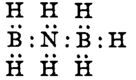
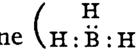
[CONTRIBUTION FROM THE GEORGE HERBERT JONES CHEMICAL LABORATORY OF THE UNIVERSITY OF CHICAGO]

Hydrides of Boron. X. The Preparation and Preliminary Study of the New Compound B_2H_7N

BY H. I. SCHLESINGER, DAVID M. RITTER,[1] AND ANTON B. BURG

In the preparation of triborine triamine ($B_3N_3H_6$) from ammonia and diborane, we[2] obtained small quantities of a new volatile compound having the molecular formula B_2H_7N. The formation of this compound, for which the structural formula  $\overset{\text{H}}{\ddot{\text{B}}}:\overset{\text{H}}{\ddot{\text{N}}}:\overset{\text{H}}{\ddot{\text{B}}}:\text{H}$ with $\ddot{\text{H}}\ \ddot{\text{H}}\ \ddot{\text{H}}$ below seems most appropriate, is an important part of the evidence in favor of the hypothesis that many of the reactions of diborane are caused by its dissociation into unsaturated borine  $\left(\text{H}:\overset{\text{H}}{\ddot{\text{B}}}:\text{H}\right)$ molecules.[3] It is, therefore, of interest to describe the preparation and properties of the new compound, as well as to present further evidence concerning its structure.

Preparation.—The observation that B_2H_7N was obtained only when diborane was used in excess of that required by the formula $B_2H_6 \cdot 2NH_3$, suggested that it is formed by the action of diborane upon the "diammoniate,"[4] rather than by the direct reaction of diborane with ammonia. It therefore seemed likely that the yield of B_2H_7N would be improved considerably if diborane were passed over the "diammoniate," under conditions subject to close control.

The apparatus used for this flow method was the one which had been employed before, in the preparation of B_4H_{10} and B_5H_{11}.[5] Ammonia was condensed as a thin layer upon the walls of the first U-tube (U4A in the article referred to above) and converted to the "diammoniate" by exposing it to an excess of diborane while the tube was warmed slowly from −130° to room temperature.[6] Then a large sample of diborane was condensed in the graduated tube M, and allowed to evaporate at −80°; the gas passed through the U-tube containing the ammoniate, at a rate limited by the capillary tube C. All condensable gases and vapors were trapped in the second U-tube (at −195°), while the hydrogen passed through and registered its pressure upon a manometer in the main vacuum apparatus beyond. The proper temperature for the first U-tube was determined by warming that U-tube until the movement of the mercury in the manometer indicated a satisfactory rate of reaction.[7] After the evaporation of the last of the diborane, the major part was recovered from the material trapped in the second U-tube; in most cases it was passed through the system again, until no important quantities of hydrogen were evolved in the process. The conditions and results of four such experiments are given in Table I.

TABLE I

FLOW METHOD OF PREPARING B_2H_7N

Ammonia, cc.[a]	Total B_2H_6, cc.	No. of passages	Flow rate, cc./min.	Temp., °C.	Diborane destroyed, cc.	B_2H_7N formed, cc.	% yield (based on diborane)
105	422	1	10	100	75	14.7	19
120	730	1	5	85	83	25.0	30
173	613	2	12	85	100	29.0	29
142	877	2	30	88	108	36.0	33

[a] All gas volumes in this paper refer to standard conditions.

The product was purified by fractional condensation: it passed through a U-tube at −55°, and condensed completely at −80°.

Analysis and Molecular Weight.—Measured samples of the vapor were treated with known volumes of standard hydrochloric acid in sealed tubes. The resulting hydrolyses were completed in ten minutes at room temperature.[8] The hydrogen was collected for measurement over mercury by means of a Töpler pump with a trap at −196°; the contents of the trap and of the hydrolysis tube were then washed into a flask. The excess acid was titrated to the methyl red end-point; the difference between the quantity of acid originally used and that found by this titration represents ammonia nitrogen. Subsequent titra-

TABLE II

ANALYTICAL DATA FOR B_2H_7N

Sample	Hydrogen Quantity	Hydrogen Ratio	Boric acid Quantity	Boric acid Ratio	Ammonia Quantity	Ammonia Ratio
0.0846	0.418	4.94[a]	0.167	1.97	..	..
.0589	..	..	..	..	0.0587	1.00
.428	..	..	..	..	.406	0.95
.196	.985	5.02	..	..	..	..
.166	.848	5.10	..	..	..	..
.303	..	..	.594	1.96	..	..

[a] In this case, the sample was heated for five hours at 100° with water containing no acid.

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(1) Much of the material of this paper was taken from the dissertation presented by David M. Ritter to the Faculty of the Division of Physical Sciences of the University of Chicago, in partial fulfilment of the requirements for the degree of Doctor of Philosophy.

(2) Schlesinger, Ritter and Burg, THIS JOURNAL, **60**, 1297 (1938).

(3) Other evidence on this subject appears in two earlier papers: Burg and Schlesinger, *ibid.*, **59**, 780 (1937); Schlesinger and Burg, *ibid.*, **60**, 290 (1938).

(4) For the structure of this compound, see Schlesinger and Burg, *ibid.*, **60**, 290 (1938).

(5) Burg and Schlesinger, *ibid.*, **55**, 4012 (1933).

(6) The preparation of the diammoniate by the slightly more tedious process of carrying on the reaction at −120° and removing the residual ammonia at −80°, led to no change of yield.

(7) It is important to employ the lowest feasible temperature, because higher temperatures lead to frothing, with the danger of clogging the capillary, and also facilitate the formation of traces of such impurities as B_4H_{10}, B_5H_{11}, and $B_3N_3H_6$.

(8) When pure water was used, the hydrolysis was far more difficult, probably because the free ammonia first liberated acted as a base to hinder the hydrolysis of the B-H links. Thus a sample which was left in contact with water in a sealed tube for two months at room temperature produced only 3.8 of the expected 5 volumes of hydrogen.

Table III

Corrected Vapor Pressures of B_2H_7N

$t°$	−27.2	−23.0	−16.2	−13.4	−9.6	−3.6	0.00	3.8
$p_{mm.}$, obsd.	5.3	7.65	12.0	14.6	18.9	26.1	32.3	39.3
$p_{mm.}$, calcd.	5.7	7.64	12.1	14.4	18.3	26.3	32.3	39.8
$t°$	7.9	11.0	15.4	20.0	22.6	25.4	27.3	28.9
$p_{mm.}$, obsd.	49.6	57.8	72.5	90.3	102.0	117.0	126.8	135.9
$p_{mm.}$, calcd.	49.6	58.4	72.6	90.8	102.5	116.7	126.8	136.2

tion of the solution to the phenolphthalein end-point in the presence of an adequate quantity of mannite gave the amount of boric acid present. The results are given (in millimoles) in Table II.

These results agree with the formula B_2H_7N, as shown by the equation $B_2H_7N + 4H_2O + H^+ \longrightarrow 2HBO_2 + NH_4^+ + 5H_2$.

The molecular weight calculated from the observed vapor density also agreed with the formula B_2H_7N (obsd. 42.9 and 42.2; calcd. 42.6).

The melting point was determined by observations on two separately purified samples. The values, taken by means of an ammonia vapor pressure thermometer, were −66.5 and −66.4°.

The vapor pressure at various temperatures determined the equation

$$\log_{10} p_{mm.} = -(2097/T) + 1.75 \log_{10} T - 0.00642T + 6.677$$

From this equation, the molar heat of vaporization is estimated as 7300 cal., and the Trouton constant as 21.0 cal./degree mole. The normal boiling point is calculated to be 76.2°.

Decomposition and Thermal Stability.—The substance B_2H_7N can be kept for several days at room temperature without appreciable decomposition, but a sample which had been held for six hours at 45° showed an increase of vapor pressure, corresponding to about 0.2 cc. of diborane (from a 5-cc. sample). A sample left for sixteen months in a sealed bulb at room temperature, decomposed almost completely, evidently according to the equation $2B_2H_7N \longrightarrow B_2H_6 + (BH_4N)_x$; the actual results were complicated by secondary production of hydrogen, and by the probable presence of $B_3N_3H_6$ in the original sample.[9]

The 5.6-cc. sample yielded 2.4 cc. of diborane, 0.6 cc. of hydrogen, and 0.4 cc. of material having approximately the volatility of $B_3N_3H_6$. The diborane was fully identified by its vapor pressure (226 mm. at −112°) and by hydrolysis, which yielded 14.4 cc. (6.1 volumes) of hydrogen and 0.214 millimole of boric acid (2.00 equivalents per mole). The non-volatile solid was not investigated further.

The Behavior of B_2H_7N toward Trimethylamine.—A stable addition product $(CH_3)_3N \cdot B_2H_7N$, is produced by the action of trimethylamine upon B_2H_7N at −80°. Heating this product with excess trimethylamine results in the removal of a BH_3 group to produce one molecule of borine trimethylammine per mole of B_2H_7N originally used.

Thus 2.7 cc. of B_2H_7N, treated with 12.2 cc. of trimethylamine at −80°, absorbed 2.8 cc. of the latter, to give a white solid which failed to react further during two hours at room temperature. During three hours at 100°, however, there resulted 2.80 cc. of material whose vapor pressures were measured as 18.6 mm. at 69.5° and 10.6 mm. at 59.8°, in good agreement with the data recorded earlier for borine trimethylammine.[10] There resulted also 2.9 cc. of hydrogen, and a further 0.9 cc. of trimethylamine was used up. A trace (0.3 cc.) of material which seemed to be $B_3N_3H_6$, also was found among the products. The residual solid thus seemed to have the composition $BNH_2 \cdot {}^1/_2N(CH_3)_3$.

The Behavior of B_2H_7N toward Ammonia.—Like trimethylamine, ammonia adds to B_2H_7N to give a stable solid mono-ammoniate, $B_2H_7N \cdot NH_3$. By the sudden heating of this substance to 200°, a 45% yield of $B_3N_3H_6$ is obtained; this yield is somewhat higher than that obtained directly from the "diammoniate of diborane."

In a typical experiment, 5.2 cc. of B_2H_7N and 17.7 cc. of ammonia were left together for one hour at −80°. Then the excess ammonia was distilled to another part of the vacuum apparatus, while the reaction tube was being warmed to room temperature. The removed ammonia was measured as 12.6 cc., indicating that the white solid residue contained 5.1 cc. of combined ammonia. Five minutes of heating of the product at 50° caused the evolution of only 0.25 cc. of volatile material.

Another sample of the solid, composed of 9.65 cc. of B_2H_7N and 9.65 cc. of ammonia, was allowed to stand for two months at room temperature (25–30°): it produced 0.3 cc. of hydrogen and an even smaller trace of material which was trapped at −196°.

A sample composed of 4.8 cc. of B_2H_7N and 4.9 cc. of ammonia was heated for five minutes in a sealed tube at 200°. The products were 15.1 cc. of hydrogen, 1.4 cc. of $B_3N_3H_6$, 0.26 cc. of an unidentified substance slightly more volatile than $B_3N_3H_6$, and non-volatile solids. The yield of $B_3N_3H_6$ thus was slightly less than 45%.

The Behavior of $B_2H_7N \cdot NH_3$ toward Sodium in Liquid Ammonia.—When the compound $B_2H_7N \cdot NH_3$ is dissolved in liquid ammonia and

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(9) This particular sample had been obtained as a by-product in the preparation of $B_3N_3H_6$.

(10) Burg and Schlesinger, This Journal, **59**, 785 (1937).

treated with sodium, one gram equivalent of hydrogen is liberated, per mole of B_2H_7N originally used. After completion of the reaction and removal of excess ammonia, the residue corresponds to the empirical formula $B_2H_7N \cdot NH_2Na$. The significance of these facts is discussed later.

A 5.65-cc. sample of B_2H_7N was dissolved in liquid ammonia at −77°; the solution was treated with 30 mg. of pure sodium, in the manner described in an earlier paper.[11] The resulting evolution of hydrogen was not very rapid, but it finally amounted to one gram equivalent per mole of B_2H_7N, as shown in Table IV.

TABLE IV

REACTION OF $B_2H_7N \cdot NH_3$ WITH SODIUM IN LIQUID AMMONIA

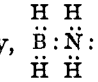
Total time, min.	Temp. during time before meas., °C.	Total H evolved, cc.	Ratio of H to B_2H_7N
16	−67	1.55	0.55
32	−55	2.45	.87
57	−60	2.90	1.03
130	−66	3.03	1.07

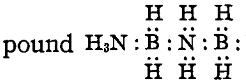
Reaction beyond that point was exceedingly slow. The major part of the ammonia was removed by distillation at −50°; a further 0.4 cc. (gas) was lost by the residue during seventy-six hours *in vacuo* at room temperature, conditions so severe that 4.0 cc. of hydrogen also was liberated. The residue was hydrolyzed completely by 3 normal hydrochloric acid; then the excess acid was distilled off and replaced by sodium hydroxide. The ammonia was determined, partly by measurement of the purified gas (9.05 cc.) and partly by titration (1.75 cc.). The total, 10.8 cc., amounts to 1.9 moles of ammonia per mole of B_2H_7N.

The slow production of somewhat more than one equivalent of hydrogen by reaction with sodium in liquid ammonia might well be due to a secondary reaction analogous to that of the "diammoniate of diborane."[4]

Discussion

Only two of the conceivable structures for the compound B_2H_7N seem worthy of serious discussion: (1) an amine of diborane, $B_2H_5NH_2$, and (2) a structure involving a B–N–B skeleton.[12] All derivatives of diborane, not immediately ammonolyzed, take up two molecules of ammonia per molecule of diborane derivative, to form stable compounds. The substance B_2H_7N, however, takes up only one molecule of ammonia; further addition, if it occurs at all, leads to very unstable addition products. This fact is sufficient to exclude further discussion of the first formulation.

The assumption of a B–N–B skeleton leads to two possible structures: (I) BH_3NHBH_3[13] and (II) $BH_2NH_2BH_3$. Formula I not only requires assumptions with regard to electronic distribution, unjustified by any of the chemical properties thus far known for the compound, but fails to explain why one and only one molecule of ammonia can be added to it. When structure II is represented electronically,  $\underset{H}{\overset{H}{\ddot{B}}}:\underset{H}{\overset{H}{\ddot{N}}}:\underset{H}{\overset{H}{\ddot{B}}}:H$, the addition of one molecule of ammonia (to the one "unsatisfied" boron atom) is understood readily. Compounds in which boron atoms are associated with only six bonding electrons are, of course, very common (*e. g.*, BF_3, BCl_3, BR_3, and their substitution products) and, if not ammonolyzed, take up one molecule of ammonia for each such boron atom present. They are also capable of adding trimethylamine in the same ratio, as does the compound B_2H_7N. On the other hand, compounds containing the BH_3 group tend to give borine trimethylammine, $BH_3 \cdot N(CH_3)_3$, a product which actually is obtained when the addition compound $B_2H_7N \cdot N(CH_3)_3$ is heated with an excess of the amine.

According to structure II, the addition of one mole of ammonia to B_2H_7N results in the compound  $H_3N:\underset{H}{\overset{H}{\ddot{B}}}:\underset{H}{\overset{H}{\ddot{N}}}:\underset{H}{\overset{H}{\ddot{B}}}:H$. This structure is analogous to that of borine ammine (H_3NBH_3) for in each an ammonia molecule is coördinatively bound to a boron atom. Although borine ammine has not been isolated, it has been shown by indirect methods[4] to react in liquid ammonia solutions with sodium to liberate one gram equivalent of hydrogen for every mole of ammonia bound in that manner. The compound $H_3NB_2H_7N$ reacts to give the same proportion of hydrogen. This cannot mean that the original ammonia addition product was an ammonium salt, for sodium would have reacted with such a salt to remove one nitrogen atom as ammonia, leaving a residue of the composition NaB_2H_6N, instead of the salt $NaNH_2 \cdot B_2H_7N$ actually obtained as a final product.

Other details of the behavior of the compound are in full agreement with formula II. Its stability is characteristic of compounds containing

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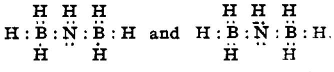
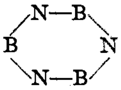
[11] Schlesinger and Burg, THIS JOURNAL, **60**, 293 (1938).

[12] Other ideas are represented by the formulas $NH_4B_2H_3$, $NH_3 \cdot B_2H_4$, $NH_3 \cdot BHBH_3$, and $H^+B_2H_6N^-$. Each of these is difficult to reconcile with some of the physical and chemical properties described in this paper.

[13] According to the usual electronic formulations, two possibilities exist for structure I:  $H:\underset{H}{\overset{H}{\ddot{B}}}:\overset{H}{\ddot{N}}:\underset{H}{\overset{H}{\ddot{B}}}:H$ and $H:\underset{H}{\overset{H}{\ddot{B}}}:\overset{H}{\ddot{N}}:\underset{H}{\overset{H}{\ddot{B}}}:H$. Neither of these avoids the difficulties pointed out for the less specific formula I.

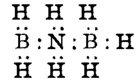
a B–N–B pattern of linking, rather than of those containing B–B bonds; the B–N–B skeleton explains why the compound, when heated, gives good yields of $B_3N_3H_6$, a substance containing the  ring; its rapid hydrolysis in acid solution to give five volumes of hydrogen suggests the existence of five B–H bonds.

Finally, attention is called to a recent paper by S. H. Bauer,[14] who, at our suggestion, investigated the electron diffraction of the vapor of this compound, and concluded that the data obtained can be explained only by the existence of a B–N–B skeleton for the molecule.

Acknowledgment.—We wish to express our thanks to the Research Corporation, for providing the liquid nitrogen used in a large part of this work.

Summary

The new volatile compound B_2H_7N (b. p. 76.2°; m. p. −66.5°) was prepared by the action of diborane upon its "diammoniate." The new substance is hydrolyzed easily in acid solution, to give five volumes of hydrogen, two equivalents of boric acid, and one equivalent of ammonium ion. Its thermal decomposition (slow at room temperature) produces diborane and a solid of undetermined character. It reacts with an equal gas volume of trimethylamine, to form a stable white solid; on heating with an excess of that amine, this product yields borine trimethylammine. With ammonia, B_2H_7N forms the stable solid $B_2H_7N \cdot NH_3$, which, on heating to 200°, gives a good yield of triborine triamine ($B_3N_3H_6$). The ammonia addition product reacts with sodium in liquid ammonia to liberate one equivalent of hydrogen; the residue after thorough removal of the solvent corresponds to the formula $NaNH_2 \cdot B_2H_7N$.

The structure  $\begin{array}{ccccccc} H & & H & & H & & \\ \ddot{B} & : & \ddot{N} & : & \ddot{B} & : & H \\ \ddot{H} & & \ddot{H} & & \ddot{H} & & \end{array}$ is proposed for the compound, and although this specific picture is not considered definitely proved, it is shown to interpret satisfactorily all of the physical and chemical properties of the substance.

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[14] S. H. Bauer, This Journal, **60**, 524 (1938).

[Contribution from the Bureau of Chemistry and Soils]

The Compressibilities of Hydrogen and of Four Mixtures of Hydrogen and Nitrogen at 0, 25, 50, 100, 200 and 300° and to 1000 Atmospheres

By R. Wiebe and V. L. Gaddy

This is a continuation of work in this Laboratory on the compressibilities of hydrogen, nitrogen and their mixtures.[1] A summary of work previous to 1930 was given by Bartlett. Townend and Bhatt measured the isotherms of hydrogen at 0 and 25° to 600 atm.[2] Isothermal measurements on hydrogen between 0 and 100° and up to 1000 atm. were made by Michels, *et al.*[3] Michels and Gerver recalculated the compressibility data of Kohnstamm and Walstra on hydrogen at 15.5 and 20° between 1000 and 2000 atm.[4] Isotherms of nitrogen between 0 and 150° and at pressures from 20 to 80 atm. were determined by Michels, *et al.*[5] This latter work was continued up to 400 atm. by Otto, Michels and Wouters.[6] A further extension to 3000 atm. including a calculation of the thermodynamic properties was made by Michels, *et al.*[7] W. Edwards Deming and Lola S. Deming have calculated the thermodynamic properties of hydrogen and nitrogen.[8]

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[1] (a) Bartlett, This Journal, **49**, 687; 1955 (1927); (b) Bartlett, *et al.*, *ibid.*, **50**, 1275 (1928); (c) **52**, 1363 (1930). Dr. Bartlett has kindly informed me that in Ref. 1b the column of figures for the compressibility of a 3:1 mixture of hydrogen and nitrogen at 99.85° was wrongly transcribed and should be as follows:

Press., atm.	Old figures	Correct
1	1.3656	1.3656
50	1.3992	1.4027
100	1.4298	1.4364
200	1.5068	1.5170
300	1.5870	1.5975
400	1.6700	1.6799
600	1.8412	1.8472
800	2.0130	2.0168
1000	2.1865	2.1865

Also in the same table, for 300 atmospheres and 0°, the figures have been transposed.

Old figure	Correct figure
1.0264	1.2064

[2] Townend and Bhatt, *Proc. Roy. Soc.* (London), **A134**, 502 (1931).

[3] Michels, Nijhoff and Gerver, *Ann. Phys.*, **12**, 562 (1932).

[4] Michels and Gerver, *ibid.*, [5] **16**, 745 (1933).

[5] Michels, Wouters and De Boer, *Physica*, **1**, 587 (1934).

[6] Otto, Michels and Wouters, *Physik. Z.*, **35**, 97 (1934).

[7] Michels, Wouters and De Boer, *Physica*, **3**, 585 597 (1936).

[8] Deming and Shupe, *Phys. Rev.*, **37**, 638 (1931), *ibid.*, **40**, 848 (1932); Deming and Deming, *ibid.*, **45**, 109 (1934).