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Microwave Spectrum, Structure, Barrier to Internal Rotation, and Dipole Moment of the Aziridine−Borane Complex ($C_2H_5N-BH_3$)

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The microwave spectrum of the aziridine−borane complex ($C_2H_5N-BH_3$) has been investigated by microwave spectroscopy in the 18−80 GHz spectral region. The spectra of the ground vibrational state and three vibrationally excited states have been assigned, and the vibrational frequencies of these states have been determined. The complex was found to have a symmetry plane (C_s symmetry) formed by the N−B bond and the bisector of the aziridine ring. The dative N−B bond is found to be as short as 161.5 pm in MP2/aug-cc-pVTZ calculations. The MP2 structure of the aziridine ring of this complex is nearly the same as that in the substitution structure of aziridine. Complex formation therefore appears to have little influence on this moiety. The dipole moment was determined to be $\mu_a = 17.72(11)$, $\mu_b = 0.0$ (by symmetry), $\mu_c = 5.70(8)$, and $\mu_{tot} = 18.62(11) \times 10^{-30}$ C m [5.581(34) D]. The barrier to internal rotation of the borane group was determined to be 12.1(3) kJ/mol using the microwave splitting method. The microwave investigation has been augmented by high-level quantum chemical calculations at the MP2/aug-cc-pVTZ and B3LYP/6-311++G** levels of theory. There is generally good agreement between the experimental results and quantum chemical predictions.

Introduction

In 1956, Burg and Good[1] isolated a substance with a melting point of 40 °C from the reaction between diborane and aziridine, which they assumed to be the donor−acceptor complex between the Lewis base aziridine (C_2H_5N) and the Lewis acid BH_3. Ten years later, Åkerfeldt and Hellström[2] synthesized the $C_2H_5N-BH_3$ complex from sodium borohydride and aziridine. A modified synthetic procedure was later reported by Åkerfeldt et al.,[3] who also determined the dipole moment of this complex to be as large as $14.8(3) \times 10^{-30}$ C m [4.45(1) debye] in benzene. The crystal and molecular structure was determined by Ringertz,[4] who concluded that the unit cell of aziridine−borane is orthorhombic and the space group is *Pmnb* with four molecules in the cell, which are bonded together with weak charge-transfer bridges. The complex was seen to have a symmetry plane formed by the N−B bond and the bisector of the aziridine ring. The NMR and IR spectra reported by Williams[5] are in agreement with these findings. Kroll and Shillady[6] using low-level ab initio, CNDO/2, and INDO calculations claimed that the N−B bond in aziridine−borane is very covalent due to substantial donation of the amino lone pair to the BH_3 group in classical dative bond fashion.

Gas-phase studies of amine−borane complexes are rare. Examples are the H_3N-BH_3[7] and $(CH_3)_3N-BH_3$ complexes.[8−10] It was therefore felt that a study of the $C_2H_5N-BH_3$ complex extended to the gas phase, using microwave (MW) spectroscopy augmented with high-level quantum chemical calculations to investigate its physical properties, would be of interest. The dative N−B bond length of $C_2H_5N-BH_3$ is of special interest and is presumably quite different from 165.76(16) pm found for H_3N-BH_3[7] and 165.6(3) pm determined for $(CH_3)_3N-BH_3$[10] because the hybridization of the nitrogen atom of the aziridine ring in the title complex is different from the hybridization of nitrogen in the H_3N-BH_3 and $(CH_3)_3N-BH_3$ complexes. An accurate determination of this bond length was therefore a major goal of this investigation.

Another important motivation to perform the present study has been to determine the barrier to internal rotation about the BN bond because very few BH_3 barriers have been reported in the past using the accurate MW splitting method. For example, the H_3N-BH_3 complex has a barrier to internal rotation of the BH_3 group that is 8.565(38) kJ/mol,[7] whereas a lower limit of 14.2 kJ/mol was found in the case of the $(CH_3)_3N-BH_3$ complex.[8]

High-level quantum chemical calculations should today be able to calculate the N−B bond length accurately, as well as many additional physical properties, while MW spectroscopy can be used to obtain structural information, the dipole moment, barrier to internal rotation, and spectroscopic characteristics of the gaseous aziridine−borane complex. All of this motivated this first MW investigation of $C_2H_5N-BH_3$.

Experimental Section

Preparation of the Aziridine−borane Complex. In a two-necked round-bottomed flask equipped with a stirring bar and a nitrogen inlet, a borane−tetrahydrofurane or borane−dimethylsulfur complex solution (5 mL of 1 M sol., 5.0 mmol) was slowly added to a cooled (−30 °C) solution of aziridine[11] (0.215 g, 5.0 mmol) in dry dichloromethane (5 mL). The reaction mixture was allowed to warm to room temperature and was stirred for 5 min at this temperature. The solvent was removed

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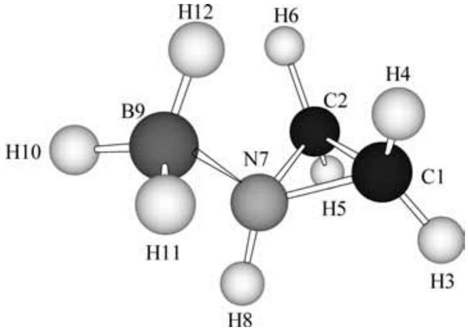

Figure 1. Model of the aziridine−borane complex with atom numbering.

in vacuo at room temperature, and the crude aziridine−borane obtained as a white solid was used without further purification. Yield: 93%. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.45 (q, 3H, $^1J_{BH}$ = 92.7 Hz, BH_3); 1.85 (dd, 2H, J_{HH} = 5.1, 5.1 Hz, 1 H of each CH_2); 2.33 (m, 2H, J_{HH} = 5.1, 6.4 Hz, 1H of each CH_2); 3.09 (s brd, 2H, NH_2). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 27.6 (t, $^1J_{CH}$ = 175.3 Hz). ^{11}B NMR ($CDCl_3$, 128.4 MHz) δ −16.1.

Microwave Experiment. The MW spectrum was recorded in the 18−80 GHz spectral region using the Stark-modulated spectrometer of the University of Oslo. Details of the construction and operation of this spectrometer, which has a 2 m Hewlett−Packard Stark cell, have been given elsewhere.[12,13] The resolution power of this instrument is about 0.5 MHz.

The spectrum was taken at room temperature. The vapor pressure of the complex was a few pascal at this temperature and was just sufficient to allow a registration of the spectrum. The spectral lines were measured with an estimated accuracy of ∼±0.10 MHz for isolated lines.

Quantum Chemical Methods. The present ab initio and density functional theory (DFT) calculations were performed employing the Gaussian 03 suite of programs,[14] running on the Titan cluster in Oslo. Electron correlation was taken into consideration in the ab initio calculations using Møller−Plesset second-order perturbation calculations (MP2).[15] Becke's three-parameter hybrid functional[16] employing the Lee, Yang, and Parr correlation functional (B3LYP)[17] was employed in the DFT calculations. Peterson and Dunning's[18] correlation-consistent triple-ζ wave function augmented with diffuse functions, aug-cc-pVTZ, was used in the MP2 calculations, whereas the 6-311++G** basis set was employed in the DFT calculations.

Results and Discussion

Quantum Chemical Calculations. The present MP2 calculations of the structure, dipole moment, harmonic vibrational frequencies, and barrier to internal rotation of the BH_3 group were performed using the large aug-cc-pVTZ basis set because it is known[19] that this procedure yields accurate molecular structures. The much less costly B3LYP/6-311++G** calculations were undertaken primarily to calculate the vibration−rotation constants (the α's)[20] because a calculation of these constants would be too expensive using MP2/aug-cc-pVTZ calculations.

All of structural parameters were allowed to vary freely in the calculations. A model of the aziridine−borane complex with atom numbering is shown in Figure 1. The resulting MP2 structure of the complex is listed in Table 1. Additional parameters of spectroscopic interest are collected in Table 2.

The MP2 calculations predict that the aziridine−borane complex possesses a symmetry plane (C_s symmetry) formed by the N7−B9 bond and the bisector of the aziridine moiety. The N7−B9 bond forms an angle of 125.7° with the aziridine ring (not given in Table 1), and the H8−N7−B9 bond is 116.8° (Table 1), which is an indication that the N7 atom is nearly sp^2-hybridized.

The N7−B9 bond length, which is a computational approximation to the equilibrium bond length, is 161.5 pm (Table 1). This is about 5 pm shorter than the corresponding r_s[21,22] bond length of 165.76(16) pm found for H_3N-BH_3[7] and the r_g bond length of 165.6(3) pm determined for $(CH_3)_3N-BH_3$.[10] A comparison of bond lengths obtained by different methods is not straightforward, but a difference as large as approximately 5 pm in the present case is likely to reflect a significant difference in the equilibrium bond lengths. The shorter N−B bond length calculated for the aziridine−borane complex may reflect the different hybridizations in the title complex on the one hand (approximately sp^2) compared to H_3N-BH_3[7] and $(CH_3)_3N-BH_3$ (∼sp^3) and/or a stronger bond.

The MP2/aug-cc-pVTZ barrier to internal rotation of the BH_3 group was calculated using the transition-state option of the Gaussian program. The transition state (not given in Table 1) was found to have an eclipsed conformation for one of the H−N−B−H chains of atoms, as expected. The barrier was found to be 10.3 kJ/mol when corrections for zero-point vibrations were taken into consideration.

The structure of the aziridine ring may be affected by complexation with the borane group. Fortunately, an accurate substitution structure is available for aziridine.[23] The r_s C−C and C−N bond lengths of aziridine are 148.1(1) and 147.5(1) pm, respectively. This is very close to their MP2 counterparts in the aziridine−borane complex (Table 1; C1−C2 and C1−N7 bond lengths). The structure of the aziridine ring therefore appears to have been little affected by the complex formation with the borane group. There is also great similarity between the B−H bond lengths (120.8 and 121.3 pm; Table 1) of our complex and the substitution bond length of the corresponding bond in H_3N-BH_3 [121.60(17) pm].

Interestingly, crystal forces seem to influence the structure significantly. For example, the MP2 N7−B9 bond length of 161.5 pm (Table 1) is significantly longer than that in the crystal (155.8(6) pm).[4] The C1−N7 bond length is 145.0(6) pm in the solid complex,[4] compared to the MP2 value of 147.0 pm. Moreover, Ringertz[4] found 146.0(9) pm for the C1−C2 bond length, whereas 148.4 pm is listed in Table 1 for this length. The bond lengths therefore appear to be shorter in the crystal than those in the free state, which the MP2 calculations mimic.

The experimental dipole moment in a benzene solution was found to be 14.8(3) × 10^{-30} C m,[3] significantly smaller than the MP2 dipole moment of 19.6 × 10^{-30} C m (Table 2).

Microwave Spectrum and Assignment of the Ground Vibrational State. The aziridine−borane complex has a large μ_a and a much smaller μ_c, whereas μ_b is 0 for symmetry reasons, according to the MP2 predictions (Table 2). A spectrum dominated by comparatively strong a-type R-branch transitions and much weaker c-type lines was therefore expected.

There are two naturally occurring isotopes of boron, namely, ^{10}B (19.9%) and ^{11}B (80.1%). The spectrum of the ^{11}B isotopologue of the complex should therefore have a spectrum that is about four times stronger than that of the ^{10}B isotopologue. The nuclear spin of ^{10}B is 3, whereas that of ^{11}B is 3/2. Quadrupole coupling of the spin angular momentum with the rotational angular momentum should therefore occur. This effect should lead to a complex quadrupole splitting of the rotational transitions. However, quadrupole splitting was not expected to be large and presumably unresolved because it has been found

TABLE 1: MP2/aug-cc-pVTZ Structure of the Aziridine−Borane Complex

bond length (pm)		bond angle (deg)		dihedral angle (deg)	
C1−C2	148.4	C2−C1−H3	118.5	H3−C1−C2−H5	0.0
C1−H3	107.9	C2−C1−H4	118.8	H3−C1−C2−H6	−153.8
C1−H4	107.8	H3−C1−H4	117.5	H4−C1−C2−H5	153.8
C1−N7	147.0	H3−C1−N7	116.4	H4−C1−C2−H6	0.0
N7−H8	101.2	H4−C1−N7	112.5	H3−C1−N7−H8	−4.4
N7−B9	161.5	C1−N7−H8	113.5	H3−C1−N7−B9	141.0
B9−H10	120.8	C1−N7−B9	120.2	H4−C1−N7−H8	−144.1
B9−H12	121.3	H8−N7−B9	116.8	H4−C1−N7−B9	1.2
		N7−B9−H10	105.7	H5−C2−N7−H8	4.4
		N7−B9−H12	103.5	H5−C2−N7−B9	−141.0
		H10−B9−H11	114.1	H6−C2−N7−H8	144.1
		H10−B9−H12	113.4	H6−C2−N7−B9	−1.2
				C1−N7−B9−H10	155.1
				C1−N7−B9−H11	−83.6
				C1−N7−B9−H12	35.7
				C2−N7−B9−H10	83.6
				C2−N7−B9−H11	−155.1
				C2−N7−B9−H12	−35.7
				H8−N7−B9−H10	−60.6
				H8−N7−B9−H11	60.6

TABLE 2: MP2/aug-cc-pVTZ Parameters of Spectroscopic Interest of the ^{11}B Isotopologue

rotational constants[a] (MHz)		centr. dist. const.[a] (kHz)		dipole moment[b] (10^{-30} C m)	
A	15402.0	Δ_J	3.33	μ_a	18.8
B	6361.0	Δ_{JK}	5.64	μ_b	0.0
C	5616.2	Δ_K	5.19	μ_c	5.5
		δ_J	0.268	μ_{tot}	19.6
		δ_K	4.69		

[a] A-reduction.[25] [b] Dipole moment components along principal inertial axes.

that the boron quadrupole coupling constants are relatively small.[24] Another factor that might lead to splitting of the rotational lines is tunneling of the BH_3 group. This effect depends strongly on the vibrational state of the torsion about the N−B bond and is much larger in excited states of this mode than that in the ground state.

Survey spectra revealed a comparatively strong and relatively dense spectrum. Only a few lines appeared to be split by quadrupole and/or BH_3 tunneling, which indicated that such effects generally amount to less than the resolution of approximately 0.5 MHz. The survey spectra also revealed that many of the strongest lines of the spectrum displayed resolved Stark effects typical for R-branch transitions, which could only be of the a-type variety. These transitions were the key to the assignment of this spectrum, using the spectroscopic constants shown in Table 2 as a starting point to predict their approximate frequencies.

Having assigned the ^{a}R-branch transitions, searches for the weaker c-type lines were undertaken. These transitions were readily assigned, and the weighted least-squares fit was gradually extended to include lines with higher and higher values of the principal J quantum number. Ultimately, a total of 193 transitions with a maximum of $J = 61$ were assigned. Transitions involving even higher values of J were searched for but not identified presumably because they were too weak, presumably due to an unfavorable Boltzmann factor. None of the ground-state transitions were detectably split. The spectrum was fitted to Watson's A-reduction Hamiltonian using the I^r-representation.[25] Only quartic centrifugal distortion constants were employed in the fit. Attempts to include sextic centrifugal distortion constants were made, but this did not improve the fit significantly, and only quartic constants were therefore retained in the final fit. The spectrum of the ground vibrational state is listed in Table 1S in the Supporting Information, while the spectroscopic constants are listed in Table 3.

Comparison of the effective rotational constants of the ground state (Table 3) with the MP2 constants (Table 2) reveals differences, which are −0.6, −1.1, and −1.2% for A, B, and C, respectively. Differences of this order of magnitude are to be expected because the MP2 and effective ground-state rotational constants are defined differently. This good agreement between the two sets of rotational constants is an indication that the structure in Table 1 is indeed accurate, as had to be expected.[19]

The theoretical quartic centrifugal distortion constants of Table 2 and the corresponding ground-state constants shown in Table 3 are also in fairly good agreement with the greatest difference (20%) found for Δ_K.

The First Excited Torsional State and the Barrier to Internal Rotation of the BH_3 Group. The uncorrected, lowest harmonic MP2 vibrational fundamentals (not given in Table 1) were calculated to be 195, 289, and 328 cm^{-1}, respectively. The first of these normal modes (195 cm^{-1}) is the torsion about the N7−B9 bond, whereas the other two vibrations (289 and 328 cm^{-1}) are the two lowest bending modes. The Boltzmann factors at room temperature of these three modes are 0.38, 0.23, and 0.20, respectively, and it should therefore be possible to assign MW spectra belonging to them. The MP2 calculations predicted that further normal modes have frequencies above 600 cm^{-1}, consequently with a low Boltzmann factor resulting in comparatively very weak spectra, which were not considered further.

The ground-state transitions were accompanied by several satellites, which display Stark effects similar to those of the ground-state lines. This behavior is typical for transitions belonging to vibrationally excited states. The spectrum of the strongest satellite was readily assigned. None of its ^{a}R lines were detectably split, but c-type lines were split into two components separated by a few MHz in many cases. These two components have A and E symmetries and equal intensities, which is characteristic for tunneling of the BH_3 group through a barrier with a height of several kJ/mol. The rotational constants of the A and E states shown in Table 3

TABLE 3: Spectroscopic Constants[a] of the ^{11}B Isotopologue of the Aziridine−Borane Complex

	vibrational state				
	ground	first torsion A-species[d]	first torsion E-species[d]	lowest bending	second lowest bending
A (MHz)	15311.1672(43)	15302.510(28)	15302.925(23)	15265.7(11)	15438.17(12)
B (MHz)	6286.8823(16)	6268.0560(82)	6268.0400(73)	6279.854(16)	6261.351(16)
C (MHz)	5548.1182(14)	5537.722(10)	5537.7056(91)	5518.832(19)	5539.414(21)
Δ_J (kHz)	3.3400(25)	3.71(12)	3.46(11)	2.95(20)	3.36(21)
Δ_{JK} (kHz)	5.3468(61)	5.17(17)	4.98(15)	5.3468[e]	5.3468[e]
Δ_K (kHz)	6.458(14)	4.8(18)	7.5(16)	6.458[e]	6.458[e]
δ_J (kHz)	0.27450(26)	0.2658(50)	0.2694(44)	0.27449[e]	0.27449[e]
δ_K (kHz)	4.397(15)	4.29(33)	3.50(29)	4.397[e]	4.397[e]
rms[b]	1.289	1.960	1.760	1.856	1.856
no. t[c]	193	66	66	24	21

[a] Reduction I^r-representation.[25] Uncertainties represent one standard deviation. [b] Root-mean-square deviation for a weighted fit. [c] Number of transitions used in the least-sqares fit. [d] See text. [e] Fixed; see text.

TABLE 4: Parameters of Relevance for the Barrier Height of the Internal Rotation of the Borane Group[a]

rotational constants:	$A = 15302.72$ MHz	$B = 6268.05$ MHz	$C = 5537.71$ MHz
direction cosines of the borane top:	$\lambda_a = 0.9112$	$\lambda_b = 0.0$[b]	$\lambda_c = 0.4120$
moment of inertia about the figure axis of the BH$_3$ top:	4.13×10^{-20} u m^2		
barrier to internal rotation[c]:	$V_3 = 12.1(3)$ kJ/mol		

[a] Splittings used to determine the barrier are found in the Supporting Information, Table 4S. [b] For symmetry reasons; see text. [c] Uncertainty represents one standard deviation.

were determined from the split c-type transitions together with the unsplit ^{a}R lines taken to be common for both symmetry species. These spectra are listed in the Supporting Information, Tables 2S and 3S.

The barrier to internal rotation was determined from the 35 splittings shown in Table 4S in the Supporting Information using the computer program MB10,[26] which is based on the principal axis method[27] and includes only even-order terms of P_z, the z-component of the angular momentum, up to fourth order. The BH$_3$ top was assumed to have an exact C_{3v} symmetry. Its moment of inertia around the figure axis was calculated to be 4.13×10^{-20} u m^2 from the structure in Table 1. This value is close to 4.150×10^{-20} u m^2 determined for H$_3$N−BH$_3$.[7] The direction cosines of the BH$_3$ top were calculated from the MP2 structure in Table 1 and are given in Table 4, where parameters relevant for the barrier determination are summarized.

The barrier was varied until each calculated splitting matched exactly the observed splitting, with the results shown in Table 4S of the Supporting Information. The average value of the V_3 barrier was calculated to be 12.1 kJ/mol from the 35 entries in this table, compared to 10.3 kJ/mol found in the MP2 calculations above. It is difficult to estimate the uncertainty of this barrier because there are several systematic sources of errors, but one standard deviation of 0.3 kJ/mol seems appropriate. The barrier of the aziridine−borane complex (12.1(3) kJ/mol) is somewhat higher than that of H$_3$N−BH$_3$ [8.565(38) kJ/mol][7] but less than that found for the (CH$_3$)$_3$N−BH$_3$ complex [>14.2 kJ/mol].[8] A torsional frequency of 196 cm^{-1} has been calculated from the 12.1 kJ/mol barrier of the title complex, whereas relative intensity measurements performed on rotational transitions yielded 193(20) cm^{-1}, close to 196 cm^{-1} obtained from the barrier height.

The vibration−rotation interaction constants (the α's)[20] defined by $\alpha_X = X_0 - X_1$, where X_0 are the ground-state rotational constants and X_1 are the rotational constants of a particular excited vibrational state, were found to be $\alpha_A = 9.1$, $\alpha_B = 20.5$, and $\alpha_C = 10.9$ MHz in the B3LYP calculations (not given in Table 2). These values are in good agreement with their experimental counterparts (8.5, 18.8, and 10.4 MHz, respectively), which have been derived from the entries in Table 3.

Spectra of the First Excited States of the Two Lowest Bending Vibrations. The spectra of two further vibrationally excited states were assigned. Only ^{a}R lines were assigned for these two states, whose spectra are displayed in Tables 5S and 6S of the Supporting Information. The lowest bending mode of these two spectra was found to have a frequency of 263(25) cm^{-1}, as determined by relative intensity measurements. The uncorrected MP2 result was 289 cm^{-1}. The B3LYP vibration−rotation constants were $\alpha_A = 56.4$, $\alpha_B = 2.7$, and $\alpha_C = 25.4$ MHz. These values are in good agreement with their experimental counterparts (45.5, 7.0, and 29.3 MHz, respectively), which have been derived from the entries in Table 3.

The frequency of the second lowest bending mode was found to be 327(30) cm^{-1} by relative intensity measurements, compared to the MP2 value of 329 cm^{-1}. The theoretical vibration−rotation constants were $\alpha_A = -128.7$, $\alpha_B = 20.7$, and $\alpha_C = 4.2$ MHz in this case, which compare well with experiment (−127.5, 25.6, and 8.7 MHz, respectively).

Spectra of the ^{10}B Isotopologue. The structure in Table 1 was used to predict the shifts in the rotational constants by substituting the ^{11}B isotope with ^{10}B. The constants were used to predict the ^{a}R spectrum of the H$_5$C$_2$N−^{10}BH$_3$ isotopologue, which was immediately assigned. The spectrum of the ground state is shown in Table 7S in the Supporting Information. ^{a}R lines of the first excited state of the BH$_3$ torsion were also assigned (Table 8S, Supporting Information). None of these transitions were split by BH$_3$ tunneling. The spectroscopic constants of the two vibrational states of the ^{10}B isotopologue are shown in Table 5.

The substitution coordinates of the boron atom were calculated from the ground-state rotational constants of the ^{11}B and ^{10}B isotopologues shown in Tables 3 and 5 using Kraitchman's equations.[28] The results were $|a| = 165.36(7)$ and $|c| = 19.0(6)$ pm, whereas a small imaginary value was found for $|b|$, which is typical for a coordinate that is exactly 0 for symmetry reasons. The uncertainties in the a- and c-coordinates have been obtained following van Eijck's recommendations.[29] The corresponding

TABLE 5: Spectroscopic Constants[a] of the ^{10}B Isotopologue of the Aziridine−Borane Complex

	vibrational state ground	first excited N7−B9 torsion[d]
A (MHz)	15329.0438(86)	15320.0(12)
B (MHz)	6514.5847(69)	6494.913(23)
C (MHz)	5722.2029(69)	5711.538(23)
Δ_J (kHz)	3.57(12)	3.09(26)
Δ_{JK} (kHz)	5.663(22)	5.663[e]
Δ_K (kHz)	5.59(28)	5.59[e]
δ_J (kHz)	0.29743(54)	0.29743[e]
δ_K (kHz)	4.461(27)	4.461[e]
rms[b]	1.042	1.705
no. t[c]	117	16

[a–e] Comments as those for Table 3.

TABLE 6: Second-Order Stark Coefficients[a] and Dipole Moment of the Aziridine−Borane Complex

transition		$\Delta\nu\ E^{-2}/10^{-6}$ MHz V^{-2} cm^2 obs.	calc.
$4_{1,4} \leftarrow 3_{1,3}$	$M = 0$	−4.09(5)	−4.11
$4_{1,4} \leftarrow 3_{1,3}$	$M = \|1\|$	5.99(10)	5.79
$4_{0,4} \leftarrow 3_{0,3}$	$M = \|1\|$	−1.41(2)	−1.47
$4_{0,4} \leftarrow 3_{0,3}$	$M = \|2\|$	8.57(10)	8.20
$4_{1,3} \leftarrow 3_{1,2}$	$M = \|1\|$	−10.30(15)	−10.52
$4_{1,3} \leftarrow 3_{1,2}$	$M = \|2\|$	−32.0(60)	−30.86
$5_{1,5} \leftarrow 4_{1,4}$	$M = \|2\|$	6.09(7)	5.87
$5_{1,5} \leftarrow 4_{1,4}$	$M = \|3\|$	14.99(30)	15.88
$5_{0,5} \leftarrow 4_{0,4}$	$M = \|1\|$	−1.79(3)	−1.73
$5_{0,5} \leftarrow 4_{0,4}$	$M = \|2\|$	1.54(2)	1.60
$5_{1,4} \leftarrow 4_{1,3}$	$M = \|2\|$	−6.41(10)	−6.20
$6_{1,6} \leftarrow 5_{1,5}$	$M = \|1\|$	−0.54(2)	−0.607
$6_{1,6} \leftarrow 5_{1,5}$	$M = \|2\|$	1.54(3)	1.50
$6_{0,6} \leftarrow 5_{0,5}$	$M = 0$	−1.43(3)	−1.57

dipole moment (10^{-30} C m)			
$\mu_a = 17.72(11)$	$\mu_b = 0.0$[b]	$\mu_c = 5.70(8)$	$\mu_{tot} = 18.62(11)$[c]

[a] Uncertainties represent one standard deviation. [b] By symmetry; see text. [c] In debye units, 5.581(34) D. Conversion factor: 1 D = 3.33564 × 10^{-30} C m.

values obtained from the structure in Table 1 are $|a| = 164.8$ and $|c| = 19.3$ pm, respectively. The close agreement is another indication that the MP2 structure is accurate.

Dipole Moment. The dipole moments of $H_3N{-}BH_3$ were determined in a least-squares fit using the experimental second-order Stark coefficients listed in Table 6. The weight of each Stark coefficient was taken to be the inverse square of its standard deviation shown in this table. The calculations of the theoretical values of the Stark coefficients were made using program MB04,[30] which is based on the second-order perturbation theory of Golden and Wilson,[31] using the rotational constants of the ground state (Table 3). The cell was calibrated using OCS, whose dipole moment was taken to be 2.38568(61) × 10^{-30} C m.[32]

Initially, all three dipole moment components were varied in the least-squares fit. However, it was found that μ_b is 0 within the measurement uncertainty. This is yet another indication that this complex indeed possesses a symmetry plane. In the final fit, which is reported in Table 6, μ_b was therefore fixed at 0. The μ_a is 6% smaller, and μ_c is 4% larger than the MP2 values (Table 2). The total dipole moment (18.62(11) × 10^{-30} C m) is significantly larger than the value found in a benzene solution (14.8(3) × 10^{-30} C m).[3] There is no obvious explanation for this difference.

Conclusions

The present MW and quantum chemical study of the aziridine−borane complex ($C_2H_5N{-}BH_3$) is one of a few investigations reported for gaseous amino−borane complexes. The complex was found to have a symmetry plane (C_s symmetry) formed by the N−B bond and the bisector of the aziridine ring, which is the same structure as was found in a previous X-ray study of the crystal.[4] The bond lengths of the free complex appear to be longer than those in the crystalline state. The dative N−B bond is calculated to be as short as 161.5 pm, approximately 5 pm shorter than the corresponding bond lengths in $H_3N{-}BH_3$[7] and $(CH_3)_3N{-}BH_3$.[10] This difference is perhaps caused by a different hybridization of the nitrogen atom in aziridine−borane (sp^2) than what is the case in $H_3N{-}BH_3$ and $(CH_3)_3N{-}BH_3$ (sp^3). The dipole moment of 17.72(11) × 10^{-30} C m in the gaseous state is significantly larger than the dipole moment measured in a benzene solution[3] (14.8(3) × 10^{-30} C m). The barrier to internal rotation of the borane group was determined using the MW splitting method and found to be 12.1(3) kJ/mol, somewhat higher than that of $H_3N{-}BH_3$ [8.565(38) kJ/mol][7] but less than that found for the $(CH_3)_3N{-}BH_3$ complex [>14.2 kJ/mol].[8] The MP2 value for this barrier in the aziridine−borane complex is 10.3 kJ/mol, which is in good agreement with the values obtained from the MW spectrum.

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Supporting Information Available: The microwave spectra. This material is available free of charge via the Internet at http://pubs.acs.org.

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