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chemical bonding involving elements in the thrid row. We have focused on only one such insight in this paper, the resonance ffect, but the fundamental ideas discussed here can be applied to illucidate concepts basic to chemical reactions.

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Registry No. Benzene, 71-43-2; fluorobenzene, 462-06-6; phenol, 108-95-2; aniline, 62-53-3; chlorobenzene, 108-90-7; bromobenzene, 108-86-1; anisole, 100-66-3.

Microwave Spectra and Molecular Structure of $BH(NH_2)_2$

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Abstract: The effective molecular structure of boranediamine, $BH(NH_2)_2$, has been determined from the microwave spectra of eight isotopic species. The molecule has planar C_{2v} symmetry, with $r(\text{B–H}) = 1.193 \pm 0.001$ Å, $r(\text{B–N}) = 1.418 \pm 0.001$ Å, $r(\text{N–H}_{\text{cis}}) = 1.005 \pm 0.005$ Å, $r(\text{N–H}_{\text{trans}}) = 1.000 \pm 0.003$ Å, $\angle\text{NBN} = 122.0 \pm 0.3°$, $\angle\text{BNH}_{\text{cis}} = 121.1 \pm 0.1°$, and $\angle\text{BNH}_{\text{trans}} = 123.7 \pm 0.6°$, where the amine hydrogens are cis or trans relative to the boron-bonded hydrogen. The dipole moment is 1.245 ± 0.017 D.

The molecular structures of the boranamines have attracted interest since the first electronic structure calculations[1] developed for simple organic molecules were used to treat isoelectronic B–N-containing compounds. These and later calculations[2-6] showed that the B–N bonds of boranamines have partial double-bond character that results from delocalization of the nitrogen lone-pair electrons into the vacant boron $2p_z$ orbital. The degree of delocalization has important structural consequences. With no delocalization, the torsional barrier about the B–N bond is low, and the three nitrogen bonds assume a pyramidal configuration due to repulsion by the nitrogen lone pair. On the other hand, with sufficient delocalization, the three nitrogen bonds are coplanar, the torsional barrier is high, and the B–N bond length is shortened. In either situation, microwave spectroscopy permits determination of the molecular structure, the molecule's planarity, the height of the torsional barrier (if it is less than 5 kcal mol^{-1}) and the magnitude of the electric dipole moment.

Despite considerable theoretical interest, however, there has been a notable lack of experimental data on the structures of the unsubstituted boranamines, $BH_{3-n}(NH_2)_n$ (n = 1, 2, or 3). This is due, in part, to the instability of condensed boranamine monomers,[7] which complicates their synthesis. Recently, however, boranediamine, $BH(NH_2)_2$, was isolated under normal conditions, and we reported its molecular structure based on preliminary microwave data.[8] Shortly thereafter, the microwave spectrum and partial structure of boranamine, BH_2NH_2, were reported by Suggie, Takeo, and Matsumura.[9] In the present paper we report the results of further investigation of the microwave spectrum of $BH(NH_2)_2$ and seven of its isotopic species. This study has yielded more accurate values for the rotational constants, molecular structure, and dipole moment than had been reported previously.

Experimental Section

The microwave spectrometer used to measure the rotational spectra of boranediamine has been described in detail previously.[10,11] It employs Stark modulation at one of a number of selectable frequencies in the range 5–20 kHz. Both the microwave source and the data acquisition system are controlled by a laboratory minicomputer. The spectrometer has a large dynamic range and is capable of recovering weak signals by means of signal averaging and digital filtering of the data.

Reflex klystrons are used as microwave sources in the 8–40 and 44–48-GHz ranges. These sources are phase-locked to a 100-kHz, crystal-controlled secondary frequency standard by means of a harmonic multiplier and a series of phase-locked loops. Shottky diodes are used to detect the microwave signals in the 8–18-GHz region; point-contact diodes are used in all other frequency regions. The microwave cell is operated at −45 °C and 5–20-μm pressure, as monitored by a capacitance manometer.

Boranediamine was synthesized following a procedure developed by Briggs et al.,[8] in which a stream of dry ammonia is passed over molten borane ammoniate ($BH_3 \cdot NH_3$). Obtaining high yields of boranediamine required excess ammonia, which was sublimed from the product at −104 °C. Samples free of detectable amounts of ammonia were difficult to prepare, both because the purification was not complete and because boranediamine decomposes to yield ammonia. The handling of boranediamine was complicated by its strong tendency to polymerize in the liquid phase and its high reactivity toward water. Gas samples below

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Table I. Observed and Calculated Rotational Transition Frequencies for Various Isotopic Species of $BH(NH_2)_2$[a]

	$^{10}BH(NH_2)_2$		$^{11}BH(NH_2)_2$		*cis*-$^{11}BHNDHND_2$[c]		*trans*-$^{11}BHNDHND_2$[c]	
transition	obsd	obsd − calcd	obsd	obsd − calcd	obsd	obsd − calcd	obsd	obsd − calcd
1(0,1)-1(1,0)	45976.88	0.12	44635.75	0.21	33830.73	0.47	38574.68	0.14
1(1,1)-2(0,2)	10949.28	−0.80	9636.99	−0.56			9201.75	−0.37
2(0,2)-2(1,1)	47320.55	0.22	46012.20	0.46	35174.59	−0.52	39699.02	0.08
2(1,2)-3(0,3)	7120.68	−0.02	8426.46	0.28	12433.84	0.12		
3(0,3)-3(1,2)	49389.09	0.05	48133.52	−0.16	37264.53	0.43		
3(1,3)-4(0,4)	25695.31	−0.39	26996.74	−0.57	28647.61	−0.34	21525.88	−0.21
3(2,2)-4(1,3)								
4(2,3)-5(1,4)			37787.93	−0.07	16910.86	−0.10	35232.72	−0.02
4(2,2)-5(1,5)					37061.43	−0.11		
σ^b		0.532		0.490		0.454		0.321

	$^{10}BH(ND_2)_2$		$^{11}BH(ND_2)_2$		$^{10}BD(ND_2)_2$		$^{11}BD(ND_2)_2$	
transition	obsd	obsd − calcd	obsd	obsd − calcd	obsd	obsd − calcd	obsd	obsd − calcd
0(0,0)-1(1,1)					39095.59	−0.52	38553.97	−0.84
1(0,1)-1(1,0)	34701.79	−0.20	33801.40	−0.12	26969.35	0.35	26462.86	0.07
2(0,2)-2(1,1)	35867.10	0.23	34990.48	−0.21	28383.03	0.14	27897.66	0.24
2(1,2)-3(0,3)	8575.48	0.29	9448.30	0.20	15954.40	0.32	16434.29	0.63
2(2,1)-3(1,2)							32803.72	0.79
3(0,3)-3(1,2)	37667.06	0.00	36830.91	0.01	30601.48	−0.10	30151.56	−0.23
3(1,3)-4(0,4)	23729.92	−0.18	24597.66	−0.01	30992.80	0.05		
3(2,2)-4(1,3)					18250.77	0.16	16687.65	−0.32
4(2,3)-5(1,4)	25483.73	0.03	22698.35	0.12				
4(0,4)-4(1,3)			39388.54	0.17				
σ^b		0.261		0.189		0.372		0.698

[a] All values in MHz. [b] Root-mean-square deviation between observed and calculated transition frequencies in MHz. [c] Cis and trans refer to the positions of the amine hydrogens relative to the B–H-bonded hydrogen.

Table II. Effective Rotational Constants *A*, *B*, and *C* (MHz) and Inertial Defects, Δ (amu Å^2) for the Species Given in Table I

parameter	$^{10}BH(NH_2)_2$	$^{11}BH(NH_2)_2$	*cis*-$^{11}BHNDHND_2$[b]	*trans*-$^{11}BHNDHND_2$[b]
A	53754.36 ± 0.710	52383.74 ± 0.305	40484.45 ± 0.277	45098.23 ± 0.233
B	9092.56 ± 0.068	9093.56 ± 0.062	7960.48 ± 0.057	7624.20 ± 0.048
C	7777.60 ± 0.029	7748.20 ± 0.121	6654.19 ± 0.069	6523.69 ± 0.100
Δ	−0.0045 ± 0.0022	−0.0013[a] ± 0.0004	−0.0203 ± 0.0004	−0.0241 ± 0.0011

parameter	$^{10}BH(ND_2)_2$	$^{11}BH(ND_2)_2$	$^{10}BD(ND_2)_2$	$^{11}BD(ND_2)_2$
A	40991.39 ± 0.163	40069.30 ± 0.117	33032.55 ± 0.172	32508.80 ± 0.347
B	7425.91 ± 0.033	7426.65 ± 0.024	7424.62 ± 0.042	7425.30 ± 0.101
C	6289.40 ± 0.067	6267.78 ± 0.042	6063.56 ± 0.081	6046.01 ± 0.183
Δ	−0.0310 ± 0.0007	−0.0308 ± 0.0004	−0.0204 ± 0.0011	−0.0188 ± 0.0021

[a] This value was obtained from the data in Table I using the program CDANAL.[10] [b] Cis and trans refer to the positions of the amine hydrogens relative to the B–H-bonded hydrogen.

100-torr pressure could be kept in clean dry Pyrex for several days with less than 20% decomposition.

The various deuterated species of boranediamine used in this study were synthesized from selectively deuterated borane ammoniate[3,12] and deuterioammonia. N-Deuterated borane ammoniate was prepared by exchanging the amine hydrogens in D_2O; the B hydrogens do not exchange under these conditions.[12] For B deuteration, it was necessary to prepare the borane ammoniate directly from sodium borodeuteride, $NaBD_4$. Partially N-deuterated boranediamines were prepared from $ND_3{\cdot}BH_3$ and partially deuterated ammonia.

Microwave Spectra and Structure

Microwave Spectra and Rotational Constants. The 8–50-GHz microwave spectrum of boranediamine is characteristic of a light slightly asymmetric-top molecule having a permanent *b* dipole moment; that is, the spectrum is sparse, and the transitions do not appear in closely spaced regular patterns except for a single high-frequency Q-branch series. The initial assignment of the spectra was aided by a rigid-rotor calculation based on a planar molecular geometry with bond lengths and angles typical of related compounds. After at least two transitions (not both Q-branch transitions) for a given species were correctly identified by their Stark structure, a least-squares fit to these transitions was used to refine the rotational constants and predict the frequencies of other transitions. In this preliminary stage of refinement, the planar constraint, $I_c - I_a - I_b = 0$ was added to reduce the number of correctly assigned transitions required to perform the least-squares refinement.[3] These predictions were sufficiently accurate (within 30 MHz) to speed the assignment procedure greatly. The success of this procedure validated the initial assumption of an approximately planar molecular structure. Ultimately, the frequencies of all transitions with $J \leq 5$ within the frequency range of the spectrometer were measured for eight isotopic species of boranediamine (Table I).

Measurement of the low-*J* transition frequencies of boranediamine was complicated by the broad irregular line shape caused by the nuclear electric quadrupole coupling of the boron and nitrogen nuclear spins to the overall rotation of the molecule. To first order, however, the unperturbed rotational transition frequency is given by the intensity-weighted mean of the line shape.[13] This mean was determined by numerically integrating over the line shape and finding the frequency corresponding to half the value of the integral. Transition frequencies measured with this procedure were reproducible to 0.1 MHz.

The effective rotational constants given in Table II were determined, within the rigid-rotor approximation, by using a

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Table III. High-*J* Rotational Transitions of $BH(NH_2)_2$[a]

transition	$^{10}BH(NH_2)_2$	$^{11}BH(NH_2)_2$
4(1,4)-5(0,5)		45974.76
5(2,4)-6(1,5)	21288.61	17105.40
6(2,4)-7(1,7)		35549.24
7(2,5)-8(1,8)	29062.90	26087.25
7(2,6)-8(1,7)	21626.74	25920.40
8(2,6)-9(1,9)	20799.20	18179.88
9(2,7)-10(1,10)	14186.57	11998.36
10(2,8)-11(1,11)	9378.56	7699.61
10(3,8)-11(2,9)	27036.93	19625.90

rotl const[b]	$^{10}BH(NH_2)_2$	$^{11}BH(NH_2)_2$
A	53755.10 ± 0.21	52385.83 ± 0.36
B	9092.88 ± 0.09	9093.86 ± 0.13
C	7777.77 ± 0.07	7748.91 ± 0.09

[a] All values in MHz. [b] Distortion-free rotational constants determined from the combined data of Tables I and II.

least-squares procedure to fit the transition frequencies given in Table I. The closeness of the calculated rigid-rotor spectrum to the observed spectrum indicates that there are no significant perturbations of the transition frequencies other than the slight effect of centrifugal distortion and nuclear electric quadrupole splitting.

The inverse of the variance–covariance matrix, **M**, for the rotational constants was calculated for each species for later use in the molecular structure calculation. As a typical example, $\mathbf{M}^{-1}$ and the correlation matrix, ρ, for $^{11}BH(NH_2)_2$ are given in eq 1a and 1b. The notation of ref 14 is used for the statistical quantities.

$$\mathbf{M}^{-1} = \begin{bmatrix} 47.1 & -110.4 & -30.9 \\ -110.4 & 39.33 & 34.4 \\ 30.9 & 34.4 & 61.1 \end{bmatrix} \quad (1a)$$

$$\rho = \begin{bmatrix} 1.00 & 0.858 & 0.700 \\ 0.858 & 1.00 & 0.516 \\ 0.700 & 0.516 & 1.00 \end{bmatrix} \quad (1b)$$

The rows and columns are labeled in the order *A*, *B*, and *C*, left to right and top to bottom, and $\mathbf{M}^{-1} = \mathbf{A}^{T}\mathbf{A}/\hat{\sigma}^2$, $\hat{\sigma}^2 = \mathbf{V}^{T}\mathbf{V}/(n - 3)$, $\hat{\sigma}_i = (M_{ii})^{1/2}$, and $\rho_{ij} = M_{ij}/\hat{\sigma}_i\hat{\sigma}_j$. Here *A* is the Jacobian matrix, **V** is the vector of residuals, $\hat{\sigma}$ is the standard deviation of the least-squares fit, $\hat{\sigma}_i$ is the least-squares estimated uncertainty in the rotational constant *i*, and *n* is the number of transitions used in the fit. In all cases the measurement errors were assumed to be uncorrelated and all transitions were given the same statistical weight. The high correlation between the rotational constants, indicated by ρ, results from fitting a limited number of transitions—in this case only *b*-dipole-type transitions from three or four subbranch wings. This situation is not easily improved, since only *b*-dipole-type transitions are allowed for the boranediamines that have C_{2v} symmetry, because the *a*-dipole transitions are very weak for the asymmetrically substituted species and because additional low-*J* transitions of the other subbranch wings occur at frequencies above the usual range of the spectrometer.

To estimate the contribution of centrifugal distortion to the effective rotational constants determined from low-J transitions, several high-*J* transitions were measured for the normal ^{10}B and ^{11}B species, and distortion-free rotational constants were determined with the computer program CDANAL[15] (Table III). The root-mean-square difference between the two sets of rotational constants (those of Table II and Table III) is 0.9 MHz. It will be shown later that this is not the limiting source of error in the determination of the molecular structure.

In addition to the rotational transitions of the ground state, several vibrational satellites were observed. The satellites have the same general line shape as the corresponding ground-state transition. Transition frequencies of the satellites are very sensitive to the *A* rotational constant and, consequently, are shifted by 700–1200 MHz from the corresponding ground-state transition.

Dipole Moment. The magnitude of the dipole moment was determined from analysis of the Stark effect. Similar to the zero-field transitions, the Stark components of boranediamine are split by nuclear electric quadrupole coupling, so the center of mass of the line shape was taken as the transition frequency. The measurements were made at high field so that the Stark perturbation was much greater than the nuclear quadrupole perturbation. Measurements were made for all $\Delta M = 0$ Stark components of the 1(0,1)–1(1,0) and 1(1,1)–2(0,2) transitions of $^{10}BH(NH_2)_2$ and $^{11}BH(NH_2)_2$. Within experimental error, all transitions showed second-order Stark behavior and extrapolated back to the observed zero-field transition frequency. The electric field strength in the microwave cell was calibrated by using the commonly accepted value for the dipole moment of OCS, 0.71521 D.[16] By using the *A* and *B* Stark coefficients calculated within the rigid-rotor approximation, we found the dipole moment to be $|\mu| = 1.245 \pm 0.017$ D.

The sign of the dipole moment cannot be determined from the Stark effect, but by symmetry it is restricted to lie along the *b* axis (coaxial with the B–H bond). Two recent ab initio calculations[2,5] disagree on the sign of the molecular dipole moment, but arguments presented in the Discussion support the sign $^{-}(BH){-}((NH_2)_2)^{+}$.

Molecular Structure. The molecular structure of boranediamine was calculated from the effective rotational constants from two different methods to give the effective structure coordinates (r_0) and the substituted structure coordinates (r_s). The r_0 structure was determined by a least-squares fit[3] to the observed rotational constants; the r_s structure was determined by means of Kraitchman's equations.[17]

Both of these methods require the rotational constants of several isotopically substituted species. Because of the large number of such species and the effort required to make a spectral assignment, a procedure was developed to determine, in advance, which of the species would contribute most to the refinement of the structural parameters. Rotational constants for a set of isotopic species are calculated, based on preliminary structure,[8] and then used in the effective structure calculation as "synthetic data" to further refine the structural parameters. Isotopic species that most reduced the standard deviations of each parameter and the correlations between the calculated structural parameters were chosen for study.

Effective Structure. The effective structure of boranediamine was determined from the rotational constants given in Table II with the computer program INTCORD.[3] In a procedure similar to merged least squares,[18] this program reduces the root-mean-square difference between the observed and calculated rotational constants by adjusting the structural parameters. The weight matrix, **P**, used in this calculation is the block-diagonal supermatrix formed from the inverse of the variance–covariance matrices, $\mathbf{M}^{-1}$, obtained from the calculation of the rotational constants of the eight isotopic species. In previous studies **P** has been omitted or only its diagonal elements have been used.[19] However, the full **P** matrix must be used when uncertainties in the rotational constants are highly correlated. This is because nonlinear least squares will not converge to the true minimum, nor will the uncertainties in the adjusted parameters be calculated correctly, if significant correlations are ignored.[14] The relatively high correlation between the rotational constants in the case of the boranediamine dictates the need for **P**.

The results of the effective structure calculation for boranediamine, assuming a planar structure, are given in Table IV. The

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Table IV. Effective Structures for $BH(NH_2)_2$[a]

structural parameter[b,i]	eff struct I[c,d]	eff struct II[c,e]	eff struct III[f]	corr errors,[g] II − I	model errors,[h] III − I
r(B–H)	1.193 ± 0.001	1.193 ± 0.001	1.194 ± 0.001	0.0005	0.0012
r(B–N)	1.418 ± 0.001	1.418 ± 0.001	1.414 ± 0.002	0.0040	0.0039
$r(\mathrm{N{-}H_{cis}})$[j]	1.005 ± 0.005	0.998 ± 0.006	1.015 ± 0.006	−0.0068	0.0096
$r(\mathrm{N{-}H_{trans}})$[j]	1.000 ± 0.002	1.000 ± 0.001	1.003 ± 0.002	0.0005	0.0030
$\angle\mathrm{NBN}$	121.98 ± 0.02	121.97 ± 0.03	121.95 ± 0.04	−0.01	−0.03
$\angle\mathrm{BNH_{cis}}$	121.14 ± 0.09	121.06 ± 0.24	121.27 ± 0.10	−0.08	−0.13
$\angle\mathrm{BNH_{trans}}$	123.66 ± 0.34	124.02 ± 0.61	124.68 ± 0.50	0.36	−1.02
σ[g]	7.26	5.93	5.27		

[a] We regard effective structure I as the most accurate effective structure (see Discussion). [b] Bond lengths in Å; angles in degrees. [c] Includes $^{10}BH(NH_2)_2$, $^{11}BH(NH_2)_2$, *cis*-$^{11}BHNHDND_2$, *trans*-$^{11}BHNHDND_2$, $^{10}BH(ND_2)_2$, $^{11}BH(ND_2)_2$, $^{10}BD(ND_2)_2$, and $^{11}BD(ND_2)_2$. [d] All-species correlation, P included. [e] All-species correlation, P not included. [f] Includes *cis*-$^{11}BHNHDND_2$, *trans*-$^{11}BHNHDND_2$, $^{10}BH(ND_2)_2$, $^{11}BH(ND_2)_2$, $^{10}BD(ND_2)_2$, and $^{11}BD(ND_2)_2$. Deuterated species, P included. [g] Calculation based on more significant figures than reported in table. [h] RMS difference between observed and calculated rotational constants in MHz. [i] Error limits are one standard deviation. [j] Cis and trans refer to the positions of the amine hydrogens relative to the B–H-bonded hydrogen.

Table V. Correlation Matrix for Structural Parameters of $BH(NH_2)_2$[a,b]

	r(B–N)	$r(\mathrm{N{-}H_{cis}})$	$r(\mathrm{N{-}H_{trans}})$	$\angle\mathrm{NBN}$	$\angle\mathrm{BNH_{cis}}$[c]	$\angle\mathrm{BNH_{trans}}$[c]
r(B–H)	−0.41[c]	0.41	−0.26	−0.70	−0.19	0.23
r(B–N)		−0.26	−0.29	0.47	−0.08	0.33
$r(\mathrm{N{-}H_{cis}})$[c]			−0.82	−0.11	−0.53	0.79
$r(\mathrm{N{-}H_{trans}})$[c]				−0.23	0.68	−0.93
$\angle\mathrm{NBN}$					−0.05	0.14
$\angle\mathrm{BNH_{cis}}$						−0.41

[a] Bond lengths in Å; angles in degrees. [b] Based on effective structure I (see Table IV). [c] Cis and trans refer to the positions of the amine hydrogens relative to the B–H-bonded hydrogen.

effective structure was computed by using three different sets of data to estimate the model errors and to show the influence of correlation, **P**, on the calculated structure. As can be seen by comparing structures I and II, including **P** changes the parameters slightly and redistributes the errors in the structural parameters, as evidenced by the parameter standard deviations. Furthermore, **P** has the effect of altering the correlations between the parameters (Table V). By way of example, the correlation between $\angle$NBN and r(B–N) is 0.47 when **P** is included in the calculation and −0.74 when P is omitted.

For structure III the rotational constants of $^{10}BH(NH_2)_2$ and $^{11}BH(NH_2)_2$ were omitted from the calculation, and only the rotational constants of the deuterated species were used to determine the effective structure. Thus, comparing structures I and III gives a measure of the model errors, that is, of the sensitivity of the computational model (rigid rotor, effective structure) to changes in the data base. A small difference between structures I and III is reasonable, since the effective structure does not account for vibration–rotation effects, which do, in fact, change upon deuterium substitution. Thus, the model errors should be largest when predominantly deuterated species are compared with predominantly normal species. As can be seen from Table IV, the errors resulting from omitting **P**, though small, are significant and may be nearly as large as model errors. This is further evidence for the necessity of including **P** in the effective structure calculation.

The error introduced into the effective structure by not using distortion-free rotational constants is small, as mentioned earlier. The root-mean-square deviation of the observed rotational constants and those calculated from the effective structure is 5 MHz. This is much larger than the 0.9-MHz deviation between the distortion-free rotational constants and the rotational constants determined by using only low-J transitions, $J \leq 5$.

Substituted Structure. Substituted structure I for boranediamine was determined from Kraitchman's equations[17] and the effective rotational constants of the single substitution series $^{11}BH(ND_2)_2$, $^{10}BH(ND_2)_2$, $^{11}BD(ND_2)_2$, ^{11}BH-*cis*-$NHDND_2$, and ^{11}BH-*trans*-$NHDND_2$ (where cis and trans refer to the positions of the amine hydrogens relative to the B–H hydrogen). From these data, r_s coordinates were calculated for all atoms except nitrogen. The b coordinates of the nitrogens were calculated from the center-of-mass equation $\sum m_i b_i = 0$ and the a coordinates from the second-moment equation for I_b and $I_c - I_a$.

Table VI. Substituted Structure for $BH(NH_2)_2$

structl parameter[a]	substd struct I,[b] r_s
r(B–H)	1.197 ± 0.001
r(B–N)	1.414 ± 0.001
$r(\mathrm{N{-}H_{cis}})$[c]	1.000 ± 0.001
$r(\mathrm{N{-}H_{trans}})$[c]	1.002 ± 0.002
$\angle\mathrm{NBN}$	122.4 ± 0.1
$\angle\mathrm{BNH_{cis}}$	121.7 ± 0.1
$\angle\mathrm{BNH_{trans}}$	123.8 ± 0.2

[a] Error limits are one standard deviation. Bond lengths in Å; angles in degrees. [b] From Kraitchman's equations. [c] Cis and trans refer to the positions of the amine hydrogens relative to the B–H-bonded hydrogen.

The resulting r_s coordinates and their uncertainties are given in Table VI. The uncertainty for each structural parameter was calculated from the uncertainty in the associated Cartesian coordinates. This was taken as the root-mean-square of the uncertainty due to vibration–rotation interaction estimated by the Costain rule[20] and the uncertainty resulting from the planar second moments.[19]

Discussion

Of the effective structures given in Table IV, we regard structure I as the most accurate, since it is based on all of the available isotopic data and the correlations between the rotational constants of each isotopic species are treated explicitly. Comparisons of this structure with the substituted structure will now be considered.

The effective structure calculations show that the positions of the amine hydrogens are the least well determined parameters. Specifically, in the case of H_{trans}, $r(\mathrm{N{-}H_{trans}})$ is highly correlated with $\angle\mathrm{BNH_{trans}}$ ($\rho = -0.93$). This is not the result of insufficient isotopic data. The synthetic data procedure shows that if ^{15}N data were available, this correlation would not be reduced. In fact, the high correlation results primarily from **P**, which, in turn, depends on the correlations, $\mathbf{M}^{-1}$, between rotational constants of the individual isotopic species. When **P** is omitted from the

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(20) Costain, C. C. *Trans. Am. Cryst. Assoc.* **1966**, *2*, 157–161.

calculation, this correlation is reduced to $\rho = -0.74$. Further, in effective structure I, $r(\mathrm{N-H})_{\mathrm{cis}} > r(\mathrm{N-H}_{\mathrm{trans}})$, but in structure II this order is reversed. In both structures, however, the amine hydrogen bond lengths are equal within their respective uncertainties. This suggests using the constraint $r(\mathrm{N-H}_{\mathrm{cis}}) = r(\mathrm{N-H}_{\mathrm{trans}}) = r(\mathrm{N-H})$ in the structure I calculation. This gives $r(\mathrm{N-H}) = 1.001 \pm 0.001$ Å. Subsequent changes in the other parameters are within the uncertainties given by structure I.

The value of $r(\mathrm{B-N})$ is sensitive to inclusion of the $^{10}\mathrm{BH(NH_2)_2}$ and $^{11}\mathrm{BH(NH_2)_2}$ data in the fit. Neither effective structure III nor the r_s structure uses data for these species. Both give $r(\mathrm{B-N}) = 1.414 \pm 0.002$ Å. When the $^{10}\mathrm{BH(NH_2)_2}$ and $^{11}\mathrm{BH(NH_2)_2}$ data are included, $r(\mathrm{B-N}) = 1.418 \pm 0.001$ Å. Because the effective structure calculation is most sensitive to the position of the heavy atoms and because the uncertainty is reduced when all isotopic data are included in the fit, 1.418 Å is probably the better effective value for $r(\mathrm{B-N})$.

All of the structure calculations for boranediamine were made by assuming a planar molecular structure. We will now examine the validity of this assumption. Since the nitrogen lone-pair electrons could repel the amine hydrogens out of the NBN plane, the question of planarity concerns the position of the amine hydrogens. No similar repulsion effect exists that could cause the B–N hydrogen to lie outside the NBN plane. Relaxing the planar constraint on the amine hydrogens in the effective structure calculations gives an out-of-plane hydrogen angle of 3 ± 2.8° where the hydrogens of one amine group are above the plane and those of the other group are below the plane. Thus, within statistical uncertainty, the amine hydrogens lie within the NBN plane. Further evidence for the planarity of boranediamine is its small inertial defect, which is between -0.031 and -0.001 amu Å^2 for all of the species studied.

The partial double-bond character of the B–N bond in boranediamine, indicated by the ab initio calculations,[2-5] is substantiated by four experimental results. The molecule is planar; the B–N bond length is much closer to the B–N double-bond length of 1.391 Å in $\mathrm{BH_2NH_2}$[9] than it is to the B–N single-bond length of 1.672 Å in $\mathrm{BH_3{\cdot}NH_3}$;[21] the torsional barrier about the B–N bond is high; and the B–N stretching force constant is high. The high torsional barrier is indicated by the absence of characteristic torsional satellites in the microwave spectrum and by the results of a recent normal coordinate analysis.[22] This analysis indicates that the two torsional vibrations occur at 464 and 422 cm^{-1}, from which an approximate barrier height of 7 kcal mol^{-1} is calculated.[23] Further, the B–N stretching force constant for boranediamine is found to be 6.25 mydn Å^{-1}. This compares with 7 mdyn Å^{-1} for $\mathrm{(CH_3)BNH_2}$[24] (double bond), 6.3 mdyn Å^{-1} for $\mathrm{(BHNH)_3}$[25] (partial double bond), and 4.56 mdyn Å^{-1} for $\mathrm{BH_3{\cdot}NH_3}$[26] (single bond).

The polarity of the B–N bond and the direction of the molecular dipole moment in boranamines have been the subjects of experimental[27] and theoretical[2,3,5] studies; however, the conclusions reached do not always agree with each other. If the B—N bond is considered to be a double bond, then the formalism of valence bond theory requires a formal positive charge on N and a negative charge on B, giving the polarity $^-\mathrm{B{=}N}^+$. By contrast, the Mulliken population analyses reported in the theoretical[2-5] studies invariably show that more electron density is transferred from B to N in the σ system that is transferred back, $\mathrm{B \leftarrow N}$, in the π system; B populations are invariably charge deficient and N populations are electron rich, indicating the bond polarity $^-\mathrm{N{-}B}^+$.

For the molecular dipole moment, two recent ab initio studies[2,5] agree on the sign for $\mathrm{BH_2NH_2}$, giving the direction $^-\mathrm{B{-}N}^+$, but disagree on the sign for $\mathrm{BH(NH_2)_2}$. Arguments presented below, based on the experimental data, support Binkley's theoretical results.[5]

To date, experimental data for the dipole moments of boranamines give only the magnitude of the dipole moment and its projection on the molecule's fixed axes, not its sign. However, if the molecular dipole is considered to be the vector sum of the dipole moments for the individual bonds, then arguments[9] can be made for boranamines having the bond polarity $^-\mathrm{B{-}N}^+$ and, in the case of $\mathrm{BH_2NH_2}$,[9] the molecular dipole having the same sign. Consider the dipole moments of $\mathrm{BHF_2}$ (0.971 D),[28] $\mathrm{BF_2NH_2}$ (2.595 D),[29] and $\mathrm{BH_2NH_2}$ (1.844 D).[9] With the electronegativity of B about the same as H but much less than F, one obtains from the dipole moment of $\mathrm{HBF_2}$ a bond moment of 0.98 D for $^-\mathrm{F{-}B}^+$, and the molecular dipole moment is assumed to have the same sign. This is in agreement with the sign of the molecular dipole moment given by the ab initio results.[5] With a bond dipole moment of 1.33 D for $^-\mathrm{N{-}H}^+$, vector addition yields for $\mathrm{BF_2NH_2}$ a $^-\mathrm{B{-}N}^+$ bond moment of 0.25 D and a molecular dipole moment with the same sign. A similar calculation gives a bond moment of 0.47 D $^-\mathrm{B{-}N}^+$ for $\mathrm{BH_2NH_2}$.

For $\mathrm{BH(NH_2)_2}$ the situation is less clear because the group moment of $\mathrm{NH_2}$ is approximately the same magnitude as the measured molecular dipole moment. This means either the B–N bond moment is nearly zero, giving a molecular dipole moment in the direction $^-\mathrm{B{-}N}^+$, or the magnitude of the B–N moment is twice as large as the $\mathrm{NH_2}$ moment and in the direction $^-\mathrm{N{-}B}^+$, thus giving a molecular moment in the direction $^-\mathrm{N{-}B}^+$. Since the B–N moment in $\mathrm{BH_2NH_2}$ is only 0.47 D, it seems unlikely that the B–N bond moment in $\mathrm{BH(NH_2)_2}$ could be as large as 2.6 D and polarized in the opposite sense. The unlikelihood of a large B–N bond moment is supported by a study[27] that indicates that the bond moments for a series of substituted boranamines is near zero. Thus, we conclude that the B–N moment in $\mathrm{BH(NH_2)_2}$ is also small and the direction of the molecular moment is $^-\mathrm{(BH){-}((NH_2)_2)}^+$ as given by Binkley.[5]

On the basis of net atomic charges calculated from Mulliken population analyses, several authors[1,30] have concluded that the B–N bond dipole moment in boranamines has the polarity $^-\mathrm{N{-}B}^+$. This is contrary to the arguments just advanced, which are based on bond dipole moments derived from experimentally determined molecular dipole moments. This apparent disagreement is understandable since both Mulliken populations and bond dipole moments derived from molecular dipole moments give only an approximate description of the charge distribution. Specifically, net atomic charge analysis does not adequately account for the asymmetry of the electron density distribution between two atoms since the overlap density is merely divided equally between the two nuclei. This can be corrected to some degree by adding a term to the dipole moment that depends on the hybridization of the atoms.[31] On the other hand, bond dipole moments determined from one molecule are not strictly transferable to another.[32] For boranamines, assigning a polarity to the B–N bond is further complicated by the small absolute value of the bond dipole moment. Nevertheless, the observed dipole moment trends in boranamines can be explained by using the bond polarity $^-\mathrm{B{-}N}^+$ and considering the Mulliken population of the B 2p$_z$ orbital as follows.

Binkley[5] has calculated the Mulliken populations for several F- and $\mathrm{NH_2}$-substituted boranes. With a 6-31* basis set, the Mulliken populations for the B 2p$_z$ orbital are, for one π donor, $\mathrm{BH_2NH_2}$ (0.26); for two π donors, $\mathrm{BHF_2}$ (0.25), $\mathrm{BH(NH_2)_2}$

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(0.36); and for three π donors, BF_2NH_2 (0.39). Increasing the basis set size by 50% to the 6-311** level gives a slight increase in the B $2p_z$ population (BH_2NH_2 (0.26) and $BH(NH_2)_2$ (0.41)), indicating that the populations are not strongly dependent on basis set size. These results show that the capacity (per substituent) of the B $2p_z$ orbital to accept electrons is reduced as more π donors are added to the borane center. This has important implications in terms of the dipole moments of boranamines. With the limited capacity of the B $2p_z$ orbital to accept electrons, adding a NH_2 group to BH_2NH_2 polarizes the B–N bond more in the direction of $^-$N–B$^+$. This results from the addition of a center that withdraws electrons through the σ system, but which is less able to donate electrons to the already "saturated" B $2p_z$. If the B–N bond in BH_2NH_2 is already polarized in the direction $^-$N–B$^+$, then $BH(NH_2)_2$ should have a dipole moment larger than BH_2NH_2. If the B–N bond in BH_2NH_2 is polarized $^-$B–N$^+$, then $BH(NH_2)_2$ should have the smaller dipole moment. Since the experimental data show that the dipole moment of BH_2NH_2 is greater than that of $BH(NH_2)_2$, the B–N polarization and molecular dipole moment must be polarized $^-$B–N$^+$ in both molecules. These conclusions are consistent with Binkley's ab initio results[5] for the molecular dipole moments of BF_2NH_2, BH_2NH_2, and $BH(NH_2)_2$, which are all in the direction $^-$B–N$^+$.

The B–N bond lengths can be rationalized on a similar basis. When additional π donors are substituted on B in BH_2NH_2, the B–N bond is expected to get longer since the additional electron density competes with the N lone-pair electrons for the limited π-accepting capacity of the B $2p_z$. This expectation is confirmed by the measured B–N bond lengths for BH_2NH_2 (1.391 Å),[9] BF_2NH_2 (1.402 Å),[29] and $BH(NH_2)_2$ (1.418 Å). As indicated by the B $2p_z$ populations for BHF_2 and $BH(NH_2)2$, N is a better π donor to B than is F.

Although rotational constants were not determined for the vibrational satellites, the vibrational mode responsible for the satellites can be tentatively assigned with the aid of results from the normal coordinate analysis[22] of boranediamine and symmetry considerations. First, the satellites must originate from excitation of a vibrational mode that has even parity with respect to a C_2 rotation about the symmetry axis (*b* axis). This must be so because the hyperfine line shape for a particular ground-state transition and its corresponding satellite is the same. This requires the ratio of the statistical weight factors for even and odd parity hyperfine components to be the same, both in the ground state and vibrational satellite transitions. For molecules having C_{2v} symmetry, this occurs only if the excited vibrational mode has even parity with respect to C_2. This eliminates B_1- and B_2-type modes from consideration. Thus, the remaining possibilities are low-frequency vibrations of A_1 or A_2 type. The two A_2-type modes involve principally out-of-plane motion of the amine hydrogens, while the lowest A_1 mode, 402 cm^{-1}, is the NBN angle deformation mode. Of these modes the NBN angle deformation mode is most likely to give the observed large frequency separation between the ground state and satellite transitions because it involves primarily motion of the heavy atoms, resulting in a large change in the A rotational constant. We conclude, therefore, that the vibrational satellites are due to the NBN angle deformation mode. Unfortunately, data taken for the temperature dependence of the satellite intensities were not sufficiently accurate to distinguish absolutely between the A_1 mode at 402 cm^{-1} and the A_2 mode at 464 cm^{-1}.

In answer to the question posed in the introduction, we find that delocalization of the nitrogen lone-pair electrons into the vacant boron $2p_z$ orbital is sufficient to increase the B–N bond strength and cause the molecule to be planar. This is somewhat surprising in light of the ab initio results, which show the Mulliken population of the boron $2p_z$ to be only ~0.3 electron.[2,3] Clearly, extensive delocalization is not required to produce dramatic structural effects.

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Note Added in Proof. The authors of ref 2 have reexamined their dipole moment calculations and now give the direction $^-BH(NH_2)_2{}^+$, in agreement with our results.

Registry No. $BH(NH_2)_2$, 18447-53-5; $^{11}BH(NH_2)_2$, 68963-53-1; $^{11}BHNDHND_2$, 81770-06-1; $BH(ND_2)_2$, 81770-07-2; $^{11}BH(ND_2)_2$, 81790-07-0; $BD(ND_2)_2$, 81770-08-3; $^{11}BD(ND_2)_2$, 68963-55-3.

Electronic Structure of the Carbyne C–Li and the Carbene Li_2C[†]

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Abstract: We have studied the electronic structure of the carbyne C–Li and the carbene Li_2C using ab initio GVB, SCF, and CI techniques. We find that C–Li has a $^4\Sigma^-$ ground state with the companion $^2\Pi_r$ state approximately 34 kcal/mol higher in energy. This should be contrasted with C–H in which the $^2\Pi_r$ is the ground state and the $^4\Sigma^-$ state is approximately 17 kcal/mol higher. In addition we find a $^2\Pi_i$ state some 49 kcal/mol above the ground $^4\Sigma^-$ state. An analysis of the bonding indicates that these states are highly polar. Li_2C is an unusual carbene having three triplets below the first singlet: $^3\Sigma_g{}^-$, $R = 3.717$ bohrs; $^3\Pi_g(3)$, $R = 3.507$ bohrs; $^3A_2$, $\theta = 88.1°$, $R = 3.815$ bohrs. At the SCF+1+2 level the $^3\Sigma_g{}^-$ is the ground state with the $^3A_2$ 6.2 kcal/mol higher. Correcting for unlinked clusters inverts this order and makes the $^3A_2$ the ground state 0.2 kcal/mol below the $^3\Sigma_g{}^-$ state. An analysis of the bonding in the $^3A_2$ states reveals a dative bond between the doubly occupied Li_2 $^2\sigma_g$ orbital and an empty pσ orbital on C. The implications of this mode of bonding for the dilithiomethanes are discussed.

In spite of their intrinsic interest, potential importance as organometallic fragments and obvious relation with CH, CH_2, and the lithiated hydrocarbon H_2CLi_2, lithium carbyne, C–Li, and dilithium carbene, Li_2C, have received very little attention in the literature.[3] Our intent in this study is to use ab initio theoretical techniques to characterize the geometry and relative energies of

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