The Microwave Spectrum, Structure, Dipole Moment, and Internal Rotation of the Methyl Isocyanide–Borane Complex

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Abstract: The molecular complex methyl isocyanide-borane ($CH_3NC\text{-}BH_3$) has been prepared, and the microwave spectra of 14 of its isotopic species have been observed in R band (26.5-40 GHz). An r_s heavy atom structure of the complex has been determined to be $r(C—N) = 1.416 \pm 0.004$ Å, $r(N{\equiv}C) = 1.155 \pm 0.006$ Å, and $r(CB) = 1.566 \pm 0.004$ Å. Assuming $r(CH) = 1.100 \pm 0.015$ Å and $r(BH) = 1.220 \pm 0.020$ Å, $\angle HCN$ and $\angle HBC$ can be evaluated by isotopic substitution as $109.0 \mp 0.5°$ and $105.7 \mp 0.6°$. The dipole moment was found to be 6.73 ± 0.07 D and the barrier to internal rotation estimated to be less than 4.2 cal/mol.

Among the most important acceptor types to be considered when donor-acceptor complexes are discussed are the vacant orbital acceptors. In this context molecular complexes of borane are of particular interest. Since the discovery of borane carbonyl and trimethylamine-borane,[2] more borane complexes have been prepared[3] and a number have been investigated by gas phase microwave spectroscopy.[4-13] No examples of characterized isocyanide-borane complexes are known to us although one such complex of trimethylborane, $t\text{-}C_4H_9NC{\cdot}B(CH_3)_3$, has been reported.[14]

We now report the preparation of the methyl isocyanide-borane complex (Figure 1) and the results of a microwave investigation of 14 of its isotopic species. The spectrum of the complex is well enough resolved to allow the molecular structure and dipole moment to be determined and an upper limit to be placed on the barrier to internal rotation.

A large number of investigations have employed shifts of characteristic group vibration frequencies on complex formation as a measure of acceptor power toward a particular donor.[15] Several complexes of methylcyanide appear to be unusual as they show an increase rather than a decrease of the $\nu(CN)$ stretching frequency on complex formation.[16] Further, x-ray structural determinations for $CH_3CN\text{-}BX_3$ (X = F, Cl) have shown a small but real decrease in CN bond length from 1.157 Å in CH_3CN[17] to 1.135 and 1.122 Å in $CH_3CN\text{-}BF_3$[18,19] and $CH_3CN\text{-}BCl_3$,[19] respectively. Subsequent force constant calculations[20,21] have shown that the CN stretching force constant increases on complex formation in agreement with the increased bond strength implied by the CN bond shortening. Corresponding studies of methyl isocyanide complexes have not been made. A structural study of methyl isocyanide-borane is of interest not only to observe if such bond shortening can be associated with methyl isocyanide complexes, but also to observe if it appears in adducts of borane itself.

In addition, the methyl isocyanide-borane complex is relatively small and structurally simple enough to be suitable for ab initio molecular orbital calculations. The experimental results reported here will provide a comparison with the corresponding quantities evaluated in a series of such calculations currently in progress.

Experimental Section

Both the common and isotopically enriched samples of methyl isocyanide-borane were conveniently prepared by mixing methyl isocyanide and diborane in the cell of the microwave spectrometer at a total pressure of 1-2 Torr. For these experiments methyl isocyanide was prepared by heating methyl iodide and silver cyanide in a 1:2 mol ratio in a sealed tube, evacuated of air, for a period of 4 h at 80 °C.[22,23] The methyl isocyanide produced was purified by vacuum distillation.

The $^{13}CH_3NC$ and CD_3NC isotopic species[24] were prepared in a similar manner by heating $^{13}CH_3I$ (10 atom % ^{13}C) and CD_3I (99 atom % deuterated), respectively, with silver cyanide.

The $CH_3{}^{15}NC$ and $CH_3N{}^{13}C$ were prepared by reacting $KC^{15}N$ (97.1 atom % ^{15}N) and $K^{13}CN$ (95 atom % ^{13}C) with an excess of silver nitrate solution to yield precipitates of the corresponding silver cyanide isotopic species.[25] These precipitates were carefully washed, dried, and then heated as above with methyl iodide. The resulting methyl isocyanide isotopes were purified by vacuum distillation.

Diborane was prepared by the method of Nöth and Beyer.[26] Typically, 26.3 mmol of trimethylamine-borane was placed in a reaction bulb connected to a vacuum line via a Teflon valve. After evacuation, 40 ml of CH_2Cl_2 and 24.0 mmol of BF_3 were condensed into the flask at −196 °C, the valve was closed, and the reactants were allowed to warm slowly to room temperature with stirring. After 18 h the reaction products were fractionated through traps held at −78, −130, and −196 °C until no more diborane was collected in the trap at −196 °C.

Diborane-d_6 was similarly prepared from trimethylamine-borane-d_3.[27] The trimethylamine-borane-d_3 was prepared by a modification of the method of Davis, Brown, Hopmann, and Kibby.[28]

All microwave spectra were recorded in R band (26.5-40 GHz) using a Hewlett-Packard Model 8460A MRR spectrometer with 33.3-KHz Stark modulation. Frequency measurements were made at 5-40 mTorr pressure and room temperature, using a small dc offset voltage (~40 V) to eliminate the $K \neq 0$ components. Cooling the microwave cell was not found to significantly improve the signal to noise ratio. Although the lines were relatively broad, no quadrupole effects could be resolved. We estimate the accuracy of frequency measurement to be ±0.20 MHz.

Results

A broadband spectrum of the common isotopic species is shown in Figure 2. It is readily assigned to $J4 \leftarrow 3$, $J5 \leftarrow 4$ transitions of the symmetric top $CH_3NC\text{-}BH_3$ with 80 atom % ^{11}B and 20 atom % ^{10}B. To low frequency of each ground state $m = 0$ transition is a series of transitions which are m components associated with internal rotation in the complex. Figure 3 illustrates a high resolution spectrum of such a series of transitions. The m assignments were made in a similar manner to that used for methylsilylacetylene.[29] On the high frequency side of each ground state transition are satellite series of low vibrational frequencies. The most prominent series is associated with the heavy atom bending vibration of the complex.

The ground state $K = 0$, $m = 0$ transition frequencies for

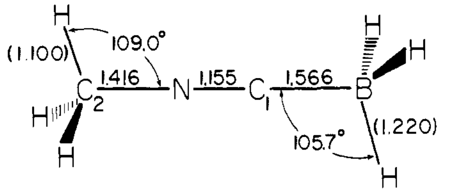

Figure 1. The structure and labeling of methyl isocyanide-borane.

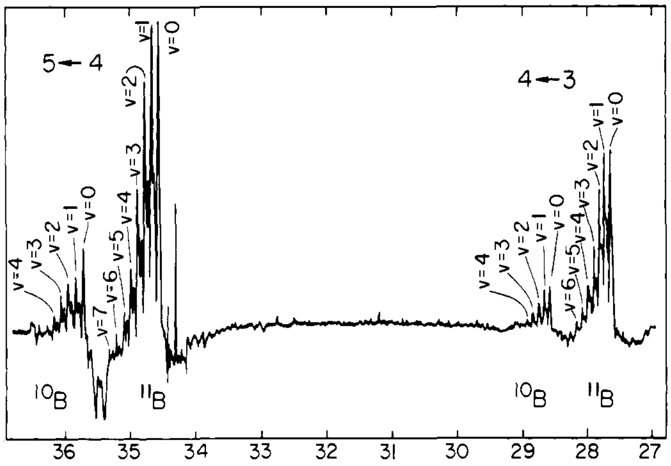

Figure 2. Rapid scan of the microwave spectrum of methyl isocyanide-borane.

Table I. Symmetric Top Rotational Transition Frequencies[a] (MHz) of Methyl Isocyanide-Borane in the Ground State: $m = 0$, $K = 0$

Isotopic species	Transition $J4 \leftarrow 3$	 $J5 \leftarrow 4$	 $J6 \leftarrow 5$
$^{12}CH_3{}^{14}N^{12}C^{11}BH_3$	27 673.90	34 592.37	
$^{12}CH_3{}^{14}N^{12}C^{10}BH_3$	28 602.25	35 752.73	
$^{13}CH_3{}^{14}N^{12}C^{11}BH_3$	26 964.35	33 705.19	
$^{12}CH_3{}^{15}N^{12}C^{11}BH_3$	27 616.01	34 519.96	
$^{12}CH_3{}^{15}N^{12}C^{10}BH_3$	28 549.01		
$^{12}CH_3{}^{14}N^{13}C^{11}BH_3$	27 607.84	34 509.72	
$^{12}CH_3{}^{14}N^{13}C^{10}BH_3$	28 521.76	35 652.11	
$^{12}CD_3{}^{14}N^{12}C^{11}BH_3$		30 947.41	37 137.01
$^{12}CD_3{}^{14}N^{12}C^{10}BH_3$		31 982.40	
$^{12}CD_3{}^{14}N^{12}C^{11}BD_3$			32 783.32
$^{12}CD_3{}^{14}N^{12}C^{10}BD_3$		28 032.86	
$^{12}CH_3{}^{14}N^{12}C^{11}BD_3$		30 454.17	36 544.8
$^{12}CH_3{}^{14}N^{12}C^{10}BD_3$		31 242.71	37 491.24
$^{12}CH_3{}^{14}N^{13}C^{11}BD_3$		30 415.05	36 498.07

[a] Estimated accuracy of frequency measurement ±0.2 MHz.

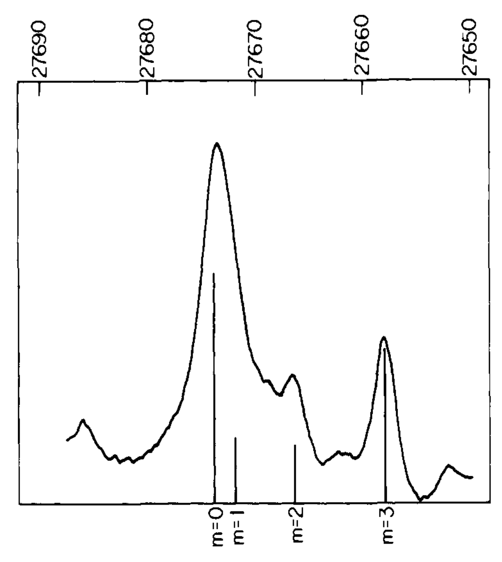

Figure 3. High resolution spectrum of the $J4 \leftarrow 3$, $v = 0$, $K = 0$, internal rotation structure of $^{12}CH_3{}^{14}N^{12}C^{11}BH_3$.

Table II. Ground State Rotational Constants (MHz) and Moments of Inertia (amu Å^2) of Methyl Isocyanide-Borane

Isotopic species	Rotational constant[a]	Moment of inertia[b]
$^{12}CH_3{}^{14}N^{12}C^{11}BH_3$	3459.24	146.095
$^{12}CH_3{}^{14}N^{12}C^{10}BH_3$	3575.28	141.353
$^{13}CH_3{}^{14}N^{12}C^{11}BH_3$	3370.53	149.940
$^{12}CH_3{}^{15}N^{12}C^{11}BH_3$	3452.00	146.401
$^{12}CH_3{}^{15}N^{12}C^{10}BH_3$	3568.63	141.616
$^{12}CH_3{}^{14}N^{13}C^{11}BH_3$	3450.98	146.444
$^{12}CH_3{}^{14}N^{13}C^{10}BH_3$	3565.22	141.752
$^{12}CD_3{}^{14}N^{12}C^{11}BH_3$	3094.75	163.301
$^{12}CD_3{}^{14}N^{12}C^{10}BH_3$	3198.24	158.017
$^{12}CD_3{}^{14}N^{12}C^{11}BD_3$	2731.94	184.988
$^{12}CD_3{}^{14}N^{12}C^{10}BD_3$	2803.29	180.280
$^{12}CH_3{}^{14}N^{12}C^{11}BD_3$	3045.41	165.947
$^{12}CH_3{}^{14}N^{12}C^{10}BD_3$	3124.27	161.758
$^{12}CH_3{}^{14}N^{13}C^{11}BD_3$	3041.51	166.160

[a] ±0.05 MHz. [b] ±0.002 amu Å^2.

Table III. Transition Frequencies[a] (MHz) of the Ground State Components of Internal Rotation for $^{12}CH_3{}^{14}N^{12}C^{11}BH_3$ and $^{12}CD_3{}^{14}N^{12}C^{11}BH_3$ Isotopic Species

	$^{12}CH_3{}^{14}N^{12}C^{11}BH_3$		$^{12}CD_3{}^{14}N^{12}C^{11}BH_3$	
m	$J4 \leftarrow 3$	$J5 \leftarrow 4$	$J5 \leftarrow 4$	$J6 \leftarrow 5$
0	27 673.90	34 592.37	30 947.41	37 137.01
1	27 672.61	34 590.59	30 946.30	37 135.46
2	27 666.70	34 583.53	30 940.47	37 128.05
3	27 657.71	34 572.33	30 931.60	37 117.61
4	27 645.87	34 557.47	30 919.15	37 110.84
5	27 629.32	34 536.63	30 903.20	37 083.99
6	27 609.21	34 511.31	30 883.35	37 060.44

[a] ±0.2 MHz.

the 14 different isotopic species are given in Table I and the corresponding rotational constants calculated using the expression $\nu_{J,J+1} = 2B(J + 1)$ are listed in Table II.

The frequencies of a number of m components associated with internal rotation for the $^{12}CH_3{}^{14}N^{12}C^{11}BH_3$ and $^{12}CD_3{}^{14}N^{12}C^{11}BH_3$ isotopic species are given in Table III.

The frequencies of the most prominent satellite series are given in Table IV for the $^{12}CH_3{}^{14}N^{12}C^{11}BH_3$ isotopic species.

Evaluation of Molecular Structure. The microwave spectrum indicates that the complex is a symmetric top. For single on-axis isotopic substitution the relationship of Kraitchman[30] can be used to determine the z coordinate of the substituted atom.

$$|z| = \left(\frac{\Delta I}{\mu}\right)^{1/2} \tag{1}$$

where ΔI is the change of moment of inertia (amu Å^2) on isotopic substitution and μ is the reduced mass (amu) defined as

$$\mu = \frac{M \Delta m}{(M + \Delta m)} \tag{2}$$

Here M is the mass of the parent isotopic species and Δm the change of mass on isotopic substitution. The r_s molecular z

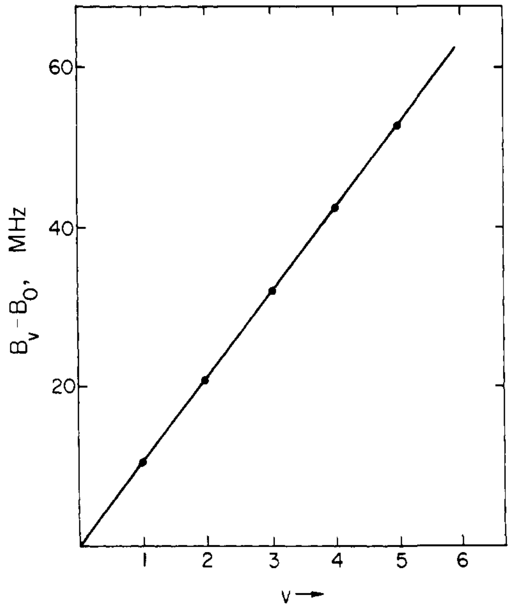

Figure 4. Plot of $B_v - B_0$ against the vibrational quantum number, v.

Table IV. Rotational Transition Frequencies[a] and Constants[b] (MHz) for the First Five Quanta of the Low Frequency Bending Vibration of $^{12}CH_3{}^{14}N^{12}C^{11}BH_3$

Quantum No.	Transitions[c] $J4 \leftarrow 3$	Transitions[c] $J5 \leftarrow 4$	Rotational constants
0	27 673.70	34 591.95	3459.23
1	27 757.85	34 697.37	3469.73
2	27 843.15	34 803.32	3480.36
3	27 928.35	34 910.71	3491.06
4	28 014.21	35 016.90	3501.73
5	28 100.73	35 124.94	3512.54

[a] ±0.4 MHz. [b] ±0.09 MHz. [c] Unresolved $m = 0, 1$; $K = 0$ components of internal rotation.

Table V. z_s Coordinates (Å) of Methyl Isocyanide-Borane

	Parent isotopic species		
Atom	$^{12}CH_3{}^{14}N^{12}C$-$^{11}BH_3$	$^{12}CH_3{}^{14}N^{12}C$-$^{10}BH_3$	$^{12}CH_3{}^{14}N^{12}C$-$^{11}BD_3$
B	−2.162 ± 0.001[a]	−2.202 ± 0.001	−2.033 ± 0.001
C_1	−0.596 ± 0.003	−0.636 ± 0.003	−0.465 ± 0.003
N	+0.559 ± 0.003	+0.519 ± 0.003	
C_2	+1.975 ± 0.001		

[a] Calculated from errors in rotational constants.

coordinates evaluated in this way from the available data are given in Table V, and the molecular parameters determined in Table VI.

The coordinates of the off-axis borane and methyl hydrogen atoms cannot be determined from the available data using Kraitchman's equations. Mono- and dideuterium substitutions were not attempted because of the complexity of the internal rotation structure which we expect would be greatly altered in the asymmetric molecules. An attempt was thus made to evaluate these coordinates using the symmetrically substituted isotopic species. If either the methyl or borinyl protons are substituted, then the change of moment of inertia is given by

$$\Delta I = \mu z_H^2 + \tfrac{3}{2}(m_D - m_H)\rho_H^2 \qquad (3)$$

where z_H is the on-axis hydrogen coordinate and ρ_H is the distance from the axis to the proton. The contribution of the first term in this expression is approximately nine times that of the second with the result that any small error in z_H causes four times that error in ρ_H. The on-axis distance, z_H, may be determined within about ±0.01 Å by double substitution giving an error of ±0.04 Å in ρ_H, which is unsatisfactory. If, however, reasonable values are assumed for r(BH) and r(CH),[17] it is possible to estimate $\angle HBC_1$ and $\angle HC_2N$ with some confidence. Choosing $r(BH) = 1.220 \pm 0.020$ Å and $r(CH) = 1.100 \pm 0.015$ Å, $\angle HBC_1$ and $\angle HC_2N$ are found to be $105.7 \mp 0.6°$ and $109.0 \mp 0.5°$. From these values $\angle HBH$ and $\angle HCH$ are calculated to be $113.0 \pm 0.6°$ and $110.0 \pm 0.5°$. The best structure we think we can propose is given in Table VII.

Table VI. r_s Structural Parameters (Å) for Methyl Isocyanide-Borane

	Parent isotopic species		
	$^{12}CH_3{}^{14}N^{12}C$-$^{11}BH_3$	$^{12}CH_3{}^{14}N^{12}C$-$^{10}BH_3$	$^{12}CH_3{}^{14}N^{12}C$-$^{11}BD_3$
$r(BC_1)$	1.566 ± 0.004	1.565 ± 0.004	1.568 ± 0.004
$r(C_1N)$	1.155 ± 0.006	1.155 ± 0.006	
$r(C_2N)$	1.416 ± 0.004		

Table VII. Molecular Structure of Methyl Isocyanide-Borane

$r(BC_1) = 1.566 \pm 0.004$ Å, $r(C_1N) = 1.155 \pm 0.006$ Å
$r(NC_2) = 1.416 \pm 0.004$ Å,
($r(BH) = 1.220 \pm 0.020$ Å),[a] ($r(CH) = 1.100 \pm 0.015$ Å)[a]
$\angle HC_2N = 109.0 \mp 0.5°$, $\angle HBC_1 = 105.7 \mp 0.6°$
$\angle HBH = 113.0 \pm 0.5°$, $\angle HCH = 110.0 \pm 0.6°$

[a] Assumed molecular parameters.

Table VIII. Rotational Constants (MHz) for Methyl Isocyanide-Borane Assuming a Small Barrier to Internal Rotation

	$^{12}CH_3{}^{14}N^{12}C^{11}BH_3$	$^{12}CD_3{}^{14}N^{12}C^{11}BH_3$
B	3459.26 ± 0.01	3094.75 ± 0.01
C	−0.094 ± 0.078	−0.149 ± 0.053
G	−0.2245 ± 0.0005	−0.1775 ± 0.0015

[a] From fitting the expression $\nu = 2(J + 1)[B + Gm^2 + C/(4m^2 - 9)]$ to the frequencies in Table III.

Table IX. Dipole Moment of Methyl Isocyanide-Borane

Transition	m	M	Dipole moment (D)[a]	Estimated[b] error
$J4 \leftarrow 3$	3	1	6.74	± 0.28
$J4 \leftarrow 3$	3	2	6.69	± 0.16
$J5 \leftarrow 4$	3	3	6.75	± 0.09
			6.73	± 0.07

[a] Stark cell calibrated using the $J2 \leftarrow 1$, $K = 0$, in the vibrational ground state of $^{12}CH_3{}^{12}C{\equiv}{}^{12}CH$, for which $\mu = 0.7840$ D. (J. S. Muenter, V. W. Laurie, *J. Chem. Phys.* **45**, 855 (1966)). [b] 95% confidence limit.

Internal Rotation. An upper limit for the barrier to internal rotation in methylsilylacetylene has been estimated by Kirchhoff and Lide.[29] Using the information in Table III and the same assumptions as those made by Kirchhoff and Lide, the upper limit for the barrier to internal rotation in methyl isocyanide-borane may be similarly evaluated as 4.2 cal/mol. The relevant parameters are given in Table VIII.

Dipole Moment. The dipole moment has been evaluated as 6.73 ± 0.07 D from the Stark effect measurements of the $K = 0, m = 3$ component of the ground state $J4 \leftarrow 3$, $M = 1, 2$, and $J5 \leftarrow 4$, $M = 3$ transitions. The results are given in Table IX.

Some Comments on the Nature of the Low Frequency Bending Vibration. A plot of the difference in rotational constants $B_v - B_0$ against quantum number v for this vibration is given in Figure 4. For the first five quanta the plot is linear, indicating an almost harmonic oscillation.

Reliable relative intensity measurements of this satellite series are exceedingly difficult to make because of the nature of the microwave spectrum. However, we have attempted these measurements and estimate the fundamental frequency of the vibration to be 186 ± 23 cm^{-1}.

Discussion

The molecular structure of methyl isocyanide-borane complex may be compared with the isolated components of the complex and also with related borane complexes.

The $r(N\equiv C_1)$ distance is shortened by 0.011 Å with respect to methyl isocyanide.[17] A similar shortening has been observed in x-ray measurements of methyl cyanide-BX_3 ($X = F, Cl$) complexes[18,19] and has been associated with an increase in the force constant on complex formation.[20,21] This indicates that some methyl isocyanide complexes may show an increase of the $\nu(N\equiv C_1)$ stretching frequency on complex formation similar to that found for the $\nu(CN)$ stretching frequencies of certain methyl cyanide complexes.[16] In contrast, the CN and OC bond lengths in trimethylamine-borane[8] and borane carbonyl[10] are both lengthened by 0.032 and 0.003 Å, respectively. It is also interesting to note that $r(C_2—N)$ in methyl isocyanide-borane is shortened by 0.008 Å compared with methyl isocyanide.[17]

The $r(BC_1)$ is observed to be 0.029 Å longer than in borane carbonyl[11] while ∠HBH = 113.0 ± 0.5°, although not so reliably determined, compares with the corresponding values of 113.3° observed in trimethylamine-borane and the recently redetermined value of 114.5° in borane carbonyl.[11]

The dipole moment of 6.73 ± 0.07 D compares with 4.84 ± 0.1 and 1.795 ± 0.01 D observed in trimethylamine-borane[8] and borane carbonyl[9] and the corresponding values of 3.83 ± 0.06, 0.612 ± 0.003, and 0.112 ± 0.005 D found in methyl isocyanide,[31] trimethylamine,[32] and carbon monoxide.[33]

As expected, the complex is almost a free internal rotator, the upper limit to the barrier to internal rotation being estimated as 4.2 cal/mol.

The number of carbon-coordinated borane adducts known is quite small, the most familiar example being borane-carbonyl. The fact that several metal complexes with isocyanide ligands are known[34] suggests that isocyanide compounds may also act as donors toward nonmetal acceptors such as borane. However, to our knowledge, only one such adduct[14] has previously been reported.

Isocyanides are thought to be stronger σ donors toward metal ions than is carbon monoxide, but comparison of IR stretching frequency shifts in metal carbonyls and metal isocyanides suggests that the two species are comparable in π donor abilities. If it is assumed that donor bonding to borane is principally σ in character, this indicates that isocyanide-borane complexes should equal or exceed borane carbonyl in stability.

Borane carbonyl may be regarded as a weak adduct because it dissociates somewhat at room temperature

$$H_3BCO \rightarrow CO + \tfrac{1}{2}B_2H_6 \tag{4}$$

and must be formed under high pressure. Methyl isocyanide-borane forms immediately on mixing B_2H_6 and methyl isocyanide at 1 Torr. Further, the dipole moment enhancement is considerably greater for methyl isocyanide-borane than for borane carbonyl. However, the longer C-B bond length of CH_3NCBH_3 compared to borane carbonyl strongly suggests that the former is the weaker adduct. Resolution of these conflicting indications may have to await direct measurements of the static dissociation of $CH_3NC{\cdot}BH_3$. Attempts to isolate the adduct are now underway.

Acknowledgments. This work was supported by Grants C-071 and E-439 of the Robert A. Welch Foundation and by Grant MPS71-03046 of the National Science Foundation.

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