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THE CHEMISTRY OF BORON HYDRIDES

AND RELATED HYDRIDES

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# OBJECTIVE

A continuation of fundamental studies on the chemistry of the hydrides of boron and related compounds.

# ABSTRACT

Monomeric ammonia-borane, $H_3NBH_3$, has been prepared directly from $B_2H_6$ and $NH_3$ by their interaction in dimethyl ether solution. $H_3NBH_3$ is monomeric in liquid ammonia and has a dipole moment in dioxane solution of $3.6 \pm .1$ Debye units.

The action of a liquid-ammonia solution of potassium on trimeric methylamino-borane gives evidence for a compound $K_2(HCH_3NBH_2)$.

The slow spontaneous decomposition of $[H_2B(NH_3)_2](BH_4)$ in diethyl ether solution containing ammonia has been noted. A microcrystalline form of $(H_3NBH_3)_n$, believed to be $[HB(NH_3)_3](BH_4)_2$, has been isolated.

The Raman spectrum of $F_3PBH_3$ is discussed and Raman spectra of $H_3NBH_3$ have been obtained but not interpreted.

A completely new type of ammonia—boron-hydride coordination compound has been isolated. It has the formula $H_3NB_3H_7$. Its structure has been determined by the methods of x-ray crystallography. Its structure and properties are reported.

## I. THE REACTIONS AND STRUCTURE OF THE "DIAMMONIATE OF DIBORANE" AND RELATED COMPOUNDS

### A. THE PREPARATION OF $H_3NBH_3$ DIRECTLY FROM DIBORANE

The preparation of $H_3NBH_3$ from $B_2H_6$ would involve symmetrical cleavage of the diborane bridge, followed by addition of $NH_3$ to the acidic borane group. Arguments previously summarized indicated that a solid-gas phase reaction between $NH_3$ and $B_2H_6$ respectively favored nonsymmetrical cleavage to give the "diammoniates of diborane." Earlier attempts by Schlesinger and Burg[1] to prepare $H_3NBH_3$ by the reaction between solid $H_3BO(CH_3)_2$ and gaseous $NH_3$ yielded the diammoniate in agreement with the foregoing arguments. On the other hand, evidence has been accumulated which indicates that symmetrical cleavage of the diborane bridge is effected in ether; hence a solution of $H_3BO(CH_3)_2$ in dimethyl ether can be obtained at low temperature by adding $B_2H_6$ to an excess of very cold ether. When $NH_3$ was dissolved in this cold (-78°C) ether solution, $H_3NBH_3$ was obtained in yields ranging up to 70% based on the equation

$$B_2H_6 \;+\; 2NH_3 \;\xrightarrow[\text{as solvent}]{(CH_3)_2O}\; 2NH_3BH_3 \;.$$
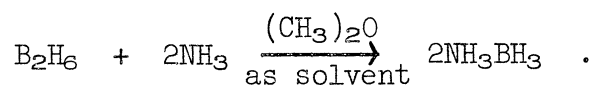
This is now the easiest method for large-scale preparation of $H_3NBH_3$.

### B. THE MOLECULAR WEIGHT OF $H_3NBH_3$ IN LIQUID AMMONIA

Previous studies have shown that $H_3NBH_3$ is monomeric in dioxane,[2] in diethyl ether, and in the solid state,[3] but data showing its molecular weight in liquid ammonia under conditions comparable to those used for studying the classical "diammoniate of diborane" were not available. Such data have been obtained using previously described[4] vapor-pressure depression methods. Data

1. H. J. Schlesinger and A. B. Burg, J. Am. Chem. Soc., 60, 290 (1938).

2. S. G. Shore and R. W. Parry, ibid., 77, 6084 (1955).

3. E. L. Lippent and W. N. Lipscomb, ibid., 78, 503 (1956); E. W. Hughes, ibid., p. 502.

4. R. W. Parry, G. Kodama, and D. R. Schultz, WADC Tech. Rept. 56-318. Final report for Contract AF 33(616)-8, E.O.R.-464 Br-1, Eng. Res. Inst., Univ. of Mich., June, 1956, p. 82.

for $H_3NBH_3$, the classical "diammoniate of diborane," $[H_2B(NH_3)_2](BH_4)$, and so-called "mistreated diammoniate" or "diammoniate (II)," $[HB(NH_3)_2](BH_4)_2$, are shown in Fig. 1. Values of the molecular weights are consistent with the formulas assigned in every case.

## C. THE DIPOLE MOMENT OF $H_3NBH_3$

The dipole moment of $H_3NBH_3$ has been measured in solution using very pure dioxane as a solvent. A high-precision heterodyne beat apparatus, kindly donated to The University of Michigan by the Chrysler Corporation of Detroit, was employed for evaluating the dielectric constants of the solutions and solvent. A value of $3.6 \pm .1$ Debye units has been obtained for the dipole moment of $H_3NBH_3$ under the conditions used. Uncertainties are largely dependent on methods of extrapolation and calculation rather than on uncertainties in actual experimental values.

The remaining members in this series, $H_3NBH_2Me$, $H_3NBH(Me)_2$, and $H_3NB(Me)_3$, will be measured in an attempt to gain information as to the effect of methyl groups on electron distribution in the amine-boranes.

A more complete report will be given upon completion of the work.

## D. EVIDENCE FOR THE CLEAVAGE OF $(HCH_3NBH_2)_3$ BY METALLIC POTASSIUM IN LIQUID AMMONIA—THE ELECTRON PAIR AS A COORDINATING LIGAND IN BOROHYDRIDE-TYPE STRUCTURES

In the previous quarterly report from this laboratory[5] the ammonolysis of the residues obtained from the action of excess sodium on the diammoniate of diborane was interpreted in terms of a preliminary reaction:

$$2Na \;+\; H_2NBH_2 \;\longrightarrow\; Na_2(H_2NBH_2) \;.$$

The product would have the structure
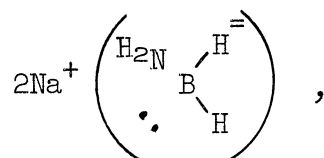


in which the electron pair serves as a coordination ligand. An extension of the foregoing postulates indicated that the compound $(HCH_3NBH_2)_3$ described by

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5. "Chemistry of Boron Hydrides and Related Hydrides," Quarterly Report No. 2, Eng. Res. Inst., Univ. of Mich., Project 2469-2-P, WADC Contract No. AF 33(616)-3343, Aug., 1956.
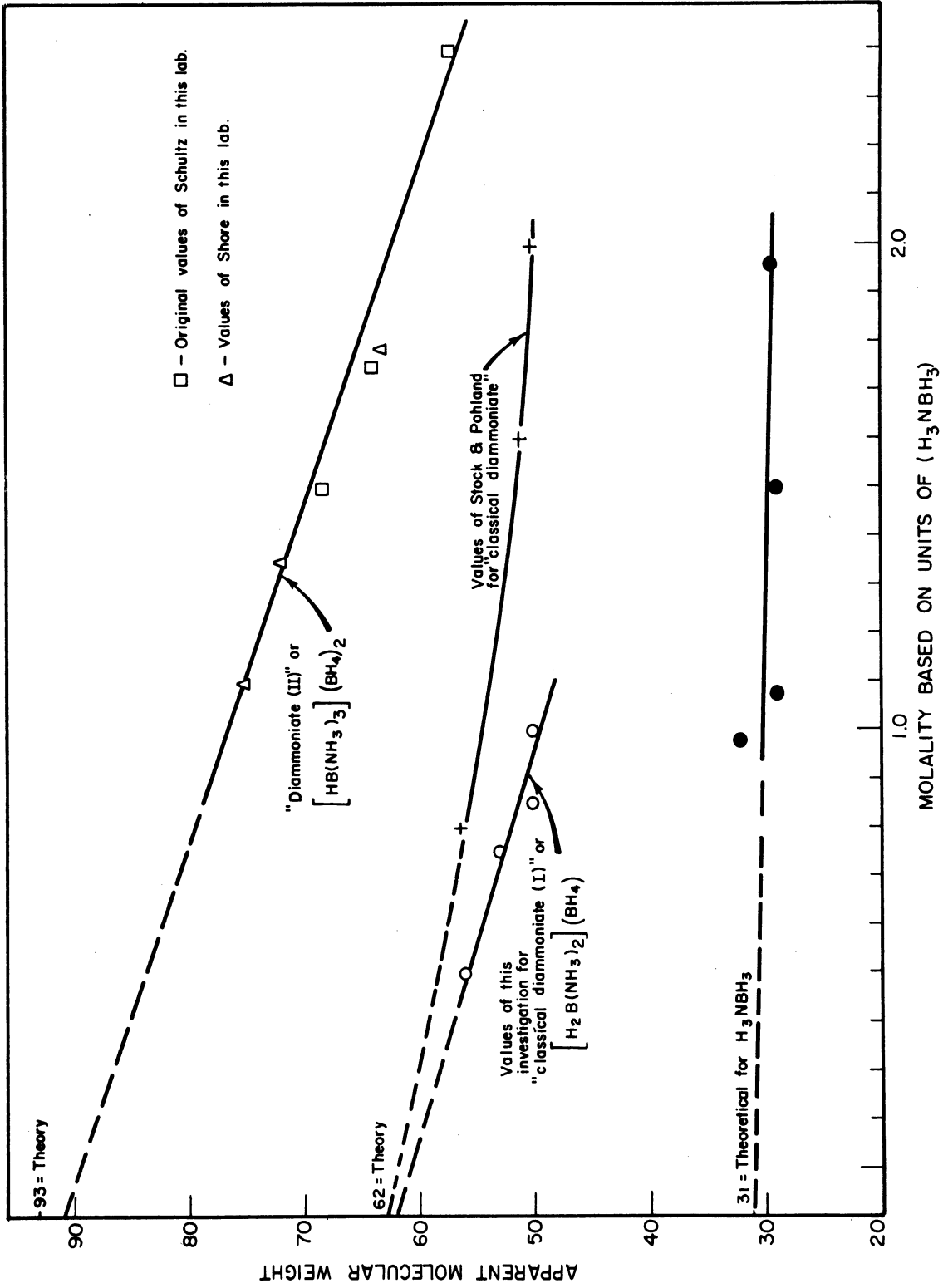
Fig. 1.  Molecular weight of ammonia-diborane addition compounds in liquid ammonia.

Bissot and Parry[6] might react with metallic potassium in liquid ammonia without hydrogen evolution. Such predictions have been confirmed. A liquid-ammonia solution of $(HCH_3NBH_2)_3$ will decolorize a liquid $NH_3$ solution of potassium without hydrogen evolution. The stoichiometry has not been established with certainty, but the following equation is indicated:

$$2K + (HCH_3NBH_2)_3 \longrightarrow K_2(HCH_3NBH_2) \ .$$
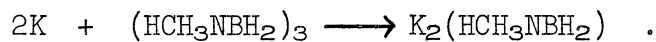
Experiments designed to isolate and purify $K_2(HCH_3NBH_2)$ are in progress.

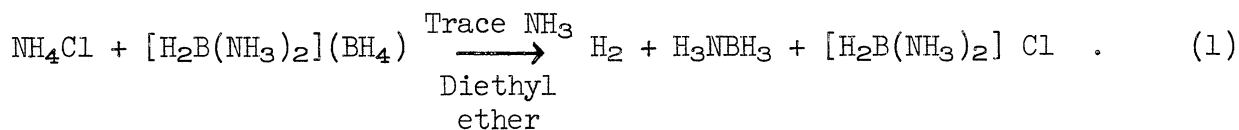E. THE SODIUM SALT OF AMMONIA-BORANE——THE $H_2N$ GROUP AS A COORDINATING LIGAND IN BOROHYDRIDE-TYPE STRUCTURES

The reaction of $H_3NBH_3$ with Na in liquid ammonia should produce $NaH_2NBH_3$ or

$$Na^+ \left( \begin{array}{c} H_2N \quad \diagup H \\ \diagdown B \diagup \\ H \diagup \diagdown H \end{array} \right) \ .$$
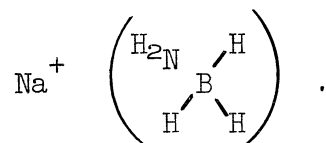
The solid product obtained from this process is extremely water sensitive and it has not been possible to characterize it by x-ray methods without preliminary decomposition. Techniques are being refined to continue the work.

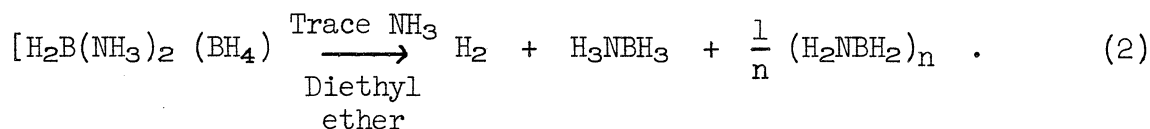F. THE DECOMPOSITION OF THE "DIAMMONIATE OF DIBORANE," $[H_2B(NH_3)_2](BH_4)$, IN AN ETHER SLURRY

In an earlier report[2] the preparation of $H_3NBH_3$ from $[H_2B(NH_3)_2](BH_4)$ was described in terms of the following equation

$$NH_4Cl + [H_2B(NH_3)_2](BH_4) \xrightarrow[\text{Diethyl ether}]{\text{Trace } NH_3} H_2 + H_3NBH_3 + [H_2B(NH_3)_2] Cl \ . \tag{1}$$

The validity of this overall equation was questioned recently when it was found that the solid reaction residues, examined by x-ray diffraction, showed only small amounts of the salt $[H_2B(NH_3)_2]Cl$.

The explanation for the discrepancy between theory and experiment is found in a very recent observation. It is now known that the "diammoniate" undergoes a competing decomposition in an ether slurry containing ammonia but NO ammonium chloride:

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6. T. C. Bissot and R. W. Parry, *J. Am. Chem. Soc.*, 77, 3481 (1955).

$$[H_2B(NH_3)_2] \ (BH_4) \xrightarrow[\substack{\text{Diethyl} \\ \text{ether}}]{\text{Trace } NH_3} H_2 + H_3NBH_3 + \frac{1}{n}(H_2NBH_2)_n \ . \qquad (2)$$

Data are summarized in Fig. 2. Reactions 1 and 2 proceeding simultaneously would be consistent with all observed facts.
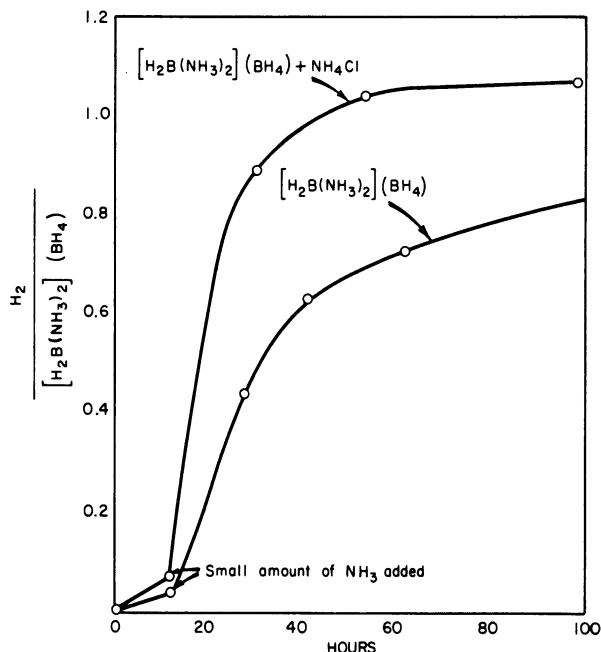


Fig. 2. The decomposition of the "diammoniate of diborane" in an ether slurry.

## G. EVIDENCE FOR THE CRYSTALLINITY OF THE "DIAMMONIATE OF DIBORANE (II)"

"Mistreated diammoniate," "diammoniate of diborane (II)," or tentatively [HB(NH$_3$)$_3$] (BH$_4$)$_2$, has been obtained in a microcrystalline form which gives a definite powder pattern. The sample is the one used previously for the determination of the molecular weight of diammoniate (II) in liquid ammonia. The application of x-ray methods to this compound looks somewhat more promising.

## II. RAMAN SPECTRAL STUDIES

## A. THE RAMAN SPECTRUM OF PF$_3$BH$_3$

Samples of PF$_3$BH$_3$ and PF$_3$BD$_3$ were prepared and purified as previously

described.[7] Samples of each compound were condensed into capillary Raman tubes which were then sealed off and maintained at liquid-nitrogen temperatures until used. Details of the experimental equipment have been given previously.[8] The spectra were obtained for the liquid at -80°C, qualitative polarization measurements being made on the hydrogen compound only, using the two-exposure method and polaroid cylinders. The data reported in Table I represent the averages from several spectra, the estimated probable error being approximately 1 $cm^{-1}$, except where indicated.

An earlier paper from this laboratory[7] proposed an ethane-type structure which would have $C_{3v}$ symmetry. Such a structure was based on known similarities between $PF_3$ and CO as coordinating ligands. The vibrational frequencies of such a structure are twelve in number and can be thought of in terms of the four vibrational frequencies of each of the two halves, considered as free molecules with $C_{3v}$ symmetry, plus four vibrations arising as a consequence of the bond between the apex atoms of the two pyramids. Since free $BH_3$ is not known, reference can be made to the Raman frequencies of $BH_3CO$ which have been determined recently.[9] In the B-H stretching region, two strong bands appear in the spectrum of $PF_3BH_3$ at 2385 and 2455 $cm^{-1}$, which appear to be $a_1$ and e type modes, respectively. Corresponding frequencies are found at 2380 and 2434 $cm^{-1}$ in the spectrum of liquid $BH_3CO$. Boron-hydrogen deformation bands are observed at 1077 and 1117 $cm^{-1}$ for the $a_1$ and e modes, which again do not differ greatly from the corresponding bands at 1073 and 1101 $cm^{-1}$ in the carbon-monoxide complex.

The frequencies associated with the $PF_3$ group likewise show a close similarity in pattern to those found in the Raman spectrum of liquid $PF_3$, which was also obtained in the present work. In this case, the $a_1$ and e P-F stretching frequencies at 832 and 874 $cm^{-1}$ shift to 994 and 958 $cm^{-1}$, respectively, in the complex while the $a_1$ and e bending frequencies shift from 484 and 351 to 441 and 370 $cm^{-1}$, respectively.

The remaining modes may be described as a P-B stretch, $BH_3$ and $PF_3$ rocking motions, and the inactive torsional mode. The first was easily identified as the strong polarized band at 607 $cm^{-1}$ while the low depolarized band at 197 $cm^{-1}$ is certainly the $PF_3$ rock. The $BH_3$ rock was assigned to the rather weak band at 697 $cm^{-1}$. No information as to the torsional frequency was obtained.

Two fundamentals of $PF_3BD_3$ were not observed directly. The position of the first, the symmetrical B-D bond, was estimated at 842 $cm^{-1}$ from its

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7. R. W. Parry and T. C. Bissot, _ibid._, 78, 1524 (1956).

8. G. L. Vidale and R. C. Taylor, _ibid_, 294 (1956).

9. R. C. Taylor, "The Chemistry of Boron Hydrides and Related Hydrides," Quarterly Reports No. 1 and 2, Eng. Res. Inst., Univ. of Mich., Project 2469, Contract No. AF 33(616)-3343, May and Aug., 1956.

TABLE I. OBSERVED RAMAN FREQUENCIES AND
ASSIGNMENTS FOR LIQUID $PF_3BH_3$ AND $PF_3BD_3$ AT $-80°C$

| Frequency in $cm^{-1}$ | | Intensity and Polarization | Symmetry | | Assignment |
|---|---|---|---|---|---|
| $PF_3BH_3$ | $PF_3BD_3$ | | | | |
| 197 | 169 | m, dp | e | $\nu_{12}$ | $PF_3$ rock |
| 370 | 362 | vw | e | $\nu_{11}$ | F-P-F deformation |
| 441 | 421 | m, p | $a_1$ | $\nu_5$ | F-P-F deformation |
| 607 | 572 | s, p | $a_1$ | $\nu_4$ | P-B stretch |
| 697±2 | - | vw | e | $\nu_{10}$ | $BH_3$ rock |
| 799 | | vw | | | diborane ? |
| 886±5 | - | vw, p? | $A_1$ | $2\nu_5$ | 2 x 441 = 882 |
| 920 | - | w, p | $A_1+A_2+E$ | $\nu_8-\nu_{12}$ | 1117 - 197 = 920 |
| 944 | 944±5 | m, p? | $a_1$ | $\nu_3$ | P-F stretch |
| 957±3 | 958±2 | m, dp | e | $\nu_9$ | P-F stretch |
| 1040±3 | - | w, p | $A_1$ | $\nu_4+\nu_5$ | 441 + 607 = 1048 |
| 1077 | - | w, p | $a_1$ | $\nu_2$ | H-B-H deformation |
| 1117 | 807 | s, dp | e | $\nu_8$ | H-B-H deformation |
| - | 1756 | w | $A_1+A_2+E$ | $\nu_8+\nu_9$ | 807 + 958 = 1765 |
| - | 1797 | vvw | E | $\nu_2+\nu_9$? | 842 + 958 = 1800 |
| - | 1980 | vvw | | | diborane-$d_6$ ? |
| 2112 | - | vvw | | | diborane ? |
| 2140±4 | 1672±2 | vw | $A_1$ | $2\nu_2$ | 2 x 1077 = 2154 |
| 2247±2 | 1602 | vw | $A_1$ | $2\nu_8$ | 2 x 1117 = 2234 |
| 2328±4 | - | vvw | | $2\nu_3+\nu_5$? | calc. 2329 |
| 2385 | 1717 | vs, p | $a_1$ | $\nu_1$ | B-H stretch |
| 2455 | 1845 | vs, dp | e | $\nu_7$ | B-H stretch |
| - | 2431 | w | | | B-H stretch (H impurity) |
| 2530 | - | vvw | | | diborane ? |
| 2655±5 | - | vvw | $A_1+A_2+E$ | $\nu_7+\nu_{12}$ | 197 + 2455 = 2652 |

first overtone, and the position of the second, the $BD_3$ rock, was estimated at $603$ cm$^{-1}$ from the comparison with $BD_3CO$. The calculated product rule ratios using these estimated values are $1.98$ and $2.53$ for the $a_1$ and e classes, which may be compared with the theoretical values of $1.97$ and $2.55$. The spectra of both molecules thus are interpreted satisfactorily in terms of the $C_{3v}$ structure.

A normal coordinate treatment is in progress and its results together with a more detailed discussion of the assignments will be published on its completion.

B. THE RAMAN SPECTRUM OF $H_3NBH_3$

Earlier attempts to obtain a Raman spectrum for $H_3NBH_3$ were consistently complicated by strong background scattering resulting from the presence of a colloidal solid which formed in the ether solution. Earlier chemical studies have shown that the formation of such a solid is accelerated by trace quantities of water in the system. By taking great pains to exclude water from the system, a clear solution of ammonia-borane in dimethyl ether was obtained.

Relatively good spectra for $H_3NBH_3$ have been obtained. Interpretation will be carried out later.
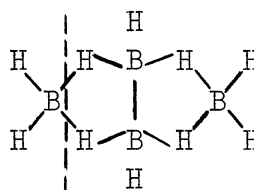
III. THE COMPLEXES OF $B_4H_{10}$

A. BACKGROUND

In earlier reports[9] symmetrical and nonsymmetrical cleavages of the double-bridge bond in $B_4H_{10}$ were postulated.
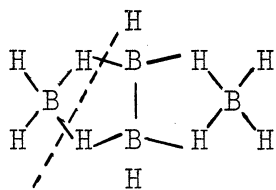


Symmetrical                                      Nonsymmetrical
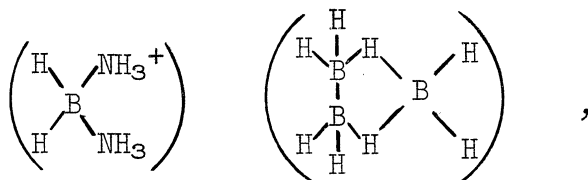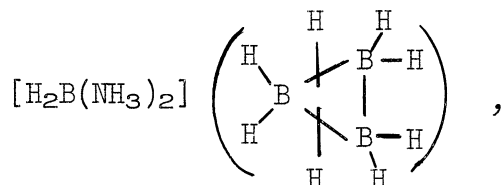Products = $H_3B$ and $B_3H_7$        Products = $H_2B^+$ and $B_3H_8^-$

Products expected in each case are indicated above.

Evidence for nonsymmetrical cleavage was contained in an earlier report[9] to the effect that a diammoniate of $B_4H_{10}$ can be obtained

$$\left(\begin{array}{c} H \diagdown \diagup NH_3^+ \\ B \\ H \diagup \diagdown NH_3 \end{array}\right) \qquad \left(\begin{array}{c} H \\ H \diagdown \overset{|}{\underset{|}{B}} \diagup H \diagdown \diagup H \\ B \\ H \diagup \overset{|}{\underset{|}{B}} \diagdown H \diagdown H \\ H \end{array}\right) \quad ,$$

or

$$[H_2B(NH_3)_2] \qquad \left(\begin{array}{c} H \diagdown \quad H \quad H \\ H \diagdown B \diagup \overset{\diagup B-H}{\underset{\diagdown B-H}{|}} \\ H \diagup \quad H \quad H \end{array}\right) \quad ,$$

which reacts with sodium in liquid ammonia to give the expected sodium salt $NaB_3H_8$, $H_2$, and $H_2NBH_2$.


B. SYNTHESIS OF A NEW AMMONIA—BORON-HYDRIDE COMPLEX, $H_3NB_3H_7$

Observations made in the synthesis of $H_3NBH_3$ suggested that a reaction between the ether soluble $NaB_3H_8$ and an ether slurry of $NH_4Cl$ should proceed as follows:

$$NaB_3H_8 \;+\; NH_4Cl \;\xrightarrow[\text{ether}]{\text{diethyl}}\; H_2 \;+\; NaCl \;+\; H_3NB_3H_7 \;.$$
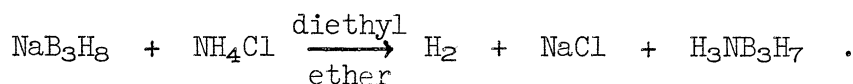
The new type of ammonia—boron-hydride coordination compound, $H_3NB_3H_7$, would be the ammonia-addition compound of the symmetrical-cleavage product, $B_3H_7$.

Using the foregoing reaction, the compound $H_3NB_3H_7$, tentatively named ammonia-triborane, has been obtained. Yields have been poor and rather erratic. Best results were obtained by the following procedure. The reaction was stopped after the evolution of about one mole of hydrogen; the solution was filtered and ether was distilled from the filtrate. From the solid filtrate residues $H_3NB_3H_7$ was sublimed under high vacuum in yields running up to 30% of the theoretical.

The white crystalline compound has been characterized by means of the following data. Analysis. Calculated for $H_3NB_3H_7$: H(hydridic) = 14.15%, N = 24.8%, B = 57.4%. Found: H(hydridic) = 14.10%, N = 24.4%, B = 57.2%. Molecular weight by vapor-pressure depression in diethyl ether was 55; theoretical for $H_3NB_3H_7$ is 56.5.

The compound dissolves in organic solvents such as benzene, ether acetone, and alcohol without decomposition. It will pick up ether vapor avidly to give an ether solution of the compound. It is only slightly soluble in petroleum ether. The compound also dissolves in water and in liquid ammonia.

It is surprisingly resistant to hydrolysis, requiring periods of up to one week at 120°C in 6NHCl for complete reaction. It melts at 73° to 75°C with loss of hydrogen.

The solid was attacked by an equimolar quantity of trimethylamine at room temperature to give a stoichiometric quantity of trimethylamine-borane and an unidentified solid residue which slowly gave off hydrogen.

$H_3NB_3H_7$ in liquid ammonia reacts slowly with sodium to give $H_2$. Only $NaBH_4$ was detected in the solid residues. The reaction is being explored farther in the hope of isolating $Na(NH_2B_3H_7)$ and following the cleavages which occur.

## C. THE STRUCTURE OF $H_3NB_3H_7$ AS DETERMINED BY X-RAY DIFFRACTION

X-ray powder and single-crystal studies of $H_3NB_3H_7$ have been conducted in this laboratory by Dr. C. E. Nordman. The solid undergoes two phase transitions between room temperature and -74°C. The room-temperature form has a structure as follows: Unit cell = tetragonal a = 6.11 Å, c = 6.57 Å. There are two formula units per cell. The space group is $C_{4v}^g$ - I4 mm.

A structure predicted from the chemical data has been confirmed. The boron atoms form an equilateral triangle with a B-B distance of 1.75 Å. The N atom lies on the normal to the plane of the borons through the center of the triangle. The distance of the N atom from the plane of the boron triangle is 2.53 Å. The hydrogen positions have not been established with certainty from the data currently available.

A fourfold axis of symmetry runs through the nitrogen atom and the center of the boron triangle. The molecules are either freely rotating or disordered about the fourfold axis.

The parameters are being refined by the method of least squares. The structure of the molecule as determined by currently available data is shown in Fig. 3. The hydrogens are placed arbitrarily since current data do not permit their precise location.

## D. THE ELECTRONIC STRUCTURE OF $H_3NB_3H_7$

The compound $H_3NB_3H_7$ poses problems in so-called "electron deficiency," as do most of the other boron hydrides. It can be formulated in relatively simple terms, using hybridized atomic orbitals to build up appropriate molecular orbitals. Hybridization of $sp^2$ orbitals gives an equilateral triangle with a third p orbital perpendicular to the plane of the triangle. Combination of the three unhybridized p orbitals of boron permits formation of molecular orbitals pointing up and down from the plane. The bottom hydrogen and the coordinated ammonia are bound through these orbitals. See Fig. 4.
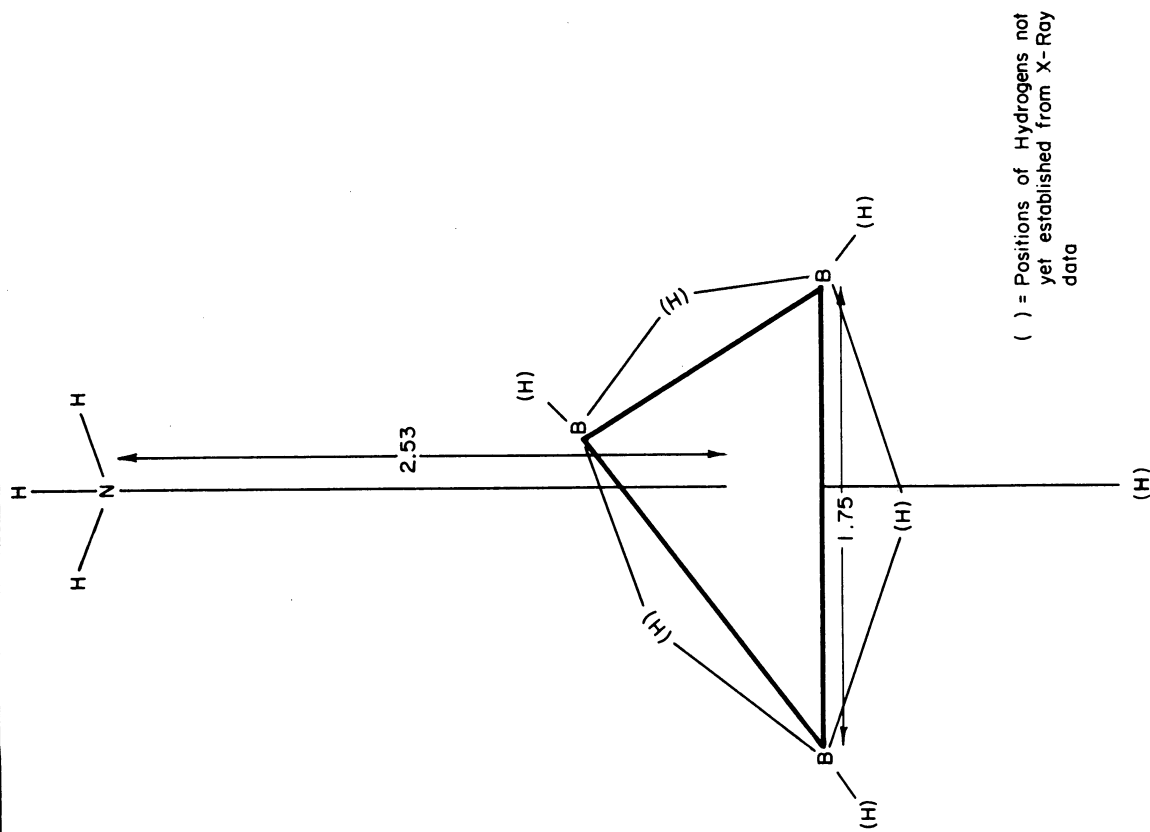
Planar sp$^2$
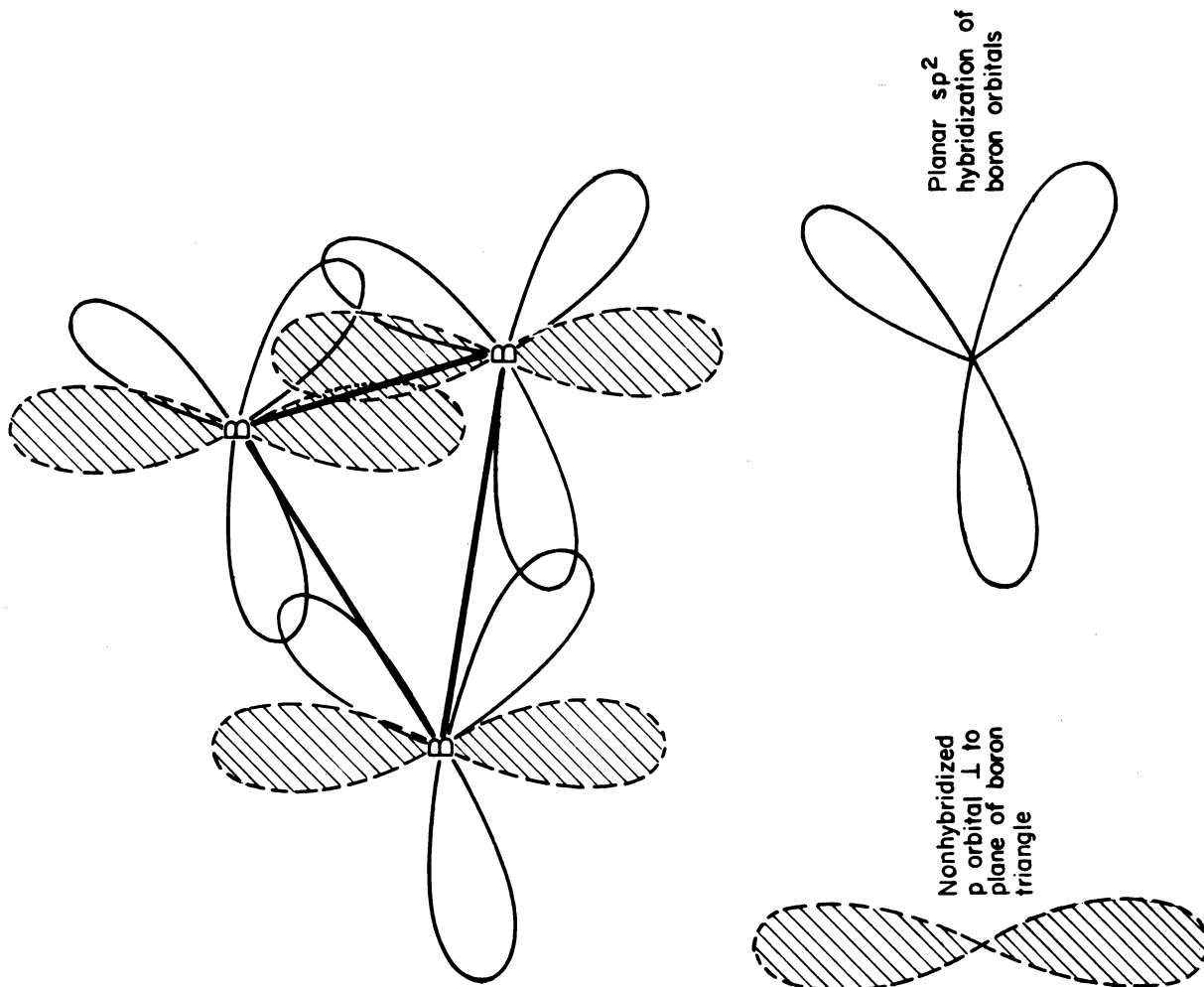hybridization of
boron orbitals

Nonhybridized
p orbital ⊥ to
plane of boron
triangle

Fig. 4.   The electronic structure of H$_3$NB$_3$H$_7$.



H

H —— N

H

2.53

(H)

(H)

B

(H)

B

(H)

1.75

(H)

(H)

B

(H)

( ) = Positions of Hydrogens not
yet established from X-Ray
data

Fig. 3.   Structure of H$_3$NB$_3$H$_7$.