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Microwave Spectrum, Structural Parameters, and Quadrupole Coupling for 1,2-Dihydro-1,2-azaborine

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Abstract: The first microwave spectrum for 1,2-dihydro-1,2-azaborine has been measured in the frequency range 7−18 GHz, providing accurate rotational constants and nitrogen and boron quadrupole coupling strengths for three isotopomers, $H_6C_4{}^{11}B^{14}N$, $H_6C_4{}^{10}B^{14}N$, and $H_5DC_4{}^{11}B^{14}N$. The measured rotational constants were used to accurately determine coordinates for the substituted atoms and provide sufficient data to determine most of the important structural parameters for this molecule. The spectra were obtained using a pulsed beam Fourier transform microwave spectrometer, with sufficient resolution to allow accurate measurements of ^{14}N, ^{11}B, and ^{10}B nuclear quadrupole hyperfine interactions. High-level *ab initio* calculations provided structural parameters and quadrupole coupling strengths that are in very good agreement with measured values. The rotational constants for the parent compound are $A = 5657.335(1)$, $B = 5349.2807(5)$, and $C = 2749.1281(4)$ MHz, yielding the inertial defect $\Delta_0 = 0.02$ amu·Å^2 for the ground-state structure. The observed near-zero and positive inertial defect clearly indicates that the molecular structure of 1,2-dihydro-1,2-azaborine is planar. The least-squares fit analysis to determine the azaborine ring structure yielded the experimental bond lengths and 2σ errors $R(\text{B}-\text{N}) = 1.45(3)$ Å, $R(\text{B}-\text{C}) = 1.51(1)$ Å, and $R(\text{N}-\text{C}) = 1.37(3)$ Å for the ground-state structure. Interbond angles for the ring were also determined. An extended Townes−Dailey population analysis of the boron and nitrogen quadrupole coupling constants provided the valence p-electron occupancy $p_c = 0.3e$ for boron and $p_c = 1.3e$ for nitrogen.

I. Introduction

The aromaticity and reactivity of boron−nitrogen-containing heterocycles have attracted much interest for decades. Earlier work has demonstrated that substitution of the B−N bond in place of the C═C bond provides an interesting chemical strategy to augment molecular and electronic properties of conjugated aromatic systems.[1] The 1,2-dihydro-1,2-azaborine molecule (BNC_4H_6) is an interesting case in particular because it is closely related to benzene, the quintessential aromatic molecule (Figure 1).

1,2-Dihydro-1,2-azaborine represents a hybrid structure between organic benzene and inorganic borazine.[2] The nature of the B−N bonding in 1,2-azaborines is of fundamental interest. Interestingly, the opposing σ- and π-electron polarization of the B−N bond in 1,2-azaborine structures results in a somewhat less polarized B−N bond (Figure 1).[3] The calculated Mulliken charges on N ($-0.3e$) and B ($0.2e$) indicate that the σ-polarization dominates and there is not complete cancellation. Structural studies, in particular the B−N bond distance, of substituted 1,2-azaborine derivatives using X-ray diffraction have demonstrated that 1,2-azaborines possess delocalized structures consistent with aromaticity.[4] The unsubstituted 1,2-dihydro-1,2-azaborine molecule is free from substituent effects and should provide an excellent model to further investigate the B−N bond interactions in BN heterocycles.

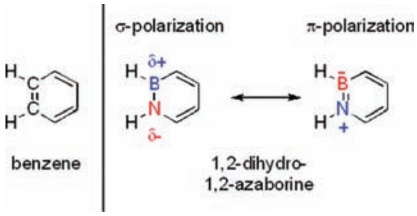

Figure 1. Opposing σ- and π-electron polarizations in 1,2-dihydro-1,2-azaborines.

Liu and co-workers[2] have reported the synthesis, NMR, and UV spectrum of 1,2-dihydro-1,2-azaborine, but a crystal structure was not obtained. Calculations comparing 1,2-dihydro-1,2-azaborine with borazine and benzene have been published,[5] but to the best of our knowledge gas phase experimental data on these heterocyclic ring systems have remained largely elusive

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Table 1. Spectroscopic Constants for 1,2-Dihydro-1,2-azaborine[a]

parameter	$H_6B^{11}N^{14}C_4$	$H_6B^{10}N^{14}C_4$	$H_5B^{10}DN^{14}C_4$	MP2/6-31+G(d,p)	MP2/6-311+G(d,p)
A	5657.335(1)	5794.049(3)	5642.9571	5635.595	5633.597
B	5349.2807(5)	5352.383(1)	5059.2583	5354.980	5344.391
C	2749.1281(4)	2781.7927(6)	2669.6747	2745.937	2742.593
$B\chi_{aa}$	−1.71(1)	−3.42(2)		−1.51	−1.6
$B\chi_{bb}$	−1.33(2)	−1.83(5)		−1.32	−1.4
$B\chi_{cc}$	3.03(2)	5.26(3)		2.83	3.0
$N\chi_{aa}$	0.46(1)	0.43(1)		0.50	0.47
$N\chi_{bb}$	0.78(6)	0.79(3)		0.55	0.57
$N\chi_{cc}$	−1.25(6)	−1.22(3)		−1.05	−1.0
σ, kHz	8	17			
$N_{\text{total}}/N_{\text{distinct}}$	139/92	73/58	3		

[a] Values in MHz. $\chi = eQq$, calculated rotational constants are for the $H_6C_4C^{11}B^{14}N$ isotopomer. The ground-state inertia defect ($\Delta = I_{cc} - I_{aa} - I_{bb}$) is $\Delta_0 = 0.02$ amu·Å^2 for $H_6B^{11}N^{14}C_4$.

to date.[6] Here, we report microwave spectroscopy measurements and structural parameters for 1,2-dihydro-1,2-azaborine. Rotational transitions for 1,2-dihydro-1,2-azaborine and its ^{10}B and ^{2}H isotopologues were measured at 7−15 GHz to obtain rotational constants and nuclear quadrupole coupling strengths for the ground electronic and vibrational state. Results from our microwave molecular beam experiments can be directly compared with *ab initio* theory.

Microwave spectroscopy has been the most accurate and useful method for the determination of gas phase structures of many small molecules. Some examples containing boron and nitrogen are H_2NBH_2,[7] H_3NBF_3,[8] and BH_3NH_3.[9] Studies of amine-boron complexes have revealed a very strong interaction between boron and nitrogen. In the HCN-BF_3 dimer, a very short van der Waals bond distance between boron and nitrogen has been observed.[10] Microwave spectroscopy of borazine is not possible due to the lack of permanent dipole moment. 1,2-Dihydro-1,2-azaborine on the contrary has a strong permanent dipole moment (2 D), and thus its microwave spectrum can be readily measured. Another advantage of microwave spectroscopy is the high sensitivity, which allows measurements of the minor ^{10}B isotopic species in natural abundance, thus providing additional data for structure determination. Our work complements the detailed work of Marwitz[2] et al. and provides new experimental data on the bond lengths and nuclear quadrupole coupling constants for this molecule.

Experimental determination of the nuclear quadrupole coupling constants for ^{14}N, ^{11}B, and ^{10}B allows the determination of the valence p-orbital electron occupation on those atoms from the Townes−Daily model.[11] It is of interest to compare the latter with the calculated natural bond orbital occupation for boron and nitrogen. The experimental molecular parameters and the π-electron occupancies on boron and nitrogen can provide additional information regarding the aromaticity for 1,2-dihydro-1,2-azaborine.

II. *Ab Initio* Studies

Quantum electronic structure calculations were performed to obtain a starting structure for microwave frequency predictions. The predicted structure and derived rotational constants were accurate and reduced the effort in searching for transitions. The calculations were done using the Gaussian 03[12] suite running on the University of Arizona ICE high performance computing cluster. The structure, nuclear quadrupole coupling constants, and rotational constants for 1,2-dihydro-1,2-azaborine were computed using the Møller−Plesset second-order perturbation theory (MP2). Sufficiently large double- and triple-ζ atomic basis sets, 6-31+G(d,p) and 6-311G+(d,p), were chosen to accurately describe the wave functions and to study the optimization performance of the basis sets.[13] Geometry optimizations were done in redundant internal coordinates at tight convergence criteria without any symmetry constraints. Harmonic frequency calculations were computed on a *fine* grid to verify that the optimized structure is at the global minimum. Theoretical rotational constants and nuclear quadrupole coupling constants obtained for the optimized structures at the MP2/6-31+G(d,p) and MP2/6-311+G(d,p) levels of calculations are given in Table 1. The ground-state geometry of 1,2-dihydro-1,2-azaborine was predicted to be planar with a near-oblate asymmetric-top rotor. As shown in Figure 2, the nitrogen atom lies very close to the *a*-inertial axis and the boron atom lies near the *b*-inertial axis (the *c*-inertial axis is perpendicular to the molecular plane).

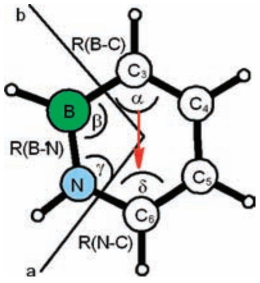

Figure 2. Molecular bond lengths and angles that were determined from the fit to the rotational constants obtained experimentally. Angles α and δ are not directly determined from the data and have not been given an experimental uncertainty. The *a*- and *b*-axes are the principal inertial axes. The dipole moment direction is given (red arrow, negative to positive) and lies along a line between the C3 and C6 carbons adjacent to B and N, respectively.

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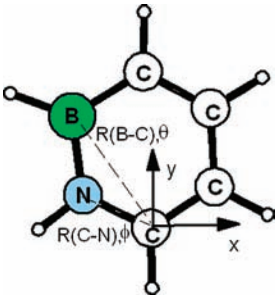

Figure 3. Polar coordinate parameters, $R(C_6-B),\theta$ and $R(C_6-N),\phi$, were used as variable parameters in the least-squares structure fit analysis. The B−N bond length, $R(B-N)$, was then obtained from these parameters. The atoms are constrained to lie in the *xy*-plane and the $-C_4H_4-$ bond geometry was fixed to the theoretical values.

Calculations indicate that both *a* and *b* dipole rotational transitions are allowed. The predicted dipole strengths are $a = 1.6$ D and $b = 1.4$ D for 1,2-dihydro-1,2-azaborine, and both types were observed in this experiment as described below. Several accounts of electronic structure calculations for BNC_4H_6 exist in the literature for direct comparison with our results.[14] The present computations of the BNC_4H_6 structure are in good agreement with the earlier calculations, including those employing higher order electron correlation methods. Calculated bond lengths and angles for the C−C−C−C portion of the molecule did not change significantly when larger basis sets (i.e., 6-311+G(d,p)) were used in the calculations. However, nuclear quadrupole coupling constants determined by MP2 seemed to depend somewhat on the basis set size for boron but were more consistent for nitrogen. Natural bond analysis (NBO) was carried out using the MP2 method to study valence p-electron occupancy in the B−N bond environment and the relation to the nuclear quadrupole coupling interaction strengths.

To better understand the relationship between the molecular structure and π-electron density distribution, we investigated the total electron density distribution and provide an electrostatic potential map (see Figure 4) for the azaborine molecule. For these calculations, the isosurface of total electron density was computed at the MP2/6-31+G(d,p) level. The illustrated isosurface was mapped with the electrostatic potential from total SCF density (Iso Val = 0.001) to provide qualitative data on the electronic charge density distribution. For direct comparison, a mapped isosurface of benzene was computed at the same level of calculations. Figure 4 shows the results of the isosurface plots for benzene and 1,2-dihydro-1,2-azaborine, where red indicates the most negative (most electron rich) regions and blue indicates the most positive (most electron poor) regions. The overall dipole moment for 1,2-dihydroazaborine is predicted to lie along a line connecting the two carbons that are adjacent to nitrogen (C_6) and boron (C_3) (see Figures 2 and 4). The calculated dipole moment is 2 D, pointing from C_3 (most negative, adjacent to B) toward C_6 (most positive, adjacent to N) (this is the physics convention, not the same as many chemistry textbooks). From the Mulliken charges it is observed that the carbon nearest boron (C_3) has a region of strongest negative charge, $-0.5e$, and the carbon closest to nitrogen (C_6) has a charge $+0.2e$. This is in agreement with the charge isosurface plot (Figure 4). The Mulliken charges on N ($-0.3e$) and B ($0.2e$) give a B−N bond dipole in a direction opposite the overall dipole moment for the molecule. The NBO (from MP2) charges indicate a more polarized B−N bond, with B ($0.5e$) and N ($-0.7e$).

III. Experimental Methods

1,2-Dihydro-1,2-azaborine arrived as a clear liquid (in dodecane) from the Liu laboratory at the University of Oregon, in a two-neck sample cell, which allowed for vacuum transfers. Details of the synthesis of the compound are reported in Marwitz et al.[2] 1-Deutero-2-hydro-1,2-azaborine was prepared simply by adding a small concentration of CH_3OD to 1,2-dihydro-1,2-azaborine and allowing the mixture to exchange at room temperature to make D-NBC_4H_5. The D-enriched sample that was shipped to our laboratory had a yellowish color and might have contained some impurities or decomposition products. We were able to obtain some spectra for this D-substituted isotopomer.

To prepare the sample for microwave measurements, the sample cell was loaded onto the spectrometer sample chamber and subsequently placed into a liquid nitrogen bath to freeze the liquid sample. This cell was then evacuated, charged to 0.8−1.0 atm with neon, and allowed to warm to 0 °C. The temperature of 0 °C was then maintained by placing the cell in the ice bath. The azaborine molecules seeded in neon were introduced into the spectrometer resonator cavity with the nozzle beam transverse to the microwave radiation, at 2 Hz using a pulsed valve (General valve series 9). The pressure inside the spectrometer chamber was maintained at $10^{-6}-10^{-7}$ Torr prior to the valve opening, and the backing pressure of neon was kept at approximately 0.8 atm during the frequency scanning. Following the molecular pulse (about 1 ms delay), a $\pi/2$ microwave excitation pulse (1 μs duration) was injected into the resonator to coherently excite the molecules, using a Herley SPDT microwave switch. The molecular FID signal was transmitted via the same SPDT switch, passed to a Miteq 6−18 GHz low-noise amplifier, and sent to the rf circuit for further signal processing. The details of the homodyne mixing and detection system and the spectrometer have been given previously.[15]

IV. Data Analysis and Results

A. Microwave Spectrum. 1,2-Dihydro-1,2-azaborine displayed an asymmetric-top spectrum with complicated nuclear quadrupole hyperfine splittings. Many of the observed *a*-type and *b*-type lines appeared fairly congested due to the unresolved hyperfine splittings. The $J = 0 \rightarrow 1$ line was observed for both *a*-type and *b*-type dipole transitions, which aided spectral assignment for the fit. Figure 5 illustrates a subset of the transitions measured for $0_{00} \rightarrow 1_{01}$. Nine distinct *a*-type and *b*-type rotational transitions for the parent 1,2-dihydro-1,2-azaborine species were measured at 7−15 GHz. We were able to assign a total of 92 resolved hyperfine components to the parent species. Eight *a*-type and *b*-type rotational transitions were measured for the ^{10}B isotopologue in natural abundance, and 39 hyperfine components were assigned to this isotopomer. Our spectral assignment of the ^{10}B isotopologue in natural abundance helped to confirm unambiguously the identity of the parent species. The measured transition frequencies and deviations for the spectral fits are given in Tables S1 and S2 in the Supporting Information. Also, the observed ^{14}N nuclear quadruple coupling constants for ^{10}B and ^{11}B isotopologues are nearly identical and agree within the experimental error limits. The larger fit standard deviation obtained for the ^{10}B isotopologue is largely due to the measurement uncertainty, as spectral lines for this isotopomer are weaker and more likely to be blended with other transitions. Our experimental line widths (fwhm) are 10−20

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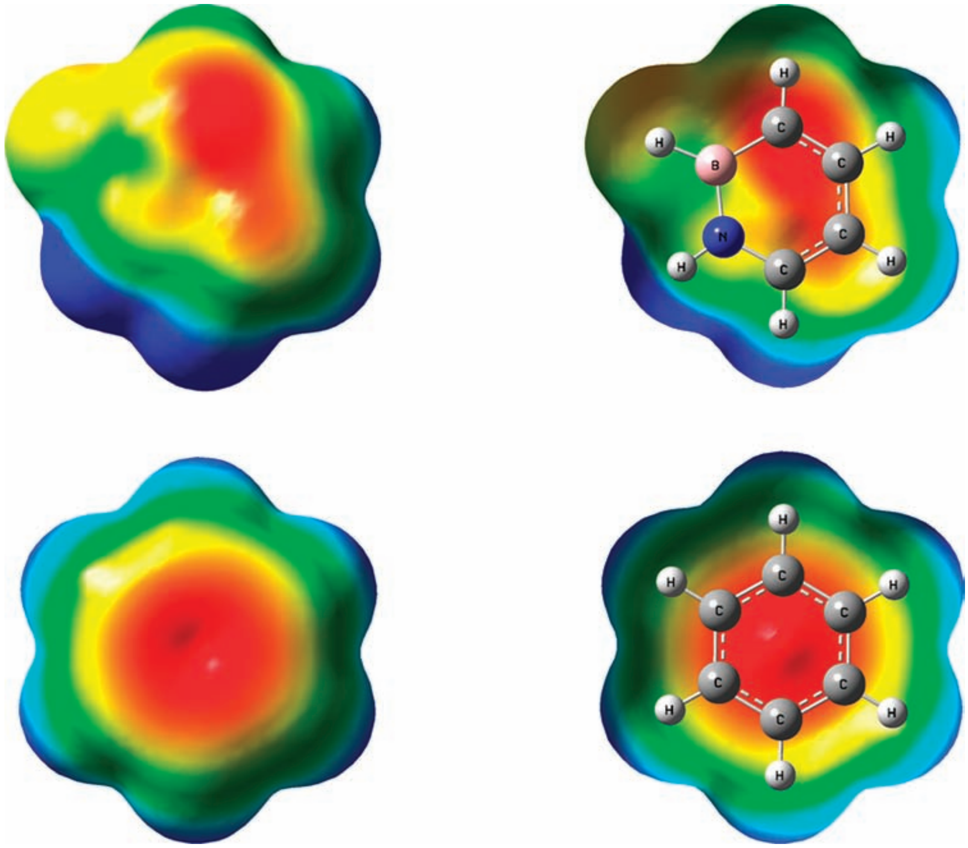

Figure 4. Electron density maps for the MP2-optimized structures of 1,2-dihydro-1,2-azaborine and benzene mapped with the electrostatic potential (Iso Val = 0.001) from the total SCF density. Red is most negative (electron rich) and blue is most positive.

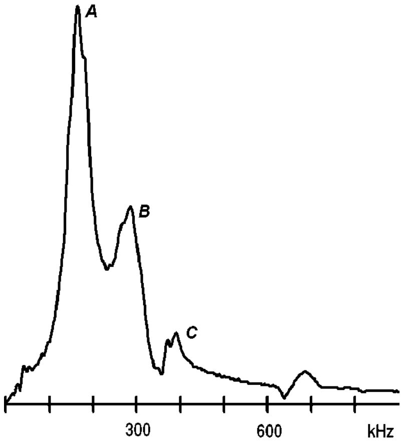

Figure 5. Hyperfine components of the $1_{01}-0_{00}$ transition at 8099 MHz (not all components are shown since they span a 2 MHz range for this transition). The stimulation frequency is 8098.770 MHz, and frequencies on the *x*-axis are relative to the stimulation frequency with *A* measured to be 8097.959, *B* at 8098.073, and *C* at 8908.172 MHz.

kHz with a measurement uncertainty of about 5 kHz for resolved transitions. We have high confidence that our current spectral assignment is correct, although some hyperfine components were not assigned due largely to the spectral line congestion. Only three rotational transitions were observed for the D-enriched species. Further frequency searches using refined rotational constants were performed for the D-enriched species, but no additional lines were found.

Nuclear quadrupole coupling of two nuclei, ^{11}B (I = 3/2) and ^{14}N (I = 1), and ^{10}B (I = 3) and ^{14}N, with the molecular rotation yielded rich hyperfine spectral patterns. This quadrupole data (i.e., the hyperfine splittings) allow us to determine the electric field gradient environment and *p* valence electron density at the B and N nuclei. The ^{10}B nuclear quadrupole moment is approximately twice as large as that of ^{11}B. Herb Pickett's SPFIT[16] program was used to analyze and fit the observed hyperfine splittings. Resolved hyperfine transitions were assigned and fit using a rigid Watson's *s*-reduced Hamiltonian in the I^r representation. The variable parameters are *A*, *B*, *C*, eQq$_{aa}$, and eQq$_{bb}$ − eQq$_{cc}$. The off-diagonal element eQq$_{ab}$, which could be nonzero for a planar molecule, was not determined from the current fits. The angular momentum coupling scheme used in this analysis is the $\mathbf{I_B} + \mathbf{J} = \mathbf{F_1}, \mathbf{I_N} + \mathbf{F_1} = \mathbf{F}$ coupling scheme. In this coupling scheme, the boron nucleus is coupled to the rotational angular momentum to give $\mathbf{I_B} + \mathbf{J} = \mathbf{F_1}$. The nitrogen nucleus was coupled to $\mathbf{F_1}$ to give $\mathbf{I_N} + \mathbf{F_1} = \mathbf{F}$. Table S1 (Supporting Information) lists the observed hyperfine transition frequencies for $^{11}B^{14}NC_4H_6$, Table S2 (Supporting Information) lists the observed hyperfine transition frequencies for $^{10}B^{14}NC_4H_6$, and Table S3 lists the three transitions observed for $^{11}B^{14}NC_4H_5D$. The assignments are specified by the quantum numbers $|J\ K_a\ K_c\ F_1\ F\rangle$, where *F* represents the total angular momentum. The molecular parameters determined by fitting the experimental transition frequencies are given in Table 1.

B. Structure Determination. It was not possible to experimentally determine all of the structural parameters since the rotational constants for only three isotopologues were measured. Because the molecule has low molecular symmetry, a complete

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Table 2. Bond Lengths and Interbond Angles from the Least-Squares Fit to the Experimental Rotational Constants[a]

parameter	microwave	MP2/6-31+G(d,p)	MP2/6-311+G(d,p)
R(B−N)	1.45(3) Å	1.438 Å	1.437 Å
R(B−C)	1.51(1) Å	1.510 Å	1.516 Å
R(N−C)	1.37(3) Å	1.369 Å	1.368 Å
α	119°	119.2°	119.1°
β	115(3)°	114.3°	114.5°
γ	123(3)°	124.4°	124.1°
δ	120°	120.4°	120.4°
σ	0.9 MHz		

[a] The listed error limits are 2σ.

analysis of the ring structure would require five isotopologues with different ring substitutions. In the present analysis a number of important structural parameters for the ring are obtained. Since the ^{10}B and ^{2}H isotopologues were measured, we can accurately determine some structural parameters by fitting the effective moments of inertia. The identified structural parameters, which depend on the boron position, are the bond distances R(B−C) and R(B−N). We performed a least-squares structure fit analysis to determine the polar coordinates of boron and nitrogen from the carbon atom indicated in Figure 3. The variable parameters R(C$_6$−B),θ and R(C$_6$−N),ϕ can subsequently be used to determine the R(B−N) bond length. Using the structure with the best fit to the nine rotational constants, the bond lengths and internal angles (α, β, γ, δ) shown in Figure 2 were obtained, with results given in Table 2. In this least-squares analysis, the structural parameters R(B−H), and R(N−H) were varied incrementally. It was found that changing the R(N−H) bond length from the calculated value did not significantly improve the fit and so was fixed at 1.02 Å. This value was obtained from the MP2/6-31+G(d) calculation and agreed with the value of 1.02 Å obtained from the structure fit. The value for R(B−H) obtained using it as a fit parameter is 1.19 Å. Correlation effects are reduced, and we prefer the value of 1.21 Å obtained by increasing fixed values for R(B−H) and looking for the lowest standard deviation for the fit. The difference in these values is not significant. Kraitchman analysis was less useful for this study because it provides only values for the coordinates of boron in the center of mass system. Measurements using isotopically labeled ^{13}C and ^{15}N isotopologues would allow refinement of R(B−C), R(B−N), and R(N−H) bond lengths and angles in the ring. However, because no isotopologues were measured for any ring carbon and nitrogen atoms in this work, the bond distances and angles in the C−C−C−C part of the azaborine ring could not be directly obtained and were fixed to the theoretical values, MP2/6-31+G(d,p). The results of this least-squares fit analysis are given in Table 2. Error limits for the angles are only reported for γ and β, as they are the only angles completely determined from the fit. The errors for the angles were determined two ways. The first way involved the propagation of error through the parameters using the law of sines and, second, by moving the nitrogen atom 2σ along R(N−C) in each direction to determine the effect on γ and β. Both give similar results with an upper limit 2σ estimate for the errors of 3°.

C. Townes−Dailey Population Analysis. The measured nuclear quadrupole coupling constants were used to determine the p$_c$ valence electron occupancy in boron and nitrogen using an extended Townes−Dailey population analysis.[11] Because the electric field gradients are primarily dependent on the p-electron density, useful information about the p-electron occupancy can be directly determined from the measured eQq value. Boron has three electrons to form the three sigma bonds (sp^2 hybridized), but has an empty, unhybridized p$_c$-orbital. Nitrogen has two electrons occupying the p$_c$-orbital and is expected to have p valence electron occupancy p$_c$ closer to 2e, given a model where three sp^2 orbitals are formed to make three sigma bonds. A natural bond orbital calculation at the MP2/6-311+G(d,p) shows electron density in the valence p$_c$-orbital of ^{11}B to be 0.35 and that of ^{14}N to be 1.6. The occupancy of the orbital can be experimentally determined by comparison of the molecular coupling constants and the atomic coupling constants. With the constraint that the sum of p$_a$, p$_b$, and p$_c$ populations is 2 for ^{11}B and 4 for ^{14}N, the populations of p$_c$ were experimentally determined to be 0.3 for ^{11}B and 1.3 for ^{14}N. It is expected that the hybridization promotes one electron from the s- into the p-orbitals, giving a total of two for boron and four for nitrogen. Results from this simple model are surprisingly close to calculated occupations for nitrogen and boron and reveal that contributions to the coupling constants along the a- and b-axis by the hybridized orbitals have atomic p-orbital character. These p$_c$-orbital electron densities may have been modified by π-bonding in the ring.

An alternative analysis for nitrogen can be performed if we assume that the nitrogen atom has pyrrole-like hybridization and that the eQq$_{zz}$(^{14}N) = eQq$_{cc}$(^{14}N) (i.e., the inertial c-axis is parallel to the z-axis of the quadrupole coupling tensor so the molecule lies in the xy-plane with nitrogen on the y-axis). We can estimate the p$_c$-electron occupation number and π_c, the amount of π-bonding associated with the nitrogen p$_c$-orbital (the 2p-orbital that lies orthogonal to the molecular plane). For this case the following Townes−Dailey equation can be applied to 1,2-azaborine: $\mathrm{eQq}_{zz}/\mathrm{eQq}_{210} = (1 - 0.375 i_\sigma(\mathrm{NC}) - 0.375 i_\sigma(\mathrm{NB}) - 0.25 i_\sigma(\mathrm{NH}) - \pi_c)/(1 + 0.3[c^-])$.[17] The best estimate of eQq$_{210}$ for a single 2p electron in atomic nitrogen is −11.2(2) MHz,[18] and c^-, the negative charge on nitrogen, is taken from the natural bond orbital estimate of 0.3. i_σ(NC), i_σ(NB), and i_σ(NH) are the ionic character for the σ-bond, which can be obtained from the electronegativites using the relation, $i_\sigma = |x_a - x_b|/2$, giving $i_\sigma(\mathrm{NC}) = 0.25$ and $i_\sigma(\mathrm{NH}) = i_\sigma(\mathrm{NB}) = 0.5$. The p$_c$ occupation number is expressed as $n_z = 2 - \pi_c$. From these equations, we obtained the amount of π-bonding ($\pi_c = 0.5$), clearly indicating delocalization of π-electrons. This gives the value of electron occupation number in the p$_c$-orbital as $n_z = 1.5$. The value of $n_z = 1.5$ is in good agreement with the theoretical value (1.6) and is only slightly larger than the 1.3 obtained using the value of extended Townes−Dailey analysis discussed above.

Bonding around the nitrogen in 1,2-dihydro-1,2-azaborine is in principle similar to that of pyrrole. Pyrrole[19] thus serves as a molecule for comparison of quadrupole coupling strengths of the nitrogen nucleus along the c-axis. In both molecules, the nuclear quadrupole coupling constant along the c-inertial axis, eQq$_{cc}$, is perpendicular to the ring plane; the nitrogen atom is sigma bonded to hydrogen. The measured eQq$_{cc}$ for 1,2-dihydro-1,2-azaborine is −1.25 MHz, and for pyrrole the value is[19] −2.70 MHz (note that in ref. 19 the reported nitrogen quadrupole coupling constants have correct values but are assigned to incorrect inertial axes; a and c are swapped). MP2/6-31+G(d,p) calculations similar to those above, when applied to pyrrole,

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give an NBO population for the p_c orbital of 1.6e. Applying the Townes-Dailey analysis to pyrrole, with corrected quadrupole coupling constants gives the n_z population for the p_c orbital of 1.5e, as obtained for 1,2-dihydro-1,2-azaborine. This implies that p-electron electronic charge distribution around the nitrogen atom of 1,2-dihydro-1,2-azaborine is very similar to that of pyrrole. The observed similarities indicate that, for both molecules, a nitrogen unshared electron pair, which lies orthogonal to the ring plane, participates in the π-electron system.

V. Discussion

The microwave spectrum for 1,2-dihydro-1,2-azaborine has been measured in the 7−18 GHz range, providing important structural parameters for the isolated BNC_4H_6 molecule. Analysis of the rotational spectrum has shown that this molecule is a near-oblate asymmetric top (asymmetry parameter $\kappa = 0.79$). Measured rotational constants and nuclear quadrupole coupling constants for the ground-state structure are in good agreement with the theoretical calculations. The r_0 structural parameters $R(B-N) = 1.45(3)$ Å, $R(B-C) = 1.51(1)$ Å, and $R(N-C) = 1.37$ (3) Å have been determined from the least-squares fit analysis. Measured quadrupole coupling constants of ^{14}N, ^{10}B, and ^{11}B are consistent with previous measurements on small B−N molecules. The nuclear quadrupole moments of boron and nitrogen have the same sign, with the value for ^{11}B being twice and ^{10}B four times that of ^{14}N. The measured nitrogen quadrupole coupling constants for the two boron isotopomers in the principal axis system are essentially the same within the given uncertainty limit. As expected, these ^{14}N eQq values should not change for the different boron isotopomers.

Our measurements of rotational constants permitted us to directly measure the planarity of this molecule from the inertial defect. From the measured rotational constants, we calculated the ground-state inertial defect to be $\Delta_0 = 0.02$ amu·Å^2. The observed near-zero and positive inertial defect indicates that the molecular structure of 1,2-dihydro-1,2-azaborine is planar. If the ring were to be nonplanar or have large anharmonicity, a negative inertial defect would have been observed. Frequency calculations (MP2/6-311+G**) showed there are three ring-puckering modes that can distort the molecule from planarity. These three modes have anharmonic vibration frequencies ranging from 325 to 465 cm^{-1} and contribute little to the total zero-point vibrational energy. We estimated the vibrational temperature in the molecular beam to be about 10 K for our experiment. The calculated asymmetrically reduced distortion constant for 1,2-dihydro-1,2-azaborine is $\Delta_J = 0.7$ kHz. Data from both experiment and theory suggested that the ring is planar with a very small centrifugal distortional constant.

Several theoretical calculations predicted that 1,2-dihydro-1,2-azaborine would show more aromatic character than borazine but would have approximately half the aromatic stabilization energy as benzene. Studies by Martitz et al.[2] confirmed that this is most likely to be the case. A key aspect of the present work was to provide high-resolution spectroscopic data that would provide additional information to support the current hypothesis regarding the aromatic properties of 1,2-dihydro-1,2-azaborine. One requirement of aromaticity for a heterocyclic ring molecule is that the ring must be planar. We have shown that this is the case for 1,2-dihydro-1,2-azaborine (see above discussion). Because the ring is planar, we can infer that there is some π-electron overlap in the B−N bond. Our least-squares fit analysis of the BNC_4H_6 structure showed the measured bond distance between boron and nitrogen, $R(B-N) = 1.45$ Å. This distance is closer to the double bond found in H_2NBH_2 ($R(B-N) = 1.39$ Å) than the single bond found in H_3NBH_3 ($R(B-N) = 1.65$ Å). The measured bond length $R(B-C) = 1.51$ Å is longer compared with the C−C bond distance in benzene due to the increased atomic radius of boron. The gas phase bond lengths for BNC_4H_6 are in good agreement with the bond lengths determined by single-crystal X-ray diffraction of substituted 1,2-azaborine derivatives.[4]

Table 3. B−N Bond Distances Reported in the Literature

molecule	$R(B-N)$/Å
H_2NBH_2	1.391(2)[a]
H_3NBF_3	1.59(2)[b]
BH_3NH_3	1.6576(16)[c]
HCN-BF_3* [e]	2.47(2)[d]

[a] Reference 7. [b] Reference 8. [c] Reference 9. [d] Reference 10. [e] *van der Waals dimer.

Our interpretation of the nuclear quadupole coupling constants reveals additional information regarding the aromaticity. The component perpendicular to the *c*-axis for nitrogen is consistent with other nitrogen-containing aromatic molecules. The electric field gradients experienced by nitrogen in 1,2-dihydro-1,2-azaborine and pyrrole are nearly equal. Additionally, using an extended Townes−Daily analysis, we "see" approximately 0.3*e* in the boron valence p_c-orbital. This result is consistent with a π-electron delocalized structure for 1,2-dihydro-1,2-azaborine.

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Supporting Information Available: The measured transition frequencies for all isotopomers and all lines included in the spectra fits, including the fit deviations, are given in Tables S1, S2, and S3. Also included is the complete author list for ref 12. This material is available free of charge via the Internet at http://pubs.acs.org.

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