

Figure 4. ORTEP drawing of the  $[\text{CuL}]^{2+}$  cation in  $[\text{CuL}]\text{Br}_2 \cdot 3\text{H}_2\text{O}$ , showing the numbering scheme adopted.

inertness toward strong acid solutions, no change being observed over a period of months in both  $\text{HCl}$  and  $\text{HClO}_4$  3 mol  $\text{dm}^{-3}$  aqueous solutions. Such a high kinetic inertness toward acidic decomposition, which has been also observed for  $\text{Cu}(\text{II})$  complexes of the related cages,<sup>4,5,22</sup> has been considered good experimental evidence for  $\text{Cu}(\text{II})$  encapsulation.

To confirm the ability of L to encapsulate the  $\text{Cu}(\text{II})$  ion, an X-ray crystal structure determination of  $[\text{CuL}]\text{Br}_2 \cdot 3\text{H}_2\text{O}$  has been carried out, and the ORTEP drawing of the cation  $[\text{CuL}]^{2+}$  is reported in Figure 4. The copper ion lies inside the cavity of the macrobicyclic and is five-coordinated by the nitrogen donors of the ligand. The coordination geometry of  $\text{Cu}^{2+}$  is trigonal bi-

pyramidal with a symmetry plane through  $\text{N}(1)$ ,  $\text{N}(4)$ ,  $\text{N}(3)$ , and  $\text{Cu}$ , slightly more distorted than that of  $\text{Li}^+$  in  $[\text{LiL}]\text{ClO}_4$ . Actually, the basal angles are 112 (1), 122 (1), and 127 (1) $^\circ$ , whereas the angles among the apical and basal bonds range from 87.8 (9) to 92.4 (8) $^\circ$ . However, the conformation adopted by the ligand is less strained in the copper complex than in the lithium analogue, as shown by the values of the bond angles within the chelate rings. Apparently, the shorter  $\text{Cu}-\text{N}$  distances (average 1.98 Å; 1.88–2.04 Å) are more appropriate to the small cavity of this macrobicyclic than the  $\text{Li}-\text{N}$  ones (2.04 Å). In fact, the mean  $\text{Cu}-\text{N}$  distance of 1.98 Å is a little shorter than that of 2.07 Å (2.03–2.11 Å) found with  $[\text{CuL1}][\text{ClO}_4] \cdot \text{H}_2\text{O}$ .<sup>4</sup> In both lithium and copper complexes the  $\text{M}-\text{N}$  apical distances are shorter than those in the equatorial plane. Finally, it can be noted that, with these trigonal-bipyramidal complexes  $[\text{CuL}]^{2+}$  and  $[\text{LiL}]^+$ , the three substituents on the basal nitrogens, i.e. two methyl groups and a hydrogen atom, assume a "head-to-tail" orientation. A different arrangement holds with the square-pyramidal complexes  $[\text{CuL1}][\text{ClO}_4] \cdot \text{H}_2\text{O}$  and  $[\text{LiL2}][\text{BPh}_4]$  of the [7.5.5] cryptates.<sup>4,6,8</sup> In such cases the two methyl substituents point toward the  $\text{NH}$  group.

**Conclusions.** The marked difference in basicity behavior of L with respect to the related cage L1 is indicative of the key role played by the molecular preorganization in determining the proton-transfer properties. The high thermodynamic stability of  $[\text{LiL}]^+$  complex in aqueous solution and the crystal structure indicate that L has the right cavity size to selectively encapsulate lithium. Further improvements on the lithium-binding capability could be achieved by inserting an appropriate substituent group on the secondary, apical nitrogen.

**Supplementary Material Available:** Tables of complete bond lengths and angles and positional and thermal parameters (6 pages); a listing of observed and calculated structure factors (10 pages). Ordering information is given on any current masthead page.

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## Gas-Phase Structures of Dimethylboron Azide and Dimethylboron Isocyanate. Electron Diffraction and ab Initio Study

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The gas-phase structures of  $(\text{CH}_3)_2\text{BN}_3$  and  $(\text{CH}_3)_2\text{BNCO}$  have been determined by electron diffraction. Both molecules have planar heavy-atom skeletons with bent  $\text{BN}_3$  and  $\text{BNCO}$  moieties. Their geometries differ mainly in the  $\text{BNY}$  bond angle ( $Y = \text{N}$  or  $\text{CO}$ ), which is small ( $\sim 120^\circ$ ) in the azide and large ( $\sim 150^\circ$ ) in the isocyanate. The following skeletal distances ( $r_s$ ) and bond angles ( $\angle_s$ ) with  $3\sigma$  estimated uncertainties have been derived.  $(\text{CH}_3)_2\text{BN}_3$ :  $\text{BC} = 1.569$  (4) Å,  $\text{BN}_\alpha = 1.436$  (6) Å,  $\text{N}_\alpha\text{N}_\beta = 1.252$  (4) Å,  $\text{N}_\beta\text{N}_\omega = 1.128$  (5) Å,  $\text{CBC} = 122.8$  (5) $^\circ$ ,  $\text{N}_\alpha\text{BC}_1 = 115.8$  (8) $^\circ$ ,  $\text{N}_\alpha\text{BC}_2 = 122.1$  (8) $^\circ$ ,  $\text{BN}_\alpha\text{N}_\beta = 118.9$  (8) $^\circ$ , and  $\text{N}_\alpha\text{N}_\beta\text{N}_\omega = 175.0$  (18) $^\circ$ .  $(\text{CH}_3)_2\text{BNCO}$ :  $\text{BC} = 1.563$  (4) Å,  $\text{BN} = 1.425$  (5) Å,  $\text{NC} = 1.206$  (6) Å,  $\text{CO} = 1.167$  (5) Å,  $\text{CBC} = 123.6$  (7) $^\circ$ ,  $\text{NBC}_1 = 115.3$  (11) $^\circ$ ,  $\text{NBC}_2 = 121.1$  (11) $^\circ$ , and  $\text{BNC} = 153.8$  (26) $^\circ$ . ( $\text{C}_1$  is the methyl carbon trans to  $Y$ .) Structure analyses with a large amplitude model for  $(\text{CH}_3)_2\text{BNCO}$  and a double minimum potential for the  $\text{BNCO}$  in-plane bending motion suggest that the barrier at the linear configuration is  $\geq 0.2$  kcal/mol. HF calculations with 6-31G\* basis sets reproduce the experimental structure of the azide satisfactorily. Relative to the ground state, a configuration with a linear  $\text{BN}_3$  group and one with the azide group pointing out of the plane are respectively 15.0 and 12.1 kcal/mol less stable. For  $(\text{CH}_3)_2\text{BNCO}$  the ab initio method predicts a linear  $\text{BNCO}$  structure, which is at variance with the experimental result.

### Introduction

It was recognized long ago<sup>2-4</sup> that structural and physical properties of boron-nitrogen compounds parallel those of the isoelectronic carbon-carbon species. In particular, the bond in amine-boranes  $\text{X}_3\text{B}-\text{NY}_3$  can be compared to the single bond in alkanes, the bond in aminoboranes  $\text{X}_2\text{B}=\text{NY}_2$  to the double bond

in alkenes, and the bond in iminoboranes  $\text{XB}=\text{NY}$  to the triple bond in alkynes. Differences in chemical behavior and the higher reactivity of boron-nitrogen compounds have been attributed to the polarity and to the weakness of the  $\text{BN}$  bonds relative to the  $\text{CC}$  bonds. Haaland<sup>5</sup> explains these differences in bonding properties by differentiating between covalent and dative bonds. Whereas all  $\text{CC}$  bonds (single, double, and triple) are covalent  $\sigma$  or  $\pi$  bonds, the single bond in amine-boranes is a dative  $\sigma$  bond and the  $\pi$  bond in aminoboranes and one  $\pi$  bond in iminoboranes are dative  $\pi$  bonds between the nitrogen lone pair and the empty

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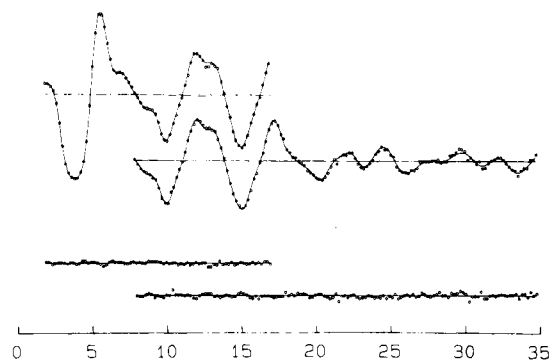
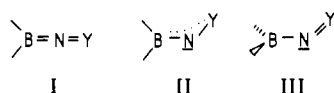


Figure 1. Experimental (dots) and calculated (full line) molecular intensities and differences for  $(\text{CH}_3)_2\text{BN}_3$ .

boron  $p_z$  orbital. In this article we follow the suggestion of Paetzold,<sup>4</sup> indicating such bonds in structural formulas with dashes, just as for covalent bonds.

Aminoboranes with BN double bonds and tricoordinated nitrogen ( $\text{X}_2\text{B}=\text{NY}_2$ ) have been studied quite extensively, but very little is known about structural properties of aminoboranes with two-coordinated nitrogen of the type  $\text{X}_2\text{B}=\text{N}=\text{Y}$ . For such compounds three different geometric structures are feasible. If the parallelism with the isoelectronic carbon analogues  $\text{X}_2\text{C}=\text{C}=\text{Y}$  is extended to this type of compounds, a linear arrangement of the cumulated double bonds is expected (I). In this structure



the BN and NY  $\pi$  bonds are orthogonal to each other, similar to those in the carbon analogues. An alternative bonding model with a three-center BNY  $\pi$  bond perpendicular to the molecular plane leads to a planar  $\text{X}_2\text{B}\text{N}\text{Y}$  structure with a bent BNY moiety (II). In structure III the NY group points out of the plane that is defined by the three boron bonds and no BN  $\pi$  bond is formed.

$\text{Mes}_2\text{B}=\text{N}=\text{CPh}_2$  is an example of an  $\text{X}_2\text{B}\text{N}\text{Y}$  compound ( $\text{Y} = \text{CPh}_2$ ) that adopts structure I with a linear skeleton and the mesityl and phenyl groups in planes perpendicular to each other.<sup>6</sup> Other examples of  $\text{X}_2\text{B}\text{N}\text{Y}$  compounds are boron azides ( $\text{Y} = \text{NN}$ ) and boron isocyanates ( $\text{Y} = \text{CO}$ ). Syntheses and properties of some boron azides have been described in the literature,<sup>7</sup> but no structural studies have been reported so far. Structure determinations of these azides in the solid state are hampered by the strong tendency for trimerization. Dimethylboron azide,<sup>8</sup> which is a highly volatile liquid at room temperature, has been characterized by NMR ( $^{11}\text{B}$  and  $^1\text{H}$ ) and infrared spectroscopy. These data do not allow for a choice among structures I–III. In analogy to known azide structures, where the bond angles at the  $\alpha$ -nitrogen are near  $120^\circ$ , a bent structure II with  $C_s$  symmetry was chosen for assignment of the infrared spectrum. The first synthesis of a boron isocyanate,  $(\text{CH}_3)_2\text{BNCO}$ , was reported by Goubeau and Gräbner in 1960.<sup>9</sup> Again, the infrared spectrum gives no conclusive information about the structure type, and a linear arrangement of the BNCO entity (structure I) was favored on the basis of the BN force constant ( $\sim 6 \text{ mdyn}/\text{\AA}$ ).

In the present study we report structure determinations of dimethylboron azide and dimethylboron isocyanate by gas-phase electron diffraction. The experimental studies are augmented by ab initio calculations to obtain additional information about the electronic structures and energy differences among structures I–III.

### Experiments

$(\text{CH}_3)_2\text{BN}_3$  was synthesized according to the literature method.<sup>8</sup>  $(\text{CH}_3)_2\text{BNCO}$  was prepared in a vacuum apparatus by reaction of gaseous

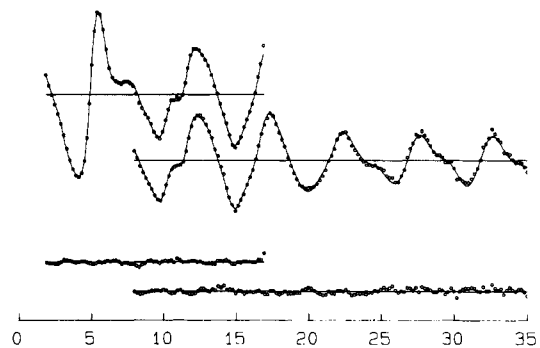


Figure 2. Experimental (dots) and calculated (full line) molecular intensities and differences for  $(\text{CH}_3)_2\text{BNCO}$ .

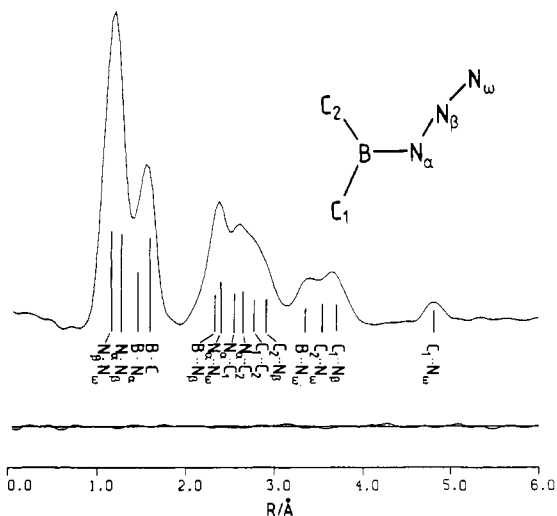


Figure 3. Experimental radial distribution function and difference curve for  $(\text{CH}_3)_2\text{BN}_3$ .

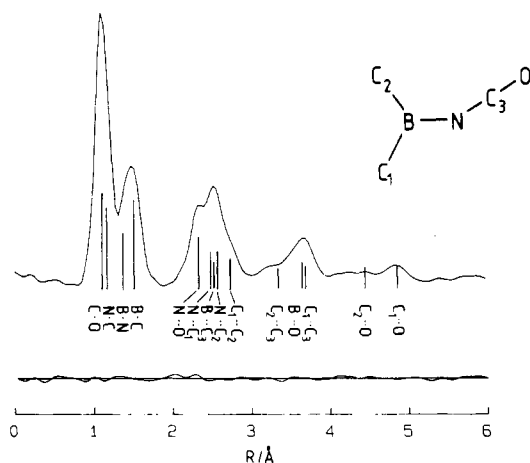


Figure 4. Experimental radial distribution function and difference curve for  $(\text{CH}_3)_2\text{BNCO}$ .

$(\text{CH}_3)_2\text{BBr}$  with  $\text{AgNCO}$  following the method of Goubeau and Gräbner.<sup>9</sup> The reaction mixture consisting of  $(\text{CH}_3)_2\text{BNCO}$  and some  $(\text{CH}_3)_2\text{BBr}$  was cooled to  $-78^\circ\text{C}$  and the volatiles were pumped off, until the remaining dimethylboron isocyanate had the desired purity. The purity of both samples was checked by infrared spectroscopy before and after the electron diffraction experiments, and no impurities  $\geq 2\%$  were detected.

The electron diffraction intensities were recorded with the Model KD-G2 gas diffractograph<sup>10</sup> at two camera distances (25 and 50 cm) on Kodak electron image plates. The electron wavelength ( $\sim 60 \text{ kV}$  accelerating voltage) was calibrated with  $\text{ZnO}$  diffraction patterns. The

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**Table I.** Vibrational Amplitudes (in Å) for (CH<sub>3</sub>)<sub>2</sub>BN<sub>3</sub> and (CH<sub>3</sub>)<sub>2</sub>BNCO<sup>a</sup>

(CH <sub>3</sub> ) <sub>2</sub> BN <sub>3</sub>		(CH <sub>3</sub> ) <sub>2</sub> BNCO	
C-H	0.070 <sup>b</sup>	C-H	0.070 <sup>b</sup>
N <sub>β</sub> ·N <sub>w</sub>	0.039 (7) l <sub>1</sub>	C-O	0.038 (6) l <sub>1</sub>
N <sub>α</sub> ·N <sub>β</sub>		N·C <sub>3</sub>	
B·N <sub>α</sub>	0.042 <sup>b</sup>	B-N	0.042 <sup>b</sup>
B·C <sub>1,2</sub>	0.047 (4) l <sub>2</sub>	B·C <sub>1,2</sub>	0.049 (4) l <sub>2</sub>
N <sub>α</sub> ·N <sub>w</sub>	0.053 (6) l <sub>3</sub>	N·O	0.044 (8) l <sub>3</sub>
B·N <sub>β</sub>		B·C <sub>3</sub>	
N <sub>α</sub> ·C <sub>1</sub>	0.066 (11) l <sub>4</sub>	N·C <sub>1</sub>	0.060 (8) l <sub>4</sub>
N <sub>α</sub> ·C <sub>2</sub>		N·C <sub>2</sub>	
C <sub>1</sub> ·C <sub>2</sub>	0.089 (3) l <sub>5</sub>	C <sub>2</sub> ·C <sub>3</sub>	0.204 (36) l <sub>5</sub>
C <sub>2</sub> ·N <sub>β</sub>		C <sub>2</sub> ·O	
B·N <sub>w</sub>	0.078 (10) l <sub>6</sub>	B·O	0.103 (18) l <sub>6</sub>
C <sub>1</sub> ·N <sub>β</sub>		C <sub>1</sub> ·C <sub>3</sub>	
C <sub>1</sub> ·N <sub>w</sub>		C <sub>1</sub> ·O	

<sup>a</sup> Without nonbonded distances involving hydrogen atoms. For atom numbering, see Figures 3 and 4. Estimated uncertainties are 3σ values. <sup>b</sup> Not refined.

sample reservoir was kept at 10 °C (azide) and -30 °C (isocyanate), and the stainless steel inlet system and nozzle were at room temperature in all experiments. The camera pressure never exceeded 1.5 × 10<sup>-5</sup> Torr. Two photographic plates for each compound and camera distance were analyzed with the usual procedures.<sup>11</sup> The averaged molecular intensities in the *s* range from 1.4 to 17 Å<sup>-1</sup> and from 8 to 35 Å<sup>-1</sup> in steps of Δ*s* = 0.2 Å<sup>-1</sup> are shown in Figures 1 and 2, and numerical values of the total scattering intensities are available as supplementary data.

### Structure Analyses

Model calculations demonstrate clearly that the experimental radial distribution functions of both compounds (Figures 3 and 4) can be reproduced qualitatively only with structures of type II, i.e. with a planar skeleton and bent BN<sub>3</sub> and BNCO moieties. Structures with linear BN<sub>3</sub> and BNCO arrangements (I) or nonplanar skeletons (III) are not compatible with the radial distribution functions. The preliminary structural models of the two compounds differ mainly in the BNY bond angle, which is small (~120°) in the azide and large (~150°) in the isocyanate. The preliminary models were refined by least-squares analyses on the basis of the molecular intensities. A diagonal weight matrix was applied to the intensities, and scattering amplitudes and phases of Haase<sup>12</sup> were used. C<sub>3v</sub> symmetry was assumed for the methyl groups. Tilt angles between the C<sub>3</sub> axis of CH<sub>3</sub> and the B-C bond direction converged toward values that were smaller than the estimated uncertainties (3σ values) and were set to zero in the final refinements. If these tilt angles were set to the ab initio values (see below; the methyl groups are tilted away from each other), the skeletal geometric parameters remained unchanged within their standard deviations. Ab initio calculations predict both methyl groups to eclipse the BN bond. In the structure analyses, however, the fit of the experimental intensities improved if an "effective" torsional angle was introduced. The deviation of the NCO group from linearity was smaller than the corresponding uncertainty, and therefore the NCO angle was constrained to 180° in the final refinement. Vibrational amplitudes were grouped according to the length and type of the distances. Since the BNY bond angles differ by about 30° between the azide and the isocyanate, the vibrational amplitudes were grouped slightly differently in the two compounds. This grouping and further constraints for vibrational amplitudes are evident from Table I. With the above assumptions, 11 (azide) and 10 (isocyanate) geometric parameters were refined simultaneously together with 6 vibrational amplitudes. The following correlation coefficients had values larger than |0.6|. (CH<sub>3</sub>)<sub>2</sub>BN<sub>3</sub>: CH/N<sub>β</sub>N<sub>w</sub> = -0.71, BN/BC = 0.64, BNN/Δ = 0.69, CH/l<sub>1</sub> = 0.84, BNN/l<sub>4</sub> = 0.68, Δ/l<sub>4</sub> = 0.78. (CH<sub>3</sub>)BNCO:

**Table II.** Experimental and Calculated Geometric Parameters (in Å and deg) for (CH<sub>3</sub>)BN<sub>3</sub><sup>a</sup>

	expt <sup>b</sup>	HF/6-31G*		
		structure II	structure I	structure III
BC <sub>1</sub>	1.569 (4)	1.591	1.588	1.585
BC <sub>2</sub>		1.583		
BN <sub>α</sub>	1.436 (6)	1.446	1.415	1.462
N <sub>α</sub> N <sub>β</sub>	1.252 (4)	1.241	1.117	1.202
N <sub>β</sub> N <sub>w</sub>	1.128 (5)	1.094	1.108	1.105
CH <sup>c</sup>	1.093 (10)	1.088	1.088	1.088
C <sub>1</sub> BC <sub>2</sub>	122.8 (5)	120.7	120.8	120.8
Δ = N <sub>α</sub> BC <sub>2</sub> - N <sub>α</sub> BC <sub>1</sub>	7.0 (9)	7.1	0.0	0.0
N <sub>α</sub> BC <sub>1</sub> <sup>d</sup>	115.1 (8)	116.1		
N <sub>α</sub> BC <sub>2</sub> <sup>d</sup>	122.1 (8)	123.2		
BN <sub>α</sub> N <sub>β</sub>	118.9 (8)	118.8	180.0	129.8
N <sub>α</sub> N <sub>β</sub> N <sub>w</sub>	175.0 (18)	174.1	180.0	176.3
HCH <sup>c</sup>	110.6 (12)	108.2	108.2	108.3
tilt(CH <sub>3</sub> ) <sup>e</sup>	0.0 <sup>f</sup>	2.7	2.3	2.4
τ(CH <sub>3</sub> ) <sup>g</sup>	28 (6)	0.0	0.0	0.2
Δ <i>E</i> , kcal/mol		0.0	15.0	12.1

<sup>a</sup> For atom numbering, see Figure 3. <sup>b</sup> *r*<sub>a</sub> values from electron diffraction experiment; estimated uncertainties are 3σ values and include a possible scale error of 0.1% for bond lengths. <sup>c</sup> Average value of the calculated parameters. <sup>d</sup> Dependent parameter. <sup>e</sup> The tilt angles are an approximate description of the calculated distortions of the methyl groups. The groups are tilted away from each other. <sup>f</sup> Not refined. <sup>g</sup> The experimental value is an effective torsional angle due to large amplitude torsional vibrations.

CH/CO = -0.61, NC/CO = -0.83, NC/l<sub>1</sub> = -0.91, CO/l<sub>1</sub> = 0.90, Δ/l<sub>4</sub> = 0.82. The results for vibrational amplitudes are summarized in Table I, and those for the geometric parameters are given in Tables II and III.

The large BNC angle in the isocyanate (153.8 (26)°), as well as vibrational amplitudes for some nonbonded distances, suggests that the barrier to inversion at the nitrogen atom is small and that the molecule exhibits nonrigid behavior with a large amplitude BNC bending motion. Therefore, additional analyses of the electron diffraction intensities based on a large amplitude model were performed. A double-minimum potential of the form

$$V = V_0 \left[ \left( \frac{\Phi}{\Phi_e} \right)^2 - 1 \right]^2$$

was assumed for the bending motion, with *V*<sub>0</sub> the barrier at the linear configuration, Φ = 180 - BNC, and Φ<sub>e</sub> corresponding to the potential minimum. The difference Δ between the two BNC angles was assumed to increase linearly with increasing deviation from the linear BNCO configuration; i.e., Δ = *a* × Φ. The inversion barrier *V*<sub>0</sub> could not be refined simultaneously with the other parameters (including the constant *a*) because of high correlations with some geometric parameters and vibrational amplitudes. In a series of least-squares refinements with different but fixed values for *V*<sub>0</sub>, the agreement factor for the long camera distance data (*R*<sub>50</sub>) has a shallow minimum at *V*<sub>0</sub> = 0.9 kcal/mol. If we discard refinements where *R*<sub>50</sub> increases by more than 20%, inversion barriers from 10 kcal/mol (rigid model) down to 0.2 kcal/mol are compatible with the electron diffraction intensities. For a very flat single-minimum potential the agreement factor increases by 40%, indicating disagreement between model and experiment. Thus, it is not possible to determine the barrier to inversion from the electron diffraction experiment; all that is suggested is a lower limit of 0.2 kcal/mol for *V*<sub>0</sub>. All geometric parameters, which are obtained with the large amplitude model, agree within their standard deviations with the values derived in the rigid analysis (Table III), except for the BNC angle. For *V*<sub>0</sub> = 0.9 kcal/mol the equilibrium value Φ<sub>e</sub> = 29.8 (25)°, corresponding to BNC = 150.2 (25)°.

### Ab Initio Calculations

Structure optimizations for both compounds were performed with the GAUSSIAN 86 program system<sup>13</sup> in the HF approximation

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**Table III.** Experimental and Calculated Geometric Parameters (in Å and deg) for (CH<sub>3</sub>)<sub>2</sub>BNCO<sup>a</sup>

	expt <sup>b</sup>	HF/6-31G*		expt <sup>b</sup>	HF/6-31G*
BC	1.563 (4)	1.584	NBC <sub>1</sub> <sup>d</sup>	115.3 (11)	} 119.4
BN	1.425 (5)	1.433	NBC <sub>2</sub> <sup>d</sup>	121.1 (11)	
NC	1.206 (6)	1.176	BNC	153.8 (26)	180.0
CO	1.167 (5)	1.156	NCO	180 <sup>f</sup>	180.0
CH <sup>c</sup>	1.098 (8)	1.087	HCH <sup>c</sup>	107.6 (12)	108.2
C <sub>1</sub> BC <sub>2</sub>	123.6 (7)	121.2	tilt(CH <sub>3</sub> ) <sup>e</sup>	0.0 <sup>f</sup>	2.4
Δ = NBC <sub>2</sub> - NBC <sub>1</sub>	5.8 (12)	0.0	τ(CH <sub>3</sub> ) <sup>g</sup>	26 (8)	0.0

<sup>a</sup> For atom numbering, see Figure 4. <sup>b-f</sup> See corresponding footnotes of Table II.

and with 6-31G\* basis sets. Calculations with different torsional positions of the methyl groups demonstrate that both groups prefer the eclipsed position with respect to the BN bond, but barriers to internal rotation of the CH<sub>3</sub> groups are very low. If one of the two methyl groups in the azide is rotated to the staggered position, the energy increases by only 0.2 kcal/mol. For (CH<sub>3</sub>)<sub>2</sub>BN<sub>3</sub> the experimental structure is reproduced satisfactorily by the calculations (see Table II). For the isocyanate, however, the ab initio method predicts a linear configuration of the B=N=C=O moiety. A similar failure of the HF method to reproduce correct equilibrium structures has been observed for other "near-linear" or "pseudolinear" molecules, such as H<sub>2</sub>C=C=C=O,<sup>14</sup> CF<sub>3</sub>-C=SF<sub>3</sub>,<sup>15</sup> or SiH<sub>3</sub>-N=C=O.<sup>16</sup> No further attempts were made to reproduce the experimental structure of the isocyanate by increasing the basis set and/or including electron correlation. In the case of (CH<sub>3</sub>)<sub>2</sub>BN<sub>3</sub> additional geometry optimizations were performed for the linear (I) and perpendicular (III) configurations (see Table II).

### Discussion

The aminoboranes with two-coordinated nitrogen (CH<sub>3</sub>)<sub>2</sub>BN<sub>3</sub> and (CH<sub>3</sub>)<sub>2</sub>BNCO adopt structures of type II, i.e. bent BN<sub>3</sub> and BNCO moieties with the azide and isocyanate groups in the molecular plane. The large BNC angle in the isocyanate (153.8 (26)°) indicates considerable contribution of structure I. These results imply that formation of a three-center BNY π bond is energetically favored relative to two BN π and NY π bonds perpendicular to each other (structure I). The BN bonds in these compounds (1.436 (6) Å in the azide and 1.425 (5) Å in the isocyanate) are longer than those in H<sub>2</sub>B=NH<sub>2</sub> (1.403 (5) Å),<sup>17</sup> (CH<sub>3</sub>)<sub>2</sub>B=NHCH<sub>3</sub> (1.397 (2) Å),<sup>18</sup> or Mes<sub>2</sub>B=N=CPh<sub>2</sub> (1.38 (2) Å).<sup>6</sup>

The ab initio calculations for (CH<sub>3</sub>)<sub>2</sub>BN<sub>3</sub> allow for a discussion of the differences in structural and bonding properties of the three possible configurations. The linear structure I is predicted to be higher in energy by ΔE = 15.0 kcal/mol relative to structure II. The shortening of the BN bond in the linear configuration (1.415 Å relative to 1.446 Å) is due to increased σ bonding (0.37 au vs 0.35 au for the overlap population), whereas the Mulliken π bond overlap population is equal for both configurations (0.10 au). The calculations predict an extreme shortening of the N<sub>α</sub>N<sub>β</sub> bond from

1.241 Å in structure II to 1.177 Å in structure I. The configuration (structure III) with the azide group out of the plane that is defined by the three boron bonds represents an energy maximum with respect to rotation around the BN bond but a minimum with respect to the BNN angle. This structure lies 12.1 kcal/mol above the ground-state structure (II), indicating that internal rotation around the BN bond is energetically favored relative to inversion of the azide group in the molecular plane (15.0 kcal/mol). The BN bond in this structure is longer (1.462 Å) than in structure II, and this lengthening can be attributed to decreased π bonding (0.05 au vs. 0.10 au). The ab initio calculations thus support the structural formulas given in the Introduction, i.e. BN double bonds for structures I and II and a single bond for structure III, although the difference between the π-bond contributions in structures I and II on one side and structure III on the other side is small.

The structural properties of the boron compounds of this study show a striking similarity to those of the analogous silanes SiH<sub>3</sub>N<sub>3</sub> and SiH<sub>3</sub>NCO. In both azides the nitrogen bond angles are close to 120° (118.9 (8)° in (CH<sub>3</sub>)<sub>2</sub>BN<sub>3</sub> and 123.8 (10)° in SiH<sub>3</sub>N<sub>3</sub>),<sup>19</sup> and in the isocyanates these angles increase to ca. 150° (153.8 (26)° in (CH<sub>3</sub>)<sub>2</sub>BNCO and 151.7 (12)° in SiH<sub>3</sub>NCO<sup>20</sup>). Silyl isocyanate is a pseudolinear molecule, and a very low barrier to inversion of 91.8 (6) cal/mol has been derived from spectroscopic data.<sup>21</sup> Unfortunately, the electron diffraction intensities do not allow for a reliable estimate of this barrier in the boron compound and only future spectroscopic studies (far-infrared and/or microwave) could supply more information about the dynamic properties of this compound.

In the Introduction we pointed out that the parallelism between boron-nitrogen and carbon-carbon compounds suggests linear conformations for molecules of the type X<sub>2</sub>B=N=Y. This parallelism holds for Mes<sub>2</sub>B=N=CPh<sub>2</sub>, where an allene type structure has been determined for the crystalline state. For the azide this analogy can not be tested, since the corresponding carbon derivative X<sub>2</sub>C=C=N<sub>2</sub> does not exist. An analogous carbon derivative of Me<sub>2</sub>BNCO is propadienone, H<sub>2</sub>C=C=C=O, which has—contrary to chemical intuition—a zigzag conformation with the CCCO chain bent in the molecular plane by CCC = 144.5 (15)° and CCO = 169.4 (35)°.<sup>22</sup> Thus, dimethylboron isocyanate and propadienone form a pair of analogous compounds that are an additional example for the structural parallelism between boron-nitrogen and carbon-carbon compounds.

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**Supplementary Material Available:** A table of numerical values for total electron diffraction intensities of (CH<sub>3</sub>)<sub>2</sub>BN<sub>3</sub> and (CH<sub>3</sub>)<sub>2</sub>BNCO (4 pages). Ordering information is given on any current masthead page.

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