A quantitative interpretation of the state of polymerization represented by the shaded circles in Fig. 1 did not seem justified because it would have involved several assumptions unwarranted at the present time.

The authors wish to acknowledge the assistance of Dr. John Bonner and Mr. Robert Vosteen for assembling and maintaining the counting equipment.

ROCHESTER 20, NEW YORK RECEIVED AUGUST 31, 1951

CONTRIBUTION FROM THE MALLINCKRODT LABORATORY OF THE DEPARTMENT OF CHEMISTRY OF HARVARD UNIVERSITY]

Boron–Nitrogen Systems. I. Dimethylaminoboron Dichloride[1,2]

BY CHARLES A. BROWN[3] AND ROBERT C. OSTHOFF[4]

Some physical and chemical properties of monomeric and dimeric dimethylaminoboron dichloride are reported. The monomer reacts quantitatively with trimethylamine and hydrogen chloride to form one-to-one addition compounds. Some physical properties of these addition compounds are given. The trimethylamine adduct reacts with hydrogen chloride to yield trimethylamine hydrochloride and monomer hydrochloride. Thermal decomposition of the amine adduct yields $Cl_3B:N(CH_3)_3$, $[(CH_3)_2N]_3B$ and trimethylamine. Measurement of the dipole moment of dimeric dimethylaminoboron dichloride leads to the assignment of a cyclic structure consisting of a four-membered ring of alternate boron and nitrogen atoms.

I. Introduction

The bonds between boron and nitrogen atoms present two extremes in type. In one case the nitrogen atom donates a pair of electrons to boron with the formation of a coördinate covalent or donor–acceptor complex. The second possibility is the formation of a "normal" covalent bond between these two atoms. Bonds intermediate between these extremes, *i.e.*, contribution of both types to the resonance hybrid, probably account for the shortening of the boron–nitrogen distance in such compounds as boron nitride, borazole ($B_3N_3H_6$) and some of its derivatives.[5]

Although a large number of studies have been published concerning the properties of coördinate covalent boron–nitrogen systems,[6,7] the character of the normal covalent bond and the intermediate bond types deserves a more detailed investigation. This paper is the first of a series directed toward the properties of some simple compounds which illustrate these types of bonding.

Experimental

II. Monomeric Dimethylaminoboron Dichloride

Preparation.—The monomer was prepared in a manner similar to that which has been described by Wiberg and Schuster.[8] Anhydrous dimethylamine (Eastman Kodak Co. "White Label") was added without further purification to boron trichloride at liquid nitrogen temperatures. The reaction mixture was allowed to warm slowly to room temperature and the volatile products fractionated by means of traps maintained at −20, −80 and −196°. The pure product, which was collected in the trap at −80°, was stored in an evacuated bulb at Dry Ice temperature until used.

The best yields of monomeric dimethylaminoboron dichloride (35% based upon the amount of dimethylamine employed) were obtained at a mole ratio $[BCl_3/HN(CH_3)_2]$ of 0.72. Although the equation

$$BCl_3 + 2HN(CH_3)_2 \longrightarrow (CH_3)_2NBCl_2 + (CH_3)_2NH{\cdot}HCl$$

was used in the calculation of yields, the formation of the hydrogen chloride adduct of the monomer and higher substitution products of boron trichloride, *i.e.*, bis-dimethylaminoboron chloride and tris-dimethylaminoboron, probably account for the low yields.

The purity of the monomer was checked by a determination of the melting point (obsd. −43°; previous value, −46°); the entire vapor pressure curve gave excellent agreement with the previously reported values.[8] Measurements of vapor density of monomeric dimethylaminoboron dichloride gave a value of the molecular weight in the vapor phase of 129 at 25°; calcd., 125.8.

When monomeric dimethylaminoboron dichloride is allowed to stand at room temperature for a period of several days, a crystalline solid dimeric modification forms. This dimer was first described by Wiberg and Schuster[9] and a more complete description of its properties is given below. However, the dimerization reaction is suppressed at low temperatures, and it is possible to store the monomer at −80° *in vacuo* for a period of several weeks.

Density of Liquid Monomer.—Densities of liquid monomer were evaluated by means of a pycnometric method. A 2-ml. dilatometric pycnometer was constructed with a stem of Tru-bore Pyrex tubing. The volume was carefully calibrated with mercury and the volume change per unit stem length determined. A sample of monomer was distilled into the pycnometer and sealed off. The pycnometer was then placed in a constant temperature bath and the level of the liquid monomer in the capillary determined by means of a cathetometer.

The results which were obtained from two independent samples are summarized in Table I. The analytical expression for the density as a function of Centigrade temperature in the range −40 to 22° is

$$d = 1.1629 - 0.001177t$$

with an average deviation of 0.0008.

Surface Tension and Parachor.—Surface tensions were determined with the liquid monomer under its own vapor pressure by the application of the method of Mills and Robinson.[10] In Table I the data obtained from two independent samples in the temperature range −40 to 35° are summarized along with the observed parachor at each temperature. The equation representing the surface tension as a function of temperature in °C. is

$$\gamma = 29.24 - 0.1238t \text{ (dynes per cm.)}$$

with a mean deviation of 0.02. The measurement of density and surface tension above room temperature leads to less reliable results since the liquid monomer slowly dimerizes to solid $[(CH_3)_2NBCl_2]_2$. The rate of the dimerization increases as the temperature is increased up to at least 80°.

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[1] Presented before the Division of Physical and Inorganic Chemistry, American Chemical Society Meeting, Chicago, Ill., September 4, 1950.

[2] In part taken from the Ph.D. Thesis of Robert C. Osthoff, Harvard University, 1951.

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[4] Procter and Gamble Fellow in Chemistry, Harvard University, 1951.

[5] S. H. Bauer, *Chem. Revs.*, **31**, 43 (1940).

[6] A. W. Laubengayer and G. F. Condike, THIS JOURNAL, **70**, 2274 (1948).

[7] D. R. Martin, *Chem. Revs.*, **34**, 461 (1944).

[8] E. Wiberg and K. Schuster, *Z. anorg. Chem.*, **213**, 77 (1933).

[9] E. Wiberg and K. Schuster, *ibid.*, **213**, 89 (1933).

[10] H. Mills and P. L. Robinson, *J. Chem. Soc.*, 1823 (1927).

TABLE I

DENSITIES, SURFACE TENSIONS AND PARACHORS OF MONOMERIC DIMETHYLAMINOBORON DICHLORIDE

t, °C.	$d_{\text{obsd.}}$	$\gamma_{\text{obsd.}}$, dynes/cm.	Parachor
−40.0	1.2093	33.39	250.1
−35.0	1.2039	33.23	251.0
−30.0	1.1991	32.95	251.4
−25.0	1.1926	32.70	252.2
−20.0	1.1875	32.13	252.7
−15.0	1.1815	30.85	252.7
−10.0		30.56	251.0
− 9.0	1.1742		
− 5.0		29.77	251.4
− 3.0	1.1641		
0.0	1.1634	29.15	251.5
3.0	1.1595		
5.0		28.82	252.5
8.0	1.1526		
10.0		28.25	252.1
13.0	1.1491		
15.0		27.40	251.3
16.0	1.1446		
20.0		27.09	252.0
21.8	1.1362		
25.0		26.07	251.4
30.0		25.06	250.5
35.0		24.90	251.7
		Mean value of parachor	251.5

The boron–nitrogen bond of dimethylaminoboron dichloride, $(CH_3)_2NBCl_2$, should have a bond order which lies between about one $(> \mathrm{B{-}\ddot{N}} <)$ and two $(> \overset{-}{\mathrm{B}}{=}\overset{+}{\mathrm{N}} <)$ depending on the extent to which the nitrogen contributes its extra electron pair to the normal covalent bond. Any participation of this pair of electrons produces partial charges on the boron and nitrogen atoms, $>\overset{\delta-}{\mathrm{B}}\leftarrow\overset{\delta+}{\ddot{\mathrm{N}}}$, and it should be noted that this polarity is opposite to that which arises from the difference in the electronegativities of the two atoms.

The value of the molar parachor of borazole, $B_3N_3H_6$, of 208 parachor units constitutes the only case in which the parachor of a boron–nitrogen compound has been reported.[11] Combination of the molar parachor of borazole with Sugden's atomic parachor values[12] gives a value of the atomic parachor of boron of 20.6 parachor units. If this value of the atomic parachor of boron is used, the molecular parachor of monomeric dimethylaminoboron dichloride is calculated to be 253.9 parachor units. This value is within 1% of the observed parachor. Since boron has a variable radius, the small difference between the calculated and the observed values does not permit any definite conclusion to be drawn concerning the bond order of the boron–nitrogen bond in monomeric dimethylaminoboron dichloride.

Reaction with Trimethylamine.—2.678×10^{-3} mole of Eastman Kodak Co. "White Label" trimethylamine (vapor pressure 675.5 mm. at 0°; calcd., 681 mm.[13]) was introduced into an evacuated 120-ml. bulb by means of a compensating gas buret. The bulb was attached to a vacuum chain and the pressure of the completely vaporized sample of trimethylamine was carefully measured with a mercury manometer. Successive weighed samples of monomeric dimethylaminoboron dichloride were then condensed by the use of liquid nitrogen into the flask containing the amine. After each addition of monomer the reaction bulb was allowed to warm to room temperature and the gas pressure determined. In this manner it was possible to calculate the mole ratio of dimethylaminoboron dichloride to trimethylamine which corresponded to each value of the pressure, the experiment being conducted at constant volume and constant temperature. In Fig. 1 the pressure is plotted against the mole ratio for two determinations of this system. Since the addition compound has only a small vapor pressure at room temperature (8 mm. at 22.5°), the minimum at a mole ratio of one indicates the quantitative formation of $(CH_3)_2NBCl_2{:}N(CH_3)_3$ under the conditions of the experiment.

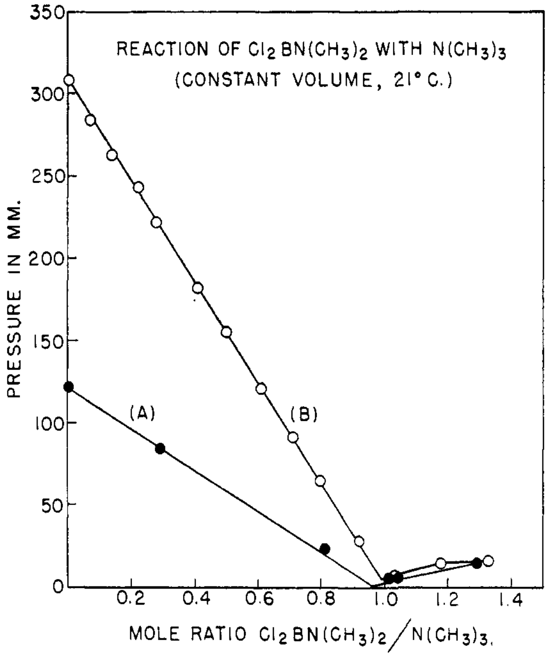

Fig. 1.—Reaction of $Cl_2BN(CH_3)_2$ with $N(CH_3)_3$ (constant volume, 21°).

The adduct of the monomer and trimethylamine is a colorless, crystalline solid at room temperature which melts at 76–77° with decomposition.

Anal. Calcd. for $(CH_3)_2NBCl_2{:}N(CH_3)_3$: C, 32.40; H, 8.11; Cl, 38.38; B, 5.87. Found: C, 32.11; H, 8.03; Cl, 38.23; B, 5.67.

Reaction with Hydrogen Chloride.—Gaseous hydrogen chloride reacts with monomeric dimethylaminoboron dichloride at low temperatures (about −30°) to form a white solid one-to-one addition compound, $(CH_3)_2NBCl_2{\cdot}HCl$. This reaction was studied by the same method as the reaction of monomer with trimethylamine. In Fig. 2 the mole ratio $[(CH_3)_2NBCl_2/HCl]$ is plotted against the pressure. An examination of the graph indicates that the substance having the composition $(CH_3)_2NBCl_2{\cdot}HCl$ is formed under the experimental conditions. The product melts at 135–139° with decomposition.

Anal. Calcd. for $(CH_3)_2NBCl_2{\cdot}HCl$: C, 14.82; H, 4.30; N, 8.66; Cl, 65.20. Found: C, 15.10; H, 4.46; N, 8.79; Cl, 64.41.

Reaction with Boron Trifluoride.—When a small sample of monomeric dimethylaminoboron dichloride was introduced into boron trifluoride vapor, a slow and apparently complex reaction occurred. The rate of the reaction, as estimated from the observation of the decreases in the pressure, was found to be about the same order of magnitude as the dimerization reaction. In typical runs in which small amounts of monomeric dimethylaminoboron dichloride were added to an excess of gaseous boron trifluoride, gradual decreases in pressure were observed over a period of three or four days. Calculations based only on the pressure decreases would in-

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(11) E. Wiberg and A. Bloz. *Ber.*, **73**, 209 (1940).

(12) S. Sugden. *J. Chem. Soc.*, **127**, 1540 (1925).

(13) A. Simon and J. Hunter. *Z. Elektrochem.*, **41**, 28 (1935).

TABLE II

VAPOR PRESSURES OF $(CH_3)_2NBCl_2:N(CH_3)_3$

t, °C.	30.0	33.0	35.0	37.5	40.0	45.0	50.0	55.0	60.0	65.0
P_{mm}(obsd.)	14.8	19.0	21.4	26.1	31.1	48.3	72.1	103.8	157.8	215.5
P_{mm}(calcd.)	13.7	18.8	21.1	26.1	32.1	48.1	71.0	100.3	151.3	210.6

dicate an empirical formula of $(CH_3)_2NBCl_2{\cdot}1.1BF_3$. However, in no case was a sufficient amount of any product isolated to obtain an analysis and it is probable that more than one compound is formed in the reaction. Complex disproportionations of the type which have been described by Burg and Randolph[14] in the case of $(CH_3)_2NBH_2$ may occur.

No reaction between the monomer and boron trimethyl was detected under the conditions used in the above experiments.

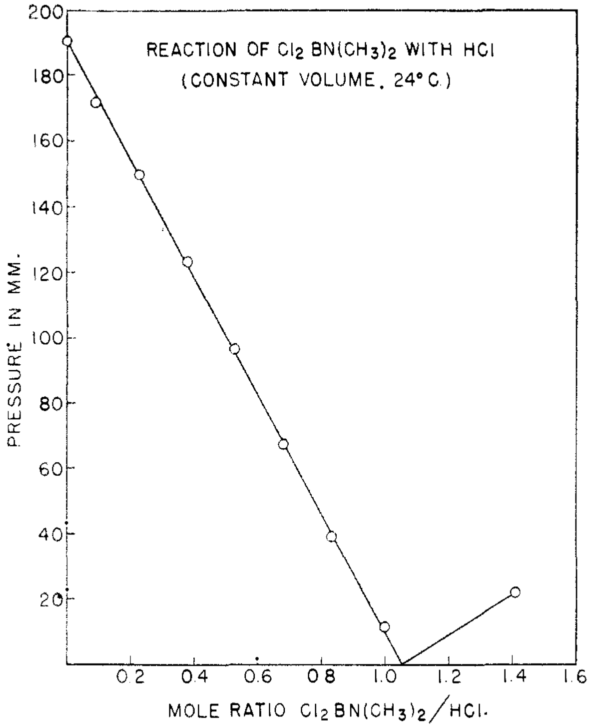

Fig. 2.—Reaction of $Cl_2BN(CH_3)_2$ with HCl (constant volume, 24°).

Stereochemically, both the boron and nitrogen atoms can show a coördination number of four under favorable conditions. Hence addition compounds of dimethylaminoboron dichloride are to be expected. According to the generalized acid–base theory of Lewis, a compound of the type X_2BNY_2 might be expected to show *both* acid and basic properties. The fact that dimethylaminoboron dichloride reacts quantitatively with trimethylamine to yield the covalent addition compound $(CH_3)_2NBCl_2:N(CH_3)_3$ illustrates the acidic behavior of the boron atom. Furthermore, it is to be concluded that trimethylamine is a stronger base than the $-N(CH_3)_2$ group which is already attached to the boron.

An example of the basic behavior of dimethylaminoboron dichloride is its reaction with hydrogen chloride to form a one-to-one addition compound of the empirical formula $(CH_3)_2NBCl_2{\cdot}HCl$. The properties of this compound indicate that the salt-like structure, $[(CH_3)_2NHBCl_2]^+Cl^-$ is probably the correct formulation of the substance.

III. Properties of $(CH_3)_2NBCl_2:N(CH_3)_3$

Preparation.—$(CH_3)_2NBCl_2:N(CH_3)_3$ was prepared in a quantitative manner by introduction of monomeric dimethylaminoboron dichloride into excess trimethylamine. After standing for one hour at room temperature the excess amine was pumped off and the $(CH_3)_2NBCl_2:N(CH_3)_3$ was purified by vacuum sublimation.

Vapor Pressure.—The vapor pressure of solid $(CH_3)_2NBCl_2:N(CH_3)_3$ was studied in the temperature range of 20 to 69° by means of a modified isoteniscope of the type which has been described by Smith and Menzies.[15] By application of the method of least squares to the data of three individual runs, the constants of the Antoine equation[16] were evaluated. It was observed that the vapor pressure of $(CH_3)_2NBCl_2:N(CH_3)_3$ may be represented in the temperature range 20 to 69° by the expression

$$\log_{10}P_{mm} = 11.1445 - \frac{2602}{t + 230}$$

From this equation the heat of sublimation was calculated to be 15.8 ± 0.4 kcal. per mole. Calculated and observed values of the vapor pressure of $(CH_3)_2NBCl_2:N(CH_3)_3$ at selected temperatures are given in Table II.

At temperatures above 70° residual pressures remained in the isoteniscopes when they were cooled to 0° showing the system to be irreversible above this temperature. A discussion of the thermal decomposition which occurs at these temperatures is given below.

The samples of $(CH_3)_2NBCl_2:N(CH_3)_3$ could be sublimed out of the isoteniscopes at the end of the runs in which the temperatures involved were not greater than 70°. The volatility of the samples indicated that no $Cl_3B:N(CH_3)_3$ had been formed due to a disproportionation of $(CH_3)_2NBCl_2:N(CH_3)_3$. Also the vapor pressures of Table II are considerably below the saturation pressures of either bis-dimethylaminoboron chloride or tris-dimethylaminoboron. This indication of the absence of higher substitution products in the isoteniscopes further substantiates the view that no disproportionation of $(CH_3)_2NBCl_2:N(CH_3)_3$ occurs below 70°.

Molecular Weight.—As a result of two independent experiments in which modified isoteniscopes were used, the vapor density of $(CH_3)_2NBCl_2:N(CH_3)_3$ in the temperature range of 27 to 60° was found to be approximately normal. A mean molecular weight in the temperature range studied was found to be 181 (calcd. molecular weight, 184.9). The somewhat low value of the molecular weight indicates that the compound may be about 2% dissociated.

Hydrolysis.—When 0.2032 g. of $(CH_3)_2NBCl_2:N(CH_3)_3$ was added to a limited amount of 10% aqueous sodium hydroxide at 3°, 0.0624 g. of trimethylamine was liberated (calcd., 0.0638 g.) and identified by its infrared absorption spectrum. Once the trimethylamine had been liberated, it is assumed that the hydrolysis of the monomer proceeds with the formation of boric acid, hydrogen chloride and dimethylamine. Thus the over-all hydrolysis reaction may be written as

$$(CH_3)_2NBCl_2:N(CH_3)_3 + 3H_2O \longrightarrow (CH_3)_3N + H_3BO_3 + 2HCl + HN(CH_3)_2$$

Reactions of $(CH_3)_2NBCl_2:N(CH_3)_3$.—The reaction of $(CH_3)_2NBCl_2:N(CH_3)_3$ with hydrogen chloride was followed by observation of the pressure changes which accompanied the addition of weighed amounts of the coördination compound to a measured volume of hydrogen chloride in the manner described in connection with the reactions of the monomer. An examination of Fig. 3 indicates that two moles of hydrogen chloride react with one mole of $(CH_3)_2NBCl_2:N(CH_3)_3$. It may thus be inferred that the boron–nitro-

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[14] A. B. Burg and C. L. Randolph, THIS JOURNAL, 71, 3451 (1949).

[15] A. Smith and A. W. C. Menzies, *ibid.*, 32, 1412 (1910).

[16] G. W. Thomson, *Chem. Revs.*, 38, 1 (1946).

gen coördinate covalent bond is ruptured with the subsequent formation of trimethylamine hydrochloride and $(CH_3)_2NBCl_2{\cdot}HCl$

$$(CH_3)_2NBCl_2{:}N(CH_3)_3 + 2HCl \longrightarrow (CH_3)_3N{\cdot}HCl + (CH_3)_2NBCl_2{\cdot}HCl$$

Because of the similarity of the physical properties of the products, the separation of the components was not possible.

2.560×10^{-3} mole of boron trimethyl reacted with 2.591×10^{-3} mole of $(CH_3)_2NBCl_2{:}N(CH_3)_3$ to produce $(CH_3)_3B{:}N(CH_3)_3$ and monomeric dimethylaminoboron dichloride. The reaction products were identified by means of their infrared spectra. Thus the reaction may be formulated as

$$(CH_3)_2NBCl_2{:}N(CH_3)_3 + B(CH_3)_3 \longrightarrow (CH_3)_3B{:}N(CH_3)_3 + (CH_3)_2NBCl_2$$

The resulting monomer slowly dimerized upon standing at room temperature for several days.

2.521×10^{-3} mole of boron trifluoride reacted with 2.344×10^{-3} mole of $(CH_3)_2NBCl_2{:}N(CH_3)_3$. $F_3B{:}N(CH_3)_3$ remained in the reaction flask after the liberated liquid monomeric dimethylaminoboron dichloride had been distilled off. Again each of the reaction products was identified by means of its infrared spectrum. The reaction is thus

$$(CH_3)_2NBCl_2{:}N(CH_3)_3 + BF_3 \longrightarrow F_3B{:}N(CH_3)_3 + (CH_3)_2NBCl_2$$

Since somewhat more boron trifluoride was consumed than the amount required by this equation, it was concluded that some boron trifluoride reacted with the monomer as has been described above in this paper.

The little investigated phenomenon of the rupture of the boron–nitrogen coördinate covalent bond by chemical means in compounds of this type has been reported but once in the literature, *i.e.*, the reaction of $(CH_3)_3B{:}N(CH_3)_3$ with hydrogen chloride[17] which produces trimethylamine hydrochloride and boron trimethyl. It should be noted that boron trifluoride, boron trimethyl and hydrogen chloride all constitute stronger acids than dimethylaminoboron dichloride, since they replace trimethylamine from the addition compound, $(CH_3)_2NBCl_2{:}N(CH_3)_3$.

Thermal Decomposition.—When $(CH_3)_2NBCl_2{:}N(CH_3)_3$ is heated in the absence of air in a sealed tube to 120° for 24 hours, a disproportionation reaction occurs in which trimethylamine, tris-dimethylaminoboron and $Cl_3B{:}N(CH_3)_3$ are formed.

$$3(CH_3)_2NBCl_2{:}N(CH_3)_3 \xrightarrow{120^\circ} (CH_3)_3N + 2Cl_3B{:}N(CH_3)_3 + [(CH_3)_2N]_3B$$

In a typical experiment 0.3356 g. of $(CH_3)_2NBCl_2{:}N(CH_3)_3$ was pyrolyzed for 40 hours in a sealed tube. 0.0360 g. of trimethylamine (calcd., 0.0356 g.), 0.2080 g. of $Cl_3B{:}N(CH_3)_3$ (calcd., 0.2126 g.) and 0.0916 g. of tris-dimethylaminoboron (calcd., 0.0870 g.) were obtained. There was no evidence found to indicate that bis-dimethylaminoboron chloride was formed in these experiments. Carbonization of the methyl groups begins to take place in the neighborhood of 230°.

IV. Properties of $(CH_3)_2NBCl_2{\cdot}HCl$

Preparation.—Small quantities of $(CH_3)_2NBCl_2{\cdot}HCl$ were prepared conveniently by the action of excess anhydrous hydrogen chloride upon monomeric dimethylaminoboron dichloride *in vacuo*. $(CH_3)_2NBCl_2{\cdot}HCl$ may be purified by recrystallization from anhydrous ether. The white crystalline solid is stable in air for short periods of time, but the ultimate hydrolysis products are boric acid, dimethylamine and hydrogen chloride.

Vapor Pressure.—The vapor pressure of solid $(CH_3)_2NBCl_2{\cdot}HCl$ was investigated by the use of an isoteniscope.

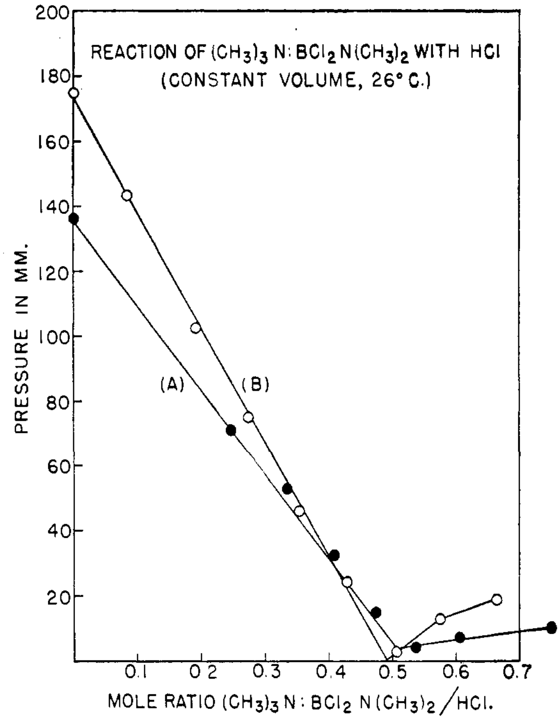

Fig. 3.—Reaction of $(CH_3)_3N{:}BCl_2N(CH_3)_2$ with HCl (constant volume, 26°).

Residual pressures of 1 to 2 mm. were observed invariably when the isoteniscopes were cooled to room temperature. The presence of these small pressures is interpreted as an indication that the following irreversible reaction takes place to a slight extent

$$2(CH_3)_2NBCl_2{\cdot}HCl \longrightarrow [(CH_3)_2NBCl_2]_2 + 2HCl$$

Dimeric dimethylaminoboron dichloride does not react with hydrogen chloride at the temperatures involved. As a result of this complication, it was not possible to evaluate the vapor pressures of the compound with a precision of greater than 5%. The vapor pressure equation which is applicable in the temperature range of 90 to 135° is

$$\log_{10} P_{\text{mm}} = 8.758 - \frac{3038}{T}$$

From this equation in which T represents the absolute temperature, the heat of sublimation of the compound was found to be 13.9 ± 0.7 kcal./mole.

In Table III are presented some observed and calculated vapor pressure data for $(CH_3)_2NBCl_2{\cdot}HCl$.

Table III

Vapor Pressures of $(CH_3)_2NBCl_2{\cdot}HCl$ (Solid)

t, °C.	90	98	110	124	130	135
P_{mm}(obsd.)	1.3	2.7	6.4	13.0	17.1	21.6
P_{mm}(calcd.)	1.0	2.5	6.6	12.7	16.6	20.5

Vapor Density.—A study of $(CH_3)_2NBCl_2{\cdot}HCl$ in the vapor phase was carried out by a modified isoteniscope method in which the volume of the vaporization bulb was about 500 ml. In the temperature range of 135 to 170° it was found that the equilibrium constant for the equilibrium

$$(CH_3)_2NBCl_2{\cdot}HCl(g) \rightleftharpoons (CH_3)_2NBCl_2(g) + HCl(g)$$

may be expressed by the equation

$$\log_{10} K_p\ (\text{atm.}) = 7.893 - \frac{3950}{T}$$

The constants in this expression were evaluated from the data of two independent runs. This equation leads to a value of the heat of dissociation of the compound of 18.1 ± 1.8 kcal./mole. Some of the dissociation data for $(CH_3)_2NBCl_2{\cdot}HCl$ are presented in Table IV.

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[17] H. I. Schlesinger, N. W. Flodin and A. B. Burg, This Journal, 61, 1078 (1939).

TABLE IV

DISSOCIATION DATA FOR $(CH_3)_2NBCl_2\cdot HCl$

t, °C.	$-\log_{10} K_p$ (atm.)	Degree of dissociation, α
135.0	1.652	0.728
140.1	1.591	.746
152.0	1.511	.782
158.0	1.196	.843
165.0	1.158	.887
170.0	1.047	.928

The standard free energy of formation of $(CH_3)_2NBCl_2\cdot HCl$ may be represented as

$$\Delta F^0 = 18.07 - 0.0361T \text{ (kcal. per mole)}$$

In all probability the structure of the hydrochloride of monomeric dimethylaminoboron dichloride is salt-like, *i.e.*, $[(CH_3)_2NHBCl_2]^+Cl^-$. J. F. Brown[18] has recently found that when pyridine is added to the hot benzene solution of boron trichloride and dimethylamine, *i.e.*, the solution of the compound of empirical formula $(CH_3)_2NBCl_2\cdot HCl$, an addition compound is formed. It may be assumed that this compound is $C_5H_5N:BCl_2N(CH_3)_2\cdot HCl$. From this it would appear that the structure of the hydrochloride should be the salt-like one.

The alternate structure, that of the isomeric addition compound, $Cl_3B:NH(CH_3)_2$, may also be discarded on the basis of the fact that there appears an immediate precipitate of silver chloride when the compound is placed in an aqueous solution of silver nitrate. This rapid hydrolysis is in sharp contrast to the behavior of the rather difficultly hydrolyzed $Cl_3B:N(CH_3)_3$[19] and $F_3B:N(CH_3)_3$.[20] Of course, there may exist a rapidly established equilibrium involving the slight ionization of the compound. It must be pointed out that there is not yet sufficient chemical evidence to definitely assign a correct structure.

V. Dimeric Dimethylaminoboron Dichloride

The spontaneous polymerization of monomeric dimethylaminoboron dichloride at room temperature to a solid modification results in a radical change in physical and chemical properties. Wiberg and Schuster[9] first described this dimorphism which is somewhat analogous to that of similar aluminum compounds.[21]

Preparation.—It has been reported that dimeric dimethylaminoboron dichloride can be obtained in a high state of purity by sublimation of the crude dimer which forms when the monomer is allowed to stand at room temperature for several days. In all attempted purifications of the dimer in this manner the sublimate invariably contained some easily hydrolyzable chloride. Samples of pure dimer were obtained in the following manner. Pure dimethylaminoboron dichloride monomer was distilled into anhydrous benzene (in which the monomer is miscible in all proportions while the dimer is but sparingly soluble) and stored at room temperature in a sealed tube. Crystals of dimer began to appear at the end of about 24 hours and continued to form for about 3 days; at the end of this time the dimerization process was essentially complete. The crystals were filtered, washed with anhydrous benzene, washed with distilled water, and finally rinsed with anhydrous methyl alcohol and dried in vacuum.

Anal. Calcd. for $[(CH_3)_2NBCl_2]_2$: C, 19.18; H, 4.78; N, 11.14. Found: C, 19.32; H, 5.15; N, 11.05.

The melting point of the solid dimer (sealed tubes) was found to be 142.5° (previous value, 142°[9]). The dimer is stable in air and was observed to be only slightly hydrolyzed after standing in contact with water at 25° for 24 hours. However, when the dimer was refluxed with 10% aqueous sodium hydroxide to which 5% of ethyl alcohol had been added, it was found that the dimer was about 80% hydrolyzed after 16 hours of reflux.

Crystal Properties.—Crystallographic examination of the dimer showed that at 24.0° the three indices of refraction of the dimer as determined by the immersion method are: $\alpha = 1.545 \pm 0.003$; $\beta = 1.580 \pm 0.003$; $\gamma = 1.59$. Crystals of the dimer were found to be biaxial and optically negative, and the crystals were apparently monoclinic as reported by Wiberg and Schuster.[9]

By combination of the three indices of refraction in the usual fashion and employing the value of the density of the dimer which has been reported previously[8] (1.552 g. per cm.^{3}), the molar refraction was found to be 53.5 cm.^{3} ($\sqrt[3]{\alpha\beta\gamma} = 1.572$). From the bond refractivities of Denbigh[22] and an assumption that the bond refraction of the boron–nitrogen bond is equivalent to that of a carbon–carbon single bond, the calculated molar refraction of dimeric dimethylaminoboron dichloride is 51.4 cm.^{3} It is seen that the agreement between the calculated and the observed molar refractions is good in view of the assumption that the boron–nitrogen and carbon–carbon bond refractions are equivalent.

Molecular Weight.—Cryoscopic measurements of molecular weight in anhydrous benzene solution gave a value of the molecular weight of 251 (calcd., 251.7).

Vapor Pressure.—The vapor pressure of dimeric dimethylaminoboron dichloride was investigated in the temperature range of 90 to 126° by means of an isoteniscope. In this range the vapor pressure may be expressed by the equation

$$\log_{10}P_{\text{mm}} = 26.736 - \frac{8564}{t + 230}$$

In Table V some observed and calculated values of the vapor pressure are given.

TABLE V

VAPOR PRESSURES OF DIMERIC DIMETHYLAMINOBORON DICHLORIDE

t, °C.	90	96	110	118	122	126.5
P_{mm}(obsd.)	0.96	2.2	37.8	139	253	517
P_{mm}(calcd.)	1.1	2.9	40.4	134	258	518

Vapor Density.—Measurements of vapor density in the temperature range of 102 to 177° were made by the use of a modified isoteniscope procedure. In two independent runs in which the volumes of the isoteniscope vaporization bulbs were 100 and 200 ml., close agreement of the molecular

TABLE VI

VAPOR DENSITY OF DIMERIC DIMETHYLAMINOBORON DICHLORIDE AT VARIOUS TEMPERATURES

Calcd. molecular weight of monomer = 125.8; calcd. molecular weight of dimer = 251.6

t, °C.	$M_{\text{obsd.}}$	Run
104.0	124.2	1
118.2	124.3	1
124.0	132.8	1
135.0	129.3	2
148.0	129.6	2
159.0	127.8	2
167.0	129.1	2
177.0	126.6	2

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[18] J. F. Brown, Research Laboratory, General Electric Co., Schenectady, N. Y., private communication, 1951.

[19] E. Wiberg and W. Sutterlin, *Z. Elektrochem.*, **41**, 151 (1935).

[20] H. Meerwein, *et al.*, *J. prakt. Chem.*, **154**, 83 (1939).

[21] N. Davidson and H. C. Brown, THIS JOURNAL, **64**, 316 (1942).

[22] K. G. Denbigh, *Trans. Faraday Soc.*, **36**, 936 (1940).

weights in the vapor phase was observed. In Table VI some typical data from each of the two runs are presented.

The mean value of the molecular weight of the vapor in the temperature range studied was 127.8. This indicates that the vapor of dimethylaminoboron dichloride is no more than 2% associated. From the data obtained in the study of the vapor density and of the vapor pressure, it was possible to evaluate the equilibrium constant for the process

$$[(CH_3)_2NBCl_2]_2(s) \rightleftarrows 2(CH_3)_2NBCl_2(g)$$

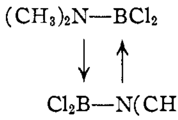
The equilibrium constant may be expressed as

$$\log_{10}K_p \text{ (atm.)} = 54.851 - \frac{22{,}040}{T}$$

where T represents the absolute temperature. The standard free energy of formation of the solid dimer from gaseous monomer may be expressed approximately as

$$\Delta F^0 = 101.2 - 0.251T \text{ (kcal. per mole dimer)}$$

Dipole Moment.—Wiberg and Schuster[9] first proposed that dimeric dimethylaminoboron dichloride possesses a cyclic structure which consists of a four-membered ring of alternate boron and nitrogen atoms.



$$\begin{array}{ccc}(CH_3)_2N & — & BCl_2\\ \downarrow & & \uparrow\\ Cl_2B & — & N(CH_3)_2\end{array}$$

Since dimeric dimethylaminoboron dichloride is relatively inert, it is apparent that any satisfactory structure which is assigned to the compound must allow for covalent saturation of both the boron and nitrogen atoms of the molecule. Wiberg's cyclic structure is the only configuration consistent with general chemical principles which would give to boron and to nitrogen their maximum covalencies.

The planar four-membered ring structure would have no dipole moment, and hence an evaluation of the electric moment of the dimer would either confirm or disprove the structure assigned by Wiberg. Other structures which may be written for the dimer all require that the dipole moment be large.

A modified heterodyne beat apparatus which will be described in a subsequent paper[23] was employed for the determination of the dielectric constants of the various dilute benzene solutions of the dimer. The densities of the solutions were evaluated by means of a capillary-dilatometric pycnometer of about 25-ml. capacity. All measurements were made with anhydrous benzene solutions of the dimer at 25°.

By taking the dielectric constant of benzene as 2.273[24] at 25° the data of Table VII were obtained.

TABLE VII

DATA FOR THE EVALUATION OF THE DIPOLE MOMENT OF DIMERIC DIMETHYLAMINOBORON DICHLORIDE

Mole fraction of solute c_2	Dielectric constant ϵ	Density d	Total molar polarization of solution $P_{1,2}$	Total molar orientation polarization of solute P_2
0.005152	2.295	0.87844	27.119	99.72
.003768	2.291	.87625	27.030	102.91
.003263	2.289	.87587	26.997	104.58
.002281	2.285	.87527	26.898	94.48
.001575	2.283	.87506	26.829	82.50
				$P_{2\infty} = 58.6$

It has been shown above that the molecular refraction of the dimer is 53.5 cm.^3 If 5% of this value is allowed for atomic polarization, the sum of the electronic polarization and the atomic polarization is calculated to be 55.97 cm.^3 If this value is used in combination with the value of $P_{2\infty}$ as described by Smyth[25] in the calculation of the electric moment, it is found that the dipole moment of dimeric dimethylaminoboron dichloride is 0.34 ± 0.11 debye unit. The small value of the dipole moment is strong evidence in favor of the four-membered ring structure which has been proposed for the dimer. The fact that the observed moment of the compound is not zero is probably due to the presence of traces of impurities in the solutions and the low sensitivity of the dielectric apparatus to solutions of substances of small dipole moments.

Chemical Properties.—Wiberg and Schuster have reported that the dimeric modification of dimethylaminoboron dichloride does not react with trimethylamine at room temperature. However, if samples of the dimer are heated to 140° in the presence of trimethylamine, a disproportionation reaction takes place in which tris-dimethylaminoboron and $Cl_3B:N(CH_3)_3$ are formed. The reaction was carried out in sealed tubes in the presence of a large excess of trimethylamine.

$$3[(CH_3)_2NBCl_2]_2 + 4N(CH_3)_3 \xrightarrow{140^\circ} 2[(CH_3)_2N]_3B + 4Cl_3B:N(CH_3)_3$$

In a typical run 0.5038 g. of dimeric dimethylaminoboron dichloride produced 0.468 g. of $Cl_3B:N(CH_3)_3$ (calcd., 0.472 g.). $Cl_3B:N(CH_3)_3$ was identified by means of its infrared spectrum. Tris-dimethylaminoboron was identified by means of its vapor pressure. Since the dimer was shown to be almost completely dissociated in the vapor phase, it is probable that $(CH_3)_2NBCl_2:N(CH_3)_3$ is first formed, and then this compound disproportionates.

Below 120° no reaction of the dimer with boron trifluoride was observed. Anhydrous hydrogen chloride was found to be without action upon dimeric dimethylaminoboron dichloride at room temperature.

CLEVELAND, OHIO RECEIVED OCTOBER 22, 1951

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[23] C. A. Brown and R. C. Osthoff, paper to be submitted shortly.

[24] J. Hadanard, *Compt. rend.*, **204**, 1234 (1937).

[25] C. P. Smyth, "Dielectric Constant and Molecular Structure," Chemical Catalog Co., (Reinhold Publ. Corp.), New York, N. Y., 1931.