branched hydrocarbons is 0.000850, a little lower than that of the symmetrical isomer which is 0.00089.

In conclusion, we wish to acknowledge the helpful suggestions offered by G. Calingaert and his co-workers of the Ethyl Corporation, and also that of R. Delavault, who, as mentioned before, took great pains to prepare a model for us.

Summary

1. The density of hexamethylethane has been measured over a temperature range of from 20° to 103.5°.

2. Two transition points were obtained upon cooling from the liquid, one at 99.65° and the other at 74.25°.

3. The contraction and re-expansion of the hydrocarbon between 100.63 and 99.65° might be considered as part of the freezing process.

4. The existence of the two forms can be explained in a similar manner as that of normal paraffins except that in this case the stable form has a cubic structure with the molecule standing upright in the 001 plane instead of being tilted as are the long hydrocarbon chains.

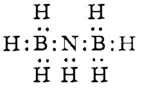
VANCOUVER, B. C. RECEIVED MARCH 17, 1949

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF SOUTHERN CALIFORNIA]

The N-Methyl Derivatives of B_2H_7N[1]

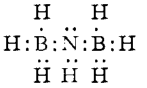
BY ANTON B. BURG AND CARL L. RANDOLPH, JR.

The structure of the aminoboron compound B_2H_7N has not been intelligible in terms of the known chemical facts,[1a] and the application of current theories of electron-deficient bonding has awaited knowledge of the positions of the hydrogen atoms on the B–N–B skeleton. The early electron-diffraction studies[2] suggest an arrangement in which the boron atoms are equivalent, like carbon atoms in dimethylamine. A resonance-structure composed of models such as I and II was suggested but the less symmetrical model III accounts far better for the 1:1 addition compounds formed by B_2H_7N with bases such as ammonia or trimethylamine. On the other hand, the electron-deficiency of the right-hand boron atom in III would demand an irreversible dimerization like that of CH_3BH_2,[3] $(CH_3)_2BH$[4] or $(C_2H_5)_2BH$.[5] Actually B_2H_7N does not dimerize in the least degree.



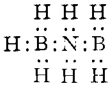
$$\mathrm{H}:\overset{\overset{\mathrm{H}}{\cdot\cdot}}{\underset{\underset{\mathrm{H}}{\cdot\cdot}}{\mathrm{B}}}:\underset{\underset{\mathrm{H}}{\cdot\cdot}}{\mathrm{N}}:\overset{\overset{\mathrm{H}}{\cdot\cdot}}{\underset{\underset{\mathrm{H}}{\cdot\cdot}}{\mathrm{B}}}:\mathrm{H}$$

I



$$\mathrm{H}:\overset{\overset{\mathrm{H}}{\cdot}}{\underset{\underset{\mathrm{H}}{\cdot\cdot}}{\mathrm{B}}}:\overset{\cdot\cdot}{\underset{\underset{\mathrm{H}}{\cdot\cdot}}{\mathrm{N}}}:\overset{\overset{\mathrm{H}}{\cdot}}{\underset{\underset{\mathrm{H}}{\cdot\cdot}}{\mathrm{B}}}:\mathrm{H}$$

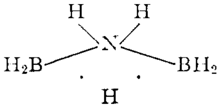
II



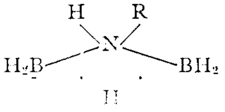
$$\mathrm{H}:\overset{\overset{\mathrm{H}}{\cdot\cdot}}{\underset{\underset{\mathrm{H}}{\cdot\cdot}}{\mathrm{B}}}:\overset{\overset{\mathrm{H}}{\cdot\cdot}}{\underset{\underset{\mathrm{H}}{\cdot\cdot}}{\mathrm{N}}}:\overset{\overset{\mathrm{H}}{\cdot\cdot}}{\underset{\underset{\mathrm{H}}{\cdot\cdot}}{\mathrm{B}}}$$

III

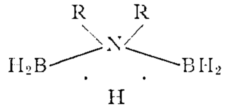
The present paper describes the N-methyl derivatives of B_2H_7N, prepared from diborane and methylamine or dimethylamine. Both are more stable and more volatile than B_2H_7N itself, but present the same structural problem. The existence of the N-dimethyl derivative, $(CH_3)_2NB_2H_5$, narrows the problem by eliminating models I and II, but III remains unsatisfactory unless a way can be found to shift electrons toward the tercovalent boron atom. Earlier concepts of the electronic structure of diborane threw no light on this problem, but the recent proposal that each of the two hydrogen atoms of Dilthey's bridge structure[6] is "half-bonded" to two boron atoms without resonance-relation to the other,[7] justifies the replacement of one bridge-hydrogen atom by nitrogen, thus:



IV



V



VI

These models are like III, except that one hydride unit has moved into a position suitable for sharing electrons equally with the two boron atoms, improving the symmetry and orbital-filling, and achieving a lower energy state by the resonance principle. Base-addition still can occur in terms of structure III, by suppressing one side of the B–H–B bridge linkage in structure IV. Thus structure IV is not only in agreement with the chemical behavior of B_2H_7N, but is also compatible with the suggestion of equivalent boron atoms advanced by Bauer.

The bridge-model for B_2H_7N and its derivatives was suggested by Professor Arthur J. Stosick of this Department in October, 1947.[8] With the as-

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(1) Presented in part in the Symposium on Organometallic Compounds at the Chicago Meeting of the American Chemical Society, April, 1948.

(1a) H. I. Schlesinger, D. M. Ritter and A. B. Burg, THIS JOURNAL, **60**, 2297 (1938).

(2) S. H. Bauer, *ibid.*, **60**, 524 (1938).

(3) H. I. Schlesinger, N. W. Flodin and A. B. Burg, *ibid.*, **61**, 1078 (1939).

(4) H. I. Schlesinger and A. O. Walker, *ibid.*, **57**, 621 (1935).

(5) H. I. Schlesinger, L. Horwitz and A. B. Burg, *ibid.*, **58**, 407 (1936).

(6) W. Dilthey, *Z. angew. Chem.*, **34**, 596 (1921).

(7) R. E. Rundle, THIS JOURNAL, **69**, 1329 (1947).

(8) Essentially the same suggestion has been made independently by E. Wiberg, A. Bolz and P. Buchheit, *Z. anorg. Chem.*, **256**, 286 (1948).

sistance of Dr. Kenneth W. Hedberg and Mr. George B. Guthrie at the California Institute of Technology, he has obtained electron-diffraction photographs over a wide range of intensities for B_2H_7N and $(CH_3)_2NB_2H_5$. The results agree with models having BNB angles of 96 and 89°, respectively. Without the postulated hydrogen-bridging the angles should have been nearly tetrahedral. Structures such as IV, V, and VI thus are fully supported by physical and chemical facts.

Aside from the structural problem, the compounds B_2H_7N, $CH_3NHB_2H_5$ and $(CH_3)_2NB_2H_5$ offer interesting series comparisons of both physical and chemical properties. They also imply the existence of many other new compounds based upon the same bonding principle.

The nomenclature of such compounds is difficult, but it seems most satisfactory to follow the convention established by the mono-halogen derivatives of diborane. It seems highly probable that bromodiborane is bridged through bromine and that chlorodiborane is similarly B–Cl–B bonded. Hence $(CH_3)_2NB_2H_5$ may be called dimethylaminodiborane without creating new language.

Dimethylaminodiborane, $(CH_3)_2NB_2H_5$

The preparation of the compound $(CH_3)_2NB_2H_5$ was accomplished by two methods, both dependent upon dimethylaminoborine, $(CH_3)_2NBH_2$, a substance discovered by Wiberg and his co-workers.[9,10] We describe first a procedure for making $(CH_3)_2NBH_2$, a method more adaptable to large-scale operation than the original, and involving less secondary aminolysis.

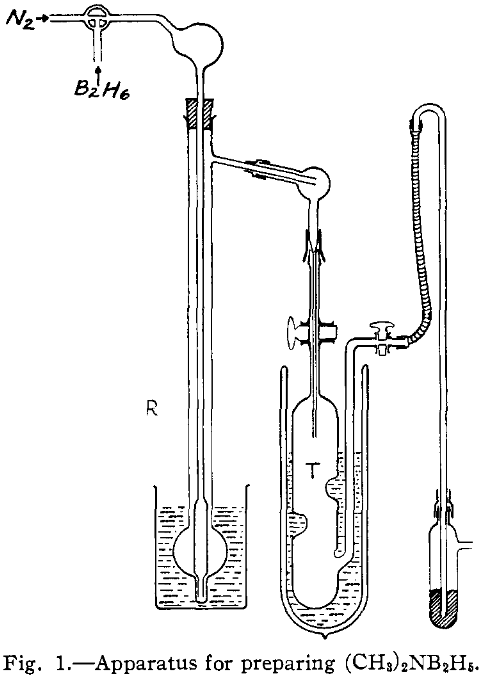

Fig. 1.—Apparatus for preparing $(CH_3)_2NB_2H_5$.

Preparation of $(CH_3)_2NBH_2$.—Diborane is passed into dry liquid dimethylamine at −42°, in the bottom of a 25 × 650 mm. test-tube. This container then is attached through a sealed-on ground joint to the high vacuum system, and the excess amine is pumped off, at room temperature, leaving the liquid compound $B_2H_6{\cdot}2(CH_3)_2NH$ (structure uncertain). Dry nitrogen now is admitted to bring the pressure to 400 mm., and the lower part of the tube is heated to 130° by a tubular electric furnace. Hydrogen is evolved and $(CH_3)_2NBH_2$ sublimes into the cool upper part of the tube, escaping further aminolysis. The yield thus is nearly quantitative. The crude product, containing little of the more volatile bis-dimethylaminoborine[9] and a trace of less volatile liquid, is purified by means of a fractionating column, operating at 98° and 400 mm. pressure (dry nitrogen) and delivering into the vacuum system. The elevated pressure and temperature are necessary to avoid solidification during the process.

A sample produced by this method was purified still further by recrystallization from low-boiling petroleum ether. Its purity was checked by hydrolysis in aqueous hydrochloric acid at 110°: 18.7 mg. yielded 14.78 cc. of hydrogen (gas at S. C.)—theoretical, 14.72. The melting range was determined as 74.5–75° (previous value, 73.5°)[10] and the vapor tension as 9.1 mm. at 23°. Precise measurements of the variation of the vapor density with temperature are in course.

Preparation of $(CH_3)_2NB_2H_5$.—Of two methods of preparing $(CH_3)_2NB_2H_5$ the more direct is the addition-reaction of diborane with dimethylaminoborine, a reaction which can be completed slowly in a sealed bulb at 80°, or very rapidly at 135° in a flow system. By either process, the reaction

$$2(CH_3)_2NBH_2 + B_2H_6 \longrightarrow 2(CH_3)_2NB_2H_5$$

is essentially quantitative, occurring in preference to the thermal decomposition of the diborane. If a large-scale preparation is desired, one proceeds without isolating the $(CH_3)_2NBH_2$, for the small loss of yield (due to secondary reactions) is more than offset by the speed and convenience of this procedure. Diborane is passed into dimethylamine at −42°, in the bottom of the tube R, Fig. 1; then the excess amine is distilled off and the bath temperature slowly raised to 135°. As the resulting $(CH_3)_2NBH_2$ begins to reflux in the upper part of tube R, diborane is bubbled in at the rate of 100–200 cc. per minute. The product is caught at −196° in the trap T, from which it later is distilled into the vacuum system and separated from unused diborane and $(CH_3)_2NBH_2$. About 75–85% of the diborane undergoes reaction and the remainder is recovered. By this process, it is convenient to prepare 25 g. of $(CH_3)_2NB_2H_5$ in the course of two hours, but there is no doubt that a much higher rate would be feasible with larger apparatus.

Small samples of $(CH_3)_2NB_2H_5$ are best purified by a slow high-vacuum distillation from a tube at −78.5° into a trap at −112°, with a second trap at −196° to catch more volatile impurities. The portion condensed at −112° should have a constant vapor tension of 101 mm. (uncor.) at 0°. If a large sample is to be purified by a fractionating column, the reflux temperature should be near −55°. Total elimination of $(CH_3)_2NBH_2$ is difficult.

The second method of preparing $(CH_3)_2NB_2H_5$ was discovered during an attempt to form a boron fluoride addition compound of $(CH_3)_2NBH_2$. The reaction was found to require a temperature of 90°; it was then tried in a sealed bulb (16 hours, 90°), with 142.5 cc. of $(CH_3)_2NBH_2$ (gas at S. C., determined by weight) and 176 cc. of boron trifluoride. Separation of the $(CH_3)_2NB_2H_5$ from diborane and the solid products of low volatility was readily accomplished by fractional condensation in traps at −42, −112 and −196°. The desired product was trapped at −112°. The material balance could be interpreted by the following equations, in which R designates methyl and the coefficients represent cc. of gas at standard conditions (equivalent to molar relationships):

$$19.6R_2NBH_2 + 9.8BF_3 \longrightarrow 9.8(R_2N)_2BH{\cdot}BF_3 + 4.9B_2H_6$$

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[9] E. Wiberg and A. Bolz, *Ber.*, **73B**, 209 (1940).

[10] E. Wiberg, A. Bolz and P. Buchheit, *Z. anorg. Chem.*, **256**, 285 (1948).

TABLE I

VAPOR TENSIONS OF $(CH_3)_2NB_2H_5$

t, °C.	−35.6	−21.0	−17.7	−12.7	−5.5	−1.7	0.0	2.9
$p_{mm.}$ obsd.	12.5	32.7	39.7	52.5	77.2	93.3	101.4	116.1
$p_{mm.}$ calcd.	13.0	32.7	39.6	52.3	76.6	92.8	101.0	116.1
t, °C.	9.5	13.0	22.4	28.2	33.3	38.9	45.7	50.3
$p_{mm.}$ obsd.	158.1	184.3	274.0	345.2	419.2	515.0	652.1	760.2
$p_{mm.}$ calcd.	157.8	184.2	274.5	346.6	419.8	515.0	652.1	760.4

$$61.8R_2NBH_2 + 41.2BF_3 \longrightarrow 30.9(R_2N)_2BF \cdot BF_3 + 20.6B_2H_6$$

$$13.9R_2NBH_2 + 4.6BF_3 \longrightarrow 4.6(R_2N)_3B \cdot BF_3 + 4.6B_2H_6$$

$$47.2R_2NBH_2 + 23.6B_2H_6 \longrightarrow 47.2\ R_2NB_2H_5 \text{ (obsd. yield)}$$

The reaction actually used 57.5 cc. of boron trifluoride (calcd., 55.6). The resultant diborane was 6.0 cc. (calcd., 6.5). The white solid was treated with trimethylamine to remove boron trifluoride and the resulting inseparable mixture, assumed to be $(R_2N)_2BH$ and $(R_2N)_2BF$, was distilled off and weighed as 201.8 mg. (calcd. 206.4). The mixture, having a vapor tension of 11 mm. at 0°, was hydrolyzed to yield 9.1 cc. of hydrogen (calcd., 9.8). The original white solid was closely similar to $(R_2N)_2BH \cdot BF_3$, which was especially prepared for comparison. The postulated compound $(R_2N)_3B$, which may have resulted from the amine treatment of the solid, was not isolated.

Proof of Formula.—The molecular weight of the new compound was determined from vapor density measurements as 71.8 (calcd., 70.6). Boron-linked hydrogen was determined by acid hydrolysis: an 11.08-cc. sample yielded 56.30 cc. of hydrogen (calcd., 55.40 cc.). Aminoid nitrogen was determined as 11.09 cc. gas (calcd., 11.08), by a modified Kjeldahl-type distillation and titration. Boron was determined on a separate 9.16-cc. sample by hydrolysis, neutralization to the methyl red end-point, and titration of the mannitol spirane to the phenolphthalein end-point. The result was equivalent to 18.28 cc. of gaseous B (calcd., 18.32).

Carbon was converted to carbon dioxide by fuming nitric acid at 200° during forty-eight hours. Gases volatile at −80° were passed over copper at 300°, after which the carbon dioxide was trapped out of the gas stream. A 6.72-cc. sample, treated in this way, gave 13.88 cc. of carbon dioxide (calcd., 13.54 cc.).

That the $(CH_3)_2N$ group is conserved as such in the formation of $(CH_3)_2NB_2H_5$, was confirmed by the recovery of 14.40 cc. of $(CH_3)_2NH$ after hydrolysis of 17.65 cc. of the compound. The non-condensable gas from this hydrolysis was proved to be hydrogen (88.70 cc.) by reaction with hot copper oxide to form only water. These results leave no doubt of the formula $(CH_3)_2NB_2H_5$.

Volatility.—The vapor tensions of a highly purified sample of dimethylaminodiborane, measured over the temperature range −36 to 50° are given in Table I. They determine the equation $\log_{10} P_{mm} = -1727.64/T + 1.75 \log T - 0.004661\ T + 5.3370$, which implies a boiling point of 50.3°. The heat of vaporization at the boiling point is estimated as 6670 cal./mole, and the Trouton constant is 20.6 cal./deg. mole.

Melting Point.—The melting range, determined visually, using the ammonia vapor tension thermometer[11] was −54.7 to −54.4° and −54.8 to −54.4° in two separate determinations.

Liquid Density.—A small capillary-dilatometric pycnometer was used to determine the density equation $d = 0.6456 - 0.001066t$ in the range 0–25°. For comparison, the densities of B_2H_7N were measured in the same range, determining the equation $d = 0.6486 - 0.0075t$.

Thermal Stability.—A relatively high degree of thermal stability sharply differentiates dimethylaminodiborane from the parent compound B_2H_7N: while the latter is appreciably decomposed in the vapor state at 45° during several hours heating, samples of $(CH_3)_2NB_2H_5$ are unaffected over much longer periods of time at temperatures as high as 90°. Vapor or liquid samples standing at room temperature for five months showed no signs of decomposition, whereas B_2H_7N is almost wholly decomposed under similar conditions.

Reaction with Trimethylamine.—Dimethylaminodiborane adds trimethylamine at low temperatures to give the stable product $(CH_3)_2NB_2H_5 \cdot N(CH_3)_3$, paralleling the behavior of aminodiborane (B_2H_7N) toward nitrogen bases. Thus when a purified sample of $(CH_3)_2NB_2H_5$ amounting to 7.53 cc. was treated with 17.83 cc. of $(CH_3)_3N$ at −80° and warmed slowly to −42° during two hours, only 9.98 cc. of amine could be regained from the reaction, implying the absorption of 7.8 cc. of $(CH_3)_3N$, and the formation of the compound $(CH_3)_2NB_2H_5 \cdot (CH_3)_3N$. This equimolar addition constitutes strong chemical evidence of the structural similarity of $(CH_3)_2NB_2H_5$ and B_2H_7N.[1a]

On warming to room temperature, the addition-product appeared as a white solid, exhibiting a saturation pressure of 4 mm. at room temperature—much more volatile than $B_2H_7N \cdot N(CH_3)_3$. There is no indication that further amine addition occurs, since the $(CH_3)_2NB_2H_5 \cdot (CH_3)_3N$ absorbed no more trimethylamine during a two-hour treatment at −42°. Although the material appears to be stable indefinitely at room temperature, heating to 85° causes almost complete decomposition according to the equation

$$(CH_3)_2NB_2H_5 \cdot N(CH_3)_3 \longrightarrow (CH_3)_2NBH_2 + (CH_3)_3N \cdot BH_3$$

Thus a homogeneous sample of $(CH_3)_2NB_2H_5 \cdot (CH_3)_3N$, amounting to 0.846 mmole, gave 0.724 mmole $(CH_3)_3N \cdot BH_3$ and 0.756 mmole of $(CH_3)_2NBH_2$. These products were effectively separated by repeated fractional condensation through a U-tube at −18°. The $(CH_3)_2NBH_2$ passing this trap was identified by its vapor tension of 9.5 mm. at 18°, while the $(CH_3)_3N \cdot BH_3$, retained at 18°, was recognized by its orthobaric melting point of 92–92.5°.

Reaction with Ammonia and with Sodium in Liquid Ammonia.—Like trimethylamine, ammonia adds in a 1:1 ratio to dimethylaminodiborane, but it is also possible to form a diammoniate. This may be the salt $NH_4^+(CH_3)_2NB_2H_5NH_2^-$, for a 9.86-cc. sample of $(CH_3)_2NB_2H_5$, dissolved in liquid ammonia and allowed to react with 27.9 mg. of sodium at −70°, yielded 4.63 cc. of hydrogen during twenty minutes, increasing to 4.89 cc. (1.01 equiv.) during two hours. In a typical addition experiment, 5.58 cc. of $(CH_3)_2NB_2H_5$, treated with three volumes of ammonia, absorbed 10.4 cc. of ammonia during two and one-half hours at −80°. At −40°, evacuation brought the ratio of ammonia to $(CH_3)_2NB_2H_5$ to 1.47, but no lower. At 0° the compound decomposed, yielding $(CH_3)_2NBH_2$ and a non-volatile solid.

Behavior toward Boron Fluoride.—Dimethylaminodiborane (24.3 cc.) and boron fluoride (22.5 cc.) were heated together in a sealed tube for one hundred and forty hours at 100°, to yield 1.6 cc. of diborane at the expense of 4.0 cc. of boron trifluoride and 3.5 cc. of $(CH_3)_2NB_2H_5$. These results seemed most simply explained by assuming the equilibrium $(CH_3)_2NB_2H_5 + BF_3 \rightleftarrows {}^1/_2B_2H_6 + (CH_3)_2NBH_2 \cdot BF_3$—a displacement of a borine group by boron fluoride. On the other hand, there is a possibility that disproportionation reactions, like those observed in the reaction of boron fluoride with $(CH_3)_2NBH_2$, occur.

A Chloro Derivative of Dimethylaminodiborane.—In view of the probable applicability of the structural prin-

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(11) A. Stock, *Z. Elektrochem.*, **29**, 354 (1921).

ciple of the aminodiboranes to bromodiborane and chlorodiborane (halogen-bridge instead of N-bridge), it seemed both feasible and theoretically of interest to synthesize a halogenated aminodiborane, involving parallel B–Cl–B and B–N–B linkages in the same molecule. Accordingly, the thermally unstable compound $(CH_3)_2NB_2H_4Cl$ was prepared by the reaction of dimethylaminodiborane with chlorodiborane at 25°.

In a typical experiment, 193 cc. of diborane and 63 cc. of boron trichloride were allowed to react to form the equilibrium amount of B_2H_5Cl during two hours at room temperature. A sample of dimethylaminodiborane amounting to 187 cc., was then condensed into the reaction flask by means of liquid nitrogen. After standing fourteen hours at 25°, the crude product was separated from the more volatile components of the mixture by rapid distillation through a trap cooled to −42°.

Final purification of the product was effected by the use of a micro fractionating column[12] operating at a reflux temperature of −42°. After removal of impurities volatile at this temperature, the reflux temperature was raised to −25° and the chloro compound distilled out. The pure material was kept at −196° except during brief periods of experimentation.

The composition of the material was found by analysis of weighed samples for hydrogen, boron and nitrogen as previously described, and for chlorine by an adsorption-indicator titration of the hydrolysis residue. The resulting empirical formula $[(CH_3)_2N]_{0.97}B_{1.9}H_{4.0}Cl_{1.1}$ indicated the ideal formula to be $(CH_3)_2NB_2H_4Cl$.

This compound, formally named B-chloro-N-dimethylaminodiborane, spontaneously inflames in air. Its vapor tension at 0° is 6.5 mm.; at 20°, 18 mm. Good measurements at higher temperatures proved unfeasible on account of the increased rate of decomposition.

This decomposition was studied by allowing a pure sample of $(CH_3)_2NB_2H_4Cl$ (35.0 cc.) to stand at room temperature for six days, during which the original liquid phase disappeared, leaving a white, semicrystalline solid. The mixture then yielded 7.12 cc. of B_2H_6, 7.21 cc. of $(CH_3)_2NB_2H_5$ and 12.9 cc. of $(CH_3)_2NB_2H_4Cl$, implying the equation

$$3(CH_3)_2NB_2H_4Cl \longrightarrow B_2H_6 + (CH_3)_2NB_2H_5 + (CH_3)_4N_2B_2Cl_3H$$

The solid product was unaffected by a hot solution of hydrochloric acid or sodium hydroxide, and was removed from the apparatus only by boiling nitric acid.

Methylaminodiborane, $CH_3NHB_2H_5$

The high stability and volatility of dimethylaminodiborane, relative to aminodiborane, appears to result from the influence of the two methyl groups bonded to the central nitrogen atom. Hence it was reasonable to expect that methylaminodiborane, possessing a single methyl group, would represent a situation intermediate between that of the parent compound and its N-dimethyl derivative.

The synthesis of this compound has been accomplished by the reaction of methylamine with diborane, and, as expected, the chemical and physical properties of the new material fall between the previously studied extremes.

Preparation.—The formation of methylaminodiborane in good yields required a flow method like that used for aminodiborane,[1a] for closed-bulb heating methods involving diborane with the liquid $B_2H_6 \cdot 2CH_3NH_2$ complex or with its decomposition product $(CH_3NHBH_2)_x$ gave only negligible yields. Evidently $CH_3NHB_2H_5$ is more stable than B_2H_7N, for it forms in better yields under less critical conditions, as indicated in Table II. These yields are based upon the diborane used up in single passages over a larger quantity of methylaminated diborane.

TABLE II

Temp., °C.	Flow rate, cc./min.	Total B_2H_6, cc.	Used B_2H_6, cc.	Product, cc.	Yield, %
92-97	30	337	48	66	69
90-95	40	340	42	75	90

The product was readily purified by passage through a trap at −42° and fractional condensation at −90°; it then showed a constant and reproducible vapor tension of 47.5 mm. at 0°.

Proof of Formula.—The empirical formula of this methyl derivative was established by analysis for hydrolyzable hydrogen, nitrogen, boron and carbon. The methods were as given for $(CH_3)_2NB_2H_5$. A 6.43-cc. sample gave 31.1 cc. of hydrogen, 6.51 cc. of ammonia and 13.3 "cc." of B, while 11:5 cc. of the vapor yielded 11.8 cc. of carbon dioxide. These data are represented by the literal formula $(CH_3)_{1.03}(NH)_{1.01}B_{2.06}H_{4.84}$, or essentially $CH_3NHB_2H_5$.

The molecular weight, calculated from the vapor density, was 56.9 (calcd. 56.73), clearly confirming the formula.

Vapor Tensions.—Intermediate in volatility between B_2H_7N and $(CH_3)_2NB_2H_5$, methylaminodiborane has an extrapolated boiling point of 66.8°, as determined from the vapor pressure equation derived from the data of Table III, namely

$$\log P_{\text{mm}} = -2158.56/T + 1.75 \log T - 0.00806T + 7.51883$$

The heat of vaporization thus is estimated to be 6,666 cal./mole, while the Trouton constant is 19.6, a value consistent with this type of equation.

TABLE III

VAPOR TENSIONS OF $CH_3NHB_2H_5$

t °C.	−33.0	−26.3	−19.6	−14.1	0.0	11.4	29.6	39.4
$P_{\text{obs.}}$, mm.	5.9	9.4	14.6	20.7	47.6	84.9	195.7	290.6
$P_{\text{calcd.}}$, mm.	5.8	9.4	14.7	21.0	47.6	86.2	195.8	288.2

Behavior toward Trimethylamine.—The structural similarity of methylaminodiborane to aminodiborane and dimethylaminodiborane is indicated by the formation of a 1:1 addition compound with trimethylamine. This fact is interpreted, as before, in terms of a B–N–B skeletal pattern. Thus 7.88 cc. of methylaminodiborane absorbed 8.16 cc. of a 17.25-cc. portion of trimethylamine during two hours at −42°. The amine in excess of the 1:1 ratio was removed only with difficulty on warming to room temperature. The white solid product of composition corresponding to the formula $CH_3NHB_2H_5 \cdot N(CH_3)_3$, showed no detectable vapor tension at room temperature, nor did any increase in volatility occur on standing. It is concluded that the decomposition typical of such compounds, yielding $(CH_3)_3N \cdot BH_3$, does not take place at room temperature.

Thermal Stability.—A slow and highly reversible dissociation of methylaminodiborane into diborane and polymeric methylaminoborine places it as expected, between aminodiborane and dimethylaminodiborane in order of increasing thermal stability. Although no deviation from ideal behavior could be detected on heating a gas sample at constant volume to 90° over a five-hour period, a 17.50-cc. sample, held as a liquid at 45° for thirteen days, yielded 2.7 cc. of hydrogen, 3.17 cc. of diborane and solid methylaminoborine polymer. The original sample was 39% decomposed. The mixture appeared to be approaching equilibrium according to the equation

$$2xCH_3NHB_2H_5 \rightleftarrows (CH_3NHBH_2)_x + xB_2H_6$$

The reversible nature of the reaction was shown by the fact that when solid CH_3NHBH_2[13] was treated with a

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[12] A. B. Burg, THIS JOURNAL, **56**, 500 (1934).

[13] Prepared by heating diborane and methylamine at 100° for two hours, and pumping off the volatile products.

17.28-cc. sample of diborane during three days at 40°, 0.8 cc. of diborane was absorbed, producing 1.03 cc. of $CH_3NHB_2H_5$ and 0.7 cc. of hydrogen. Shorter reaction periods, typified by an experiment in which diborane under 100 mm. pressure was passed over polymeric CH_3NHBH_2 at 100°, produced no detectable amount of methylaminodiborane.

Discussion

The observed regular trend toward increased thermal stability as methyl groups are successively substituted for N-bonded hydrogen atoms in the aminodiborane series appears to be inversely related to the stability of the polymeric forms of the aminoborines from which these compounds are formally derived.

Thus it is noteworthy that NH_2BH_2, CH_3NHBH_2 and $(CH_3)_2NBH_2$ show volatility characteristics indicative of a progressively lower degree of polymerization, while the corresponding aminodiboranes exhibit a complementary increase in thermal stability. Formation of a stable polymer withdraws aminoborine units from equilibria such as $B_2H_6 + 2BH_2NH_2 \rightleftarrows 2B_2H_7N$, accounting for the relative instability of B_2H_7N. This effect is lessened in the case of methylaminodiborane, and becomes immeasurable in dimethylaminodiborane, due to the low free energy change in the association of $(CH_3)_2NBH_2$—approximately 1.8 kcal./mole at 100°, according to preliminary experiments in this Laboratory.

The decrease of polymerization energy with N-methylation of the aminoborines might be related to the electron-releasing (+I) effect of the methyl groups, permitting resonance-contribution by structures in which boron has a complete octet. However, steric effects may well be more important.

The regular increase in volatility from B_2H_7N to dimethylaminodiborane is most convincingly attributed to steric factors; thus the reverse trend of boiling points (76.2, 66.8 and 50.3°) with increasing molecular weights, is in harmony with the suggestion that more methyl groups force the molecular dipoles farther apart, sharply lowering the intermolecular attraction.

Acknowledgment.—The generous support of this work by the Office of Naval Research is gratefully acknowledged.

Summary

The new compounds $CH_3NHB_2H_5$ and $(CH_3)_2NB_2H_5$ have been prepared from diborane and methylamine or dimethylamine. These and the parent compound, B_2H_7N, are regarded as derivatives of diborane in which a bridging hydrogen atom is replaced by N. A second hydrogen atom can be replaced by chlorine, yielding the volatile, unstable and self-inflaming $(CH_3)_2NB_2H_4Cl$. Volatility, stability and ease of preparation increase in the order $NH_2B_2H_5$, $CH_3NHB_2H_5$, $(CH_3)_2NB_2H_5$; the last can be stored permanently at ordinary temperatures.

LOS ANGELES 7, CALIF. RECEIVED JANUARY 17, 1949

[CONTRIBUTION FROM THE GEORGE M. MOFFETT RESEARCH LABORATORIES, CORN PRODUCTS REFINING COMPANY]

The Molecular Weight of the β-Amylase Limit Dextrin from Corn Starch

BY RALPH W. KERR AND FRANK C. CLEVELAND

Difficulty is experienced in the determination of the molecular weight of starch molecules by physical measurements on dispersions in appropriate solvents owing to the reluctance of these molecules or their derivatives to dissociate, or to become disentangled from each other. It is presumed that this difficulty arises because of the linear or long, thread-like structure of the amyloses, or because of the many linear branches on the large amylopectin molecules. On occasion, some branched starch derivatives are found to be so highly associated that they swell but do not dissolve to any very great extent in any neutral solvent. Accordingly, although molecular weight determinations on the amyloses have been reported frequently,[1–5] examinations of the amylopectins have either been approached with considerable caution, or the results have been given with the qualification that the error may be very large.[1,2,6] However, it appeared that if the linear terminal branches were removed, such as, by hydrolysis with β-amylase, association effects would be minimized when observations were made on the residual portion of the amylopectin molecules. Furthermore, inasmuch as branched starch molecules are thought to be of considerable size and measurements such as osmotic pressure determinations are of a very low order, it is obvious that by removing the end branches which constitute, on the average, nearly half the weight of amylopectin molecules, material would be provided the molecular weight of which could be estimated with very much greater accuracy. Lastly, since it has now generally been concluded that the action of β-amylase on amylopectin stops at a definite end-point, leaving the molecule intact behind points of branching, then it fol-

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(2) F. E. Horan, Dissertation, Columbia University, New York, 1944.

(3) J. F. Foster and R. M. Hixon, THIS JOURNAL, **66**, 557 (1944).

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