

^{*a*} [R₃NHCl]₀ = 5 × 10⁻² M. *b* Diluents: 1,2-dichlorobenzene, DCB; 1,2-dichloroethane, DCE; carbon tetrachloride, CCl₄.
^{*c*} [H⁺]_{aq} = 6 M = [Cl⁻]_{aq}. ^{*d*} [H⁺]_{aq} = 4 M; [Cl⁻]_{aq} = 6 M.

Registry No. Mo, 7439-98-7; triisooctylamine, 25549-16-0.

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Nature of B-Monosubstituted Dimethylaminoboranes¹

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Monaminoboranes with various substituents (R_2BNR_2) have been observed as monomers, dimers, trimers, or higher polymers. The degree of polymerization is considered to be related to the interplay of a variety of factors² which include electronic, steric, thermodynamic, and mechanistic effects. When monomers are observed, the electronic effect, π bonding, has generally been considered to be sufficient to prevent association with subsequent σ -bond formation.² For example, the monomeric molecule, 3 (CH₃)₂BN(CH₃)₂, is planar and has a relatively short B-N bond, which would be consistent with π bonding. However, it should be noted that essentially all similarily organo-substituted aminoboranes are monomeric. This observation might suggest that steric factors play a significant role. For comparison, the compounds X2BN(CH3)2 $(X = H, F, Cl, Br, I)$, which do not have an organo substituent on boron, have been observed as monomers and dimers depending on the phase and experimental conditions.^{4,5} The monomers which are believed to be planar⁵ are usually observed in the gas phase at higher temperatures. The dimers, for example [Cl₂BN(CH₃)₂]₂, exist as planar four-membered rings⁶ at room temperature.

The B-monosubstituted aminoboranes, HXBN(CH3)2, offer interesting opportunities for research. The single substituent on boron in the aminoborane might have some unusual effects on the properties and structures of the compounds. In addition it might be possible to evaluate the significance of π -bonding and steric effects to the stability of the monomeric species and to the equilibrium between the monomeric and dimeric species. In this paper we report the results of our investigation of the preparation and physical and spectral properties of HClB- $N(CH_3)_2$ and HBrBN(CH₃)₂. Attempts to extend this study to other monosubstituted derivatives with more unusual substituents, such as -CN, -NCO, and -NCS, were unsuccessful. The compounds could not be prepared.

Experimental Section

All compounds described in this investigation were manipulated in a vacuum system or a purified nitrogen atmosphere. The solvents and reagents were purified by conventional means.

Preparation of HXBN(CH3)2 (X = Cl, Br). The compounds HClBN(CH₃)₂ and HBrBN(CH₃)₂ were prepared by heating [H₂BN(CH₃)₂]₂ and HgCl₂ or HgBr₂ at 110 °C. In a typical reaction, 1.11 g (9.93 mmol) of $[H_2BN(CH_3)_2]_2$ was vacuum distilled into a pyrolysis tube containing 2.74 g (10.1 mmol) of HgCl₂. The tube, equipped with a break-seal side arm, was sealed under vacuum. The mixture was heated at 110 °C for 24 h. Hydrogen (9.73 mmol) and elemental Hg were produced in the reaction. A small pressure of a condensable gas, believed to be monomeric HClBN(CH₃)₂, was observed in the pyrolysis tube after the H_2 had been removed. The crystalline product remaining in the tube was purified by vacuum sublimation at 25 °C to a Dry Ice cold finger and identified as [HClBN(CH₃)₂]₂ by its melting point, 96–97 °C (lit.⁷ mp 95–97 °C). The compound $[HBrBN(CH_3)_2]_2$, which was prepared and purified in an identical manner, was also identified by its melting point, 122-124 °C (lit.⁸ mp 122-124 °C). Both compounds were further confirmed by elemental analyses and molecular weight studies. The molecular weights of [HClBN(CH₃)₂]₂ and [HBrBN(CH₃)₂]₂ as measured

Table I. Vapor Pressure Data

| $T, \degree C$ | $P, \, \text{mm}$ | $T, \degree C$ | P , mm | |
|----------------|-------------------|----------------|----------|--|
| | $HClBN(CH_3)$, | | | |
| 50.5 | 4.50 | 119 | 440.7 | |
| | | | | |
| 57.0 | 8.00 | 114 | 336.2 | |
| 67.5 | 23.00 | 103 | 198.4 | |
| 75.0 | 46.20 | 95 | 127.2 | |
| 87.5 | 88.40 | 91 | 103.7 | |
| 88.0 | -90.90 | 85 | 76.40 | |
| 93.5 | 115.8 | 80 | 58.20 | |
| 102.5 | 189.3 | 72 | 35.85 | |
| 108 | 245.1 | 63 | 13.55 | |
| | $HBrBN(CH_3)_2$ | | | |
| 84.0 | 14.05 | 136 | 239.0 | |
| | | | | |
| 94.0 | 27.25 | 127 | 155.6 | |
| 106 | 50.15 | 118 | 103.1 | |
| 116 | 86.85 | 101 | 42.40 | |
| 128 | 155.3 | 79 | 12.50 | |

cryoscopically in benzene were 186 (calcd 182) and 270 (calcd 273), respectively. There was no dependence of molecular weight on concentration. These compounds exist as dimers in benzene solution.

Other routes to these compounds were also attempted. The reagents, [H2BN(CH3)2]2 and HgC12, were combined under a variety of other conditions. There was no reaction at $25 °C$ using diethyl ether or pentane as solvents. These are the solvents and conditions used for reactions of HgCl₂ with H₃B₃N₃H₃,⁹</sup> H₃B₃N₃(CH₃)₃,⁹ and H₃BN(CH₃)₃.¹⁰ The use of refluxing hexane (68 °C) led to reaction but the products were $[HCIBN(CH_3)_2]_2$ and $H_2ClBN(CH_3)_2H$. Apparently HC1 had been formed in the reaction and then combined with $H_2BN(CH_3)_2$ to form $H_2CBN(CH_3)_2H$. The compound $H_2CIBN(CH_3)_2H^{10}$ can be converted to $[HCIBN(CH_3)_2]_2$ by pyrolysis at 110 °C. The product obtained from this reaction was identical in every respect to that obtained from the HgC12 reaction.

Attempted Preparation **of** [H(CN)BN(CH3)2]2. A variety of attempts were made to prepare H(CN)BN(CH3)2. However, we were never successful in obtaining a product which we considered to be a pure compound. As the reagent, AgCN, had been useful for preparing H₂(CN)BN(CH₃)₃¹⁰ from H₃BN(CH₃)₃, AgCN was combined with [H2BN(CH3)2]2 under a variety of conditions. Pyrolysis of the reaction mixture at 150 "C for 36 h in a sealed tube gave only a partial yield of the H₂ expected¹⁰ and a liquid which could not be identified. Higher temperatures or longer reaction times led to products, which indicated decomposition. The compound $H_2(CN)BN(CH_3)_2H$, obtained by previously described methods,¹⁰ did not eliminate H₂ at 147 °C (18 h). Higher temperatures led to decomposition rather than dehydrogenation and formation of the desired compound. Attempts to prepare derivatives¹⁰ with the substituents, -NCO and -NCS, were also unsuccessful.

Vapor Pressure and Gas-Phase Molecular Weight Studies. The equilibrium vapor pressure and gas-phase molecular weights were measured using an isoteniscope and standard procedures.11 Mercury levels were measured by means of a cathetometer. Readings were made while both increasing and decreasing the temperature. At a given temperature, the system was allowed to equilibrate (establish constant pressure) over long periods of time. The vapor pressure, molecular weights, and values of K_p for the equilibrium (dimer \rightleftharpoons 2(monomer) are given in Tables I and 11. Thermodynamic quantities for the gas-phase monomer-dimer equilibrium reactions were calculated from plots of log K_p vs. $1/T$.

Infrared Spectra. Infrared spectra were recorded in the range 4000-400 cm-1 by means of a Perkin-Elmer Model 457 spectrometer. The spectra of [HClBN(CH3)2]2 and [HBrBN(CH3)2]2 were observed as Nujol mulls and chloroform solutions between KBr plates. Gaseous monomeric species were observed in a heatable 7-cm gas cell equipped with KBr optics. The monomeric species was identified by comparison with spectra of similar species.10 Absorption intensities were measured using the method of Durkin, Glore, and DeHayes.¹²

The following give the spectral data [frequency, cm^{-1} (intensity: s, strong; m, medium; w, weak; sh, shoulder)]: $[H_2BN(CH_3)_2]_2$ —3018 (m), 2960 (s), 2860 (m), 2810 (m), 2440 (s), 2370 (s), 2230 (m), 1470 (m), 1240 (s), 1193 (s), 1150 (s), 1048 (m), 965 (s), 812 (m); [HClBN(CH₃)₂]₂-3018 (m), 3000 (m), 2940 (s), 2880 (w), 2490 (s), 1460 **(s),** 1411 (m), 1358 (m), 1245 (m), 1198 (m), 1117 (m), 1078 (m), 1030 (m), 950 (m), 790 (m), 725 (w); HCIBN(CH3)z

Table III. Nuclear Magnetic Resonance Data^a

 a Concentration: 10% by weight. Chemical shifts in ppm; coupling constants in Hz.

(monomer)-3018 (m), 3000 (m), 2490 (s), 2880 (s), 2820 (m), 2560 (s), 1590 (w). 1525 (s), 1462 (s), 1425 (s), 1222 (s), 1150 (s), 1079 (m), 1065 (m), 960 (w), 930 (m), 785 (s), 780 (s), 770 (m); $[HBrBN(CH_3)_2]_2$ —3018 (m), 3000 (m), 2940 (s), 2880 (m), 2495 (s), 1460 (s), 1410 (w), 1357 (m), 1243 (m), 1199 (s), 1182 (s), 1117 (m), 1070 (s), 1060 (m), 1034 (s), 1007 (s), 958 (s), 949 (s), 775 (s) , 721 (w), 643 (m); HBrBN(CH₃)₂ (monomer)-3018 (m), 2940 (s), 2880 (m), 2820 (w), 2560 (s), 1590 (w), 1520 (s), 1455 (m), 1415 (s), 1215 (s), 1140 (s), 1060 **(w),** 965 (w), 790 (w), 710 (m).

Nuclear Magnetic Resonance Spectra. The 'H NMR spectra were recorded at 100 MHz by means of a Joelco MH-100 spectrometer equipped with variable-temperature capability. All chemical shifts are given in ppm and are referenced to tetramethylsilane as 0.00 ppm. There was no dependence of spectra on concentration. Boron-11 NMR spectra were recorded by means of a Varian Model HA-60 spectrometer, operating at 15.871 MHz. Chemical shifts in ppm were determined relative to $BF_3\text{-}O(C_2H_5)$ ₂ which was contained in sealed capillaries. Coupling constants are measured in hertz. The NMR data are given in Table 111.

Results and Discussion

The reagents HgClz and HgBrz are very useful for preparing a boron-halogen derivative of a borazine,9,13 amine-borane,^{10,14} and aminoborane from the corresponding boronhydrogen compound. However, the reactivities of the boron-nitrogen compound and mercury-containing products are different for the various boron-nitrogen compounds. Aminoboranes react with HgX_2 at 110 °C to give Hg and HX whereas borazines^{9,13} and amine-boranes^{10,14} react at 25 °C to give Hg2X2 and HX as products. **As** the mercury(I1) halides are believed to react with these types of boron-nitrogen compounds by a polar mechanism, $9,10,14$ the decreased reactivity of [(H2BN(CH3)2]2 compared to that of H3B3N3H3 and H3BN(CH3)3 might be related to a smaller partial negative charge on the hydrogen bound to boron¹⁰ due to electronegativity effects and steric effects. At higher temperatures, the reactivities of both $[H_2BN(CH_3)_2]_2$ and HgX_2 will be enhanced by changes in coordination number. The aminoborane dimer will dissociate into a less sterically hindered monomer and the six-coordinate mercury (II) species of the solid phase¹⁵ will be converted into a linear two-coordinate species.

There is another observation of synthetic utility which is worth noting. The compound $H_2CIBN(CH_3)$ ₂H readily loses H_2 to form [HClBN(CH₃)₂]₂. In our experiments, the reaction was observed at 110 $^{\circ}$ C. (No attempt was made to determine the lowest temperature necessary for reaction.) Conversely, the compound $H_2(CN)BN(CH_3)2H$ could not be converted to $[H(CN)BN(CH_3)_2]_2$ by loss of H₂. No reaction was observed at 147 °C and higher temperatures led to decomposition. These cyano-substituted amine-boranes also exhibit unusually high hydrolytic stability.

The 1H NMR spectra of [HClBN(CH3)2]2 and [HBrB-N(CH3)2]2 suggest some interesting structural properties. The data for both compounds are consistent with a structure involving a four-membered ring and cis-trans isomerism. The multiplicity of CH lines and their temperature dependence suggest that the rings are bent and inverting at room temperature. The ¹¹B NMR spectra of both compounds, a symmetrical doublet due to B-H coupling, are consistent with only one type of boron atom. Thus, structures involving unsymmetrical substitution, four-membered chains, ionic structures, and monomeric species are eliminated. Molecular weight measurements in solution also confirm the absence of significant concentrations of monomeric species. The room-temperature 1H NMR spectrum of [HClBN(CH3)2]2 in CDC13 consists of a broad line at **-2.58** ppm and a sharp line at -2.49 ppm. These two lines can be assigned to the N-CH3 groups of the cis and trans isomers, respectively. The spectrum at lower temperatures confirms the assignments of the lines. Upon cooling, the broad line at -2.58 ppm splits into two lines at -2.62 and -2.56 ppm at -23 °C. The line at -2.49 ppm remains a sharp singlet. These data suggest that the lower field line in the room-temperature spectrum is due to the cis isomer of a bent boron-nitrogen ring. **As** the temperature is lowered, the two types of methyl groups in the cis isomer, axial and equatorial, are observed. In benzene solution, the lines due to the isomers of $[HCIBN(CH_3)_2]_2$ are not resolved. The situation is exactly the opposite for $[HBrBN(CH_3)_2]$; the isomers are resolved in aromatic solvents but not in CDC13. The **1H** NMR spectrum of $[HBrBN(CH_3)_2]_2$ in C₆H₅Cl exhibits two CH lines (-2.31) and -2.22 ppm) at room temperature and at -40 °C, the lowest temperature we could attain. The data for this compound are also consistent with a bent but flexible boron-nitrogen ring. Apparently, the bromine-substituted molecule is inverting faster than the chlorine derivative. There is also more ring distortion in bromocyclobutanes.¹⁶ For both compounds $[HCIBN(CH_3)_2]$ 2 and $[HBrBN(CH_3)_2]$ 2, this cis isomer is more abundant than the trans isomers. Similar observations have been made for 1,3-dihalocyclobutanes,¹⁶ [Cl(CH₃)B- $N(CH_3)$ ₂]₂,¹⁷ and analogous aluminum-nitrogen compounds.¹⁸ The high cis:trans ratio for group 3-5 compounds may be dependent on the mechanism of dimer formation.

An equilibrium between the dimeric and monomeric species in the gas phase is confirmed by vapor pressure, gas-phase molecular weight measurements, and mass spectral data. The enthalpies for the gas-phase equilibrium (dimer \rightleftarrows 2(monomer)) for $[HCIBN(CH3)2]2$ and $[HBrBN(CH3)2]2$ are 30.1 and 42.0 kcal/mol, respectively. The comparison of the thermodynamic data suggest that [HBrBN(CH3)2]2 exhibits the more stable dimer. This conclusion is consistent with the observation that BBr3 is a stronger Lewis acid19 than BC13. By analogy, there might be more distortion in the bromo derivative than in the chloro to form stronger boron-nitrogen bonds in the dimer. As there is less boron-bromine π bonding than boron-chlorine, increased boron-nitrogen π bonding might be expected to stabilize the monomeric species. However, the monomeric species is certainly not very stable at 25 °C. It is regretable that there are just too many undetermined variables in the thermodynamic cycle, analogous to that used for the Lewis acidity of boron trihalides, to be able to evaluate the magnitude of boron-nitrogen π bonding in the compounds. There just might be less boron-nitrogen π bonding than we have been led to believe in the past.

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Registry No. [H₂BN(CH₃)₂]₂, 23884-11-9; HgCl₂, 7487-94-7; $HgBr₂, 7789-47-1; cis-[HClBN(CH₃)₂]$ ₂, 57652-88-7; trans-[HCIBN(CH3)2]z, 57694-03-8; cis-[HBrBN(CH3)z] **2,** 57652-89-8; trans-[HBrBN(CH3)z]z, 57694-04-9.

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Field Desorption Mass Spectrometry of inorganic Compounds

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Field desorption mass spectrometry has drawn much interest in recent years as a means to ionize and mass analyze nonvolatile and thermolabile organic compounds.¹ This technique may, however, have interesting applications in the field of