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An Ab Initio Study of the Structures and Selected Properties of 1,2-Dihydro-1,2-azaborine and Related Molecules

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Abstract: An ab initio study has been carried out to investigate the effect of replacing $[\text{HC}-\text{CH}]_n$ linkages in benzene by the isoelectronic $[\text{HN}-\text{BH}]_n$ linkages for $n = 1, 2$, and 3 . Such replacements give rise to azaborine, a set of diazaborines, borazine, and pseudoborazine. These replacements lead to significant rearrangements of electron densities in these molecules due primarily to the introduction of the polar B–N bond. As a result, azaborine and diazaborines exhibit much more localized structures than that of benzene. They are also less aromatic than benzene but have a higher degree of aromaticity than borazine. The bonding patterns can be related to the relative stabilities of the diazaborines. Among these molecules, the most stable isomer contains an N–B–N–B linkage, while the two least stable isomers have either a B–B or a N–N bond. Changes in bonding patterns are also reflected in changes in the N1–B2 coupling constant. When N1 and B2 are bonded to the less electronegative atoms C and B, $^1J(\text{N1}-\text{B2})$ increases relative to borazine, but when either N1 or B2 is bonded to N, $^1J(\text{N1}-\text{B2})$ decreases. Computed NMR chemical shifts and coupling constants are in good agreement with available experimental data.

1. Introduction

There has been a long-standing fascination with molecules in which a HC–CH group is replaced by a HB–NH one, giving an isoelectronic molecule with a B–N bond. A fundamental question is how similar or dissimilar are these two molecules?¹ Obviously, the C–C bond is nonpolar while the B–N bond is very polar, since the B atom is significantly less electronegative than the C atom, whereas the N atom has a higher electronegativity. The introduction of the polar B–N bond can significantly alter the electronic properties of the system. For example, while graphite has a very high

conductivity, the isoelectronic boron nitride, which has the graphite structure, is an insulator. Moreover, in a previous paper,² we have shown that substituent effects on the bonding properties and vibrational frequencies of iminoboranes are not only different but also opposite at times to substituent effects on the corresponding acetylene derivatives. The dissimilarities between acetylene and iminoborane derivatives are primarily a consequence of the difference in the electronegativities of B and N, which leads to a significant distortion of electron density in the B–N bonding region compared to that of the C–C region.

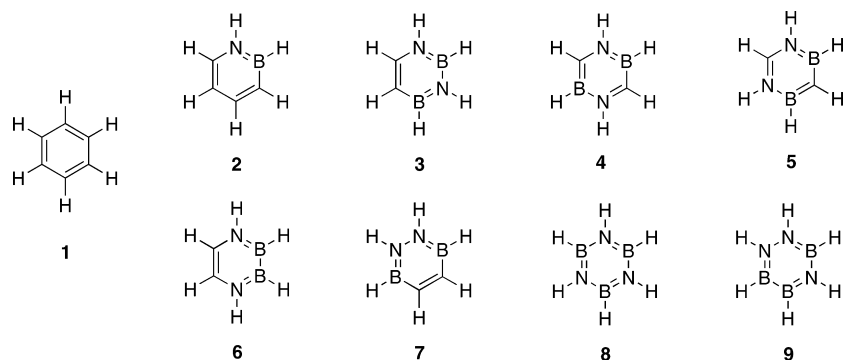
Of particular interest is the replacement of one HC–CH group of benzene (**1**) by one HN–BH group to form 1,2-dihydro-1,2-azaborine (**2**),^{3,4} or the replacement of two HC–CH groups by two HN–BH groups to form the diazaborines (**3–7**) and three HC–CH groups to give borazine (**8**) or pseudoborazine (**9**). These molecules are

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Chart 1. Benzene and the Azaborines

shown in Chart 1. It is interesting to note that while borazine (**8**) has been known experimentally since 1926,⁵ 1,2-dihydro-1,2-azaborine (**2**) was only recently prepared in 2008 by Liu et al.¹ and subsequently investigated by other authors.^{6–8} On the basis of their theoretical and experimental data, these authors concluded that 1,2-azaborine has significant aromaticity.⁸

The number of compounds which have substituents on the N and B atoms of rings containing B–N bonds are legion,^{9,10} but the parent compounds in which only H atoms are present are not common. For the most part, studies of such molecules have been restricted to theoretical investigations. A MP2/6-31G(d) study of azaborines, including **2**, was reported by Kranz and Clark,¹¹ who concluded that these compounds present a considerable degree of electron delocalization. The most stable isomer arises when B and N are directly bonded (1,2), with the stability decreasing in the order of 1,2 (**2**) \gg 1,4 > 1,3. According to Schleyer et al., borazine (**8**) is nonaromatic due to the polar BN bonds and shows little or no evidence of ring currents.¹² In contrast, the harmonic oscillator model of aromaticity (HOMA) and Bird aromaticity indexes calculated by Krygowski and co-workers indicate that the aromaticity of borazine (**8**) is only slightly less than that of benzene.¹³ Kar, Elmore, and Scheiner carried out MP2/6-31+G(d,p) studies of B- and N-containing molecules, including several of those illustrated in Chart 1, and concluded that molecules with adjacent B–N bonds are more stable than other isomers.¹⁴ Consistent with this, Dixon and co-workers concluded that **2** was aromatic on the basis of high-level computational data and experimental results.⁸ Doerksen and Thakkar calculated the vibrational frequencies and polarizabilities of the compounds shown in Chart 1 as well as azaborinines with nonadjacent B and N atoms.¹⁵ In 2009, Bosdet and Piers published a review in which molecule **2** and N- and/or B-substituted derivatives are described as well as the structures of molecules related to **3** and **5–7**.¹⁶ Didehydro derivatives (benzyne derivatives) of some of the molecules in Chart 1 were investigated by Fazen and Burke at various levels of theory up to and including coupled-cluster singles and doubles method, CCSD(T).¹⁷ Ab initio calculations up to and including CCSD(T)/CBS have been used to obtain reliable thermochemical data for borazine and related derivatives.¹⁸ We previously reported an investigation of neutral and anionic BN-containing five-member rings and found that they exhibit a significant degree of electron delocalization.¹⁹ In the present paper, we extend our studies

of BN-containing molecules and report a systematic analysis of the structures, energies, bonding, aromaticity, and NMR properties of six-member rings (**2–9**) containing one, two, or three HB–NH groups.

2. Theoretical Methods and Computational Details

Molecular geometries have been optimized at second-order Møller–Plesset perturbation theory (MP2)^{20–23} with the 6-311+G(d,p) basis set.^{24,25} Frequency calculations were performed to confirm that these structures are local minima on their potential surfaces. Improved energies were obtained using the composite G3B3 method implemented in Gaussian-03. All calculations were carried out using the Gaussian-03 package.²⁶

The electron densities of these molecules have been analyzed using the atoms in molecules (AIM) theory as implemented in the AIMPAC²⁷ and AIMAll programs.²⁸ Calculations of atomic properties were carried out by integration within the atomic basins using the default parameters in these packages, except in those cases where the integrated Laplacian was less than 1×10^{-3} au, and tighter criteria was employed. Previous reports have shown that small errors can occur in the energy and charges of systems if the values of the integrated Laplacian are less than those of the default parameters.²⁹

Further analyses of the bonding in these systems were carried out by means of the natural bond orbital (NBO) method.³⁰ This method offers a picture of the bonding of a given compound as a combination of localized hybrids and lone pairs, which can be obtained by block-diagonalizing the one-particle density matrix. In this analysis, we have allowed for the detection of three center bonds, which are rather common in B-containing compounds. Further insight into the bonding characteristics was obtained by examining interactions between occupied and unoccupied molecular orbitals (MOs) through a second-order perturbation analysis of the Fock matrix and computing Wiberg bond orders. Since the systems under investigation may have significant aromatic character, we have also used the natural resonance theory (NRT)³¹ to estimate the contributions of different resonance structures and the corresponding delocalization energy. The delocalization energy is defined as

$$E_{\text{deloc}} = E_{\text{total}} - E_{\text{Lewis}} \quad (1)$$

where E_{total} is the total energy of the compound, and E_{Lewis} is the energy of a hypothetical Lewis molecule with strictly localized bonds. E_{Lewis} is obtained by removing all off-diagonal elements from the Fock matrix and computing one self-consistent field (SCF) cycle.

The absolute chemical shieldings have been calculated at MP2/6-311+G(d,p) with the GIAO computational method, as implemented in Gaussian-03. The nuclear independent chemical shift (NICS), an aromaticity index based on magnetic criteria, has been evaluated for molecules **1–9**. This index is defined as the negative absolute magnetic shielding computed at the center of the ring.³² The NICS(1) index is calculated 1 Å above the ring center.³³ Rings with highly negative NICS values are aromatic, whereas those with positive values are antiaromatic. The so-called *para*-delocalization index (PDI), proposed by Solà and co-workers, has also been evaluated.³⁴ This index is defined as the average of Bader's electron delocalization index (DI) of atoms, which are in *para* positions in six-member rings. This index has been found to correlate strongly with HOMA, the latter being inapplicable for the molecules of interest in this study because of the lack of reference values for B–N bonds.

Spin–spin coupling constants were computed for molecules **2–9** using the equation-of-motion coupled-cluster singles and doubles method (EOM-CCSD) in the configuration interaction (CI)-like approximation^{35–38} with all electrons correlated. The Ahlrichs qzp basis set³⁹ was used on ^{13}C and ^{15}N atoms, and the qz2p basis set was used for all ^1H atoms. The recently constructed hybrid basis set was used for ^{11}B .² This basis set has the same number of contracted functions (6s, 4p, and 1d) as the Ahlrichs qzp basis for C and N and was used previously in studies of B–N, B–H, and B–Li coupling constants.^{40–43} In the nonrelativistic approximation, the nuclear spin–spin coupling constant is composed of four terms: the paramagnetic spin–orbit (PSO), diamagnetic spin–orbit (DSO), Fermi-contact (FC), and spin–dipole (SD).⁴⁴ All of the terms have been computed for all of the molecules. The EOM-CCSD calculations were carried out using ACES II⁴⁵ on the Itanium cluster at the Ohio Supercomputer Center.

3. Results and Discussion

The optimized bond distances for compounds **2–9** are given in Figure 1. The MP2/cc-pVTZ results previously reported⁸ for **2** are in good agreement with those given here. All molecules in Figure 1 have planar rings except for the molecule **9**. Total energies for molecules **2–9**, relative energies, and enthalpies of formation for molecules **2–7** and **9** are reported in Table 1. The enthalpies were computed for the isodesmic reactions (eqs 2 and 3) at the G3B3 computational level, using the experimental enthalpy of formation for molecules **1** and **8** (82.8 and $-510.03 \text{ kJ mol}^{-1}$, respectively⁴⁶). Due to the errors associated with the heat of formation of molecule **8** ($\pm 12 \text{ kJ mol}^{-1}$) and the isodesmic energies at this level (from 4 to 8 kJ mol^{-1}), the calculated heats of formation are estimated to have error bars of $\pm 20 \text{ kJ mol}^{-1}$.



Substitution of a C–C bond in benzene by a B–N bond leads to a significant rearrangement of electron density due to the polarity of the BN bond. In molecule **2**, the natural net charges on B and N are $+0.48$ and $-0.73e$, respectively. With the AIM partitioning, these values are $+2.00$ and $-1.47e$, respectively, and are in agreement with previous reports that show very large charges within the AIM methodology for bonds between atoms with very different electronegativities.⁴⁷ The Laplacian of the electron density at the BN bcp of **2** is positive, as it is in all molecules **2–9**. However, the energy density is negative, indicating that although the bond is very polar, the potential energy density dominates over the kinetic energy density as in typical covalent interactions. Replacement of one or two HC–CH linkages by HB–NH does not destroy the planarity of azaborine or diazaborines. However, pseudoborazine (**9**) is slightly nonplanar. Planar molecule **9** has one imaginary

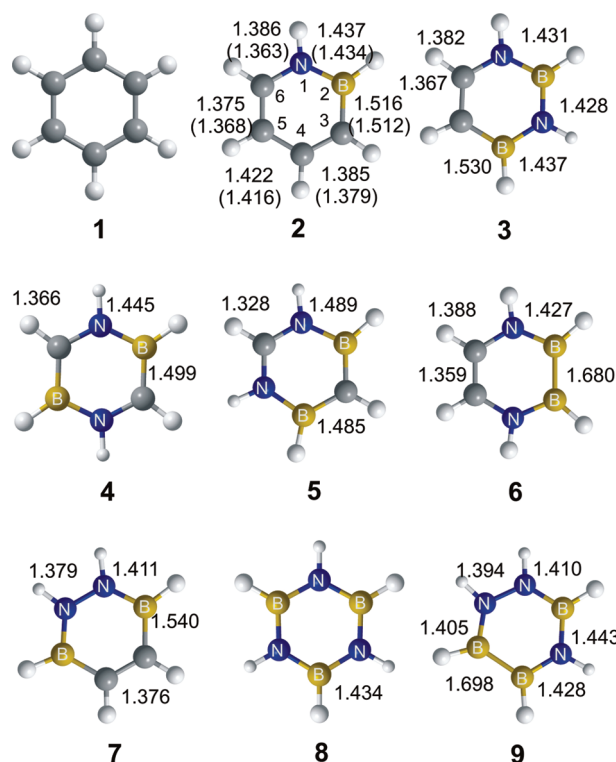


Figure 1. Optimized MP2/6-311+G(d,p) bond distances (Å). The atomic numbering used for these molecules is indicated in **2**. The MP2/cc-pVTZ results reported in ref 8 for compound **2** are given in parentheses.

Table 1. Total MP2/6-311+G(d,p) Energies, Relative Energies, and G3B3 ΔH_f° Values

molecule	symmetry	E_{total} (Hartree)	E_{rel} (kJ mol $^{-1}$)	ΔH_f° (kJ mol $^{-1}$)
2	C_s	−235.009313	—	4.8 ^a
3	C_s	−238.484585	0.0	−200.8
4	C_{2h}	−238.424084	158.8	−21.9
5	C_{2v}	−238.428974	146.0	−55.8
6	C_{2v}	−238.412937	188.1	−17.9
7	C_{2v}	−238.399569	223.2	13.4
8	D_{3h}	−242.002367	0.0	—
9	C_1	−241.850656	398.3	−127.5

^a The predicted ΔH_f° from ref 8 is $12.55 \text{ kJ mol}^{-1}$.

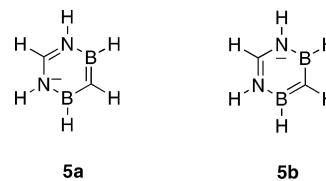
Table 2. MP2/6-311+G(d,p) Aromaticity Indexes

molecule	NICS(0)	NICS(1)	PDI
1	-7.91 (-8.76) ^a	-10.20 (-10.39) ^a	0.059
2	-5.39 (-5.62) ^a	-7.54 (-7.27) ^a	0.049
3	-2.50	-4.29	0.026
4	-4.89	-6.92	0.064
5	-4.10	-6.13	0.037
6	-2.22	-4.38	0.037
7	-2.73	-4.93	0.041
8	-1.50 (-2.02) ^a	-2.51 (-3.01) ^a	0.012
9	-0.51	-2.30	0.023

^a Values from ref 8.

frequency of -203 cm^{-1} but is only 0.07 kJ mol^{-1} less stable than the equilibrium C_1 structure. As shown previously for five-member rings,¹⁹ one of the most characteristic signatures of a B–N bond is its ability to act as either an electron donor since N is electron rich or an electron acceptor since B is electron poor. This is indeed the case for compound **2**. According to a NRT analysis, although the dominant resonance form is the Kekulé-type structure with a weight of 57%, there are also non-negligible contributions from other resonance forms which involve electron donations from the π_{C3C4} bonding orbital to the π^*_{BN} antibonding orbital and the π_{BN} bonding orbital to the π^*_{C5C6} antibonding orbital. As a result, the BN bond order (1.02) is smaller than that of a typical B=N double bond (1.257 in H_2BNH_2) and close to that of borazine (1.01). In addition, the bond orders of the C3C4 and C5C6 linkages (1.62 and 1.58, respectively) are less than those of typical C=C bonds but greater than that of benzene (1.44). The electron densities at the corresponding bcps are also greater (0.309 and 0.317 au, vs. 0.303 au). A similar conclusion can be derived from the analysis of the delocalization indexes since, as has been shown previously, they are linearly correlated with the bond orders.⁴⁸ Hence, the presence of the BN linkage produces a more localized structure than that found in benzene and is reflected in a decrease of about 20% in the delocalization energy. Similar decreases are also found in the absolute values of the NICS and the PDI indexes, as evident from Table 2. Nevertheless, these data indicate that **2** has a significant aromatic character, in agreement with the observations made previously.^{1,6–8}

When two HB–NH groups are introduced into the ring, five different isomers (**3**–**7**) can be formed. The most stable isomer (**3**) corresponds to the one in which the two groups are bonded in the order of N–B–N–B, while the least stable isomers have B–B or N–N bonds, as in **6** and **7**, respectively. The NICS and PDI indexes reported in Table 2 clearly show a decrease in aromaticity going from **2** to **3**. The delocalization energy also decreases by 9%, although **3** still exhibits a certain degree of delocalization as indicated by the existence of BNB and NCC three center bonds. Although the NICS and PDI indexes indicate that the aromaticity of **4** and **5** increases relative to **3**, both species are predicted to be much less stable. This may be attributed to the replacement of stronger C–C by weaker C–B bonds. In addition, the existence of a N–B–N–B linkage in **3** also results in the formation of a very strong C=C bond with a bond order of 1.70, which is intermediate between a pure double bond (ethylene bond order of 2.00) and an aromatic C–C bond

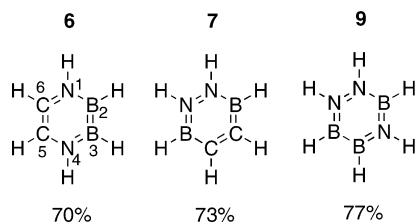
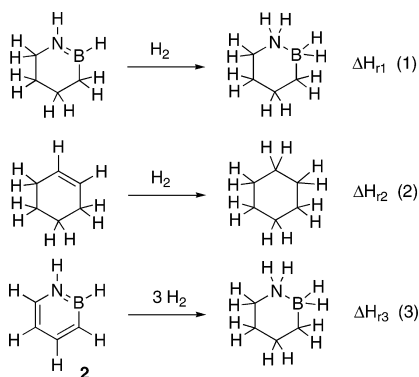
Chart 2. Mesomeric Forms of Molecule 5

of benzene (1.44). The slightly greater stability of **5** relative to **4** can be attributed to the strengths of the C–N and C–B bonds in **5** (bond orders of 1.38 and 1.32, respectively) compared to **4** (1.30 and 1.22, respectively). Similar trends are observed for the electron densities at the bcps. In **5**, the electron densities at the C–N and C–B bcps are 0.340 and 0.202 au, respectively, compared to 0.300 and 0.191 au, respectively, for **4**. These bonding differences also reflect the significant contributions (with a weight of 20% each) of the mesomeric forms **5a** and **5b**, shown in Chart 2, which are favored by the presence of a N–C–N linkage. As might be expected, the B–N bonds have very small bond orders (0.846) as a consequence of the N–C–N and B–C–B linkages.

Only in the least stable isomers **6** and **7** are no three center bonds detected in the NBO analyses, although both NICS(1) and PDI indexes suggest a slight increase in aromaticity relative to **3**. In contrast, the delocalization energies of these two molecules are 9% and 14% lower than that of **3**. In any case, it seems clear that aromaticity changes do not correlate with relative stabilities. The lower stabilities of **6** and **7** are mainly due to the presence of a B–B and a N–N bond, respectively. A B–B bond is weaker than a C–B bond, and in addition, both B atoms are bonded to N atoms. This produces a net positive charge (+0.27 e) on both B atoms and a significant electrostatic repulsion between them, which destabilizes **6** relative to **3**. This effect is even stronger for **7**, since in this isomer the negative net charge accumulated on the two bonded N atoms is much larger in absolute value (−0.56 e), and this again results in an increased electrostatic repulsion. As expected, the B–N bond orders (BO) in **6** and **7** (1.13 and 1.14, respectively) are intermediate between H_2BNH_2 (1.257) and borazine (1.02).

When all the C–C bonds of the benzene ring are replaced by B–N bonds, two possible isomers, **8** and **9**, can arise. The structure and aromaticity of borazine (**8**) has been the subject of many previous studies and will not be discussed here. It is worth mentioning, however, that its low aromaticity has been explained in terms of the polarity of the B–N bonds.¹² The very low stability of **9** is clearly due to the presence of one B–B and one N–N bond within the ring, a situation which results in large electrostatic repulsions. No three center bonds are found in **9**, and the calculated delocalization energy is about 19% less than that of borazine. Although its NICS values are reduced, its PDI is almost twice that of borazine. Of the three nonequivalent B–N bonds in **9**, the one exhibiting the most double-bond character is B5–N6 (BO = 1.203), since it is located between a B–B and a N–N bond. The B2–N3 bond has the smallest bond order (0.979) and is part of the N–B–N–B linkage.

The B–N bond lengths vary significantly from 1.405 Å in **9** to 1.489 Å in **5**, as can be seen from Figure 1. The

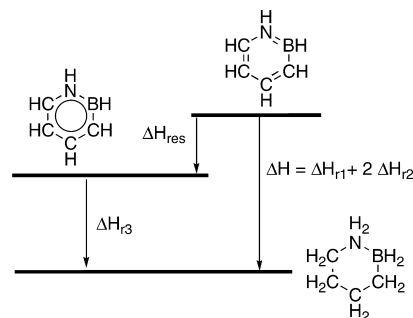
Chart 3. Dominant Mesomeric Forms of Molecules 6, 7, and 9**Chart 4.** Reaction Enthalpies

shortest B–N bonds have the N atom bonded to another N atom as in **7** and **9**. Conversely, the longest B–N bonds have B and N bonded to C atoms as in **4** and **5**. Insight into these trends can be obtained by recalling that B–B or N–N bonds within the ring significantly favor a Kekulé-type structure, which makes these bonds single bonds and the B–N bonds formally double bonds. Consistently, in **6**, **7**, and **9**, the mesomeric structures shown in Chart 3 dominate with weights of 70–80%. In contrast, the B–N bonds of **5** are long due to the presence of N–C–N and B–C–B linkages, which favor electron delocalization and leave the B–N bond a single bond.

The PDI index is obtained as an average of three individual delocalization values which may vary over a wide range. For the molecules included in this study, the largest delocalization values correspond to those involving a pair of carbon atoms. The maximum value of the DI is that of the *para*-C–C pair in **4**, with a value of 0.123. In contrast, the smallest values are associated with the boron atoms with DI values of B–B pairs ranging between 0.004 and 0.018 in **7** and **3**, respectively.

The resonance energy of benzene is usually calculated as the difference between its hydrogenation enthalpy, i.e., the energy released when benzene is converted to cyclohexane, and the hydrogenation enthalpy of cyclohexatriene, the energy released when hypothetical C₆H₆ with three localized C=C double bonds becomes fully saturated. The hydrogenation enthalpy of the latter is taken as three times the enthalpy change when cyclohexene is converted to cyclohexane.

A similar approach could be used to estimate the resonance energies of the azaborines. Since azaborines contain both C=C and B=N bonds, it is necessary to also evaluate the hydrogenation energy of a B=N bond. This can be done as illustrated by the reactions in Chart 4 for the molecule **2**. ΔH_{r1} is the enthalpy change when the B=N bond becomes

Chart 5. Resonance Energy of Azaborine**Table 3.** G3B3 Resonance Enthalpies (kJ mol^{−1})^a

compound	resonance enthalpy
2	96
3	57
6	82
7	79
8	6
9	59

^a The resonance enthalpy for benzene at the same level of theory is 201 kJ mol^{−1}.

hydrogenated. The hydrogenation enthalpy of one C=C double bond is the energy released in reaction 2, ΔH_{r2} , as in benzene. Finally, ΔH_{r3} is the energy released when azaborine is fully hydrogenated. The resonance energy then is simply $\Delta H_{\text{res}} = \Delta H_{r1} + 2 \Delta H_{r2} - \Delta H_{r3}$, as illustrated in Chart 5. By adjusting the weighting coefficients of ΔH_{r1} and ΔH_{r2} , this scheme may also be extended to estimate the resonance energies of compounds **3** and **6–9**. However, a similar scheme cannot be applied to compounds **4** and **5** since there are no C–C linkages.

The calculated resonance enthalpies are summarized in Table 3. It is interesting to note that the resonance energy is not negligible for compound **2**, although it is less than half of that calculated for benzene at the same level of theory. This is consistent with a certain aromaticity inherent in the NBO description above and with both the PDI and NICS(1) values. The resonance energies computed for **3**, **6**, and **7** clearly indicate a decrease in aromaticity relative to **2** and are consistent with both our previous observations and the calculated PDI and NICS(1) values. The resonance energies also increase slightly in going from **3** to **6**, but decrease slightly going from **6** to **7**, in contrast to the PDI and NICS(1) results.

The resonance energy of borazine suggests that it does have a certain degree of aromaticity, although it is much less than that of compound **2**, in agreement with PDI and NICS(1) descriptions. Also, the resonance energy of borazine is definitely smaller than that of compounds **3**, **6**, and **7**, again in agreement with the other aromaticity indexes [PDI and NICS(1)].

Finally, the resonance energy of compound **9** indicates that it is much more aromatic than borazine. This is not consistent with both the dominant weight of the localized resonant forms discussed above or the NICS(1) values, which predict a similar aromaticity for both systems. It should be recognized, however, that the model used to obtain the resonance energies of azaborine, the diazaborines, and borazine has

Table 4. MP2/6-311+G(d,p) Calculated Chemical Shifts (δ , ppm) for Molecules **2–9** and Experimental Chemical Shifts for Molecules **1**, **2**, and **8**

atom	1	2	3	4	5	6	7	8	9	1 exp.	2 exp.	8 exp.	1 ^a	2 ^a	8 ^a
X1	130.04	-203.98	-235.56	-173.07	-205.75	-204.62	-209.84	-250.85	-234.64	128.5		-265.8	135.2	-246.9	-287.6
X2	130.04	26.99	23.57	20.75	29.38	38.56	23.97	27.15	21.24	128.5	31	30.2	135.2	26.9	26.1
X3	130.04	136.21	-225.76	146.19	124.92	38.56	150.19	-250.85	-218.26	128.5	131.6		135.2	139.0	-287.6
X4	130.04	142.08	33.58	-173.07	29.38	-204.62	150.19	27.15	45.58	128.5	144.5	30.2	135.2	151.5	26.1
X5	130.04	116.09	112.89	20.75	-205.75	119.06	23.97	-250.85	30.77	128.5	112.1		135.2	118.8	-287.6
X6	130.04	132.44	145.00	146.19	140.80	119.06	-209.84	27.15	-203.99	128.5	134.7	30.2	135.2	140.2	26.1
H1	7.75	8.42	6.56	9.73	8.08	8.28	7.66	5.58	6.32	7.26	8.44	5.42	7.5	7.8	5.3
H2	7.75	5.49	5.00	5.29	5.51	5.74	4.99	4.94	4.65	7.26	4.90	4.46	7.5	5.4	5.0
H3	7.75	7.61	7.05	8.03	6.99	5.74	8.01	5.58	7.34	7.26	6.92	5.42	7.5	7.4	5.3
H4	7.75	8.04	5.58	9.73	5.51	8.28	8.01	4.94	6.03	7.26	7.70	4.46	7.5	8.0	5.0
H5	7.75	6.83	6.12	5.29	8.08	6.64	4.99	5.58	4.96	7.26	6.43	5.42	7.5	6.6	5.3
H6	7.75	7.52	7.57	8.03	7.75	6.64	7.66	4.94	7.61	7.26	7.40	4.46	7.5	7.3	5.0

^a B3LYP/Ahlrichs-vtzp values from ref 8.

certain limitations. Although the number of B=N and C=C bonds are accounted for, their bond orders are not those of the reference compounds. Moreover, some of the molecules considered in this study also have B–B or N–N bonds which are not present in the model compounds. These limitations mean that the calculated resonance energies are only approximate.

NMR Chemical Shifts. The calculated absolute chemical shieldings (σ) of molecules **2–9** have been transformed to the corresponding chemical shifts (δ) using those obtained for ¹H and ¹³C (in TMS), ¹⁵N (NH₃), and ¹¹B (from BF₃·OEt₂ in the gas-phase for which the experimental value is 9.4 ppm).⁴⁹ The calculated B3LYP/Ahlrichs-vtzp values from ref 8, those obtained in the present work, and the available experimental values are given in Table 4. Experimental values are available for two of the azaborines, namely **2** and **8**.^{8,50} The only value of an experimental ¹⁵N chemical shift for the molecules included in this study was measured for borazine (**8**) and was -265.8 ppm.⁵¹ ¹¹B chemical shifts have been obtained for **2** and **8**, and are 31 and 30.2 ppm, respectively.^{8,50} Thus, the computed values are consistent with the experimental.

Good correlations are obtained between the experimental and calculated ¹H and ¹³C chemical shifts (for benzene all C and H atoms have been considered), as indicated by eqs 4 and 5 which include TMS ($\delta = 0.00$ ppm).

$$\delta(\text{exp}) = (1.010 \pm 0.006)\delta[\text{MP2/6-311} + \text{G(d,p)}]$$

$$n = 34, \quad R^2 = 0.9987 \quad (4)$$

$$\delta(\text{exp}) = (0.945 \pm 0.004)\delta(\text{B3LYP/Ahlrichs-vtzp})$$

$$n = 34, \quad R^2 = 0.9993 \quad (5)$$

Equation 6 shows that the results obtained at these two levels of theory are linearly related.

$$\delta(\text{B3LYP/Ahlrichs-vtzp}) = (4.7 \pm 0.8) +$$

$$(1.114 \pm 0.008)\delta[\text{MP2/6-311} + \text{G(d,p)}]$$

$$n = 37, \quad R^2 = 0.9984 \quad (6)$$

Both theoretical methods yield comparable results, with R^2 slightly better at B3LYP/Ahlrichs-vtzp, but the slope closer to 1 at MP2/6-311+G(d,p).

NMR Spin–Spin Coupling Constants. Liu and co-workers reported experimental one- and three-bond spin–spin coupling constants as part of their spectroscopic characteriza-

Table 5. ¹J(N–B), ¹J(N–H), and ¹J(B–H) (Hz) for Azaborine, Diazaborines, Borazine, and Pseudoborazine^a

molecule no.	¹ J(N1–B2)	¹ J(B2–N3)	¹ J(N3–B4)	¹ J(B5–N6)
2	-23.4			
3	-29.6	-27.7	-21.9	
4	-23.4			
5	-16.5			
6	-19.6			
7	-28.9			
8	-26.8			
9^b	-34.9	-28.0	-18.0	-24.0

molecule no.	¹ J(N1–H)	¹ J(N3–H)	¹ J(N6–H)
2	-79.6 (-80) ^c		
3	-82.4	-75.0	
4	-75.9		
5	-79.6		
6	-78.5		
7	-76.9		
8	-76.7 (-77.4) ^d		
9^b	-88.6	-73.5	-84.9

molecule no.	¹ J(B2–H)	¹ J(B4–H)	¹ J(B5–H)
2	126.4 (130) ^c		
3	134.5	123.1	
4	129.5		
5	125.4		
6	115.9		
7	112.4		
8	131.4 (138.4) ^d		
9^b	133.1	114.1	116.4

^a Coupling constants correspond to ¹H, ¹¹B, and ¹⁵N isotopes.^b Values computed for the structure of C_s symmetry. ^c Experimental value from ref 8. ^d Experimental value from ref 50.

tion of azaborine (**2**).^{8,52} For this molecule, they determined ¹J(B–H) with ¹¹B = 130 Hz and ¹J(N–H) with ¹⁴N = 57 Hz. This value for ¹J(N–H) with ¹⁴N corresponds to 80 Hz for ¹⁵N. In addition, they measured six three-bond H–H couplings, ³J(H–H). The signs of these coupling constants were not determined. Experimental values of ¹J(B–H) and ¹J(N–H) for borazine (**8**) are 138.4 and 55.1 Hz for ¹¹B and ¹⁴N, respectively.⁴⁶ The ¹⁴N = 55.1 Hz corresponds to ¹⁵N = 77.4 Hz. Table 5 reports the computed values of ¹J(N–B), ¹J(N–H), and ¹J(B–H) for molecules **2–9**. The computed values of ¹J(B2–H) and ¹J(N1–H) for **2** are 126.4 and -79.6 Hz, and the computed values for **8** are 131.4 and 76.7 Hz, respectively. Thus, the computed values are in good agreement with the experimental values,⁸ with the sign of ¹J(N–H)

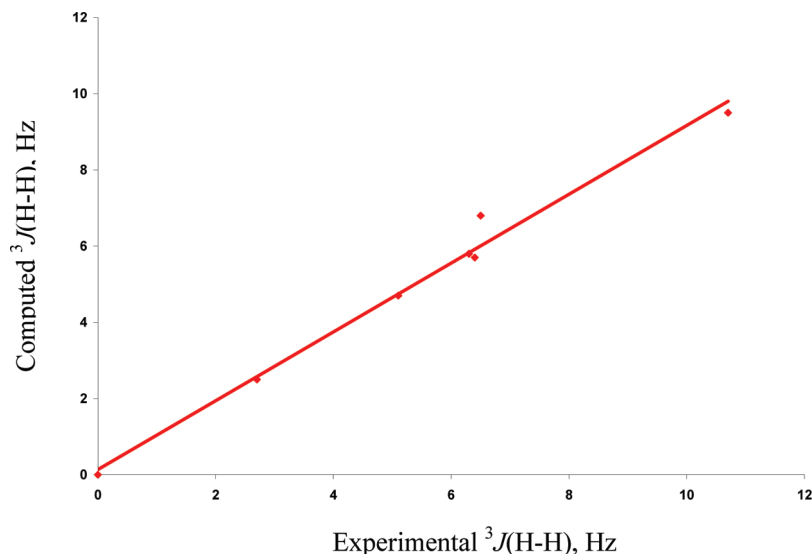


Figure 2. Computed vs experimental values of $^3J(\text{H-H})$ for azaborine (**2**).

negative and $^1J(\text{B-H})$ positive. In addition, Figure 2 shows a plot of computed versus experimental values of $^3J(\text{H-H})$, which are much smaller, varying from 2 to 11 Hz. A reference point at (0,0) has been added. From Figure 2, it can be seen that the computed values are linearly related to the experimental as

$$^3J(\text{H-H})(\text{calc}) = 0.903[^3J(\text{H-H})(\text{exp})] + 0.136$$

$$n = 6, \quad R^2 = 0.986 \quad (7)$$

Thus, for those cases in which comparisons can be made, there is good agreement between the computed and the experimental values of coupling constants for molecule **2**.

Table 5 also lists $^1J(\text{N-B})$, $^1J(\text{N-H})$, and $^1J(\text{B-H})$ for the diazaborines (**3-7**), borazine (**8**), and pseudoborazine (**9**). It is advantageous to examine the values of $^1J(\text{N1-B2})$, $^1J(\text{N1-H})$, and $^1J(\text{B2-H})$ for molecules **2-7** relative to borazine, since variations in these coupling constants may also be viewed as arising from the substitution of one or two HC-CH groups for one or two HN-BH groups. Relative to $^1J(\text{N1-B2})$ for borazine, this coupling constant decreases in absolute value for molecules **2** and **4-6**, but increases for molecules **3** and **7**. Some insight into these changes can be obtained by examining the bonding patterns in these molecules. In molecules **2** and **4-6**, the N1-B2 group is bonded to either two C atoms or one C and one B. In contrast, N1-B2 is bonded to one C and one N in molecules **3** and **7**. Thus, it is apparent that changes in the N1-B2 bond, which occur in these molecules as the atoms bonded to N1 and B2 change, are reflected in the changes in $^1J(\text{N1-B2})$. When N1 and B2 are bonded to the less electronegative atoms C and B, $^1J(\text{N1-B2})$ decreases in absolute value, whereas when either N1 or B2 is bonded to a N atom, $^1J(\text{N1-B2})$ increases. This relationship is also consistent with an increase of $^1J(\text{B2-N3})$ and a decrease of $^1J(\text{N3-B4})$ for **3**, and a significant increase in $^1J(\text{N1-B2})$ for pseudoborazine (**9**) in which both N1 and B2 are bonded to N atoms. Moreover, the increase in $^1J(\text{N1-B2})$ when either N1 or B2 is bonded to the more electronegative N

atom, and the decrease in $^1J(\text{N1-B2})$ when N1-B2 is bonded to C and B, are consistent with the effects of F and Li substitution in borazine.⁴⁰ Fluorine substitution at either N1 or B2 of borazine increases the one-bond N1-B2 coupling constant, whereas Li substitution decreases $^1J(\text{N1-B2})$. This is also consistent with substituent effects in benzene, in which case $^1J(\text{C-C})$ increases upon F substitution but decreases with Li substitution. Since values of $^1J(\text{N1-B2})$ for molecules **2-9** are dominated by the Fermi-contact (FC) terms, it is evident that changes in the s electron densities in both the ground and excited states of these molecules must respond to the different bonding patterns in these systems. It should also be noted that the FC term underestimates $^1J(\text{N-B})$ by about 2 to 3 Hz, the contribution from the PSO term. This situation was also found for borazine and its derivatives.⁴⁰

Relative to its value of -76.7 Hz for borazine, $^1J(\text{N1-H})$ increases in absolute value in azaborine (**2**) and the diazaborines (**3-7**), except for molecule **4**, in which case it decreases but by less than 1 Hz. The largest absolute value of $^1J(\text{N1-H})$, -82.4 Hz, is found for molecule **3**. The value of $^1J(\text{B2-H})$ is 131.4 Hz for borazine, and it decreases in the same set of molecules except for molecule **3**, in which case it increases to 134.5 Hz. Moreover, $^1J(\text{N1-B2})$ also has its greatest absolute value in molecule **3**. What makes molecule **3** unique among these six-member rings? The answer must be related to the retention of the borazine connectivity N1-B2-N3-B4 in molecule **3**, which is also the most stable of the diazaborazine isomers, as noted above. It is also interesting to note that the largest absolute values of both $^1J(\text{N1-B})$ and $^1J(\text{N1-H})$ in the entire set of molecules are found for pseudoborazine (**9**), while $^1J(\text{B-H})$ has its second-largest value in this molecule. Once again, the N1-B2-N3-B4 connectivity is retained in this molecule. No simple relationships could be found between $^1J(\text{N-B})$, $^1J(\text{N-H})$, and $^1J(\text{B-H})$ and the corresponding N-B, N-H, and B-H distances. Moreover, values of

$^1J(\text{N}-\text{B})$, $^1J(\text{N}-\text{H})$, and $^1J(\text{B}-\text{H})$ do not appear to correlate with each other.

Conclusions

An ab initio study has been carried out to investigate azaborine, the diazaborines, and borazine. These molecules can be considered as arising when one or more HC—CH linkages in benzene are replaced by HB—NH linkages. Such replacements lead to a significant rearrangement of electron density due primarily to the polarity of the BN bond. Azaborine (**2**) exhibits a much more localized structure than that of benzene, with a dominant contribution (57%) of the Kekulé-type structure. Azaborine and the diazaborines lose aromaticity relative to benzene but are more aromatic than borazine. The bonding characteristics influence the lengths of the B—N bonds in these molecules as well as the relative stabilities of the diazaborines. The most stable isomer has the N—B—N—B linkage, while the least stable have either a B—B or N—N bond.

NMR chemical shifts and coupling constants have been computed and found to be in good agreement with available experimental data. Changes in the N1—B2 bond in these molecules are reflected in the changes in $^1J(\text{N1}-\text{B2})$. When N1 and B2 are bonded to the less electronegative atoms C and B, $^1J(\text{N1}-\text{B2})$ increases in absolute value relative to borazine, but when either N1 or B2 is bonded to N, $^1J(\text{N1}-\text{B2})$ decreases. No simple relationships exist between $^1J(\text{N}-\text{B})$, $^1J(\text{N}-\text{H})$, and $^1J(\text{B}-\text{H})$ and the corresponding N—B, N—H, and B—H distances, respectively. Moreover, values of $^1J(\text{N}-\text{B})$, $^1J(\text{N}-\text{H})$, and $^1J(\text{B}-\text{H})$ do not appear to correlate with each other.

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Supporting Information Available: MP2/6-311+G-(d,p) geometries for molecules **2–9**. Also included are the full references for 26 and 45. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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