Boron and Nitrogen Hyperfine Structure in the Microwave Spectrum of Trimethylamine-Borane

W. Kasten and H. Dreizler
Abteilung Chemische Physik im Institut für Physikalische Chemie der Universität Kiel

R. L. Kuczkowski
Department of Chemistry, University of Michigan, Ann Arbor, MI 48 109

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We investigated the microwave spectrum of trimethylamine-borane by microwave Fourier transform spectroscopy and determined the quadrupole coupling constants of ^{11}B and ^{14}N and the rotational and centrifugal distortion constants for the ^{11}B isotopic species. The B–N bond order is discussed and a value for $eQq_{210}(^{14}N)$ is determined.

We investigated the microwave spectrum of trimethylamine-borane, $(CH_3)_3N-BH_3$ with the higher resolution of microwave Fourier transform (MWFT) spectroscopy to resolve the nitrogen and boron hfs. Previous investigations by Schirdewahn [1], Durig et al. [2] and Cassoux et al. [3] did not obtain this information. The interpretation of the quadrupole coupling constants results in the order of the B–N bond and a value of $eQq_{210}(^{14}N)$ [4] under certain assumptions. Trimethylamine-borane was prepared according to

$$B_2H_6 + 2N(CH_3)_3 \rightarrow 2(CH_3)_3N-BH_3\,.$$

In the frequency range of our MWFT spectrometer the $J = 1-0$ and $J = 2-1$ transitions of $(CH_3)_3N-{}^{11}BH_3$ were measured at a temperature of $-50\,^{\circ}C$ and pressures of approximately 0.25 mTorr. The transitions are given in Table 1.

The multiplet patterns were assigned and analysed on the basis of a centrifugally distorted symmetric rotor with the rotational hamiltonian [5] $H_R = BP^2 + (A-B)P_z^2 - D_J P^4 - D_{JK} P^2 P_z^2 - D_K P_z^4$ containing two coupled nuclei.

The coupling scheme $\boldsymbol{I}_1(^{14}N)+\boldsymbol{P}=\boldsymbol{F}_1$, $\boldsymbol{F}_1+\boldsymbol{I}_2(^{11}B)=\boldsymbol{F}$ [6] was used. The hamiltonian matrix of $H_R + H_{Q_1} + H_{Q_2}$ with H_{Q_i} the hamiltonian for the hfs diagonal in K, I_1, I_2, F, M_F and nondiagonal in J and F_1 was diagonalised (program SYM2Q.FOR). As the $J = 2-1$ transition is not well resolved the quadrupole coupling constants $eQq(^{11}B)$ and $eQq(^{14}N)$ were calculated from the splittings of the $J = 1-0$ transition only. With fixed eQq's B, D_J, and D_{JK} were fitted to both transitions.

The results are given in Table 2. In Tables 3 and 4 we give measurements and analysis of $J = 1-0$ transitions of two unassigned vibrationally excited states.

Table 1. Observed frequencies ν_{obs} [MHz] of the ^{11}B- and ^{14}N-hyperfine components of the $J = 1-0$ and $2-1$ transitions of trimethylamine-borane. The values ν_{calc} [MHz] were calculated with the parameters of Table 2. $\Delta\nu = \nu_{obs} - \nu_{calc}$ [MHz].

$J'-J$	K	$F'-F$	$F_1'-F_1$	ν_{obs}	ν_{calc}	$\Delta\nu$
1–0	0	1.5–0.5	1–1	9 031.692	9 031.704	−0.012
		1.5–1.5	1–1	9 031.692	9 031.704	−0.012
		1.5–2.5	1–1	9 031.692	9 031.704	−0.012
		0.5–0.5	1–1	9 032.014	9 032.006	0.008
		0.5–1.5	1–1	9 032.014	9 032.006	0.008
		2.5–1.5	1–1	9 032.014	9 031.999	0.015
		2.5–2.5	1–1	9 032.014	9 031.999	0.015
		3.5–2.5	2–1	9 032.726	9 032.744	−0.018
		0.5–0.5	2–1	9 032.726	9 032.736	−0.010
		0.5–1.5	2–1	9 032.726	9 032.736	−0.010
		1.5–0.5	2–1	9 032.868	9 032.853	0.015
		1.5–1.5	2–1	9 032.868	9 032.853	0.015
		1.5–2.5	2–1	9 032.868	9 032.853	0.015
		2.5–1.5	2–1	9 033.148	9 033.156	−0.008
		2.5–2.5	2–1	9 033.148	9 033.156	−0.008
		1.5–0.5	0–1	9 034.202	9 034.203	−0.001
		1.5–1.5	0–1	9 034.202	9 034.203	−0.001
		1.5–2.5	0–1	9 034.202	9 034.203	−0.001
2–1	0	2.5–1.5	1–0	18 064.625	18 064.589	0.036
		3.5–2.5	2–1	18 065.239	18 065.275	−0.036
		4.5–3.5	3–2	18 065.392	18 065.392	0.000
	±1	3.5–2.5	2–1	18 064.714	18 064.717	−0.003
		3.5–2.5	3–2	18 065.963	18 065.960	0.003

Reprint requests to Prof. Dr. H. Dreizler, Abt. Chemische Physik im Institut für Physikalische Chemie der Universität Kiel, Olshausenstr. 40, D-2300 Kiel.

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Table 2. Rotational, centrifugal, and hfs coupling constants of trimethylamine-borane, $(CH_3)_3{}^{14}N-{}^{11}BH_3$. The hfs analysis is based on $J = 1-0$ transition only.

		[1]
B	= 4 516.3558(25) MHz	4 516.353(15) MHz
D_J	= 1.5(5) kHz	1.32(11) kHz
D_{JK}	= − 24.7(36) kHz	
$eQq(^{11}B)$	= 2.064(33) MHz	
$eQq(^{14}N)$	= − 2.832(15) MHz	

Table 3a. Observed frequencies ν_{obs} [MHz] of the ^{11}B- and ^{14}N-hyperfine components of the $J = 1-0$ transition of an unassigned vibrational state. The values ν_{calc} [MHz] were calculated with the parameters of Table 4a.

$J'-J$	K	$F'-F$	$F_1'-F_1$	ν_{obs}	ν_{calc}	$\Delta\nu$
1−0	0	1.5−0.5	1−1	9 026.923	9 026.933	−0.010
		1.5−1.5	1−1	9 026.923	9 026.933	−0.010
		1.5−2.5	1−1	9 026.923	9 026.933	−0.010
		0.5−0.5	1−1	9 027.257	9 027.238	0.019
		0.5−1.5	1−1	9 027.257	9 027.238	0.019
		2.5−1.5	1−1	9 027.257	9 027.243	0.014
		2.5−2.5	1−1	9 027.257	9 027.243	0.014
		3.5−2.5	2−1	9 027.964	9 027.983	−0.019
		0.5−0.5	2−1	9 027.964	9 027.989	−0.025
		0.5−1.5	2−1	9 027.964	9 027.990	−0.026
		1.5−0.5	2−1	9 028.098	9 028.097	0.001
		1.5−1.5	2−1	9 028.098	9 028.097	0.001
		1.5−2.5	2−1	9 028.098	9 028.097	0.001
		2.5−1.5	2−1	9 028.430	9 028.416	0.014
		2.5−2.5	2−1	9 028.430	9 028.416	0.014
		1.5−0.5	0−1	9 029.452	9 029.451	0.001
		1.5−1.5	0−1	9 029.452	9 029.451	0.001
		1.5−2.5	0−1	9 029.452	9 029.451	0.001

Table 3b. Observed frequencies ν_{obs} [MHz] of the ^{11}B- and ^{14}N-hyperfine components of the $J = 1-0$ transition of an unassigned vibrational state. The values ν_{calc} [MHz] were calculated with the parameters of Table 4b.

$J'-J$	K	$F'-F$	$F_1'-F_1$	ν_{obs}	ν_{calc}	$\Delta\nu$
1−0	0	1.5−0.5	1−1	9 020.364	9 020.365	−0.001
		1.5−1.5	1−1	9 020.364	9 020.365	−0.001
		1.5−2.5	1−1	9 020.364	9 020.365	−0.001
		0.5−0.5	1−1	9 020.665	9 020.668	−0.003
		0.5−1.5	1−1	9 020.665	9 020.668	−0.003
		2.5−1.5	1−1	9 020.665	9 020.665	0.000
		2.5−2.5	1−1	9 020.665	9 020.665	0.000
		3.5−2.5	2−1	9 021.383	9 021.408	−0.025
		0.5−0.5	2−1	9 021.383	9 021.405	−0.022
		0.5−1.5	2−1	9 021.383	9 021.405	−0.022
		1.5−0.5	2−1	9 021.543	9 021.519	0.024
		1.5−1.5	2−1	9 021.543	9 021.519	0.024
		1.5−2.5	2−1	9 021.543	9 021.519	0.024
		2.5−1.5	2−1	9 021.836	9 021.827	0.009
		2.5−2.5	2−1	9 021.836	9 021.827	0.009
		1.5−0.5	0−1	9 022.865	9 022.870	−0.005
		1.5−1.5	0−1	9 022.865	9 022.870	−0.005
		1.5−2.5	0−1	9 022.865	9 022.870	−0.005

Table 4a. Rotational and hfs coupling constants of trimethylamine-borane of the unassigned vibrational state of Table 3a.

B	= 4 513.9776(18) MHz
$eQq(^{11}B)$	= 2.162(39) MHz
$eQq(^{14}N)$	+ − 2.824(19) MHz

Table 4b. Rotational and hfs coupling constants of trimethylamine-borane of the unassigned vibrational state of Table 3b.

B	= 4 510.6884(18) MHz
$eQq(^{11}B)$	= 2.098(40) MHz
$eQq(^{14}N)$	= − 2.829(19) MHz

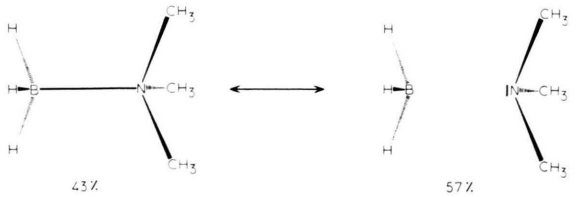

Fig. 1. Relative weight of the principal structures, which contribute to the ground state of trimethylamine-borane.

Following the procedure given in [7] we calculated from the measured quadrupole coupling constant $eQq(^{11}B) = 2.064(33)$ MHz the B−N bond order $n_B = 0.43(1)$, the number of electrons donated from the nitrogen to the boron. $eQq_{210}(^{11}B) = -5.39$ MHz [8] and $\measuredangle$ NBH = 105.32(16)° [2, 3] were used. So the B−N bond can be interpreted as given in Figure 1. The low bond order correlates with estimates of the dissociation energy to $BH_3 + (CH_3)_3N$ of 31 to 48 kcal/mol [3].

The next consideration uses the experimental value $eQq(^{14}N)$ to determine $eQq_{210}(^{14}N)$. We follow Townes and Dailey [9] and Gordy [10]. Details are given in [11].

We use

$$eQq(^{14}N) = -(Up)_z \cdot \frac{eQq_{210}(^{14}N)}{1 + [3(n_c - 1) - n_B]\,\varepsilon_N} \qquad (1)$$

with $eQq(^{14}N)$ the experimental nitrogen quadrupole coupling constant, $eQq_{210}(^{14}N)$ the quadrupole coupling constant induced by a $2p_z$ electron, $\varepsilon_N = 0.3$ [12] the shielding constant of nitrogen, n_c is the mean number of electrons occupying the orbitals directed to the methyl groups, n_B the mean number of electrons donated by the nitrogen to the boron.

The number of "unbalanced" p electrons in z-direction i.e. the N–B-bond direction may be expressed by

$$(Up)_z = -\tfrac{3}{2} \cdot n_c \cdot a_p^2(\psi_c) \cdot (3\cos^2 \sphericalangle(\mathrm{BNC}) - 1) - (2 - n_B) \cdot a_p^2(\psi_B) \quad (2)$$

with $a_p^2(\psi_c)$ the p-electron fraction of the nitrogen orbital directed to the methylcarbon and $a_p^2(\psi_B)$ that directed to boron. Assuming hybridisation mixing of s and p functions $\psi_c = s_c + \lambda\, p_c$ [13] one gets:

$$a_p^2(\psi_c) = \frac{\lambda^2}{1+\lambda^2} \quad \text{with} \quad \lambda^2 = -\{\cos \sphericalangle(\mathrm{CNC})\}^{-1} \quad (3)$$

and similar

$$a_p^2(\psi_B) = \frac{\mu^2}{1+\mu^2} \quad \text{with} \quad \mu^2 = \{\lambda \cdot \cos \sphericalangle(\mathrm{BNC})\}^{-2} \quad (4)$$

with the relation

$$\cos^2 \sphericalangle(\mathrm{BNC}) = \frac{1}{3}(1 + 2\cos \sphericalangle(\mathrm{CNC})) \quad (5)$$

and

$$a_s^2(\psi_c) = \frac{1}{1+\lambda^2}. \quad (6)$$

(1) simplifies to

$$eQq(^{14}\mathrm{N}) = \frac{3 \cdot a_s^2(\psi_c) \cdot (2 - n_c - n_B)}{1 + [3(n_c - 1) - n_B] \cdot \varepsilon_N} \cdot eQq_{210}(^{14}\mathrm{N}) \quad (7)$$

Equation (7) describes for $n_B = 0$ the quadrupole coupling constant of trimethylamine.

For trimethylamine-borane the bond angle $\sphericalangle$ CNC $= 109.0°$ is known from the structure [3] and the quadrupole coupling constant $eQq(^{14}\mathrm{N}) = -2.832$ MHz is measured in this work.

For trimethylamine the bond angle $\sphericalangle$ CNC $= 110.9°$ is determined by Wollrab and Laurie [14] and the quadrupole coupling constant $eQq(^{14}\mathrm{N}) = -5.47$ MHz was measured by Lide and Mann [15].

Assuming n_c (trimethylamine) = n_c (trimethylamine-borane) equation (7) yields two equations for n_c and $eQq_{210}(^{14}\mathrm{N})$. The results are $n_c = 1.16$ and $eQq_{210}(^{14}\mathrm{N}) = -9.38$ MHz. As there are some assumptions we do not give an error limit. The value of $eQq_{210}(^{14}\mathrm{N})$ compares well with that determined from solid nitrogen $eQq_{210}(^{14}\mathrm{N}\ \text{solid}) = -9.3$ MHz [16].

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