15	0.79	108.88	0.20	108.71
<b>N3B2_2_A</b>	B2–H7	–0.40	0.78	104.95	0.11	105.44
<b>N2B3_1</b>	B2–H7	–1.12	0.89	134.37	0.40	134.55
	B4–H9	–1.31	0.64	122.68	0.28	122.28

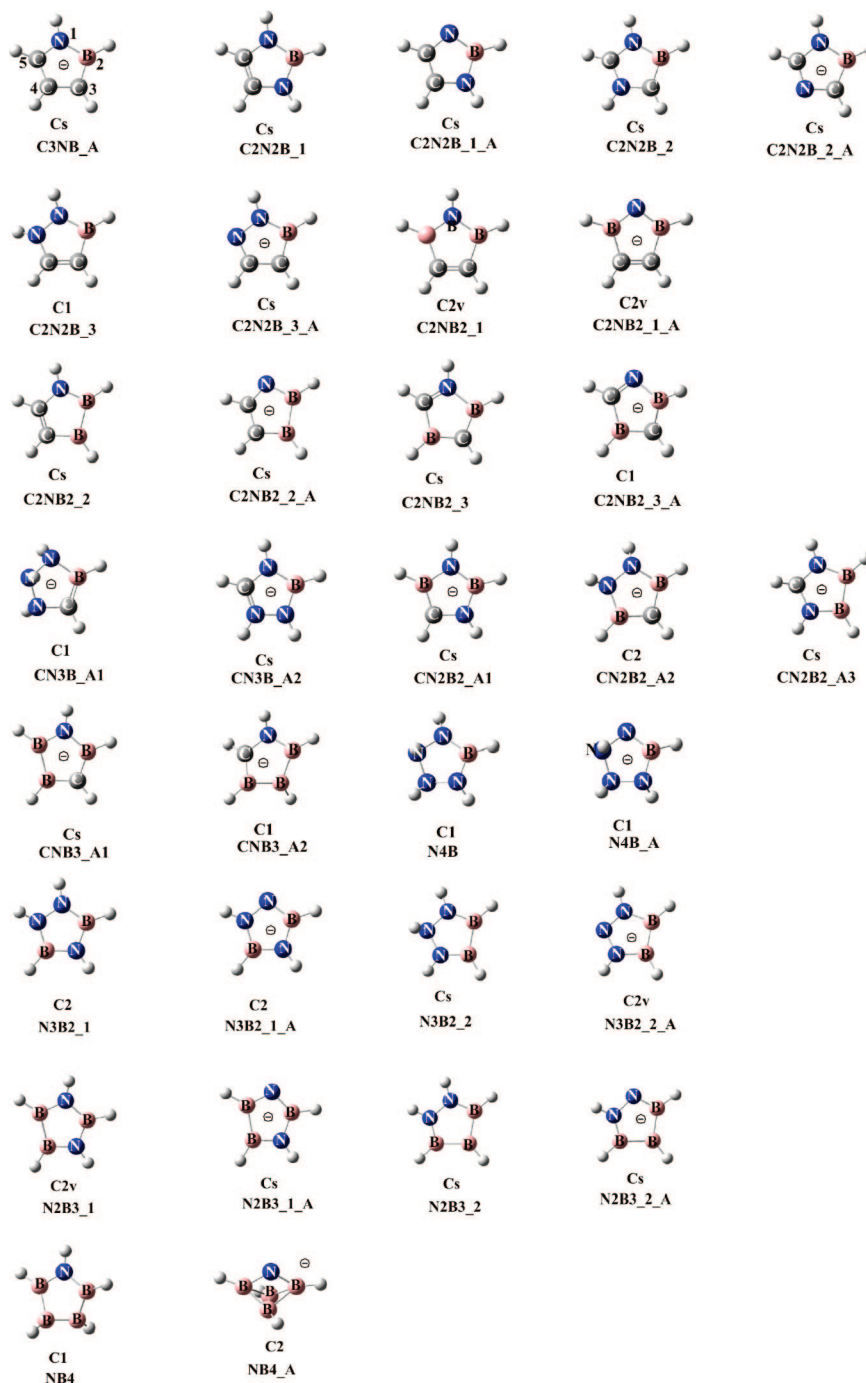
coupling constant in phosphinine.<sup>20</sup> In addition, the computed B–H coupling constant in newly synthesized diazaborole is in agreement with the experimental value of  $^1J(\text{B}-\text{H})$ .<sup>8</sup> Finally, good agreement between experimental and computed coupling constants has been found for a series of molecules  $\text{H}_m\text{X}-\text{YH}_n$  and selected F-derivatives.<sup>21</sup> Coupling constant calculations were carried out using ACES II<sup>22</sup> on the Itanium cluster at the Ohio Supercomputer Center.

## Structures and Bonding

A total of 32 neutral and anionic five-membered BN-containing rings with the general formulas  $\text{C}_x\text{N}_y\text{B}_z\text{H}_5$  ( $x + y + z = 5$ ), their most stable deprotonated anions  $\text{C}_x\text{N}_y\text{B}_z\text{H}_4^-$ , and anionic rings  $\text{C}_x\text{N}_y\text{B}_z\text{H}_5^-$  have been investigated, although calculations on additional anions obtained by deprotonation of the neutral rings were carried out so that the most stable anion could be identified. A systematic identification scheme has been developed so that the neutral molecules are listed in order of decreasing number of carbon atoms, and for a given number of carbons, decreasing number of nitrogen atoms **CxNyBz**. If a particular compound has more than one isomer, these are listed in order of relative stability, indicated by a number. For example, **N3B2\_1** is more stable than **N3B2\_2**. Anionic species have the letter **A** added to the label, as in **C2N2B\_1\_A**. Figure 1 presents the five-membered rings investigated in this study and illustrates the atom numbering adopted so that each ring has an N1–B2 bond. Usually, N1 is also the deprotonated nitrogen. An anion **CN3B\_A2** originally considered for inclusion was eliminated from this study because it presents a RHF-UHF instability, thereby invalidating both MP2 and EOM-CCSD calculations.

The Wiberg bond orders for HBNH (2.140),  $\text{H}_2\text{BNH}_2$  (1.257),  $\text{H}_3\text{BNH}_3$  (0.625), and borazine (1.011) as paradigmatic examples of triple, double, single, and aromatic BN bonds, respectively, are suitable references for the discussion which follows. The Wiberg bond orders (BOs) as well as the bond lengths for the neutral and anionic five-membered rings investigated in this study are summarized in Table 2.

In general, B and N should be expected to form double bonds because of the electron deficient character of the B atom, which facilitates N lone pair donation into the empty 2p orbital of B. This expectation is consistent with the relative stabilities of the isomers of **C2N2B** and **C2NB2** and anions  $\text{C}_x\text{N}_y\text{B}_z\text{H}_5^-$ , since the most stable isomer has the most



**Figure 1.** Five-member BN-containing rings with the numbering system illustrated in **C3NB\_A**.

BN bonds. Nevertheless, in most systems the BN bonds have BOs close to those in borazine, indicating a certain amount of electron delocalization.

As we shall discuss later in more detail, the NBO analysis reveals that some systems exhibit a clear electron delocalization through the participation of three-center bonds. Some others present what might appear to be more localized BN double bonds, but interactions involving these bonds with adjacent atoms in the rings result in BN bonds that still resemble those of borazine, with BOs close to 1.0 rather than 1.26. Why are the bond orders less than expected even though there exist both  $\sigma$  and  $\pi$  bonding components? This is a consequence of the extreme polarity of the BN bond. A particular BN bond can be either an electron donor since N

is electron rich or an electron acceptor because B is electron poor. In the first case charge transfer can occur from a BN bonding orbital to an electron acceptor within the ring, normally a C or a B atom, and this leads to a decrease in the population of this bonding orbital and a decrease in the BO. In the second case, there is charge donation from an N electron donor within the ring into a BN antibonding orbital. The increased population of this antibonding orbital also leads to a decrease of the BO. Only when these interactions are weak does the BO approach the BO of  $\text{H}_2\text{N}=\text{BH}_2$ .

As mentioned above, several systems are characterized by the presence of three-center bonds. A three-center CNB bond is found in **C3NB\_A** and **C2NB2\_2** and its anion; NBN in **C2NB2\_1** and its anion and **CN2B2\_A1**; CCB in **C2NB2\_3**

**Table 2.** Relative Enthalpies ( $\Delta H^\circ$ , kJ mol<sup>-1</sup>),<sup>a</sup> B–N and B–H Distances (R, Å), Wiberg Bonds Orders (BO), and Coupling Constants (FC, Hz) for Neutral and Anionic Five-Membered BN-Containing Rings

species	bond	neutral				anion			
		$\Delta H^\circ$	R	BO	FC	$\Delta H^\circ$	R	BO	FC
<b>C3NB_A</b>	N1–B2						1.470	0.99	–25.7
<b>C2N2B_1</b>	N1–B2	0.0	1.433	1.06	–32.4		1.426	1.27	–19.5
	B2–N3		1.433	1.06	–32.4		1.465	0.98	–24.1
<b>C2N2B_2</b>	N1–B2	123	1.468	0.97	–22.5		1.473	0.96	–25.3
<b>C2N2B_3</b>	N1–B2	182	1.427	1.10	–28.7		1.452	1.06	–27.3
<b>C2NB2_1</b>	N1–B2	0.0	1.438	0.99	–25.8		1.416	1.24	–15.6
<b>C2NB2_2</b>	N1–B2	181	1.422	1.05	–24.8		1.446	0.95	–12.7
<b>C2NB2_3</b>	N1–B2	199	1.609	0.63	–10.4		1.548	0.80	–7.9
<b>CN3B-A1</b>	N1–B2						1.528	0.84	–15.0
<b>CN2B2_A1</b>	N1–B2					0.0	1.437	1.07	–31.8
	B2–N3						1.430	1.10	–35.4
	N1–B5						1.494	0.91	–21.2
<b>CN2B2_A2</b>	N1–B2					128	1.473	0.96	–22.5
<b>CN2B2_A3</b>	N1–B2					174	1.472	1.03	–18.4
<b>CNB3_A1</b>	N1–B2					0.0	1.494	0.83	–23.0
	N1–B5						1.430	1.07	–21.3
<b>CNB3_A2</b>	N1–B2					232	1.408	1.16	–25.1
<b>N4B</b>	N1–B2		1.414	1.09	–34.8		1.386	1.50	–19.0
	B2–N3		1.444	1.02	–27.0		1.514	0.84	–14.6
<b>N3B2_1</b>	N1–B2	0.0	1.424	1.10	–32.7		1.411	1.41	–20.9
	B2–N3		1.440	1.02	–28.7		1.484	0.91	–20.5
	N3–B4		1.440	1.02	–28.7		1.438	1.05	–32.1
	B4–N5		1.424	1.10	–32.7		1.421	1.15	–35.7
<b>N3B2_2</b>	N1–B2	341	1.407	1.19	–25.9		1.467	1.09	–19.2
<b>N2B3_1</b>	N1–B2	0.0	1.451	0.94	–29.6		1.418	1.19	–17.0
	B2–N3		1.451	0.94	–29.6		1.509	0.79	–19.2
	N3–B4		1.430	1.07	–20.5		1.422	1.13	–22.2
	N1–B5		1.430	1.07	–20.5		1.419	1.30	–14.6
<b>N2B3_2</b>	N1–B2	410	1.400	1.23	–29.7		1.403	1.32	–18.5
	B4–N5		1.400	1.23	–29.7		1.395	1.55	–29.8
<b>NB4<sup>b</sup></b>	N1–B2		1.446	1.01	–18.2		1.474	0.96	–3.0

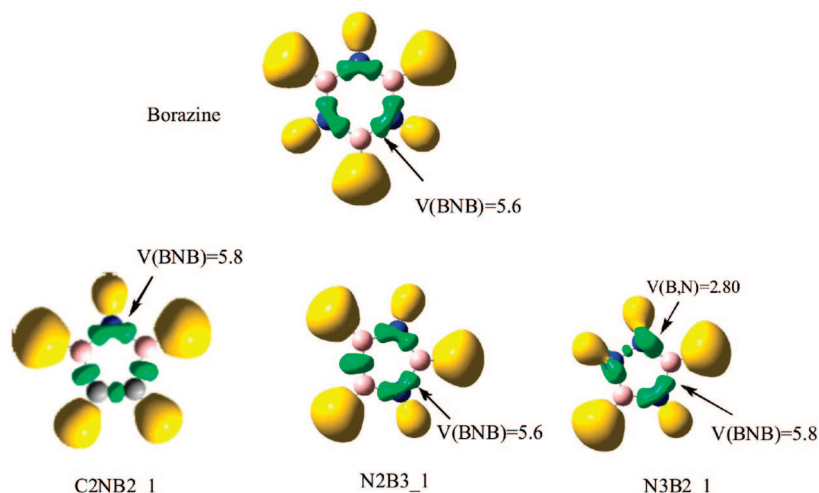
species	bond	neutral		anion	
		R	FC	R	FC
<b>C3NB_A</b>	B2–H			1.207	108.3
<b>C2N2B_1</b>	B2–H	1.185	145.3	1.207	120.6
<b>C2N2B_2</b>	B2–H	1.187	137.1	1.204	112.2
<b>C2N2B_3</b>	B2–H	1.188	134.0	1.205	110.8
<b>C2NB2_1</b>	B2–H	1.192	128.9	1.221	108.9
<b>C2NB2_2</b>	B2–H	1.191	126.8	1.215	106.0
	B3–H	1.193	122.6	1.211	101.7
<b>C2NB2_3</b>	B2–H	1.192	136.6	1.213	109.5
	B4–H	1.194	128.1	1.215	103.4
<b>CN3B-A1</b>	B2–H			1.205	111.8
<b>CN2B2_A1</b>	B2–H			1.204	116.5
	B5–H			1.207	108.3
<b>CN2B2_A2</b>	B2–H			1.213	102.7
<b>CN2B2_A3</b>	B2–H			1.210	101.9
<b>CNB3_A1</b>	B2–H			1.218	98.7
	B4–H			1.218	95.1
	B5–H			1.218	94.6
<b>CNB3_A2</b>	B2–H			1.211	102.5
	B3–H			1.216	95.1
	B4–H			1.209	107.3
<b>NB4</b>	B2–H	1.184	145.6	1.205	121.5
<b>N3B2_1</b>	B2–H	1.187	141.4	1.206	118.7
	B4–H	1.187	141.4	1.202	118.5
<b>N3B2_2</b>	B2–H	1.190	126.7	1.207	104.9
<b>N2B3_1</b>	B2–H	1.191	134.4	1.219	113.3
	B4–H	1.194	122.7	1.216	97.8
	B5–H	1.194	122.7	1.224	104.5
<b>N2B3_2</b>	B2–H	1.192	126.9	1.213	107.3
	B3–H	1.192	119.7	1.211	96.3
	B4–H	1.192	126.9	1.208	106.5
<b>NB4<sup>a</sup></b>	B2–H	1.192	132.1	1.190	160.5
	B3–H	1.189	137.0	1.191	158.8

<sup>a</sup>  $\Delta H^\circ = \Delta E^\circ + \Delta ZPE$ . <sup>b</sup> The structures of neutral and deprotonated **NB4** are very different. In the neutral ring, N1–B2 and N1–B5 are equivalent. In the anion, N1–B2 and N1–B4 are equivalent.

and its anion, **CN2B2\_A2**, and **CNB3\_A1**; and BNB in **C2NB2\_1** and its anion. Thus, the similarity between the BNB bonding pattern for **C2NB2\_1** and borazine, for instance, is nicely reflected in their corresponding ELF

descriptions, as illustrated in Figure 2. Bonding in **NB4** involves three-center BBB bonds. The BOs for rings with three-center bonds are close to 1.0 as in borazine, but there are some exceptions. The most obvious is **C2NB2\_3** and its





**Figure 2.** Three-dimensional representations of ELF isosurfaces with ELF = 0.80 for borazine and selected five-membered BN-containing rings. Yellow lobes correspond to  $V(\text{C,H})$  or  $V(\text{N,H})$  basins. Green lobes correspond to  $V(\text{C,C})$ ,  $V(\text{C,N})$ ,  $V(\text{B,N})$ , and  $V(\text{N,N})$  basins. Populations of  $V(\text{B,N})$  basins are also indicated.

anion, both of which exhibit a three-center  $\text{B2C3B4}$  bond and have N1 doubly bonded to C5. The existence of this double bond impedes conjugation between N1 and B2 with the result that the N1B2 bond in the neutral ring is the longest BN bond in the series and has the smallest BO of 0.63. B2–N1 conjugation increases slightly upon deprotonation of N1, as reflected by a BO of 0.80 in the anion, which, nevertheless, still has the longest BN bond and the smallest BO among the anions.

In all the remaining cases in which the rings present one BN bond or two equivalent BN bonds, the NBO analysis gives two components, one  $\sigma$  and one  $\pi$ . When the system presents two pairs of equivalent BN bonds, as in **N3B2\_1**, two of the bonds appear as double bonds (N1B2 and N5B4) and two (N3B2 and N3B4) as single bonds in the NBO analysis. As mentioned above, the tendency of B and N to form double bonds is due to the electron deficient character of the B atom, which facilitates N lone pair donation into the empty 2p orbital of B. These BN double bonds involve an electron rich N atom which makes a large contribution (about 80%) to the BN bonding molecular orbital. Nevertheless, although the BN bonds might appear to be typical BN double bonds as in  $\text{H}_2\text{BNH}_2$ , interactions with other atoms in the ring lead to a significant electron delocalization and to BOs similar to those of borazine. Another interesting example is found for **CN2B2\_A3**. In this molecule there is a strong charge donation from the N1B2 and N4B3  $\pi$  bonding orbitals to C5, a good electron acceptor. This favors the conjugation of C5 with the neighboring N atoms and is reflected in a CN bond order of 1.2. This donation reduces the electron population of the BN  $\pi$  orbital, and the BO of this bond approaches that of borazine. A similar change is observed for **N2B3\_1** as charge is transferred from the  $\pi$  B5N1 and B4N3 bonding orbitals into the B2 empty 2p orbital, which enhances its conjugation with N1 and N3. Hence, relative to a single bond, the N1B2 and B2N3 bonds acquire some double bond character, while the N3B4 and B5N1 bonds lose double bond character, and the BOs of both sets of bonds approach that of borazine. The ELF descriptions

**Table 3.** Intrinsic Acidities ( $\Delta_{\text{acid}}H^\circ$ ,  $\text{kJ mol}^{-1}$ ) of the Neutral Five-Membered BN Rings

molecule	$\Delta_{\text{acid}}H^\circ$
<b>C2N2B_1</b>	1551
<b>C2N2B_2</b>	1471
<b>C2N2B_3</b>	1441
<b>C2NB2_1</b>	1556
<b>C2NB2_2</b>	1514
<b>C2NB2_3</b>	1527
<b>N4B</b>	1538
<b>N3B2_1</b>	1528
<b>N3B2_2</b>	1440
<b>N2B3_1</b>	1558
<b>N2B3_2</b>	1499
<b>NB4</b>	1417

of all of the BN bonds in this system closely resemble that of borazine, as can be seen in Figure 2.

A similar but much weaker effect is observed in **N2B3\_2** because in this ring the acceptor boron atom B3 is bonded to two B atoms and has a natural charge of +0.19e (as compared to +0.81e for B2 in **N2B3\_1**). Thus, electron donation from the BN bonds to B3 is minimal, and both BN bonds of **N2B3\_2** exhibit double bond character with BOs close to 1.26, the BO of  $\text{H}_2\text{B}=\text{NH}_2$ . On the other hand, **N3B2\_1** provides an example in which the N1B2 and N5B4 bonds act as electron acceptors through lone pair donation from the N3 lone-pair into  $\pi_{\text{BN}}^*$  antibonding orbitals. This leads to a decrease of the BOs of the N1B2 and N5B4 bonds and an increase in the BOs of the N3B2 and N3B4 bonds. The net result is that the ELF descriptions of the B2N3B4 fragment closely resemble that of borazine, as illustrated in Figure 2. A similar effect is found in **N3B2\_2**, but it is significantly reduced since the electron donor is directly attached to the two electron-rich N atoms.

As expected, the most acidic site of a neutral BN ring is a NH group. The calculated intrinsic acidities, defined as the enthalpy at 0 K of reaction 1, are summarized in Table 3. All values are typically in the 1440–1560  $\text{kJ mol}^{-1}$  range, with **NB4** the only exception, most likely a reflection of the

## Scheme 1



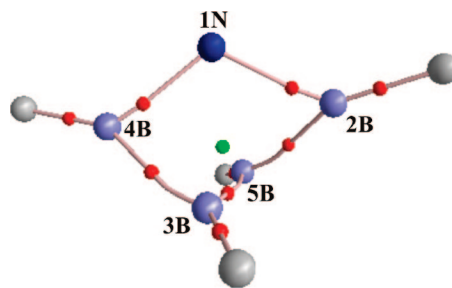
dramatic structural rearrangement that takes place upon deprotonation, as discussed below.



The question to be addressed at this point is how do the bonding patterns found for molecules change when the most acidic N–H proton is removed to form the anion. Two groups of molecules can be distinguished: those in which the deprotonated nitrogen atom participates in a BN bond and those in which the deprotonated N atom is not bonded to a B atom. Among the molecules in the first set are **C2N2B\_1**, **N3B2\_1**, **N2B3\_1**, and **N2B3\_2**. For these, the deprotonation process is accompanied by a lowering of symmetry as two BN bonds which are equivalent in the molecule are no longer equivalent in the anion. **C2N2B\_1** serves as a typical example. The N1B2N3 bonds in this molecule are three-center bonds. The orbitals involved in bonding are illustrated in Scheme 1. The first is completely bonding, while the second is BN nonbonding and NN antibonding. In contrast, in the anion the B 2p orbital contributes to the second three-center N1B2N3 orbital which then becomes B2N3 antibonding and B2N1 bonding. Hence, upon deprotonation the B2N3 BO decreases from 1.06 to 0.98, whereas the B2N1 BO increases from 1.06 to 0.98, whereas the B2N1 BO increases from 1.06 to 0.98.

Also included in the first set are the molecules **N4B** and **NB4**, both of which experience dramatic structural and bonding changes upon deprotonation. In both neutral molecules all of the BN bonds have BOs near 1.0. Deprotonation of **N4B** occurs at N1 and reduces conjugation with N3. As a result, the N1B2 BO increases, and the electron density at the BCP also increases dramatically from 0.196 au to 0.227 au, while the B2N3 BO decreases and the electron density at the BCP also decreases from 0.201 au to 0.165 au. In **NB4\_A**, a reinforcement of the N1B2 and N1B5 bonds upon deprotonation might be expected, but since the molecule contains four electron deficient centers, electron delocalization involves all of the atoms and leads to significant distortion of the five-membered ring. The molecular graph for the resulting anion which is given in Figure 3 shows bond paths only for N1B2 and N1B4. There is also a slight reduction in BOs, consistent with bond lengths of 1.473 Å. The other two BN interactions, N1B5 and N1B3, are across much longer distances of 1.798 Å and are essentially nonbonding. B3B4 and B2B5 are bonded, but no BCPs are associated with B4B5 and B2B3 at distances of 1.859 Å, so there are no B–B bonds in these two cases.

There is only one molecule, **C2NB2\_1**, for which deprotonation of the N atom participating in the BN bond is not accompanied by a symmetry change. In this case N1 deprotonation enhances conjugation of the nitrogen atom with the two neighboring B atoms. The BN BOs increase, and the electron densities at the BCPs also increase from 0.195 au to 0.215 au.



**Figure 3.** Molecular graph of **NB4\_A**. Red dots denote (3,-1) BCPs, and the green dot a (3,+3) cage critical point.

The second group of molecules are those in which the deprotonated nitrogen is not bonded to a B atom. The molecules **C2N2B\_2** and **N3B2\_2** and their anions illustrate two extremes in bonding changes. In **C2N2B\_2** deprotonation of N4 alters the conjugation of N4 with the two C atoms directly bonded to it but has only a small effect on the remote N1B2 bond. The N1B2 BO for the anion is essentially identical to that for the neutral molecule. In contrast, deprotonation of N5 in **N3B2\_2** has a significant but indirect effect on the BN bonds. In the anion, conjugation of N5 with the two N atoms directly bonded to it increases at the expense of reduced conjugation of N1 with B2 and N4 with B3. An increase in the BN bond distance and a decrease in BO are observed.

**Spin–Spin Coupling Constants.** Table 2 reports the FC terms for one-bond B–N and B–H coupling in the set of neutral and anionic five-membered rings. The values of  $^1J(\text{B–N})$  vary considerably and are always negative. Since the magnetogyric ratio of  $^{11}\text{B}$  is positive and that of  $^{15}\text{N}$  is negative, the reduced coupling constant  $^1K(\text{B–N})$  is positive and therefore in agreement with the Dirac vector model.<sup>23</sup> For the neutral rings,  $^1J(\text{B–N})$  ranges from –10.4 Hz in **C2NB2\_3** to –34.8 Hz in **N4B**, thereby bracketing the value of  $^1J(\text{B–N})$  for borazine which is –28.7 Hz.  $^1J(\text{B–N})$  spans an even greater range in the anions, from –3.0 to –35.7 Hz. It is interesting to note that the smallest absolute value of  $^1J(\text{B–N})$  among neutral molecules is found for **C2NB2\_3**, which has the weakest B–N bond. Among the anions, the smallest absolute value is found for **NB4\_A**, which is structurally unique. Nevertheless, closer examination of  $^1J(\text{B–N})$  for these systems indicates that there is no overall correlation between the value of this coupling constant and either the BN distance or the BN bond order. This is readily illustrated using the bond orders and B–N coupling constants for the N1–B2 bonds in **C2N2B\_3** and **N3B2\_1** as references. Both N1–B2 bonds have BOs of 1.10 and corresponding values of  $^1J(\text{N1–B2})$  of –28.7 and –32.7 Hz, respectively. The N1–B2 bonds in **N3B2\_2** and **C2N2B\_2** have larger (1.19) and smaller (1.05) BOs, respectively, but the corresponding coupling constants are similar (–25.9 and –24.8 Hz) and reduced relative to the reference values. The lack of correlation between coupling constants and ground-state distances and bond orders is neither new nor surprising, since coupling constants are second-order properties which depend on electron distributions in both the ground state and the excited electronic states which couple to it primarily through the FC operator.

Are there any systematic trends among these coupling constants? The data of Table 2 indicate that the absolute value of  $^1J(\text{B}-\text{N})$  decreases in the anion relative to the corresponding neutral ring if coupling involves the deprotonated N or a B atom bonded to a deprotonated N. However, if this is not the case, then  $^1J(\text{B}-\text{N})$  may increase or decrease upon deprotonation. For example,  $^1J(\text{N1}-\text{B2})$  for **C2N2B\_3** and **N3B2\_2** decrease in absolute value when N5 is deprotonated, while  $^1J(\text{B4}-\text{N5})$  for **N3B2\_1** and **N2B3\_2** increase in absolute value when N1 is deprotonated.

Why does  $^1J(\text{B}-\text{N})$  decrease when the coupled N is deprotonated or when the coupled B is bonded to a deprotonated N? Some insight into the answer to this question can be gained by noting that nitrogen deprotonation replaces an N-H bond with a nonbonding pair of electrons. The decrease in  $^1J(\text{B}-\text{N})$  which is observed is consistent with the change in  $^1J(\text{N}-\text{C})$  upon protonation of pyridine.<sup>20</sup> The experimental and computed EOM-CCSD values of  $^1J(\text{N}-\text{C})$  for neutral pyridine are quite small at 0.67<sup>24</sup> and 0.53<sup>20</sup> Hz, respectively. The FC contribution to  $^1J(\text{N}-\text{C})$  is -4.3 Hz and is counterbalanced by a PSO contribution of 5.5 Hz. In pyridinium, the absolute value of  $^1J(\text{N}-\text{C})$  increases, with experimental and computed values of -12<sup>24</sup> and -15<sup>20</sup> Hz, respectively. In the ion, the FC term increases in absolute value to -18.3 Hz and dominates the PSO term which decreases slightly to 4.2 Hz. The change in the FC term for one-bond N-C coupling is associated with s-electron density differences in the ground and excited electronic states of pyridine and pyridinium. From a sum-overstates perspective, the particular excited  $\sigma$ -type states which dominate and determine the FC term are most probably quite different depending on the presence or absence of a heteroatom with a lone pair of electrons. Thus, the presence of nonbonding electrons plays an important role in determining both the sign and magnitude of the N-C coupling constant in pyridine and pyridinium. In the BN rings, the FC term is an excellent approximation to J, and the presence or absence of a lone pair on N has a major impact on  $^1J(\text{B}-\text{N})$  when the coupled N is deprotonated or when the B is bonded to a deprotonated N.  $^1J(\text{B}-\text{N})$  decreases when the N-H bond is replaced by a nitrogen nonbonding pair of electrons.

The B-H coupling constant  $^1J(\text{B}-\text{H})$  is always positive and varies from 120 to 146 Hz in the neutral rings and from 95 to 119 Hz in the anions (excluding **NB4\_A**).  $^1J(\text{B}-\text{H})$  always decreases in the anion relative to the corresponding base, independent of whether or not the coupled B is bonded to the deprotonated N. The only exceptions are  $^1J(\text{B2}-\text{H3})$  and  $^1J(\text{B3}-\text{H4})$  for **NB4** which increase significantly upon deprotonation and, at approximately 160 Hz, are the largest B-H coupling constants found in the entire set of neutral and anionic rings. However, it should be noted that neutral and deprotonated **NB4** are significantly different structurally and that  $^1J(\text{N1}-\text{B2})$  in the anion is only -3.0 Hz and therefore smaller than any other B-N coupling constant.

## Conclusions

In this study, the structural, bonding, and NMR spectroscopic properties of a series of five-membered neutral and anionic rings containing BN bonds  $\text{C}_x\text{N}_y\text{B}_z\text{H}_5$  ( $x + y + z = 5$ ), their

most stable deprotonated anions  $\text{C}_x\text{N}_y\text{B}_z\text{H}_4^-$ , and anionic rings  $\text{C}_x\text{N}_y\text{B}_z\text{H}_5^-$  have been examined. In the majority of these rings there is significant electron delocalization which leads to BOs close to that found in borazine which contains the prototypical aromatic BN bond. Only in a few systems are localized B=N double bonds found. Electron delocalization in these rings is favored by the strong polarity of the BN bonds, which behave either as electron donors or as electron acceptors depending on their bonding environment in the ring. Some significant bonding changes are found upon deprotonation of the neutral rings. In most cases these changes accompany a loss of symmetry which occurs with proton elimination.

Computed one-bond  $^{15}\text{N}-^{11}\text{B}$  spin-spin coupling constants range from -10.4 to -34.8 Hz in the neutral rings, thereby bracketing the value of  $^1J(\text{B}-\text{N})$  for borazine, -28.7 Hz.  $^1J(\text{B}-\text{N})$  spans an even greater range in the anions, from -3.0 to -35.7 Hz. The absolute value of  $^1J(\text{B}-\text{N})$  decreases upon deprotonation if coupling involves the deprotonated nitrogen or a boron atom bonded to the deprotonated N.  $^1J(\text{B}-\text{H})$  always decreases in the anion relative to the corresponding neutral ring.

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