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Final Report

THE CHEMISTRY OF BORON HYDRIDES AND RELATED HYDRIDES

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FOREWORD

The work reported herein was conducted under Contract No. AF 33(616)-3343 with the United States Air Force, the sponsoring agency being the Aeronautical Research Laboratory of the Wright Air Development Center, Air Research and Development Command. Direct technical responsibility for the investigation was vested in the Chemistry Research Branch of the Aeronautical Research Laboratory under the supervision of Dr. James Bierlein. Dr. William Ruigh served as task scientist, representing WADC in technical matters.

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ABSTRACT

Arguments to support the structure $[H_2B(NH_3)_2]BH_4$ for the "diammoniate of diborane" were presented in WADC Technical Report 56-318. The following additional information relative to the "diammoniate of diborane" and related structures has been obtained.

(a) A microcrystalline form of $B_2H_6 \cdot 2NH_3$ has been obtained and the powder pattern is tabulated for ready compound identification.

(b) Relatively strong evidence against the structure $[HB(NH_3)_3](BH_4)_2$ has been accumulated. The so-called "diammoniate of diborane II" which was formerly assigned this structure has been shown to consist chiefly of the regular "diammoniate" with the structure $[H_2B(NH_3)_2]BH_4$.

(c) Improved methods for the synthesis of pure salts of the form $[H_2B(NH_3)_2]X$ have been developed.

(d) A complete single-crystal X-ray crystallographic study which established the structure of $[H_2B(NH_3)_2]Cl$ has been completed and the data confirm the above structure assignments in every detail. The structures of the bromide and iodide salts have also been deduced.

(e) A nuclear magnetic resonance study of $[HB(NH_3)_2]I$ can best be interpreted in terms of the accepted structure of the cation $[H_2B(NH_3)_2]^+$.

(f) The "diammoniate of diborane," $[H_2B(NH_3)_2]BH_4$, has been prepared by metathesis, a fact which offers final and complete chemical support for the above structure.

The mono-, di-, and trimethylamines have all been prepared as stable compounds, and vapor-pressure measurements, dipole-moment measurements, and Raman spectra have been obtained for the series. The data represent part of a systematic examination of the amine-boranes. Phosphorus trifluoride-borane has been examined by means of Raman spectroscopy. Preliminary studies of the reaction between F_3PBH_3 and NH_3 indicate the existence of the new compound, $(NH_2)_3PBH_3$. The Raman spectrum of carbon monoxide—borane is considered.

A strong similarity has been found between the chemistry of diborane and that of tetraborane. The new compounds $B_4H_{10} \cdot 2NH_3$ and $H_3NB_3H_7$ have been prepared. On the basis of chemical evidence the structure of $B_4H_{10} \cdot 2NH_3$ is written as $[H_2B(NH_3)_2][B_3H_8]$. A complete single-crystal X-ray study has established the detailed structure of $H_3NB_3H_7$. All attempts to prepare $F_3PB_3H_7$ have been unsuccessful.

The new compound Cl_3AlPF_3 has been prepared and characterized. The compound $H_3Al[N(CH_3)_2]$ described by Wiberg has been confirmed independently and structural studies on the molecule have been initiated.

A detailed Raman spectral study of B_2H_6 has been completed and a detailed spectroscopic study of several borohydrides is described along with force constant calculations. The dipole moment of tetraborane has been measured as 0.6D. The bridge hydrogens of decaborane display acidic character on the basis of deuteron exchange studies.

I. REACTIONS AND STRUCTURES OF THE AMMONIA ADDITION COMPOUND OF DIBORANE AND OF ITS DERIVATIVES

A. Background

1. EARLY STRUCTURAL ARGUMENTS

In most of its reactions with electron donor molecules, diborane, B_2H_6, appears to cleave symmetrically to give characteristic base-borane adducts of the type:

Base: BH_3

For example, Burg and Schlesinger[1] found that trimethylamine reacts smoothly with B_2H_6 to give $(CH_3)_3NBH_3$, and CO reacts smoothly under pressure to form the compound carbon monoxide-borane. The foregoing authors used processes of the above type as support for the postulate that the reactions of diborane proceed through a BH_3 intermediate. Extensive experimental support for the postulate was provided by the researches of Schlesinger, Burg, their students, and other workers in the field. Indeed a large body of present-day evidence supports the postulated role of the BH_3 broup,[2] and McCoy and Bauer[3] have estimated the energy relationships involved in the postulated borane-diborane equilibrium as indicated below:

$$1. \quad B_2H_6 \longrightarrow 2BH_3 \qquad \begin{array}{l} \Delta H = 28.5 \text{ kcal/mole} \\ \Delta S = 34.2 \text{ e.u. at } 300° \end{array}$$

Although most reactions between diborane and electron donor molecules can be explained easily and logically in terms of the hypothetical borane intermediate, several boron hydride products have posed real interpretive problems. For example, one might expect that the reaction between diborane and ammonia would give the simple adduct ammonia-borane, H_3NBH_3, yet Stock and Pohland[4]

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(1) A. B. Burg and H. I. Schlesinger, J. Am. Chem. Soc. 59, 780-7 (1937).

(2) R. W. Parry and L. J. Edwards, Systematics in the Chemistry of the Boron Hydrides, Paper No. 54, the Division of Inorganic Chemistry Meeting of the American Chemical Society, San Francisco, April, 1958; J. Am. Chem. Soc., in press.

(3) R. E. McCoy and S. H. Bauer, J. Am. Chem. Soc. 78, 2061 (1956).

(4) A. Stock and E. Pohland, Ber. 58, 657 (1925).

found that the reaction did not follow the expected pattern. Instead, the product was a salt-like solid whose molecular weight in liquid ammonia corresponded to that of a dimer. The dimeric solid has been called "the diammoniate of diborane." In order to rationalize this unexpected dimeric formula, Stock[5] assumed that two of the hydrogen atoms of diborane are acidic in character. Such an assumption then leads to the representation of the "diammoniate" as an ammonium salt, $(NH_4)_2[B_2H_4]$.

Since Stock's formulation of the "diammoniate of diborane" was in conflict with the borane reaction hypothesis of Burg and Schlesinger, these authors reinvestigated the ammonia-diborane addition product. In the resulting study[6] it was found that only one equivalent of hydrogen gas was liberated when sodium was allowed to react with $B_2H_6 \cdot 2NH_3$ in liquid ammonia at -77°C. It was justly held that such behavior was inconsistent with the model of Stock, since a molecule containing two ammonium ions would be expected to liberate two equivalents of hydrogen in the sodium reaction. The equation suggested by Stock's formula is:

$$2. \qquad (NH_4)_2[B_2H_4] + 2Na \longrightarrow H_2 + Na_2B_2H_4$$

Since only one equivalent of hydrogen or 1/2 mole was obtained, a new formulation, consistent with the sodium stoichiometry and the borane reaction hypothesis, was proposed; the structure was $(NH_4)(H_3BNH_2BH_3)$. Additional evidence bearing on the question of acid hydrogens in the diborane molecule was presented by Burg.[7] Nyman[8] and his coworkers showed that when the Brönsted-Lowry acid NH_4Cl is dissolved in liquid ammonia, a rapid interchange of protons occurs between the acid cation and the solvent molecule. Burg conducted experiments with $B_2H_6 \cdot 2NH_3$ in liquid ND_3 which showed that H-D interchange occurs only with the hydrogens attached to the nitrogen and not with those attached to boron in $B_2H_6 \cdot 2NH_3$. He interpreted his results as proof of the assumption that the hydrogens of diborane have no acidic character. If the hydrogens of diborane are not acidic in character, the model of Stock for the diammoniate becomes untenable. On the basis of the foregoing evidence, the model of Schlesinger and Burg (i.e., $NH_4[H_3BNH_2BH_3]$) was widely accepted for many years, particularly in the standard textbooks of the English-speaking countries.[9]

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(5) A. Stock, Hydrides of Boron and Silicon, Cornell Univ. Press, Ithaca, 1933.

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

(7) A. B. Burg, J. Am. Chem. Soc. 69, 747 (1947).

(8) C. J. Nyman, S. C. Fung, and H. W. Dodger, J. Am. Chem. Soc. 72, 1033 (1950).

(9) a) N. V. Sidgwick, The Chemical Elements and Their Compounds, Oxford Univ. Press, London, 1950; b) T. Moeller, Inorganic Chemistry, J. Wiley and Sons, N. Y., 1952; c) L. F. Audrieth and J. Kleinberg, Non-Aqueous Solvents, John Wiley and Sons, N. Y., 1953; d) D. R. Stranks and R. G. Wilkins, Chemical Reviews, 57, 743 (1957).

An alternative proposal by Agromonov[10] received equally wide acceptance in continental Europe, particularly in Germany in the laboratories of Wiberg and his students. It was suggested that $B_2H_6 \cdot 2NH_3$ is indeed a monomer, H_3NBH_3, but that its salt-like character and dimeric nature in liquid ammonia are due to dipole-dipole interaction and hence to systematic errors in molecular weight measurements in liquid ammonia solution. The assumption that H_3NBH_3 would be a solid of salt-like appearance because of its dipole moment has indeed been verified by subsequent isolation of the solid monomer, and the assumption that dipole-dipole interaction could give rise to apparent dimerization in solvents of low dielectric constant found support in the observations of Bright and Fernelius[11] on the molecular weights of boron trifluoride-amine addition compounds in benzene. It was observed that trimethylamine-boron trifluoride was 81% dimerized in an .08 molal solution in benzene, and phenyldimethylamine boron trifluoride was likewise 91% dimerized in a benzene solution which was .011 molal in solute. It has been shown more recently, however, that, because of the higher dielectric constant of liquid ammonia, H_3NBH_3 is not dimeric in that solvent, even at relatively high concentrations (1.0 molal).[12]

Since the enigma of the $B_2H_6 \cdot 2NH_3$ structure could only be resolved by additional investigation, intensive chemical work was carried on in a number of laboratories in the United States. Attempts to resolve the question by direct X-ray diffraction studies were unsuccessful because the material of the correct composition was always obtained in an amorphous condition. Although Stock reported that the "diammoniate" crystallizes out of a liquid ammonia solution in long thin needles, it was found in several American laboratories that the crystalline solid obtained from liquid ammonia appeared to be a solvate since removal of the ammonia to obtain the solid of formula $B_2H_6 \cdot 2NH_3$ invariably led to decrepitation of the crystals and formation of an amorphous powder. It is significant, however, that X-ray methods did provide the final indirect evidence for resolution of the structural question. George Schaeffer and his students[13] at the University of St. Louis examined the X-ray diffraction pattern of the residue produced by the reaction between $B_2H_6 \cdot 2NH_3$ and Na in liquid ammonia. They found that the pattern contained the characteristic lines of $NaBH_4$. Schultz, Shore, and Parry, working in the Michigan laboratories, were told by Dr. Schaeffer of the $NaBH_4$ identification and the Michigan group immediately proposed the structure $[H_2B(NH_3)_2][BH_4]$ for $B_2H_6 \cdot 2NH_3$. Such a model had been mentioned brief-

(10) a) L. J. Agromonov, J. Chim. gen. 9 (71), 1389 (1939); Chem. Zbl. 1941 I, 2362; b) E. Wiberg, A. Boltz, and P. Buckheit, Z. anorg. Chem. 256, 287, footnote p. 307 (1948); c) Gmelin's Handbuch der anorganischen Chemie, 8 Auflage, System 13, pp. 100-101 (1954).

(11) J. R. Bright and W. C. Fernelius, J. Am. Chem. Soc. 65, 735 (1943).

(12) R. W. Parry, G. Kodama, and D. R. Schultz, J. Am. Chem. Soc. 80, 26 (1958).

(13) G. W. Schaeffer, M. D. Adams, and F. J. Koenig, S. J., J. Am. Chem. Soc. 78, 725 (1956).

ly by Burg[7] in 1947 but had been rejected by him without serious examination.

Schaeffer, Adams, and Koenig[13] were reluctant to accept the unprecedented cation $(H_2B(NH_3)_2]^+$, but proposed instead a structure containing both the ammonium ion and the borohydride group, $NH_4^+(H_2BNH_2)BH_4^-$. Since Schultz[14] had shown that NH_4BH_4 is unstable, it was suggested by the St. Louis group that H_2BNH_2 groups stabilized the ammonium borohydride structure by an unspecified mechanism.

In summary, five widely recognized structural proposals for the compound $B_2H_6 \cdot 2NH_3$ have been made. The formulas suggested are: (1) $(NH_4)_2(B_2H_4)$, (2) $NH_4[H_3BNH_2BH_3]$, (3) H_3NBH_3, (4) $[NH_4][H_2BNH_2][BH_4]$, and (5) $[H_2B(NH_3)_2]BH_4$. Evidence useful in making a choice between the above possibilities will now be reviewed. Since the detailed arguments have all been presented in earlier reports to WADC from this laboratory and in a recently published series of papers,[15] only the major arguments and conclusions will be considered.

2. EXPERIMENTAL STRUCTURAL ARGUMENTS FOR $B_2H_6 \cdot 2NH_3$

(a) The Models $[NH_4]_2[B_2H_4]$ and H_3NBH_3

Strong evidence against Stock's original model, $[(NH_4)]_2B_2H_4$, was provided by Burg's exchange experiments involving ND_3 and $B_2H_6 \cdot 2NH_3$. The data indicated no acid hydrogens in diborane and thus were in direct conflict with Stock's model which assumed two acid hydrogens in the original B_2H_6 molecule. On the other hand, Burg's conditions were mild and his quantitative methods for determining the extent of exchange could be questioned since they were based on small differences in the vapor pressures of ND_3 and NH_3. A more rigorous and unequivocal argument against assuming acid character for the hydrogens of B_2H_6 was contained in the tracer study of Shore, Girardot, and Parry.[15f] If Stock's model were correct, the reaction of B_2D_6 and NH_3 should produce $[NH_3D]_2[B_2D_4]$. Subsequent reaction of this salt with sodium should then produce some HD or D_2 in the evolved gas. Detailed tracer studies showed conclusively that all hydrogen liberated in the sodium reaction came from the rupture of hydrogen-nitrogen bonds, not from the breaking of hydrogen-boron bonds. In view of this

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(14) D. R. Schultz, Ph.D. dissertation, Univ. of Mich., 1954.

(15) a) R. W. Parry, D. R. Schultz, and P. R. Girardot, J. Am. Chem. Soc. 80, 1 (1958); b) D. R. Schultz and R. W. Parry, J. Am. Chem. Soc. 80, 4 (1958); c) S. G. Shore and R. W. Parry, ibid. 80, 8 (1958); d) S. G. Shore and R. W. Parry, ibid. 80, 12 (1958); e) R. W. Parry and S. G. Shore, ibid. 80, 15 (1958); f) S. G. Shore, P. R. Girardot, and R. W. Parry, ibid. 80, 20 (1958); g) R. W. Parry, G. Kodama, and D. R. Schultz, ibid. 80, 24 (1958); h) R. C. Taylor, D. R. Schultz, and A. R. Emery, ibid. 80, 27 (1958).

evidence and Burg's earlier results, the model $(NH_4)_2B_2H_4$ became untenable. The ammonia-borane model, H_3NBH_3, for $B_2H_6 \cdot 2NH_3$ was eliminated unequivocally by Shore and Parry[15c] who synthesized an authentic sample of monomeric H_3NBH_3 by means of the reaction between NH_4Cl and $B_2H_6 \cdot 2NH_3$ in ether slurry. It was clearly established that $B_2H_6 \cdot 2NH_3$ and H_3NBH_3 are different chemical species and that no labile equilibrium exists between them at the low temperatures found in the usual liquid ammonia solutions.

(b) Evidence for The Borohydride Ion in $B_2H_6 \cdot 2NH_3$

Although the production of $NaBH_4$ in the reaction between $B_2H_6 \cdot 2NH_3$ and Na originally suggested the existence of the borohydride ion in the diammoniate of diborane, it did not offer unequivocal proof of the $B_2H_6 \cdot 2NH_3$ structure since the possibility of a slight rearrangement of the solid product to give $NaBH_4$ and H_2NBH_2 had not been eliminated. If such a rearrangement of solid products were postulated,[13] the X-ray evidence could be regarded as consistent with any of the models for $B_2H_6 \cdot 2NH_3$ outlined earlier. Clearly, more definitive evidence was needed.

Schultz and Parry[15b] found that magnesium thiocyanate in liquid ammonia reacted with the diammoniate of diborane to give a precipitate of $[Mg(NH_3)_6](BH_4)_2$. This test for the borohydride group is comparable to procedures normally used in qualitative analysis for anion identification; for example, $SO_4^=$ is identified by precipitation as $BaSO_4$. Further, it was found that solid $NaBH_4$ in intimate mixture with authentic ammonium salts such as NH_4Cl or NH_4Br reacted to give hydrogen gas and a new microcrystalline solid phase containing boron, ammonia, hydridic hydrogen, and the halide anion. The equation indicated by the data is:

$$MBH_4 + NH_4X \longrightarrow \underline{MX} + [H_2B(NH_3)_2]X + 2H_2$$
$$\text{solid phase}$$

It was found that $B_2H_6 \cdot 2NH_3$ reacts with ammonium salts under comparable conditions to give comparable products thus suggesting the presence of the borohydride ion in the solid $B_2H_6 \cdot 2NH_3$. Furthermore, Shore and Parry[15c] showed that the reactions of ether slurries of $B_2H_6 \cdot 2NH_3$ with ammonium salts, lithium halides, and aluminum chloride paralleled completely the reactions under comparable conditions of authentic borohydrides such as $NaBH_4$ or $LiBH_4$.

Additional chemical evidence supporting the existence of borohydride in the diammoniate was contained in an early observation of Stock[16] who reported that solid $B_2H_6 \cdot 2NH_3$ reacted slowly at -60°C with gaseous HCl to give significant quantities of B_2H_6. Although B_2H_6 was produced in relatively good yield, Stock

(16) A. Stock, Hydrides of Boron and Silicon (Cornell Univ. Press, Ithaca, 1933), p. 134.

considered that it was a product of a secondary reaction. He represented what he regarded as the main reaction by the equation:

$$B_2H_6 \cdot 2NH_3 + 2HCl \longrightarrow B_2H_4Cl_2 \cdot 2NH_3 + 2H_2.$$

The nature of the secondary reaction which supposedly gave B_2H_6 was not clearly delineated in Stock's work. Modern information about borohydrides suggests representation of the process as

$$MBH_4 + HCl \longrightarrow MCl + 1/2\ B_2H_6 + H_2$$

where M is any cation. A complicating side reaction which would reduce the yield of B_2H_6 would be:

$$6B_2H_6 + 6HCl \longrightarrow 6B_2H_5Cl \longrightarrow 2BCl_3 + 5B_2H_6$$

Finally, physical evidence supporting the existence of the borohydride ion in the original ammonia solution of $B_2H_6 \cdot 2NH_3$ was provided by Taylor, Schultz, and Emery.[15g] The Raman spectrum of $B_2H_6 2NH_3$ in liquid ammonia solution at -78°C revealed unequivocal evidence for the borohydride group.

(c) Evidence Related to the Identity of the Cation in $B_2H_6 \cdot 2NH_3$

Three of the five formulas proposed for $B_2H_6 \cdot 2NH_3$ contained one or more ammonium ions per mole of diammoniate; a fourth formula was the now discredited monomeric model [H_3BNH_3], and the fifth model contained the new and unrecognized cation [$H_2B(NH_3)_2$]$^+$. In view of these facts, the evidence concerning the nature of the cation, and particularly the evidence supporting the existence of the widely accepted ammonium ion deserve careful examination.

The original model containing an ammonium ion, $(NH_4)_2B_2H_4$, was written by Stock to rationalize his observations on the electrolysis of a liquid ammonia solution of $B_2H_6 \cdot 2NH_3$. It was found that a monomeric compound $H_3NB(CH_3)_3$ which would be analogous to the monomeric H_3NBH_3, had a conductivity in liquid ammonia solution which was less than 1/100th of that of $B_2H_6 \cdot 2NH_3$. On the basis of this evidence an ionic structure was indicated, but any ionic model could be made to agree with the observations on conductivity. To support his position further, Stock attempted to identify the electrolysis products and account for them in terms of his molecular model, but his interpretations were by no means unique and unequivocal. The observations have been re-interpreted in a variety of ways.

The principal evidence used by Schlesinger and Burg[6] to justify the use of an ammonium ion in their model, $NH_4(H_3BNH_2BH_3)$ was the reaction between

$B_2H_6 \cdot 2NH_3$ and sodium in liquid ammonia. The equation assumed was:

$$Na + NH_4[H_3BNH_2BH_3] \xrightarrow[-78°C]{\text{liq } NH_3} 1/2\ H_2 + NH_3 + Na[H_3BNH_2BH_3]$$

Although the sodium reaction is indeed consistent with the presence of an ammonium ion in the compound, it is important to note that the reaction is difinitely not proof of the existence of an ammonium ion in the solid "diammoniate." Rather it is evidence for the presence of any Brönsted-Lowry acid which can oxidize the active sodium metal in liquid ammonia solution. For example, $(CH_3)_3BNH_3$(17), F_3BNH_3(18), and monomeric H_3BNH_3(19) all react slowly with sodium in liquid ammonia, yet contain no NH_4^+ ions in the solid state. One might also compare the reactions of acids such as $[Al(H_2O)_6^{+3}]$ in water systems. The acid character of $Al_2(SO_4)_3 \cdot 12H_2O$ is not evidence for H_3O^+ ions in solid aluminum sulfate hydrate, but is instead evidence for the existence of water molecules whose proton donor qualities have been enhanced by coordination to an ion of relatively high field strength. Similar arguments may be applied to ammonia molecules coordinated to the boron of $[H_2B(NH_3)_2]^+$. The reaction with sodium may be written:

$$[H_2B(NH_3)_2]X + Na \xrightarrow[NH_3]{\text{liq}} NaX + H_2BNH_2 + 1/2\ H_2 + NH_3$$

See pages 11 and 52 for further details.

No direct evidence for an ammonium ion in the "diammoniate of diborane" has ever been presented. On the other hand, strong evidence against the presence of this ion is now available. For example, it is known that $NaBH_4$ in intimate mixture with authentic ammonium salts such as NH_4Cl or $(NH_4)_2SO_4$ reacts rapidly to give off H_2,(15b) yet Schultz and Parry(15b) showed that the "diammoniate of diborane" does not react with excess $NaBH_4$ under comparable conditions. On the other hand, $B_2H_6 \cdot 2NH_3$ will react with authentic ammonium salts because of the borohydride ion in the structure. If one were to assume a model for $B_2H_6 \cdot 2NH_3$ containing NH_4^+ ions, the above observations could be rationalized only by assuming that something in the solid (H_2NBH_2 has been suggested) renders the NH_4^+ ion in the solid "diammoniate" inactive toward BH_4^- even though NH_4^+ ion, when added as NH_4Cl, reacts vigorously with the BH_4^- ion of the same structure. The mechanism of such stabilization without formation of the cation $[H_2B(NH_3)_2^+]$ remains obscure.

(17) a) C.E. Coates, Organo Metallic Compounds (Methuen and Co. Ltd., London, 1956), p. 59; b) C. A. Krause, J. Chem. Ed. 29, 548 (1952); c) J. E. Smith and C. A. Krause, J. Am. Chem. Soc. 73, 2751 (1951).

(18) W. J. McDowell and C. W. Keenan, J. Am. Chem. Soc. 78, 2065 (1956).

(19) S. G. Shore and R. W. Parry, J. Am. Chem. Soc. 80, 8 (1958).

In contrast, evidence for the complex cation $[H_2B(NH_3)_2^+]$ is provided by isolation of its chloride and bromide salts. The two compounds are isostructural and are not a mixture of H_2BNH_2 and the corresponding NH_4X salt. The bromide salt reacts with sodium in liquid ammonia to give hydrogen as does the "diammoniate of diborane," and the salts containing the complex cation should be electrolytes in liquid ammonia as Stock reported for $B_2H_6 \cdot 2NH_3$. Finally, Taylor, Schultz, and Emery[15h] found that the Raman spectrum of the salt $[H_2B(NH_3)_2]Br$ plus the Raman spectrum of $NaBH_4$ gives the Raman spectrum of $B_2H_6 \cdot 2NH_3$.

In summary, all evidence cited for the existence of the NH_4^+ ion is equally good for the complex ion $[H_2B(NH_3)_2^+]$, and several discriminatory physical and chemical tests argue against the NH_4^+ ion but are consistent with the ion $[H_2B(NH_3)_2]^+$. Schultz and Parry[15b] reviewed all earlier arguments cited for the structure $[NH_4^+][H_3BNH_2BH_3]$ and found that every observation cited by earlier workers was consistent with the model $[H_2B(NH_3)_2^+](BH_4^-)$.

B. Further Studies on "The Diammoniate of Diborane," $[H_2B(NH_3)_2][BH_4]$, and Related Molecules

1. SYNTHESIS OF $B_2H_6 \cdot 2NH_3$ IN ONE GRAM-LOTS

In the past all attempts to synthesize as much as 1 g of $B_2H_6 \cdot 2NH_3$ in a single batch resulted in decomposition of the product. Schultz,[14] working in this laboratory, found that attempts to scale up the usual synthetic procedure resulted in the production of volatile products; $B_2H_5NH_2$ was probably a major component of the reaction mixture. Temperature control was a major problem. A successful synthesis of 0.6 g of $B_2H_6 \cdot 2NH_3$ in one run has been effected using the procedure described below.

A 10-millimole quantity of diborane was condensed at the bottom of a reactor tube, 30 mm in diameter and about 230 mm long. An excess quantity of ammonia was condensed along the walls of the tube by progressively raising a Dewar filled with liquid nitrogen from a height of about 50 mm above the condensed diborane to 50 mm from the top of the tube. A pentane bath at -145°C was placed around the tube. The thermostating pentane bath and the reaction tube warmed up gradually from -145°C to -80°C over a period of about 12 hours. The diborane vaporized and reacted with the ammonia. The diammoniate was isolated by subliming away the excess ammonia at -78°C. The total yield of $B_2H_6 \cdot 2NH_3$ was about 0.6 g. The product was identified by its X-ray powder pattern. The first standard X-ray powder pattern of $B_2H_6 \cdot 2NH_3$ was obtained as described in the next section.

In another attempt to prepare a relatively large quantity of "diammoniate" the reaction between diborane and ammonia was carried out in diethyl ether at -95°. A mixture of the "diammoniate" and ammonia-borane resulted. Identifica-

tion was by X-ray powder pattern.

2. THE PREPARATION OF MICROCRYSTALLINE $B_2H_6 \cdot 2NH_3$—THE X-RAY POWDER PATTERN OF "THE DIAMMONIATE OF DIBORANE"

(a) Discussion

As indicated in the literature review of Section A, all attempts to prepare crystalline $B_2H_6 \cdot 2NH_3$ for X-ray structural investigations had been unsuccessful in this and other laboratories. During the course of the study described in this report, a product with the empirical formula $[H_3NBH_3]_n$ was obtained which gave a definite and characteristic X-ray powder pattern. This product was originally prepared by a procedure which supposedly gave "diammoniate of diborane II," $[HB(NH_3)_3](BH_4)_2$.[15e] However, repetition of the experiment by a procedure known to give an authentic sample of the "diammoniate" $[H_2B(NH_3)_2][BH_4]$ gave a product with an identical x-ray diffraction pattern. These facts cast serious doubt on the existence of diammoniate (II) [see page 10 for further information], but made possible identification of $B_2H_6 \cdot 2NH_3$ by X-ray methods. Why the crystalline product is easily obtained now, but was unobtainable earlier, remains in the realm of speculation.

(b) Experimental

(1) Diammoniate of Diborane (II).—Diborane was added to frozen, excess ammonia in the same manner employed to prepare the "Diammoniate I."[15e] Then the system was aged for about 20 hours at -45° to cause conversion to "diammoniate (II)." Excess ammonia was then pumped from the system at about -65°C. Final traces of ammonia were pumped away at room temperature. The resulting solid product had the empirical formula H_3NBH_3. The following analytical ratios were obtained: B/N = 1.02; hydridic H/N = 3.02. X-ray powder data for the microcrystalline product are presented in Table I.

(2) Diammoniate of Diborane (I).—The solid was prepared according to standard procedures[15e] and solvent ammonia was removed as completely as possible at -78°C. The product, presumably $B_2H_6 \cdot 2NH_3$ (I), was then warmed to room temperature, transferred rapidly in a dry box to an X-ray capillary tube, and a powder pattern was taken. The pattern obtained was identical to that in Table I except for four very weak lines at d = 6.05, 5.18, 4.09, and 3.63.

TABLE I

INTERPLANAR SPACINGS FOR THE CRYSTALLINE FORM
OF THE "DIAMMONIATE OF DIBORANE"
$B_2H_6 \cdot 2NH_3$

Intensity	θ	d	Intensity	θ	d
W	5.78	7.62	MS-	19.40	2.32_2
W	8.18	5.42	W	21.03	2.14_9
MS	9.53	4.64	MW	21.55	2.09_9
S	10.35	4.28	W	22.75	1.97_9
S	12.65	3.52	MW	23.20	1.95_9
MS	15.18	2.94	W	25.40	1.79_8
MS	15.73	2.84	W	25.98	1.76_1
MS	16.63	2.69	W	26.35	1.73_7
MS-	17.23	2.60	W	26.98	1.70_1
MW	17.83	2.51_8	MS-	27.43	1.67_3
MW	18.65	2.41_3			

Intensity scale: S>MS>MS->MW>W>VW CuK_α radiation

3. ADDITIONAL CHEMISTRY OF $B_2H_6 \cdot 2NH_3$. EVIDENCE FOR AND AGAINST THE EXISTENCE OF "DIAMMONIATE OF DIBORANE II" WITH THE FORMULA $[HB(NH_3)_3][BH_4]_2$

(a) Decomposition of $B_2H_6 \cdot 2NH_3$ in Diethyl Ether Slurry

In an earlier report[20] the preparation of monomeric H_3NBH_3 from $[H_2B(NH_3)_2]BH_4$ was described in terms of the following equation.

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

The validity of this overall equation was questioned 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 this discrepancy between theory and experiment arises from properties of $[H_2B(NH_3)_2]BH_4$. It is now known that the "diammoniate" undergoes a competing decomposition process in an ether slurry containing ammonia but no ammonium chloride:

(20) R. W. Parry, R. C. Taylor, T. C. Bissot, D. H. Campbell, A. E. Emery, P. R. Girardot, G. Kodama, D. R. Schultz, S. G. Shore, J. T. Yoke III, WADC Tech. Report 56-318 (1956).

$$[H_2B(NH_3)_2]\ BH_4 \xrightarrow[\text{Diethyl ether}]{\text{Trace } NH_3} H_2 + H_3NBH_3 + \frac{1}{n}\ (H_2BNH_2)_n$$

The reaction is not unexpected in view of the known weak acidic character of the $[H_2B(NH_3)_2^+]$ cation in liquid ammonia and the hydridic character of the hydrogens in the borohydride group.

Data are summarized in Fig. 1. The two reactions written above proceeding simultaneously, would be consistent with all observed facts.

In a typical run 1.73mmoles of $[H_2B(NH_3)_2][BH_4]$ were prepared and isolated in one arm of a vacuum line filter system of the type described by Schultz[14,15a] [see Fig. 3.] About 10 ml of diethyl ether was then distilled into the reaction tube. About 0.15 mmole of rigorously dried ammonia was also distilled in; then the evacuated system was closed off and the reactor was warmed up to about 3 or 4 degrees below room temperature. A beaker of water just below room temperature served as a thermostating medium. This procedure prevented condensation of ether throughout the system and minimized attack on the stopcock grease by ether. The extent of reaction was determined at various intervals by quenching the reaction tube in liquid nitrogen and measuring volumetrically the quantity of hydrogen produced. Upon completion of the reaction, the contents of the reactor tube were filtered and extracted with ether. The filtration and extraction were carried out at about -75° to take advantage of the negative temperature coefficient of solubility of ammonia-borane. Crystalline ammonia-borane was obtained from the filtrate by distilling away the ether as the receiver tube was warmed from -70 to -20°C.

(b) The Reaction of "The Diammoniate of Diborane" with Sodium in Liquid Ammonia

In all earlier work considerable structural and chemical significance has been attached to the stoichiometry and rate of the reaction between sodium and $B_2H_6 \cdot 2NH_3$ in liquid ammonia. For example, the original "diammoniate" formula of Schlesinger and Burg $[NH_4][H_3BNH_2BH_3]$ was based primarily upon the stoichiometry of the sodium reaction, and Parry and Shore[15e] used the stoichiometry of this same reaction as evidence for the suggestion that there exists a second form of $B_2H_6 \cdot 2NH_3$ called the "diammoniate of diborane (II)" with the structure $[HB(NH_3)_3][BH_4]_2$. It was suggested that if the normal "diammoniate of diborane (I)," $[H_2B(NH_3)_2][BH_4]$, which was prepared and maintained below -78°C, is warmed to -45°C and stored at this temperature for about 20 hours, diammoniate (II) is produced. It is assumed that diammoniate (I) in liquid ammonia reacts with sodium to give one equivalent of H_2 per mole of $B_2H_6 \cdot 2NH_3$ in accordance with the following equation:

$$[H_2B(NH_3)_2]\ BH_4 + Na \longrightarrow 1/2\ H_2 + NaBH_4 + H_2BNH_2 + NH_3$$

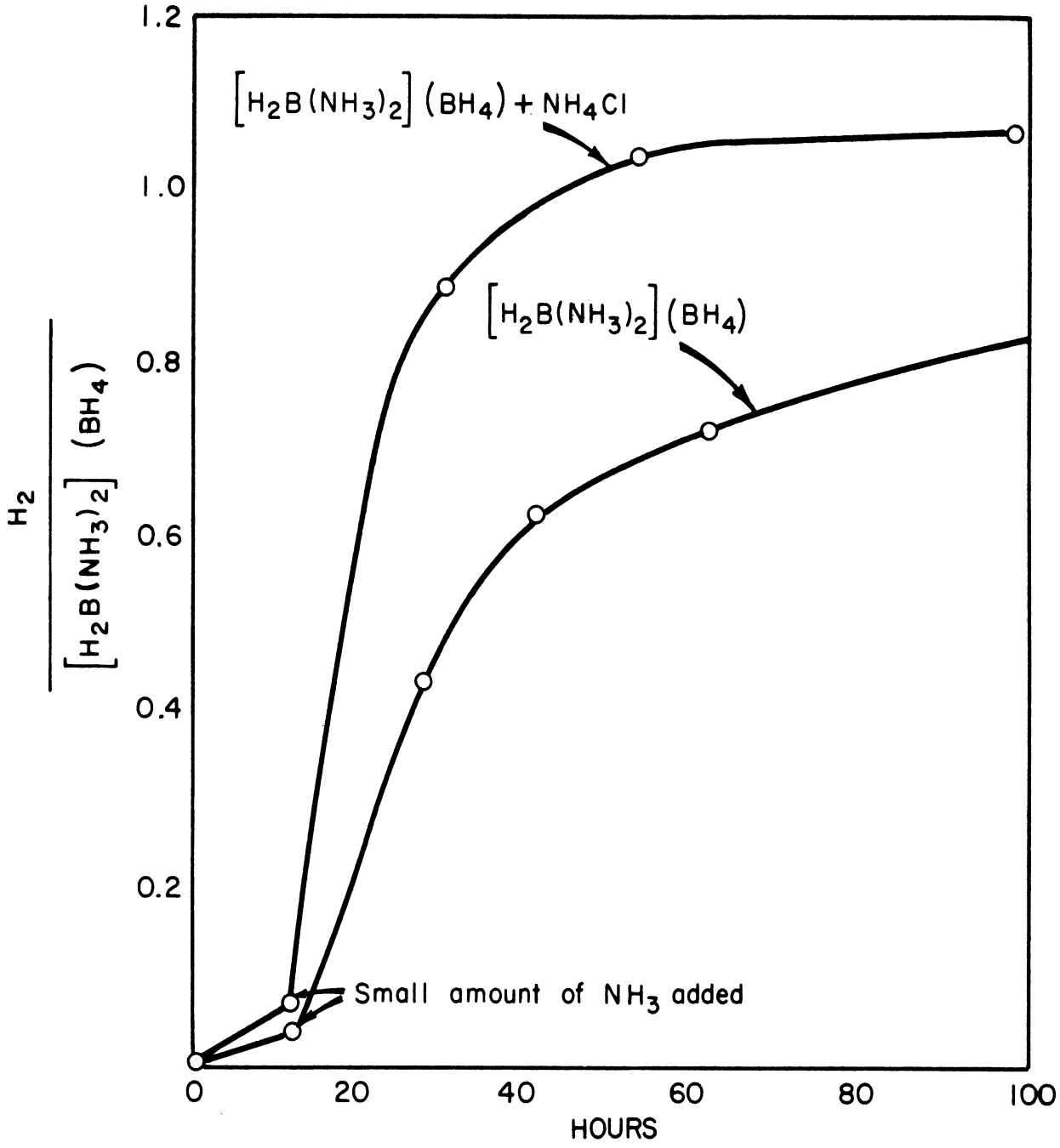

Fig. 1. The evolution of H_2 from $B_2H_6 \cdot 2NH_3$ in diethyl ether slurry. The role of NH_4Cl.

Diammoniate (II) was assumed to react to give the observed 1.33 equivalents of H_2 per formula weight of $B_2H_6 \cdot 2NH_3$. The equation written was:

$$[HB(NH_3)_3][BH_4]_2 + 2Na \longrightarrow 2NaBH_4 + H_2 + HB(NH_2)_2 + NH_3$$

Note: $[HB(NH_3)_3][BH_4]_2$ is equal to 1.5 formula weights of $B_2H_6 \cdot 2NH_3$.

$$\text{Thus: } \frac{2 \text{ equiv } H_2}{1.5 \text{ formula wts}} = 1.33 \text{ equiv } H_2/B_2H_6 \cdot 2NH_3$$

Earlier in Section B it was reported that a sample of $B_2H_6 \cdot 2NH_3$ was prepared and stored under conditions assumed to give diammoniate (II) and a second sample of $B_2H_6 \cdot 2NH_3$ was prepared carefully under conditions known to give diammoniate (I). Strangely enough, the X-ray powder patterns of both samples were identical except for four very weak lines in the diammoniate (I) pattern. To characterize further the presumed diammoniate (II), a portion of the sample from the batch used in X-ray analysis was dissolved in liquid ammonia and allowed to react with excess sodium in liquid ammonia at -78°C. In about one hour 1.28 equivalents of H_2 per formula weight of $B_2H_6 \cdot 2NH_3$ were obtained. The value is consistent with behavior attributed to diammoniate (II), but a molecular weight determination in liquid ammonia on this same material gave a value of about 55 which corresponds to diammoniate (I) [theoretical value = 61].

A reasonable interpretation of the foregoing facts is that diammoniate (I) and diammoniate (II) are the same material, but that other factors such as traces of decomposition products or other as yet undefined variables in the higher-temperature product influence the rate and stoichiometry of hydrogen evolution in the sodium reaction to such an extent that the structural significance of the data is definitely limited. Such an interpretation is supported by data on the HCl reaction described next, and by observations on the reaction of $[H_2B(NH_3)_2]Cl$ with sodium (p. 52) and of $[H_2B(NH_3)_2][B_3H_8]$ with sodium (p. 114). The assumed importance of impurities in catalyzing hydrogen evolution in boron nitrogen systems has been demonstrated by Campbell, Bissot and Parry,[21] and by Kodama and Parry,[22] and is amply supported in other sections of this report [see p. 59].

One other alternate possibility cannot be eliminated on the basis of evidence now available. In view of the extreme sensitivity of the properties of the so-called "diammoniate I" to the methods used for its preparation, it is possible that this low-temperature material is in reality a mixture consisting of $[H_2B(NH_3)_2]BH_4$ and a postulated intermediate[15e] containing a single bridged

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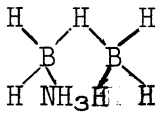
(21) D. H. Campbell, T. C. Bissot and R. W. Parry, J. Am. Chem. Soc. 80, 1549 (1958); WADC Tech. Report 56-318 (1956).

(22) G. Kodama and R. W. Parry, WADC Tech. Report 57-11 (January, 1957) p. 21; J. Am. Chem. Soc. 79, 1007 (1957); see also discussion in this report on $B_4H_{10} \cdot 2NH_3$.

bond,



On the basis of a detailed study of the sodium reaction, Shore, Girardot, and Parry suggested that the single-bridge structure would react slowly with sodium in liquid ammonia. Thus any appreciable quantity of the intermediate would reduce the rate of hydrogen evolution in the sodium reaction. A corollary to the above argument is that pure salts of the type $[H_2B(NH_3)_2]X$ would liberate one equivalent of hydrogen very rapidly in the sodium reaction and additional hydrogen more slowly in a secondary process. Studies reported on pages 52 and 114 for the salts $[H_2B(NH_3)_2]Cl$ and $[H_2B(NH_3)_2][B_3H_8]$ support this argument. Additional information relative to the postulated forms I and II of $B_2H_6 \cdot 2NH_3$ is found in the next section.

(c) The Reaction of "The Diammoniate of Diborane" with Hydrogen Chloride

In his early studies of the "diammoniate of diborane" Stock[5] investigated the reaction between $B_2H_6 \cdot 2NH_3$ and HCl. He wrote the equation:

$$B_2H_6 \cdot 2NH_3 + 2HCl \longrightarrow B_2H_4Cl_2 \cdot 2NH_3 + 2H_2 \quad ,$$

but he reported the formation of B_2H_6 by an unspecified secondary reaction. Schultz and Parry[15b] reinterpreted Stock's observations and wrote the equation between the "diammoniate of diborane (I)" and HCl as:

$$[H_2B(NH_3)_2][BH_4] + HCl \longrightarrow [H_2B(NH_3)_2]Cl + H_2 + 1/2\ B_2H_6$$

The analogous equation expected for the diammoniate of diborane (II) as suggested by Parry and Shore[15e] would be:

$$[HB(NH_3)_3](BH_4)_2 + 2HCl \longrightarrow [HB(NH_3)_3]Cl_2 + B_2H_6 + 2H_2$$

A complicating side reaction between the B_2H_6 formed as a product and HCl present in the reacting system would be:

$$6B_2H_6 + 6HCl \longrightarrow 6B_2H_5Cl + 6H_2$$
$$\downarrow$$
$$2BCl_3 + 5B_2H_6$$

To evaluate Stock's proposal more effectively and to differentiate more effectively between the two proposed forms of the diammoniate {i.e., $[H_2B(NH_3)_2](BH_4)$ and $[HB(NH_3)_3][BH_4]_2$}, the reaction between $B_2H_6 \cdot 2NH_3$ and HCl has been studied under rather well-controlled conditions.

From the foregoing equations for the reaction between the diammoniate of diborane and HCl, it is apparent that the amount of hydrogen produced in the

process will be complicated by the secondary reaction between B_2H_6 and HCl. Although the HCl-B_2H_6 reaction can be slowed up by holding the temperature at -78°C, it is still difficult to attach great structural significance to the amount of hydrogen obtained in a given period of time. Of greater structural significance is the identity of the solid product which remains after gas evolution. Three possibilities must be recognized. Stock wrote $B_2H_4Cl_2 \cdot 2NH_3$. Such a product would have a B/N/Cl ratio of 1/1/1. "Diammoniate of diborane (I)" as described by Schultz and Parry would produce $[H_2B(NH_3)_2]Cl$ which has a B/N/Cl ratio of 1/2/1, while "Diammoniate of diborane (II)" as postulated by Parry and Shore[15e] would produce $[HB(NH_3)_3]Cl_2$ which has a B/N/Cl ratio of 1/3/2.

When a slurry of "diammoniate of diborane (I)" in dimethyl ether was allowed to react with an excess of HCl at -78°C, the solid product was unequivocally identified as $[H_2B(NH_3)_2]Cl$ on the basis of its X-ray powder pattern. Some NH_4Cl contaminated the solid. When a slurry of "the diammoniate of diborane (II)" in dimethyl ether was allowed to react with HCl under conditions comparable to those used above, the solid product was again $[H_2B(NH_3)_2]Cl$ contaminated with small amounts of NH_4Cl; it was not $[HB(NH_3)_3]Cl_2$ as expected. These data, coupled with the X-ray powder patterns, lead almost unequivocally to the conclusion that diammoniate of diborane (I) and diammoniate of diborane (II) have the same major phase. Differences between the two samples in the sodium reaction or molecular weight values are attributed to small amounts of impurities in one sample or the other. Two possibilities remain and neither can be eliminated conclusively on the basis of available evidence. The possibilities are: (a) the -78° product, $B_2H_6 \cdot 2NH_3$ (I), is contaminated by products representing incomplete reaction between B_2H_6 and NH_3, or (b) the -45° product, formerly $B_2H_6 \cdot 2NH_3$ (II), is contaminated by small quantities of decomposition products which give rise to instability of the compound. The problem now resolves itself into a question of compound purification.

If $[H_2B(NH_3)_2][BH_4]$ could be obtained in high purity, its utilization in the preparation of high purity $[H_2B(NH_3)_2]Cl$ becomes immediately apparent. Studies directed toward this objective are described under the synthesis of $[H_2B(NH_3)_2]Cl$ on page 23.

The reactions referred to above were conducted as described below.

Samples of "diammoniate of diborane (I)" and "diammoniate of diborane (II)" were prepared by previously described procedures.[15e] Commercial ethers, used as solvents, were dried over $LiAlH_4$ before use. Commercial anhydrous hydrogen chloride was purified by freezing it into one arm of the purification system shown in Fig. 2. By cooling the second arm of the purification system, the gas could be slowly passed through the P_2O_5 to dry it. Six passes through the dessicant were made; HCl was then condensed into the reaction vessel for use.

In a typical run a suitable sample of $B_2H_6 \cdot 2NH_3$ (about 1 to 2 millimoles) was placed in a 24/40 reaction tube on a vacuum filter apparatus (Fig. 3). For studies on diammoniate (I) it was desirable to make the $B_2H_6 \cdot 2NH_3$ right in the

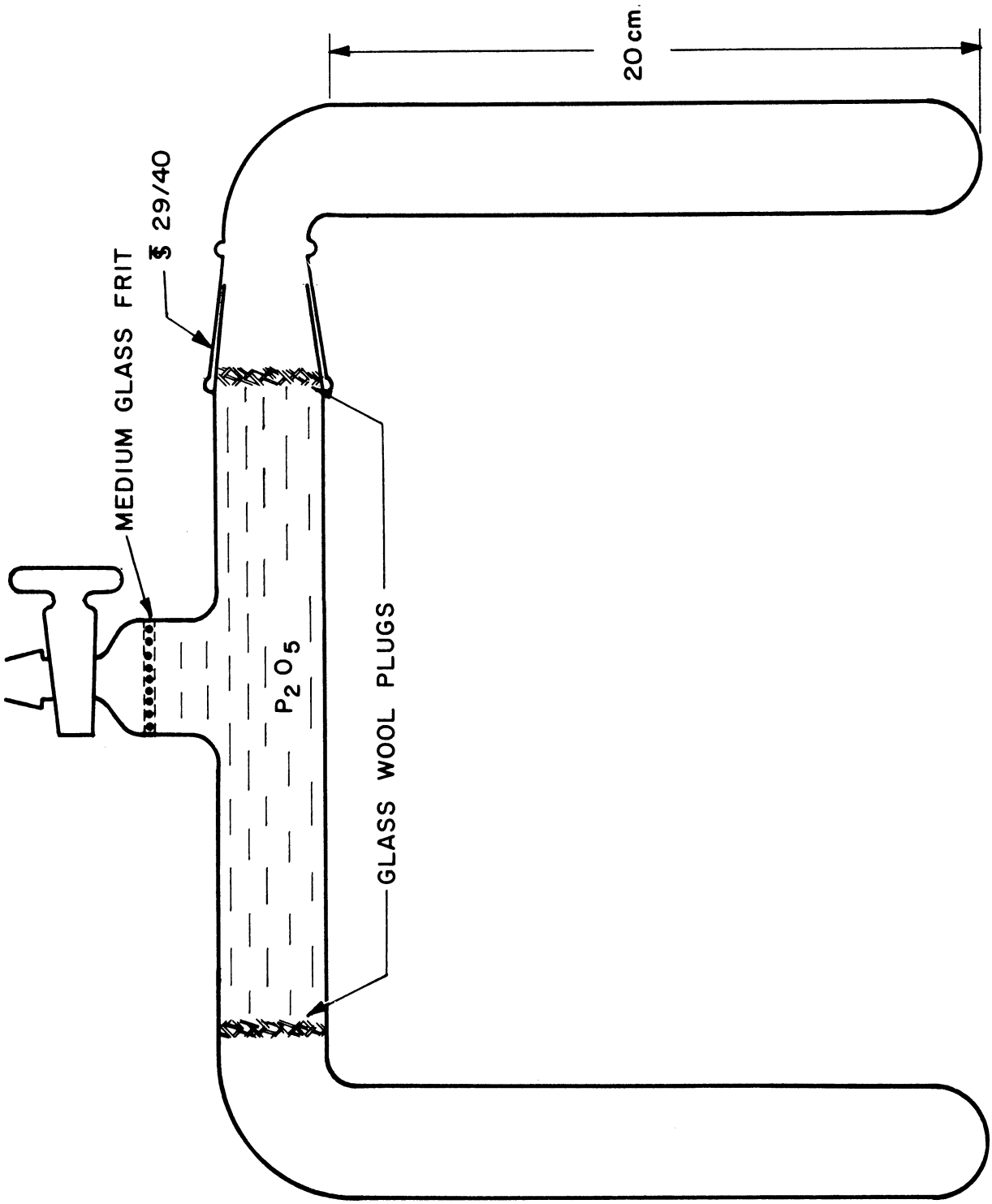


Fig. 2. Phosphorus pentoxide drying tube for HCl.

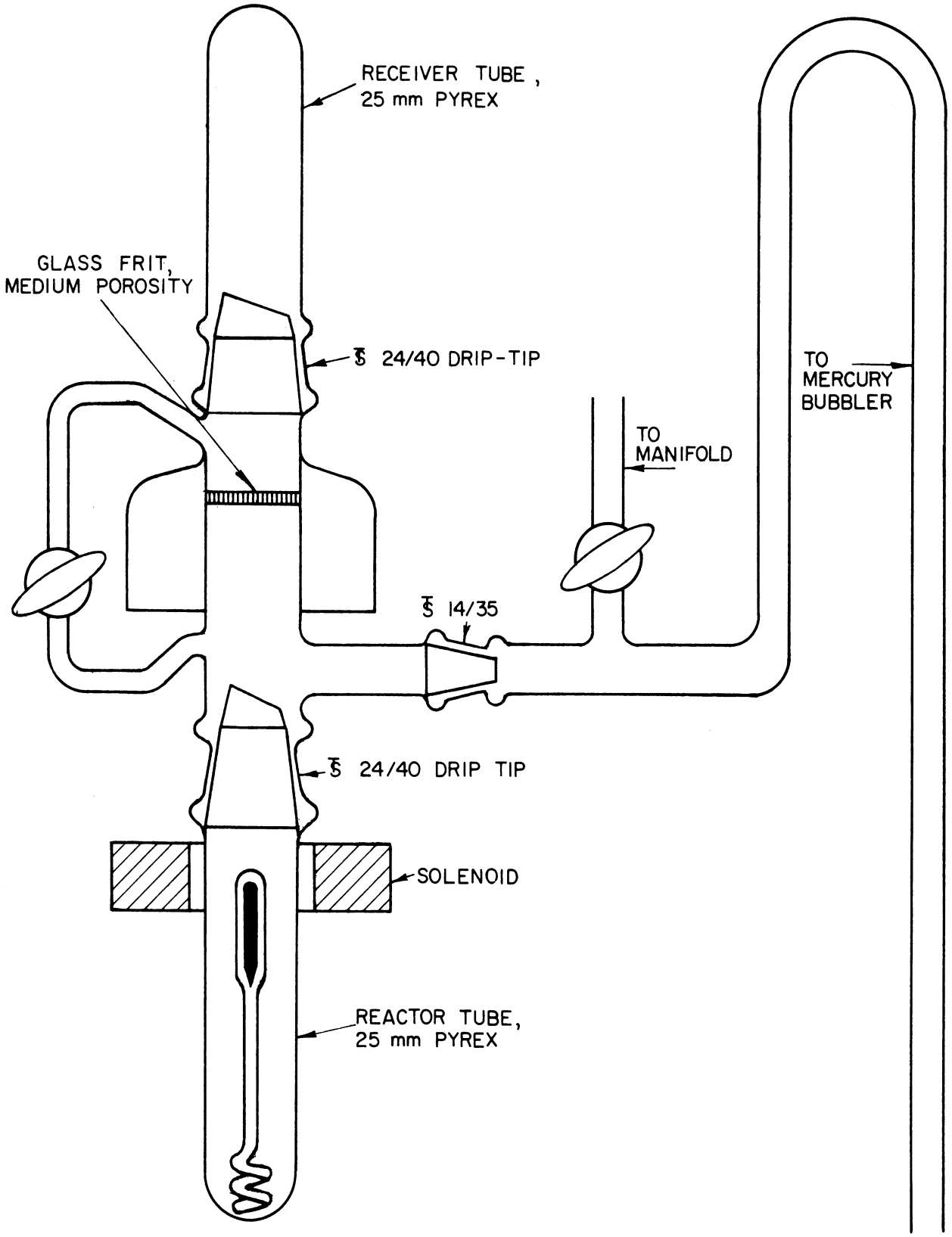


Fig. 3. Vacuum line filtration apparatus.

reaction tube so that it could be maintained at temperatures below -78°C until reaction was effected. For studies directed toward the synthesis of pure $[H_2B(NH_3)_2]Cl$, larger samples of diammoniate of diborane were prepared; then smaller aliquots were transferred to the reaction tube for use. Approximately 3 ml of anhydrous dimethyl ether was condensed onto the solid $B_2H_6 \cdot 2NH_3$, and this mixture was stirred with the conventional magnetically operated "hopper stirrer" until a uniform suspension was obtained. Then the desired quantity of previously dried HCl, ranging from an equivalent amount to a 5-fold excess, was dissolved in 1 ml of dimethyl ether and the solution was condensed onto the suspension. Hydrogen was evolved rapidly at first, then very slowly. In earlier runs where hydrogen evolution was measured, the reaction mixture was frozen down with liquid nitrogen and H_2 was pumped from the reaction vessel for measurement. When hydrogen evolution amounted to less than 0.1 millimole/hour, the reaction mixture was filtered at -78°C. The washed precipitate was extracted with ammonia and the solvent NH_3 was sublimed away leaving a white residue. The residue was identified as $[H_2B(NH_3)_2]Cl$ which was contaminated by small amounts of NH_4Cl. X-ray powder patterns served as the basis for identification. The X-ray capillary was loaded in a dry box and sealed at both ends to prevent hydrolysis of the sample during a 10- to 12-hour exposure period. $Cu_{K\alpha}$ radiation was used. Representative data are contained in Table II.

TABLE II

THE REACTION OF $B_2H_6 \cdot 2NH_3$ WITH HCl IN DIMETHYL ETHER

EVIDENCE AGAINST THE EXISTENCE OF DIAMMONIATE (II) OR $[HB(NH_3)_3](BH_4)_2$

Sample Diammoniate II	mmoles B_2H_6	mmoles HCl	Vol $(CH_3)_2O$ Solvent	Time	H_2 Evolved mmoles H_2 / B_2H_6	Product
Prepared *in situ*	2.16	9.9	3-5 ml	2 hr	1.18	$H_2B(NH_3)_2Cl$ + NH_4Cl as Impurity
				5 hr	1.33	
Prepared *in situ*	4.82	7.9	3-5 ml	1.5 hr	1.08	$H_2B(NH_3)_2Cl$ + NH_4Cl as Impurity
				5 hr	1.23	

All reactions at -78°C

4. STUDIES ON THE AMMONOLYSIS OF THE RESIDUES RESULTING FROM THE REACTION OF AN ALKALI METAL WITH "THE DIAMMONIATE OF DIBORANE" IN LIQUID AMMONIA

(a) Background

Reports by Schaeffer, Adams, and Koenig[13] and independent observations in this laboratory[20] indicated that the solid residues from the alkali metal-

diammoniate reaction (these are MBH_4 and H_2NBH_2) reacted with NH_3 at room temperature and below to give off H_2. A tracer study[15f] showed that such hydrogen arises from the interaction of a hydridic hydrogen attached to boron and a protonic hydrogen attached to nitrogen. The equation assigned to the process in this and other laboratories was:

$$H_2BNH_2 + NH_3 \longrightarrow HB(NH_2)_2 + H_2$$
$$+$$
$$NH_3 \longrightarrow B(NH_2)_3 + H_2$$

Although this equation appeared to be consistent with all earlier data on the ammonolysis reaction, it appears questionable when critically compared with analogous systems. In the first place, the ready reaction between the very slightly acidic ammonia and the residue $(H_2NBH_2)_n$ seems inconsistent with the properties expected for $(H_2NBH_2)_n$, particularly when it is compared with the formally analogous compound $(N_2BNHCH_3)_3$. The latter compound will float on a slightly acidic water solution at room temperature with only very slow hydrolysis. Complete hydrolysis is effected by a relatively long exposure to a boiling 20% hydrochloric acid solution. On the other hand, the equation written above postulates a reaction between H_2NBH_2 and the weakly acidic NH_3 molecule at temperatures below 25°C. The contrast in properties assumed for $(H_2NBH_2)_n$ and $(CH_3HNBH_2)_3$ seems remarkable.

Other observations are equally disturbing. Schaeffer, Adams, and Koenig[13] reported that the presence of an alkali metal borohydride with $[H_2NBH_2]_n$ could promote hydrogen evolution. $LiBH_4$ was very effective while KBH_4 was relatively ineffective; $NaBH_4$ occupied an intermediate position. It was suggested that an explanation for the differences might be based upon the relative abilities of $LiBH_4$ and KBH_4 to form stable ammoniates and hold ammonia in the reaction zone as the temperature of the system was raised. The foregoing uncertainties in observation and interpretation suggested that a careful experimental reexamination of the system might be appropriate.

(b) Experimental

A mixture of H_2NBH_2 and KBH_4 was prepared in liquid ammonia by allowing $[H_2B(NH_3)_2][BH_4]$ to react with a slight excess of potassium in about 2 cc of liquid ammonia. A sample containing 1.846 millimoles of $B_2H_6 \cdot 2NH_3$ was prepared; 0.922 millimole of H_2 was evolved in 75 minutes; then gas evolution stopped. After reaction was complete, all excess potassium was removed quantitatively by amalgamating it with about 0.7 cc of liquid mercury at -35°C. The solution was filtered to separate the alkali metal amalgam; then the solvent was removed from the filtrate at -78°C. The mixture of KBH_4 and H_2NBH_2 was transferred under nitrogen to a dry box where it could be weighed.

In a separate reaction vessel a sample (1.09 millimoles) of commercial $LiBH_4$ was attached to the vacuum line and dissolved in 1 cc of liquid ammonia.

Hydrogen, which evolved very slowly, was measured. After 24 hours a sample mixture consisting of .07 millimole of KBH_4 and .07 millimole of H_2NBH_2 was weighed in the dry box and introduced into the system under dry nitrogen. The entire mass was dissolved in liquid ammonia; then the solvent was distilled away and the system was allowed to warm to room temperature in contact with gaseous ammonia (1 atm). Data in Fig. 4 show that hydrogen evolution was extremely slow under these conditions, less than .018 mmole of H_2 being evolved from .07 mmole of H_2NBH_2 in 18 hours at room temperature.

While dry nitrogen was allowed to flow through the system, a glass bulb containing a slight excess of sodium was broken into the reaction vessel. The reactor was then evacuated and the system frozen with liquid nitrogen. Ammonia was distilled into the reactor and the entire reaction mass was completely dissolved in liquid ammonia at -78°C. The solvent was then removed at -78°C; then the solid residue was warmed up to room temperature in the presence of one atmosphere of ammonia vapor. As shown in Fig. 4, hydrogen evolution was rapid at room temperature as soon as sodium was added. Even in the presence of sodium, gas evolution was slow at -78°C. The data indicate unequivocally that sodium metal rather than MBH_4 was effective in promoting gas evolution at room temperature.

(c) Discussion

If, as suggested by Schaeffer, Adams and Koenig, the reaction between H_2BNH_2 and ammonia were catalyzed by the presence of a metal borohydride which served to hold the ammonia in the reacting mass, gas evolution should have been rapid when H_2BNH_2, KBH_4, NH_3 and excess $LiBH_4$ were present in the same vessel at room temperature. The fact that hydrogen evolution was slow under these conditions can be taken as strong evidence against the above explanation. On the other hand, the role of the alkali metal in hydrogen evolution seems well established by the foregoing data, particularly when one notes that in the work of Schaeffer, Adams, and Koenig excess alkali metal was not removed prior to ammonolysis reaction. With this point in mind, one notes that the earlier data are consistent with the somewhat more detailed studies described here. When excess alkali metal was rigorously removed from the system by mercury extraction, N_2BNH_2 and $LiBH_4$ reacted very slowly with gaseous ammonia at room temperature. Addition of sodium metal accelerated the reaction in a dramatic fashion.

On the basis of the above experimental evidence, the following speculative explanation may be advanced. It is postulated that the free alkali metal in the system reacts with H_2NBH_2 in accordance with the equation shown below to give a compound comparable to the "base" $Na_2[BH(CH_3)_2]$ described by Burg and Campbell:[23]

$$2Na + H_2BNH_2 \longrightarrow Na_2(H_2BNH_2)$$

(23) A. B. Burg and G. W. Campbell, Jr., J. Am. Chem. Soc. 74, 3744 (1952).

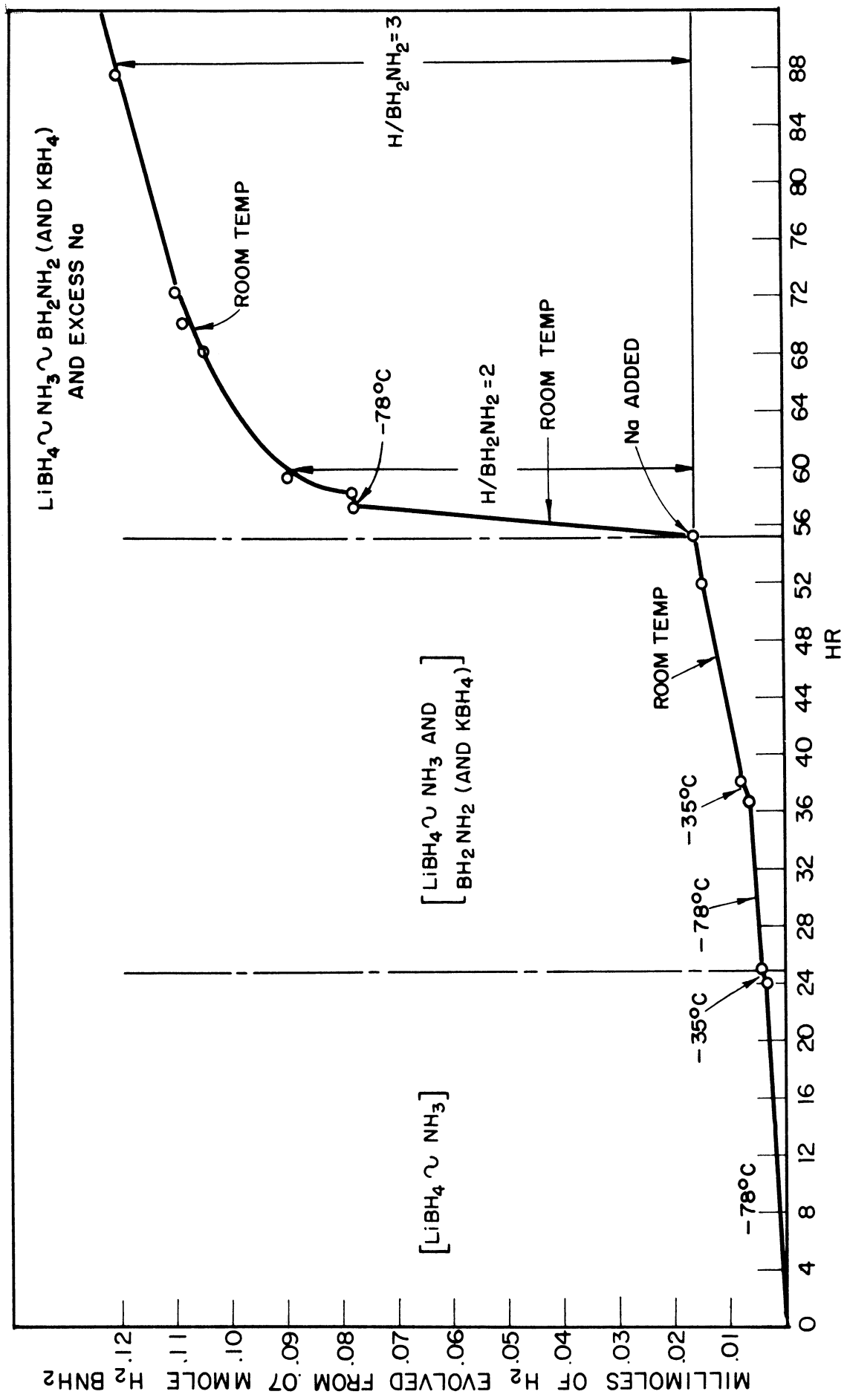


Fig. 4. Rate of hydrogen evolution in the system KBH_4-H_2BNH_2-NH_3.

Burg and Campbell found that the lone hydrogen bound to boron in their compound was extremely hydridic in character. Some evidence was accumulated which can be interpreted as indicating ammonolysis of $Na_2[HB(CH_3)_2]$ at temperatures as low as -50°C. In view of these observations ammonolysis of the related compound $Na_2[H_2BNH_2]$ at room temperature would not be surprising. The following ammonolysis equations can be written:

$$Na_2(H_2BNH_2) + NH_3 \xrightarrow{R.T.} Na_2[HB(NH_2)_2] + H_2$$

The above process would produce 1 molecule of H_2 per molecule of BH_2NH_2 present (or $2H/BH_2NH_2$); the formula suggests that a change in hydrogen evolution rate might be observed when this step is completed. Such a change in rate of hydrogen evolution is noted where the ratio of H_2/H_2BNH_2 is equal to 1 (or H/H_2BNH_2 = 2; Fig. 4). The next step in the process would be:

$$Na_2[HB(NH_2)_2] + NH_3 \xrightarrow{R.T.} Na_2[B(NH_2)_3] + H_2$$

On the basis of the above equation a maximum of $2H_2$ molecules per molecule of H_2BNH_2 should be obtained or 2-1/2 H_2 molecules per original molecule of $B_2H_6 \cdot 2NH_3$. Schultz[14] observed as much as 2.15 H_2 molecules per original molecule of $B_2H_6 \cdot 2NH_3$, and the data in Fig. 4 indicate that slow H_2 evolution is continuing even after the total ratio of $H_2/B_2H_6 \cdot 2NH_3$ exceeds 1.5 [or H/H_2BNH_2 = 3 (Fig. 4)].

If the compound $Na_2[B(NH_2)_3]$ were unstable at room temperature and dissociated in accordance with the equation

$$Na_2[B(NH_2)_3] \longrightarrow 2Na + B(NH_2)_3$$

a small amount of alkali metal could well be catalytic for hydrogen evolution. Alternatively, sodium could be consumed in the reaction. More data are needed on this point.

If one recalls that $LiBH_4$ is very proton-sensitive, $NaBH_4$ less so, and KBH_4 stable even in water solution, it is not difficult to rationalize Schaeffer's observation regarding the ammonolysis rates for the residues resulting from the reaction of Li, Na, or K with $B_2H_6 \cdot 2NH_3$. The relative proton sensitivity of $Li_2(H_2BNH_2)$, $Na_2(H_2BNH_2)$, and $K_2(H_2BNH_2)$ would decrease quite rapidly from Li to K; hence the rate of the ammonolysis reaction would be expected to fall sharply as was reported.[13]

The above arguments are definitely speculative; isolation of pure compounds of the form M_2BH_3, $M_2BH_2NH_2$, $M_2BH(NH_2)_2$, and $M_2B(NH_2)_3$ could provide a more definite test for the process proposed.

C. Halide Salts of the General Form $[H_2B(NH_3)_2]X$

1. PREPARATION OF SALTS CONTAINING THE COMPLEX CATION $[H_2B(NH_3)_2]^+$

(a) The Solid Phase Reaction of $B_2H_6 \cdot 2NH_3$ and NH_4^+ Salts

The first halide salt containing the complex cation $[H_2B(NH_3)_2]^+$ was prepared by Schultz[14] using the solid phase reaction between ammonium bromide and the diammoniate of diborane, $[H_2B(NH_3)_2]BH_4$. The equation is

$$[H_2B(NH_3)_2][BH_4] + 2NH_4Br \longrightarrow 2[H_2B(NH_3)_2]Br + 2H_2$$

A mixture of $[H_2B(NH_3)_2]BH_4$ and NH_4Br was completely dissolved in about 5 cc of liquid ammonia and held for 2 hours with continuous stirring at low temperatures ranging from -78.5 to -35 (-63.5 was used in most runs). Under these conditions hydrogen evolution was negligible. Solvent ammonia was then sublimed from the solid mixture and the temperature was raised slowly to that of the room. Hydrogen was removed with a Toepler pump; the residue was redissolved in ammonia; after stirring ammonia was again removed; the system was warmed up and H_2 was measured. This cycle was repeated 3 to 5 times. The product prepared by the above procedure was pure enough to permit original identification of the salt, but not as pure as the product obtained by the method of Kodama[24] described in the last procedure of this section.

(b) The Reaction of $B_2H_6 \cdot 2NH_3$ with HX in Ethers

In an earlier section the reaction occurring in dimethyl ether between $B_2H_6 \cdot 2NH_3$ and HCl was described in some detail. The product always showed NH_4Cl contamination. A number of other ether solvents have been investigated in an effort to prepare $[H_2B(NH_3)_2]Cl$, free of NH_4Cl.

A suspension of $B_2H_6 \cdot 2NH_3$ in diethyl ether reacted too slowly with HCl at -78°C to provide a basis for the synthesis of $[H_2B(NH_3)_2]Cl$.

Use of Ansul 121 polyether (1, 2 dimethoxyethane), dried over $LiAlH_4$ at room temperature, required a slight modification of the previously described procedure. Because of the higher melting point of the polyether, the reaction was carried out at -63°C (chloroform slush) until hydrogen evolution ceased (about 2 hours). Under these conditions diborane produced in the primary reaction was attacked readily by HCl, and BCl_3-etherate contaminated the product. The polyether was removed by distillation at -45°C; then diethyl ether was condensed into the crude salt mixture and stirred at -63°C. The contaminating Et_2OBCl_3 was removed in the filtrate; the precipitate was washed with excess Et_2O to remove last traces of Et_2OBCl_3; then $[H_2B(NH_3)_2]Cl$ was extracted from

(24) G. Kodama, Ph.D. dissertation, Univ. of Mich. (1957).

the washed precipitate using liquid ammonia in the usual manner. $[H_2B(NH_3)_2]Cl$ prepared in Ansul 121 showed no lines for NH_4Cl in the X-ray powder pattern.

The same procedure was used with Ansul 141 (diethyleneglycol dimethyl ether) except that ether had to be distilled from the reaction mixture in the vacuum system at room temperature instead of at -45°C.

Data are contained in Table III.

(c) The Reaction of $B_4H_{10}\cdot 2NH_3$ and Acids in Diethyl Ether

By methods to be described in a subsequent section, Kodama[24] in this laboratory synthesized the compound $B_4H_{10}\cdot 2NH_3$. Chemical evidence cited in a later section led unequivocally to the structure $[H_2B(NH_3)_2](B_3H_8)$ for this compound. A reaction at -78°C between an acid HX and the ether soluble compound $B_4H_{10}\cdot 2NH_3$ in diethyl ether gives the ether insoluble salt $[H_2B(NH_3)_2]X$. The equation is:

$$[H_2B(NH_3)_2][B_3H_8] + HX \xrightarrow[-78°]{Et_2O} [H_2B(NH_3)_2]X\downarrow + H_2 + Et_2OB_3H_7$$

Kodama[24] prepared pure $[H_2B(NH_3)_2]Cl$ and $[H_2B(NH_3)_2]Br$ by this procedure. Heitsch[25] working on this contract prepared and characterized a relatively pure iodide salt. Yamauchi[26], working in this laboratory, prepared a salt which has been tentatively identified as the fluoride $[H_2B(NH_3)_2]F$, although its complete characterization has been complicated by difficult analytical problems. Procedures which have given satisfactory products for each halide salt are described below.

(1) $[H_2B(NH_3)_2]Cl$.—In a typical run a 1.84-millimole sample of $B_4H_{10}\cdot 2NH_3$ was placed in the reaction tube of a vacuum filtration assembly and dissolved in about 2 ml of diethyl ether. The solution was frozen with liquid nitrogen and a 1.78-millimole sample of HCl was condensed into the tube. When the temperature was raised from -196 to -78°C, very rapid evolution of hydrogen gas and formation of a white precipitate were observed. In 15 minutes, 1.74 millimoles of H_2 gas was liberated; then gas evolution almost stopped. Even if an excess of HCl were used, H_2 gas evolution was relatively slow (see Fig. 17) after 1 mole of H_2 had been evolved from 1 mole of $B_4H_{10}\cdot 2NH_3$. The white precipitate was separated by filtration in the vacuum line filter system (Fig 3). The filter cake was washed with diethyl ether; then the receiver was changed and the precipitate was washed through the filter disc with liquid ammonia. Removal of the solvent ammonia at -45°C left 119 mg of the compound $[H_2B(NH_3)_2]Cl$ or a recovered yield of 79%, based on the $B_4H_{10}\cdot 2NH_3$ used.

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(25) C. Heitsch, doctoral dissertation, Univ. of Mich. To be published.

(26) M. Yamauchi, doctoral dissertation, Univ. of Mich. To be published.

TABLE III

THE PREPARATION OF $[H_2B(NH_3)_2]Cl$ FROM $B_2H_6 \cdot 2NH_3$ AND HCl IN VARIOUS ETHERS

	Sample $B_2H_6 \cdot 2NH_3$	mmoles $B_2H_6 \cdot 2NH_3$	mmoles HCl	Vol. and Identity of Ether	H_2 Evolved Time, min.	H_2 Evolved mmoles H_2 / $B_2H_6 \cdot 2NH_3$	Purity Solid $H_2B(NH_3)_2Cl$
1.	Prepared <u>in situ</u>	1.97*	10.35	$(CH_3)_2O$ (5 ml)	30	0.86	Traces of NH_4Cl (X-ray)
					60	0.89	(99.5%) analysis
2.	Taken from stock	1.9*	10.41	$(CH_3)_2O$ (5 ml)	40	1.15	Traces of NH_4Cl
					60	1.20	impurity from
					135	1.36	X-ray
3.	<u>In situ</u>	1.7	10.0	$(CH_3)_2O$ (5 ml)	30	1.0	Trace of NH_4Cl
					60	1.06	X-ray
					90	1.12	
4.	<u>In situ</u>	1.7	4	Ansul 121	45	0.64	No NH_4Cl but
					60	0.75	other impurities
					90	1.10	present (X-ray)
					11 hr	1.91	
5.	<u>In situ</u>	2.06	3.4	$(CH_3)_2O$ (5 ml)	15	0.87	Trace of NH_4Cl
					75	0.95	
					570	1.07	
6.	Stock**	1.29	2.1	Ansul 121 (4 ml)	120	1.78	
7.	Stock**	1.37	2.3	Ansul 141 (4 ml)	120	1.83	Pure sample No NH_4Cl
8.	Stock**	6.81	8.9	Ansul 121 (15 ml)	135	1.13	

*Small sample removed for X-ray powder pattern 0.1 mmole

**Reaction run at -63°C. Others at -78°

(2) $[H_2B(NH_3)_2]Br$.—A 0.64-millimole sample of $B_4H_{10}\cdot 2NH_3$ was allowed to react at -78°C with 3.83 millimoles of HBr in about 7 ml of diethyl ether. The procedure was identical to that given above. The hydrogen gas amounted to 0.64 millimole. After filtering the solid and washing it with 2 cc of diethyl ether, it was kept under high vacuum for one hour, then washed through the filter disc with liquid ammonia. Most solvent was removed at -78°C but the last traces were pulled off under vacuum at room temperature. The solid product was 0.50 millimole of $[H_2B(NH_3)_2]Br$ or a recovered yield of 79% based on the $B_4H_{10}\cdot 2NH_3$ used.

(3) $[H_2B(NH_3)_2]I$.—Hydrogen iodide was prepared by the reaction:

$$H_2 + I_2 \xrightarrow[500\text{-}600°C]{Pt} 2HI$$

The procedure used was a modification of that described in Inorganic Synthesis, Vol. 1, p. 159. The apparatus is shown in Fig. 5. A is a catalytic deoxygenator attached to the pressure reduction valve on the hydrogen tank. B is a Pyrex tube filled with P_2O_5; D is a Vycore reaction tube. A layer of glass wool near the inlet of the reaction tube was covered with (a) a layer of iodine crystals (Mallinkrodt Analytical Reagent), (b) a second layer of glass wool, (c) a layer of platinized asbestos, and (d) a final layer of glass wool. Joints at a, b, and g were closed with Tygon tubing. Joints d and f were sealed with de Khotinsky cement. Joint e and stopcock g were lubricated with Dow-Corning High Vacuum Silicone grease.

The furnace, E, was raised so that it surrounded the platinized asbestos but was above the iodine layer. The temperature of the furnace was then raised to 200°C and the platinized asbestos was dried in a hydrogen stream for one hour. During this period a stream of cold air was directed against the outside of that part of the tube which contained the iodine. This reduced sublimation of iodine during the drying of the asbestos. After the drying operation the furnace was dropped down around the iodine layer, its temperature was raised to 600°C, and the exit gas stream was diverted through the cold trap H (-78°) and into a trap on the vacuum system chilled with liquid N_2 (-196°C). The product from the -196° trap was sublimed through a trap cooled to -78°C and into a trap cooled to -196. The sublimation was repeated. The purified material showed no color due to iodine and had a vapor pressure of 170 mm at -63.5°C [chloroform slush]. Stull[27] reports a value of 165 mm at this temperature. The product was stored at -190°C until used.

The reaction between HI and $B_4H_{10}\cdot 2NH_3$ was carried out in the same fashion as that described for the reactions of $B_4H_{10}\cdot 2NH_3$ with HCl and HBr. The stoichiometry of hydrogen evolution was not as clean-cut as that in the two preceding cases, apparently because of the instability of HI in high-vacuum manipulation. In a typical run about 1 gram of crude $B_4H_{10}\cdot 2NH_3$ (see p. 101 for its synthesis) was leached with dry diethyl ether (about 10 cc) through a medium porosity frit into a weighed tube on the vacuum line. The solvent ether was then removed and the tube was filled with dry nitrogen and stoppered. The tube and pure crystals

(27) D. R. Stull, Ind. and Eng. Chem. 39, 517 (1947).

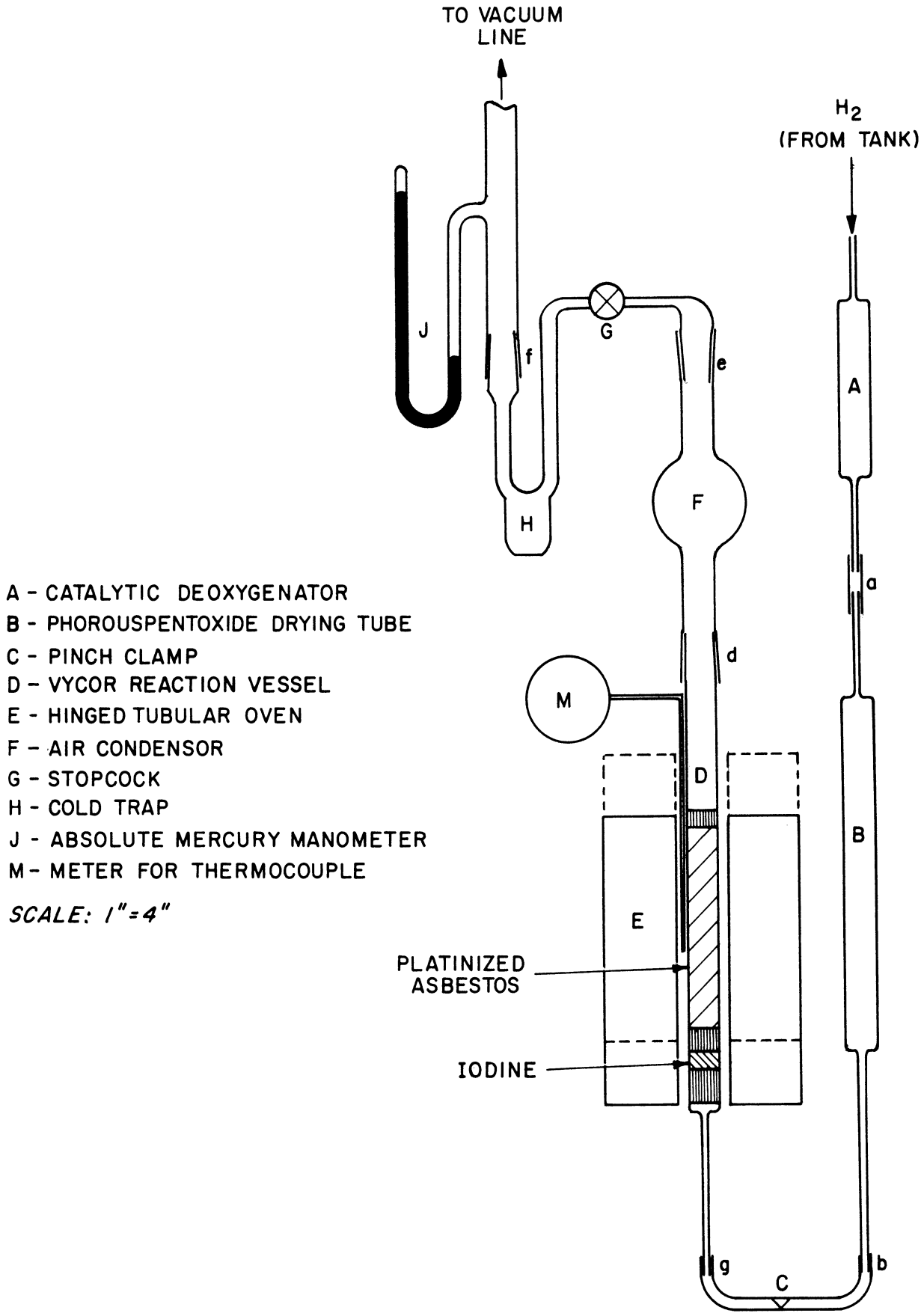

Fig. 5. Apparatus for the preparation of hydrogen iodide.

were carefully weighed. The weight corresponded to 10.1 millimoles of $B_4H_{10}\cdot 2NH_3$. The tube was replaced on the vacuum filtration apparatus and about 10 cc of dry diethyl ether was distilled into the system; then a mixture of 11.5 millimoles of HI and 5 cc of ether was distilled into the system. The mixture was then warmed from -190° to -78°C. Stirring was started as soon as the reaction mass became sufficiently fluid. Hydrogen evolution proceeded for about 2 hours. Then the rate of gas discharge dropped rapidly to almost zero. The mixture was filtered; the ether insoluble $[H_2B(NH_3)_2]I$ was washed with more ether and finally leached into a clean tube with anhydrous liquid ammonia. A total sample consisting of 1.52 grams of salt was recovered from the tube representing a yield of 87% based on the $B_4H_{10}\cdot 2NH_3$ used. The X-ray powder patterns showed weak lines for NH_4I.

(4) $[H_2B(NH_3)_2]F$ or Perhaps $[H_2B(NH_3)_2[BF_4]$.—A 2.12-millimole sample of $[H_2B(NH_3)_2](B_3H_8)$ was dissolved in 3 ml of diethyl ether in a translucent teflon tube which could be attached to the copper vacuum line. An excess of HF (about 3 millimoles), dried over commercial anhydrous CoF_3, was condensed about an inch above the solution and this was allowed to warm up slowly to -78°C with constant stirring. Rapid evolution of H_2 (identified by molecular weight measurements) took place. The amount of H_2 evolved could not be measured in this system. The ether solvent was removed at -78°C and the white residue was transferred under dry nitrogen to the vacuum filter system. The residue was washed with toluene, and diethyl ether then extracted with dimethyl ether. The solid extracted by Me_2O has been difficult to characterize by conventional techniques because of analytical difficulties. The best evidence to date suggests that it is $[H_2B(NH_3)_2]F$ or $[H_2B(NH_3)_2](BF_4)$.

(d) General Observations on the Synthesis of Salts of the Cation $[H_2B(NH_3)_2]^+$

One of the most common contaminants of $[H_2B(NH_3)_2]X$ salts is the corresponding ammonium halide, NH_4X. In general it seems that the more soluble the original diammoniate of diborane or tetraborane in the suspending solvent the less the contamination of the resulting product. For example, both bromide and chloride salts, prepared by the solid phase reaction between $B_2H_6\cdot 2NH_3$ and NH_4X, are contaminated with ammonium salts. $B_2H_6\cdot 2NH_3$ has very low solubility in diethyl ether; the reaction with HCl in this solvent was too slow for practical use and the product obtained was of low purity. Dimethyl ether is a somewhat better solvent for $B_2H_6\cdot 2NH_3$, and the resulting chloride salt, $[H_2B(NH_3)_2]Cl$, was fairly good but always contaminated with NH_4Cl. Finally, $B_2H_6\cdot 2NH_3$ is fairly soluble in Ansul 121 and 141 and the resulting product was always free of ammonium salts. These generalizations seem to be applicable as well to the reactions using $B_4H_{10}\cdot 2NH_3$ as a starting material since $B_4H_{10}\cdot 2NH_3$ is soluble in diethyl ether and the products obtained from this reaction system were always of relatively high purity.

2. CHARACTERIZATION OF THE HALIDE SALTS OF THE $[H_2B(NH_3)_2]^+$ CATION

Analytical data and molecular weight values have been obtained for all the halide salts described in the preceding section. Analytical results are sum-

marized in Table IV and analytical procedures are described below.

TABLE IV

SUMMARY OF ANALYTICAL DATA FOR THE CHARACTERIZATION OF THE $[H_2B(NH_3)_2]X$ SALTS

Salt		%B	% Hydridic H	%N	% Halide	Mol. Wt.	Solvent
$[H_2B(NH_3)_2]I$	Obs.	6.15	1.09	19.50	-	170	Ammonia
	Theor.	6.22	1.16	19.59	-	173.8	
$[H_2B(NH_3)_2]Br$	Obs.	8.46	1.59	22.15	62.5 Br^-	120	Ammonia
	Theor.	8.53	1.59	22.10	63.0 Br^-	127	
$[H_2B(NH_3)_2]Cl$	Obs.	13.2	2.42	33.9	42.7 Cl^-	95	Ammonia
	Theor.	13.1	2.44	34.0	43.0 Cl^-	82.3	
$[H_2B(NH_3)_2]F$	Obs.	*	*	*	*	90-120 above 200	Ammonia $(Me)_2O$
	Theor.	16.4	3.05	42.5	28.9 F^-	65.8	

*Problems of obtaining reliable analysis for B, N, H in presence of F not yet resolved. Identity of sample still very uncertain.

(a) Analysis for Hydridic Hydrogen

The sample was sealed with acid (usually 6N HCl) into a tube equipped with a break-off tip. The tube and contents were then heated in a 150°C oil bath for a period of about 3 days. The hydrogen gas was measured in the vacuum system by use of a Toepler pump and a gas burette.

(b) Analysis for Boron

A modification of the so-called identical pH method proposed by Foote[28] was used. The method permits the titration of boron in the presence of ammonium and substituted ammonium salts. The reliability of the procedure was considered by Bissot[29] and the magnitude of errors established. The method consists of adjusting the pH of the solution to a value of 6.7, then adding an excess of reagent such as mannitol to complex the boron, and titrating the liberated H^+ with .05N NaOH. A Beckman, Model F pH meter with a glass electrode was used to follow the pH values.

(28) F. J. Foote, Ind. Eng. Chem., Anal. Ed., 4, 39 (1932).

(29) T. H. Bissot, Ph.D. dissertation, Univ. of Mich. (1955).

(c) Analysis for Nitrogen

Nitrogen was determined using standard micro-Kjeldahl methods.[30] The Beckman pH meter described above was used for titrations. Solutions of 0.01 N H_2SO_4 and .05 N NaOH were used.

(d) Analysis for Halogens

Bromide and chloride were determined as silver halides by standard gravimetric procedures. No satisfactory procedure for the determination of fluoride in these compounds has yet been obtained.

(e) Molecular Weight Measurements

The procedure used has been described in detail elsewhere.[31] Occasional changes in thermostating liquids were demanded for some systems. The apparent molecular weight is shown as a function of concentration for each of the salts in Fig. 6.

(f) Comments on the "Fluoride" Salt

Since all results on the assumed fluoride salt are unsatisfactory at the present time, its characterization must be considered incomplete. The strongest argument supporting its identity is its use in a metathesis reaction to prepare $[H_2B(NH_3)_2]BH_4$. Work on its complete characterization is still in progress.

(g) X-ray Powder Patterns

See next section.

3. THE CRYSTAL STRUCTURE OF $[H_2B(NH_3)_2]^+$ SALTS

Although a large amount of chemical evidence has been amassed to support the existence of the cation $[H_2B(NH_3)_2]^+$, no independent and unequivocal physical evidence has yet been presented in support of the identity of this ion. The following independent structural information, provided by single-crystal and powder X-ray methods, leaves no room for reasonable doubt regarding the identity of the $[H_2B(NH_3)_2]^+$ cation.

(30) J. B. Niederl and V. Niederl, Micromethods of Quantitative Organic Analysis, John Wiley and Sons, N. Y., 1948.

(31) R. W. Parry, et al., Chemistry of the Boron Hydrides and Related Hydrides, WADC Tech. Report 56-318 (1956), p. 85. See also J. Am. Chem. Soc. 80, 24 (1958).

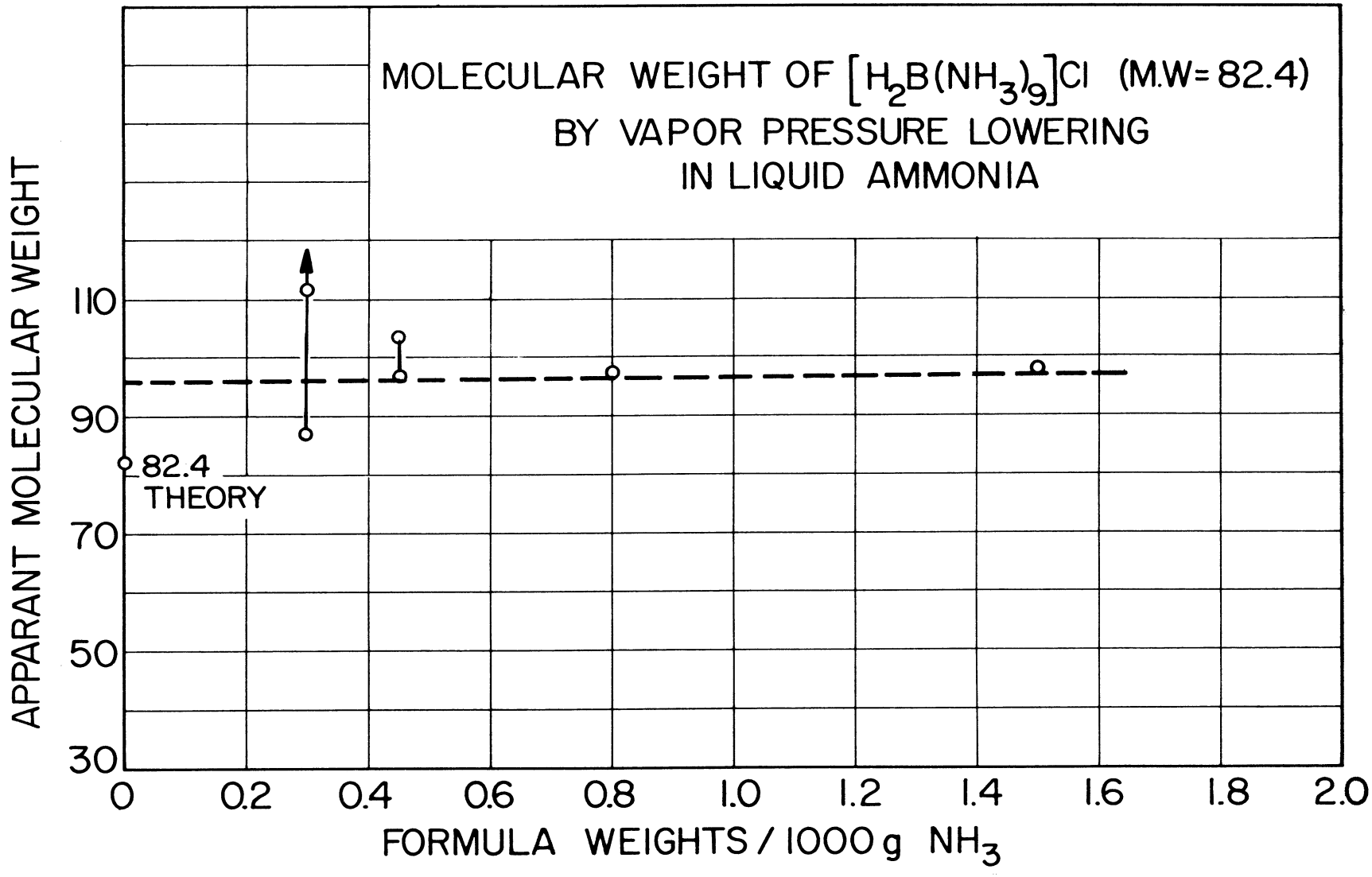

Fig. 6a. Molecular weights of the halide salts of the cation $[H_2B(NH_3)_2]^+$.

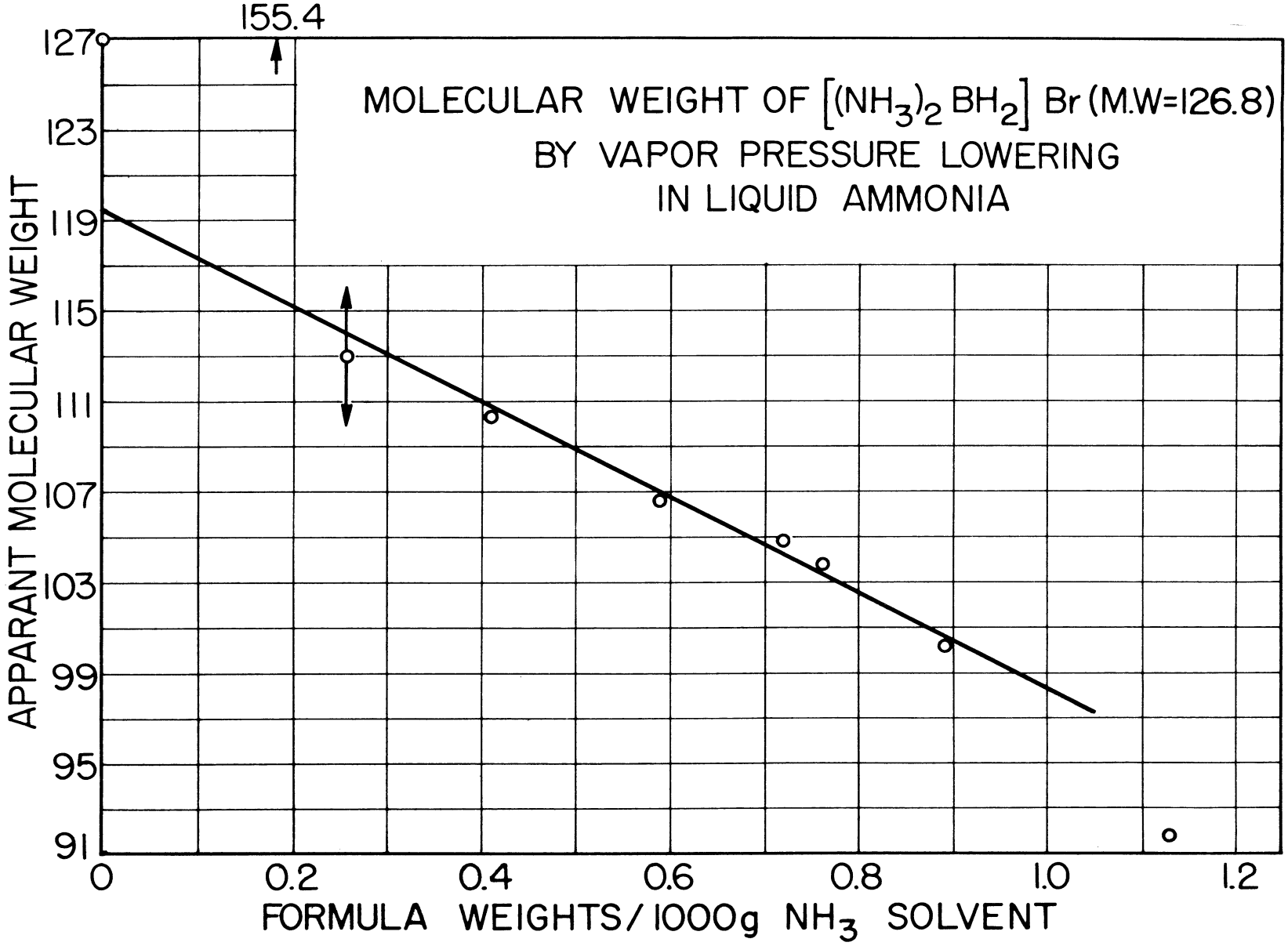

Fig. 6b. Molecular weights of the halide salts of the cation $[H_2B(NH_3)_2]^+$.

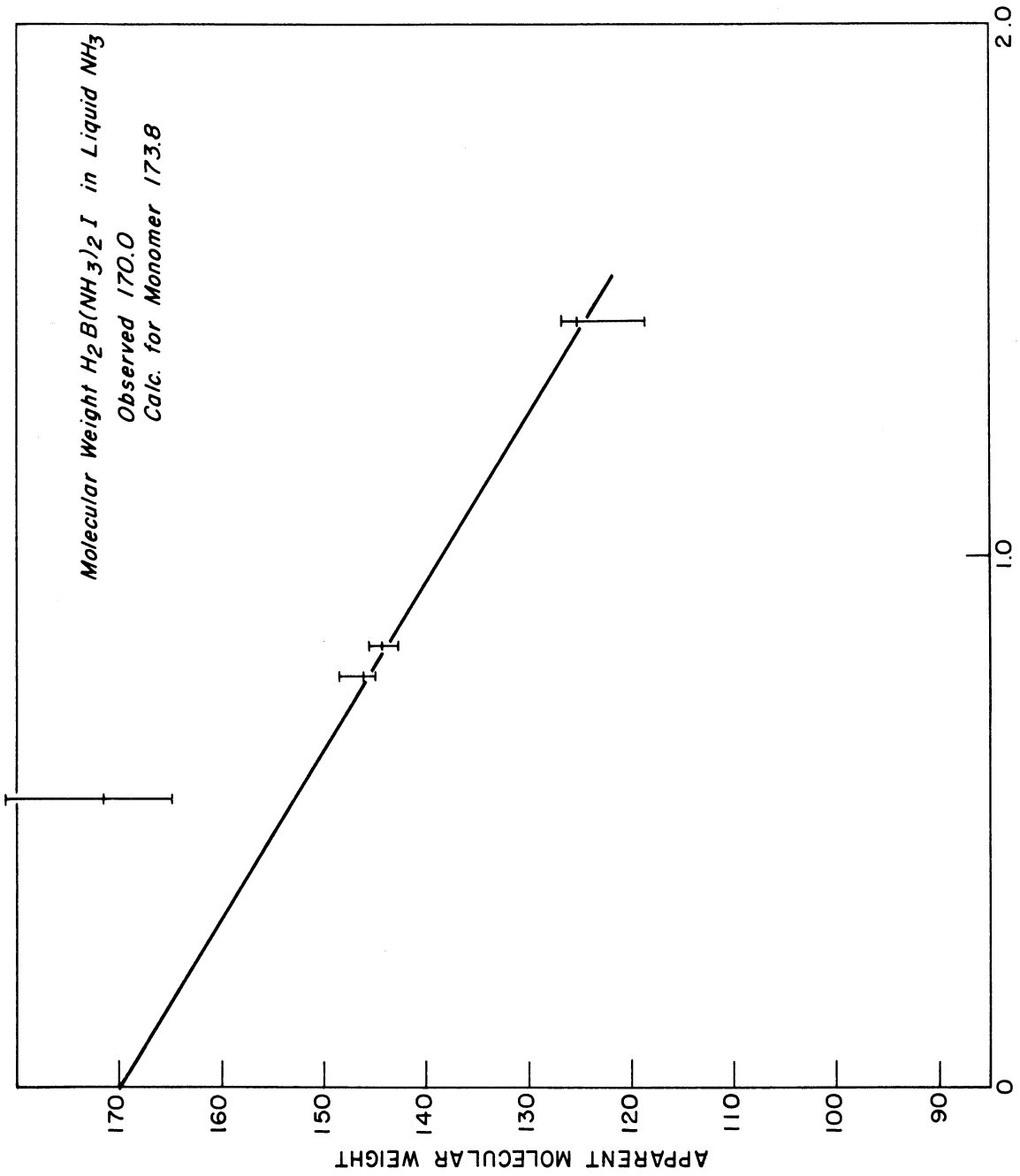

Fig. 6c. Molecular weights of the halide salts of the cation $[H_2B(NH_3)_2]^+$.

(a) The Crystal Structure of $[H_2B(NH_3)_2]Cl$ as Determined by Single-Crystal X-ray Studies

Nordman and Peters,[32] working in the University of Michigan laboratories, succeeded in the difficult task of preparing a single crystal of the chloride salt and working out an unequivocal structure for it by single-crystal X-ray methods.

(1) Experimental.—Samples of $[H_2B(NH_3)_2]Cl$ were prepared according to methods previously described from $B_4H_{10}\cdot 2NH_3$. The preparation of a single crystal suitable for X-ray work proved difficult since the compound is decomposed in solution by traces of moisture and by solvents containing protonic hydrogen. Acetone, diethyl ether, and hydrocarbons do not dissolve $[H_2B(NH_3)_2]Cl$, and crystallization from liquid ammonia yields a microcrystalline powder which gives a characteristic powder pattern, but no crystals large enough for single-crystal examination. A few imperfect single crystals were obtained, however, by dissolving the compound in Ansul 141 (diethylene glycol dimethyl ether) and layering the solution with diethyl ether. These crystals were sealed in thin-walled glass capillaries for X-ray examination. In spite of repeated attempts, only one crystal suitable for single-crystal work was obtained.

Zero-, first-, and second-level precession or Weissenberg patterns of the three principal nets were recorded using MoKα or CuKα radiation. This yielded a total of 186 independent intensities. The X-ray work was discontinued at this point due to the deterioration of the crystal.

(1.1) Unit Cell and Space Group.—The diffraction patterns showed nearly tetragonal symmetry and the axes were labeled accordingly. On the nets perpendicular to the c axis, however, systematic intensity variations were found which violated the fourfold symmetry, and led to the conclusion that the crystals were orthorhombic with two axes, a and b, of equal length. It was further observed that the only systematic absences in the hk0 net occurred when h and k were both odd. Since this is not a space group extinction, it was concluded that the crystal was a twin consisting of two fragments turned with respect to each other by 90° about the c axis. The observed absences in hk0 could then be explained as occurring for odd h in each of the fragments. Since the a and b axes were equal in length, all hk0 reflections with h and k even were overlaps of, in general, nonequivalent reflections from the two fragments. This was not the case for reflections with k odd, in view of the systematic absences for odd h. Thus, hk0 reflections with h + k odd were "pure" and afforded a means of determining the relative size, or diffractive power, of the two fragments. The ratios of the intensity of hkl, divided by the Lorentz and polarization factors, to that of khl was found to be very nearly constant for all hk0 with h + k odd, as well as for corresponding upper-level reflections. This constituted strong evidence that the crystal was indeed a twin and yielded a value for the

(32) C. Nordman and C. Peters, J. Am. Chem. Soc., in press; see earlier reports, this contract.

ratio of the sizes of the fragments.

The unit cell parameters are $\underline{a}$ = 10.20 ± 0.02 Å, $\underline{b}$ = 10.20 ± 0.02 Å, $\underline{c}$ = 8.71 ± 0.02 Å, where the limits of error are taken as three times the estimated standard deviation. The calculated density is 1.21 g/cm^3 assuming eight formula units per cell.

Systematic absences, referred to the untwinned crystal, were observed in $\underline{hkl}$ for $\underline{h}$ + $\underline{l}$ odd, in $\underline{0kl}$ for $\underline{k}$ odd and in $\underline{hol}$ for $\underline{h}$ odd. The possible space groups are then D_{2h}^{18}-Bbcm and C_{2v}^{17}-Bba2. The first of these has sixteen general positions and consequently requires at least the chloride and boron atoms to lie in special positions.

In addition to the reflections leading to the above unit cell assignment, a set of very weak and somewhat diffuse reflections was observed calling for a doubling of the $\underline{c}$ axis. The true unit cell parameters are then $\underline{a}$ = 10.20 ± 0.02 Å, $\underline{b}$ = 10.20 ± 0.02 Å, $\underline{c}$ = 17.42 ± 0.04 Å. In view of the relatively small number of clearly observable reflections in this category, no attempt was made to determine the space group applicable to the doubled cell. The reflections demanding the doubled cell were ignored in the structure analysis.

(1.2) Structure Determination.—Intensity data were obtained from the diffraction photographs by visual comparison with a series of timed exposures of spots of similar shape. Application of the Lorentz and polarization factors yielded a set of raw values of the squares of the structure factors. For every spot observed on two films, the ratios of these raw $\underline{F^2}$ values were calculated and averaged to give the ratio of the scale factors to be applied to the two films. Through appropriate averaging of such ratios the scale factors themselves were found and the raw F^2 values placed on a common scale.

Due to the twinning of the crystal, most of the values obtained were derived from spots which were overlaps of contributions from the two fragments, whereas the rest of the values arose from one or the other of the two fragments.

From the nature of the twinning and the symmetry of the reciprocal lattice, it follows that a reflection $\underline{hkl}$ from one of the fragments (A) will appear as "$\underline{khl}$" when produced by the other fragment (B). If $\underline{h}$ + $\underline{k}$ is odd, either the reflection $\underline{hkl}$ or $\underline{khl}$ produced by A must be absent, since all reflections with $\underline{h}$ + $\underline{l}$ odd are absent. For example, if $\underline{h}$ is even and $\underline{k}$ odd, a reflection with even $\underline{l}$ indexed as "khl" must in fact be the $\underline{hkl}$ reflection from fragment B. Furthermore, it must be "pure" inasmuch as it cannot contain a contribution from an overlapping reflection from A. For the same reason the reflection indexed as $\underline{hkl}$ must be a pure reflection from fragment A.

Twenty-seven independent reflections with $\underline{h}$ + $\underline{k}$ odd were observed. The ratios of the raw $\underline{F^2}$ values of these reflections $\underline{hkl}$ to the corresponding values of the reflections "$\underline{khl}$" were found to be constant within the error of measurement. The average value of this ratio, $1/\underline{r}$, expresses the size ratio, A to B, of the two crystal fragments. The value of $\underline{r}$ was found to be 0.26.

All reflections for which $h + k$ is even are overlaps of contributions from both fragments. If the raw F^2 values of these reflections are denoted $I(hkl)$, we have

$$I(hkl) = F^2(hkl) + rF^2(khl)$$

and

$$I(khl) = F^2(khl) + rF^2(hkl)$$

Consequently, the expression

$$F^2(hkl) = [I(hkl) - rI(khl)]/(1 - r^2)$$

yields the magnitudes of the individual structure factors expressed on the scale of the large fragment.

The magnitudes of the structure factors with all indices even are, on the average, considerably larger than the rest. This observation led to the conclusion that the chlorine atoms, which dominate the scattering, must lie at or near the points of a simple tetragonal lattice having one half the axial lengths of the assumed cell. The $hk0$ and $h0l$ electron density projections were therefore computed using structure factors with even indices only, with signs based on the chlorine contributions. The $h0l$ projection showed the nitrogen and boron atoms to lie in layers perpendicular to the c axis half-way between the assumed chlorine layers. This arrangement is consistent with Bbcm, the more symmetrical of the two possible space groups, if the boron and nitrogen atoms lie in mirror planes at $z = 0$ and $1/2$ and the chlorine atoms on twofold axes parallel to the c axis at $(x,y) = (0,0)$, $(0,1/2)$, $(1/2,0)$ and $(1/2,1/2)$. Since any violation of these conditions was, at most, very slight, the space group was tentatively assumed to be Bbcm.

The eightfold chlorine positions are then $(0,0,0;\ 1/2,0,1/2) + 0,0,z;\ 0,0,\bar{z};\ 1/2,\ 1/2,z;\ 1/2,1/2,\bar{z}$ where the parameter z is approximately 0.25. The nitrogen and boron atoms are located at eightfold positions of the type $(0,0,0;\ 1/2,0,1/2) + x,y,0;\ \bar{x},\bar{y},0;\ x,1/2-y,1/2;\ \bar{x},1/2+y,1/2$. Approximate x and y coordinates of the two nitrogen atoms and one boron atom were derived from the $hk0$ electron density projection. The suggested configuration was an angular N-B-N group with two approximately equal B-N distances.

The seven atomic coordinates, the scale factor k, and the isotropic temperature factor B were now refined by least-squares methods. Specifically, the quantity

$$\Sigma w(hkl)\ kF_o\ (hkl) - F_c(hkl)^2/\Sigma\ w(hkl)k^2F_o^2(hkl)$$

was minimized, where the weight $\underline{w}(\underline{hkl})$ of each reflection was taken as $3\,\underline{F}_{min}/\underline{F}\,(\underline{hkl})$ if $\underline{F}(\underline{hkl}) > 3\underline{F}_{min}$ and equal to unity otherwise

The least-squares refinement proceeded to

$$\underline{R}_1 = \Sigma|\underline{k}|\underline{F}|_o - |\underline{F}|_c|/\Sigma\underline{k}|\underline{F}|_o = 0.17$$

at which point several Fourier sections and $(F_o - F_c)$ syntheses of the electron density were computed. The chief reason for this was to check for indications of lower symmetry than that of Bbcm. Since no such indications were found, it must be concluded that the space group is Bbcm, at least to the accuracy of this determination. Anisotropy was observed in the thermal motion of the chlorine atoms, the peaks being somewhat elongated in the $\underline{z}$ direction. An anistropic temperature factor exp $-[\alpha(h^2 + k^2) + \beta l^2]$ was therefore applied to f_{Cl}- and by successive difference syntheses the best values $\alpha = -0.0030$ and $\beta = +0.0020$ were found. To account for the somewhat stronger thermal motion in the nitrogen atoms than in the boron atom, an additional temperature factor exp $(-0.75\ \sin^2\underline{\theta}/\underline{\lambda}^2)$ was applied to $\underline{f}_N$ in calculating the structure factors.

It was not possible to locate the hydrogen atoms independently; however, their presence was assumed and an approximate hydrogen contribution included in the calculation of structure factors. Two hydrogen atoms were assumed to be attached to the boron atom, and six half-hydrogens to each of the nitrogen atoms. The hydrogen scattering factors were multiplied by an additional temperature factor exp $[-1.0\ \sin^2\underline{\theta}/\lambda^2]$.

With these refinements, including several more cycles of least-squares adjustment of the seven atomic coordinates, scale and overall temperature factors were carried out. The final agreement of observed and calculated structure factors is given by

$$\underline{R}_1 = 0.137$$

and

$$\underline{R}_2 = (\underline{kF}_o - \underline{F}_c)^2/\ \underline{k}^2\underline{F}_o^2 = 0.036.$$

The observed and final calculated structure factors are listed in Table V. An additional 96 structure factors which were part of the photographed nets were found to be unobservably small. The final calculated values of these structure factors showed no significant disagreement with their observed maximum limits.

When $\underline{h} + \underline{k}$ is odd, the geometrical structure factor has the form

$$\underline{A}(\underline{hkl}) = -16\ \sin 2\pi\underline{hx}\cdot\sin 2\pi\underline{ky}\cdot\cos 2\pi\underline{lz}$$

Consequently, the chlorine atoms do not contribute to these structure factors. As a further check on the nitrogen and boron coordinates, a separate least-

TABLE V

OBSERVED AND CALCULATED STRUCTURE FACTORS FOR $[H_2B(NH_3)_2]Cl$

hkl	kFo	Fc	hkl	kFo	Fc	hkl	kFo	Fc	hkl	kFo	Fc	hkl	kFo	Fc	hkl	kFo	Fc
000	-	+352	0.12.2	15	- 17	246	20	- 24	408	22	+ 21	620	63	+ 57	880	17	+ 17
002	22	+ 37	113	34	+ 28	248	13	+ 14	410	17	- 20	622	38	- 45	882	28	- 23
004	119	+126	115	28	- 18	2.4.10	8	- 5	412	14	- 14	624	32	+ 36	8.10.0	20	+ 14
006	18	- 3	117	23	+ 18	250	19	- 18	420	75	+ 79	626	20	- 20	8.10.2	12	- 13
008	36	+ 32	119	19	- 10	252	15	- 16	422	57	- 67	628	11	+ 11	8.12.2	11	- 8
0.0.10	8	+ 1	121	47	- 48	260	75	+ 61	424	47	+ 50	630	14	+ 11	10.0.0	19	+ 23
020	89	+ 72	123	25	- 31	262	44	- 42	426	27	- 24	640	41	+ 39	10.0.2	31	- 28
022	176	-130	125	10	- 16	264	37	+ 38	428	12	+ 14	642	50	- 49	10.0.4	16	+ 17
024	35	+ 42	131	20	- 18	266	16	- 19	430	26	+ 24	650	15	- 14	10.0.6	13	- 13
026	39	- 40	141	19	- 21	268	14	+ 12	432	15	+ 19	652	13	- 13	10.2.0	24	+ 25
028	13	+ 9	161	23	- 24	280	54	+ 50	440	72	+ 76	660	68	+ 47	10.2.2	24	- 25
0.2.10	14	- 10	171	16	- 12	282	21	- 24	442	50	- 53	662	20	- 24	10.2.4	17	+ 17
040	182	+147	181	9	+ 8	284	36	+ 34	460	41	+ 36	680	36	+ 29	10.4.0	26	+ 23
042	35	- 33	200	67	+ 75	286	8	- 11	462	58	- 52	682	23	- 23	10.4.2	22	- 23
044	58	+ 69	202	110	-128	288	12	+ 11	480	27	+ 29	6.10.0	30	+ 22	10.6.0	29	+ 22
046	18	- 16	204	49	+ 43	2.10.0	28	+ 26	482	38	- 36	6.10.2	13	- 16	10.6.2	15	- 16
048	21	+ 21	206	46	- 40	2.10.2	24	- 25	4.10.0	26	+ 22	6.12.2	11	- 11	10.8.0	19	+ 14
0.4.10	6	- 2	208	15	+ 9	2.10.4	10	+ 18	4.10.2	23	- 24	711	15	- 12	10.8.2	13	- 13
060	24	+ 26	2.0.10	8	- 9	2.10.6	10	- 12	4.12.0	9	+ 15	751	11	- 9	12.0.0	17	+ 16
062	93	- 77	210	46	- 51	2.12.0	20	+ 20	4.12.2	13	- 15	771	10	+ 6	12.0.2	18	- 18
064	17	+ 18	212	31	- 40	2.12.2	10	- 13	521	15	- 17	800	36	+ 37	12.2.0	23	+ 21
066	22	- 33	220	77	+ 57	2.14.2	14	- 11	523	13	- 13	802	40	- 40	12.2.2	13	- 13
068	10	+ 5	222	134	-122	311	21	- 19	531	7	- 7	804	25	+ 23	12.4.0	15	+ 14
080	41	- 39	224	33	+ 34	321	26	+ 25	561	11	- 12	806	22	- 19	12.4.2	17	- 16
082	37	- 38	226	33	- 38	323	13	+ 17	571	11	- 10	820	57	+ 51	12.6.2	13	- 11
084	20	+ 25	228	18	+ 11	331	9	- 8	600	30	+ 31	822	19	- 23	12.8.2	9	- 9
086	11	- 18	2.2.10	7	- 7	341	22	+ 24	602	73	- 72	824	29	+ 35	14.2.2	11	- 11
0.10.0	26	+ 22	230	27	+ 27	351	9	- 8	604	21	+ 21	826	11	- 10			
0.10.2	28	- 29	232	19	+ 22	400	137	+149	606	37	- 31	840	30	+ 27			
0.10.4	13	+ 16	240	90	+ 82	402	38	- 32	608	12	+ 6	842	43	- 38			
0.10.6	12	- 13	242	69	- 65	404	73	+ 70	610	30	- 28	860	36	+ 29			
0.12.0	22	+ 18	244	43	+ 52	406	23	- 16	612	24	- 24	862	23	- 23			

squares refinement of these parameters was carried out using the 27 observed structure factors with $\underline{h} + \underline{k}$ odd only. This yielded coordinates very nearly equal to those obtained with the complete set of data, and a value of $\underline{R}_1 = 0.092$ for the set of 27 structure factors.

The final atomic coordinates (x,y,z) are (0, 0, 0.264) for Cl, (0.236, 0.064, 0) and (0.060, 0.237, 0) for N_1 and N_2, and (0.212, 0.219, 0) for B. Estimated standard deviations of these values are 0.0015, 0.002 and 0.003, respectively, for chlorine, nitrogen, and boron coordinates. The reliability of these estimates, which are based on the least-squares residuals, is doubtful since the effect of a possible error in $\underline{r}$ is unaccounted for.

(2) Discussion.—Electron density projections on (010) and (001) are shown in Figs. 7 and 8 and a perspective drawing of the structure in Fig. 9. Interatomic distances and angles are given in Fig. 10.

Each NH_3 group is surrounded by four chlorine atoms at the corners of a distorted square while each chlorine is surrounded by eight NH_3 groups belonging to six different $[H_2B(NH_3)_2]^+$ at the corners of a strongly distorted cube. The arrangement of the chlorine atoms and the N ... Cl distances indicate that the compound is ionic, namely, $[H_2B(NH_3)_2]^+Cl^-$. The four symmetrically nonequivalent distances may be compared with the N ... Cl distances in ammonium chloride (3.36 Å) and particularly methylammonium chloride[33] (3.18 Å) where the coordination is more comparable to that found in $[H_2(NH_3)_2B]Cl$. The lengthening of this distance in the present case is to be expected in view of the presumably smaller charge on each of the NH_3 groups in the $(NH_3)_2BH_2^+$ ion.

The lengths of the two N-B bonds in the cation are equal within experimental error, and also equal to the N-B bond length found in ammonia-triborane, $NH_3B_3H_7$.[34]

The complete X-ray structural analysis of $[H_2B(NH_3)_2]Cl$ leaves no question regarding the identity of the cation $[H_2B(NH_3)_2]^+$. Essentially unequivocal evidence now supports the arguments advanced earlier from the chemistry of $B_2H_6 \cdot 2NH_3$

(b) Powder Patterns and Structures for Other Halide Salts

(1) Cell Geometry.—X-ray powder patterns of $[H_2B(NH_3)_2]I$ and $[H_2B(NH_3)_2]Br$, produced by the Debye-Scherrer method, show obvious similarities in low-angle reflections with the low angle reflections for $[H_2B(NH_3)_2]Cl$. As noted in the preceding section, the structure of the chloride salt is known. By assuming that the three structures are isomorphous, it has been possible to index the thirty-one observed lines for the bromide salt and the sixty-six lines for the iodide

(33) E. W. Hughes and W. N. Lipscomb, J. Am. Chem. Soc. 68, 1970 (1946).

(34) Nordman and Reimann, this report, p. 143.

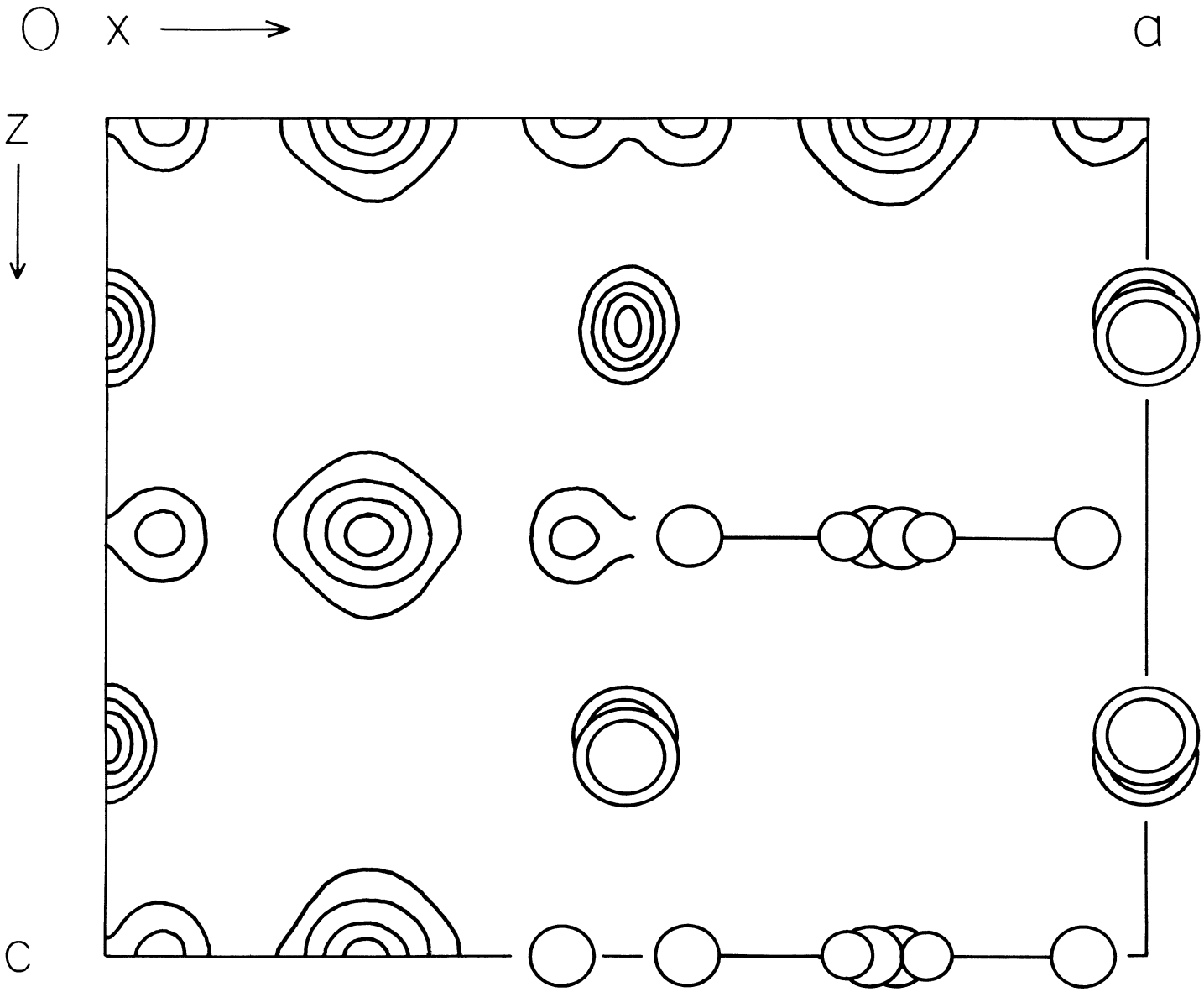

Fig. 7. Electron density projections for $[H_2B(NH_3)_2]Cl$ on 010 plane showing arrangement of boron, nitrogen, and chlorine atoms.

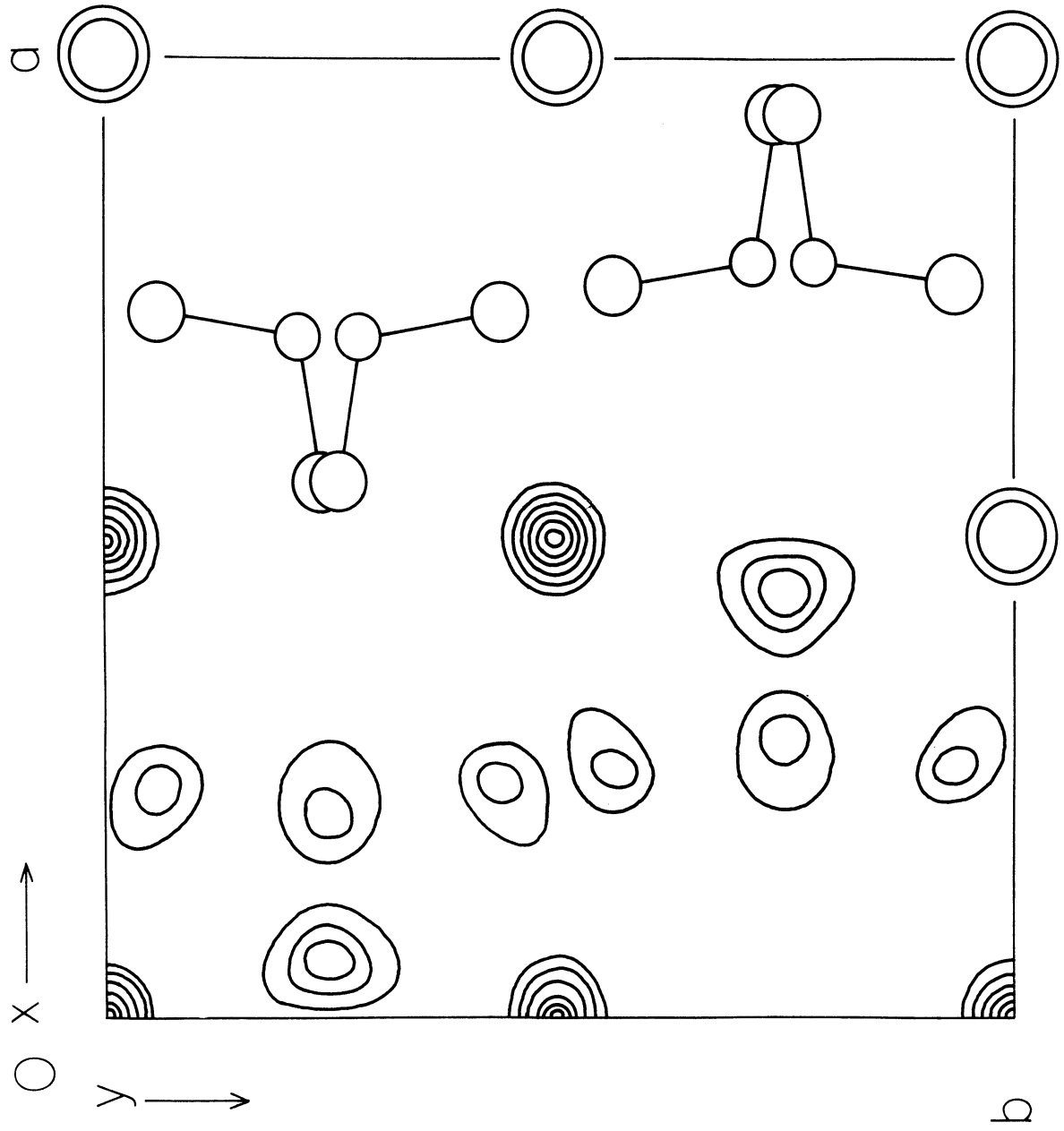

Fig. 8. Electron density projection on (001). Contours as in Fig. 7.

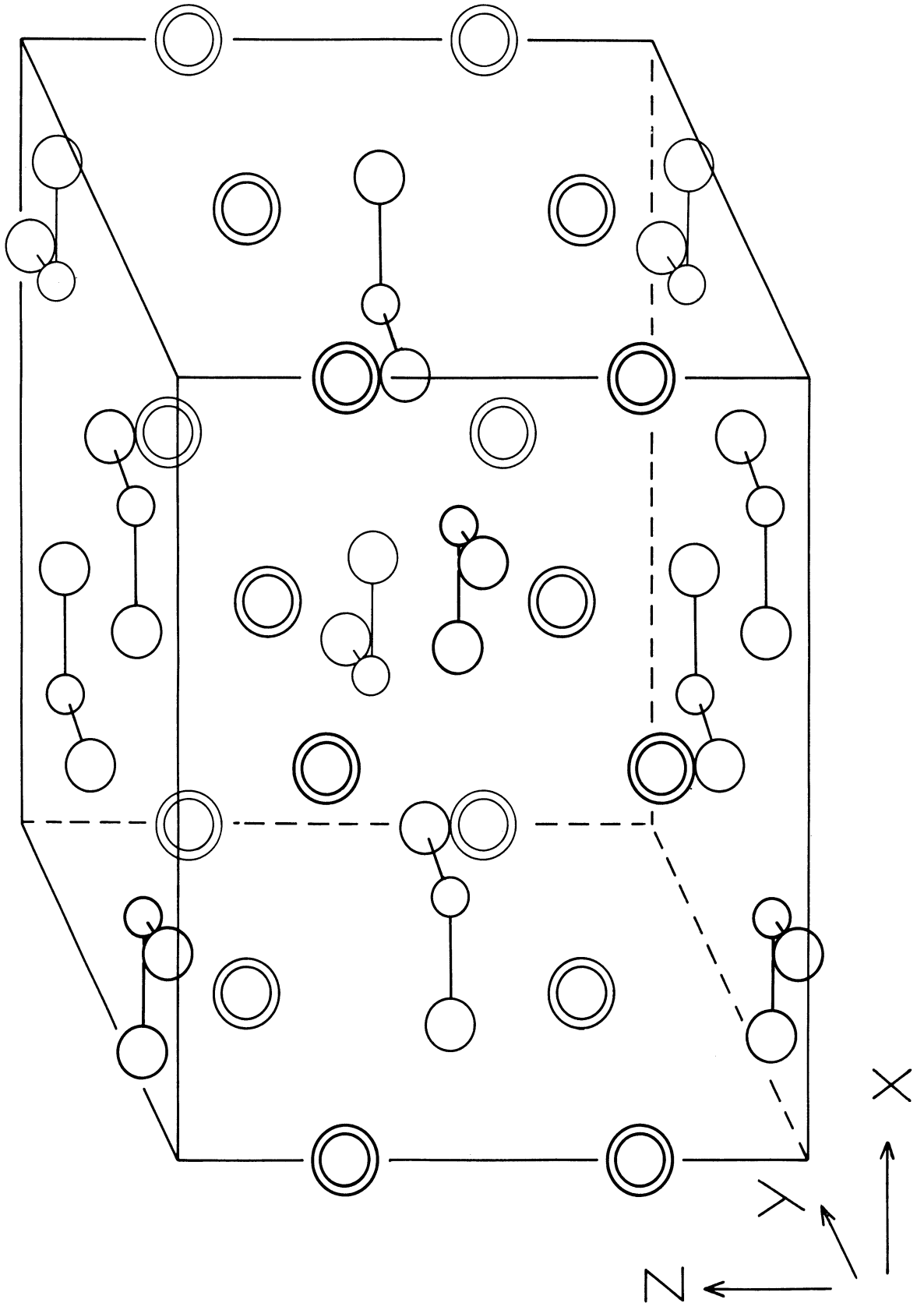

Fig. 9. The structure of $[H_2B(NH_3)_2]Cl$.

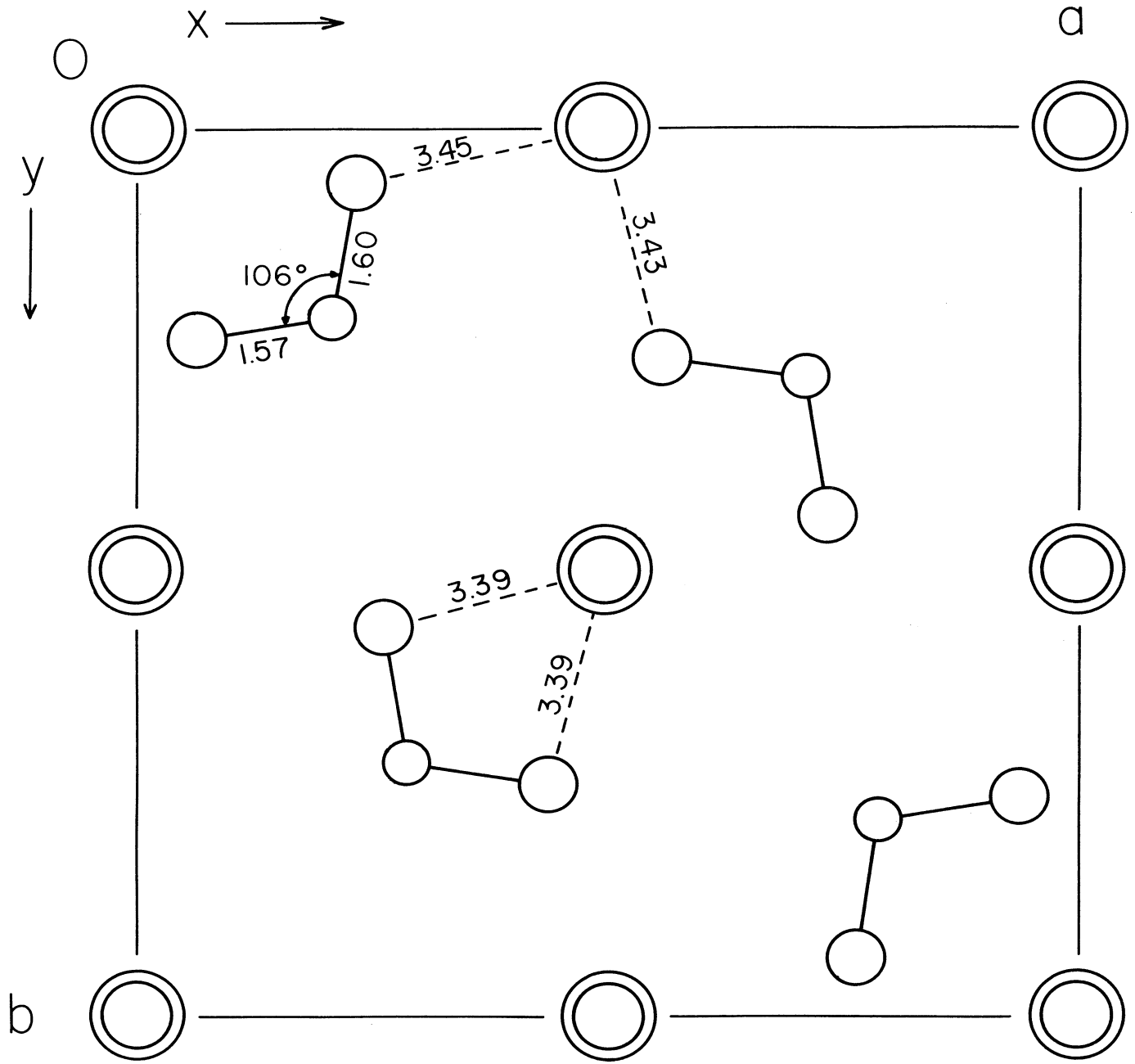

Fig. 10. Interatomic distances and bond angles in $[H_2B(NH_3)_2]Cl$.

salt. By calculating the powder pattern for the chloride salt from the single-crystal data, it has been possible to determine hkl values for each reflection, and by analogy the hkl values for the corresponding bromide and iodide reflections.* Knowing hkl values, one can then calculate dimensions of the unit cell. It should be noted that while the bromide salt is apparently pseudotetragonal (actually orthorhombic with the a and b axes equal as in the chloride salt), the iodide salt is unambiguously orthorhombic with "b" larger than "a" using the same axis designation as used in the chloride salt.

The patterns themselves do not provide an unequivocal choice between space groups Bbcm and Bba2; however, because of the striking similarities in the intensities of lines with the same index for all three salts, it is probably safe to assume that they are indeed isomorphous and all share the same space group Bbcm, determined by Nordman and Peters from their single-crystal study of the chloride salt. There are eight formula weights of each compound per unit cell. Unit-cell data are summarized in Table VI.

TABLE VI

COMPARISON OF LATTICE PARAMETERS FOR CHLORIDE, BROMIDE, AND IODIDE SALTS OF $[H_2B(NH_3)_2]^+$

	a	b	c	Density g/cc	Apparent Vol. per Ion Pair; $(Å)^3$
$[H_2B(NH_3)_2]Cl$	10.20Å	10.20Å	8.71Å	1.21	113.1
$[H_2B(NH_3)_2]Br$	10.48±.02	10.48±.02	9.03±.02	1.70	123.8
$[H_2B(NH_3)_2]I$	10.75±.02	11.01±.02	9.58±.02	2.04	141.9

(2) Procedure.—Data were fit by least-squares methods to minimize errors in cell parameters. Conventional data-reduction procedures were employed.

One may define the following:

$$d^* = 1/d,\ a^* = 1/a,\ b^* = 1/b,\ c^* = 1/c$$

where d is the distance between reflecting planes of atoms and a, b, and c are the distances on the x, y, and z axes which define the unit cell. For orthorhombic cells (1)

$$d_c^* = \sqrt{a^{*2}h^2 + b^{*2}k^2 + c^{*2}l^2}$$

*In actual practice only the low-angle reflections of the chloride, bromide, and iodide salts were sufficiently similar to provide unequivocal h, k, and l identification; however, identification of these lines provided tentative reciprocal lattice constants from which the complete indexing could be effected.

where d_c^* = the d value calculated from known h, k, l values and h, k, and l are defined as the Miller indices of the scattering plane. From the Bragg equation (2):

$$d_o^* = \frac{2 \sin \theta}{\lambda}$$

where d_o^* = the d value observed from measurements on powder photographs.

From the single-crystal data on the chloride salt, the values of a*, b*, and c* were known and d_c^* could be calculated for each known hkl plane. The powder pattern for the chloride calculated by this procedure from the single-crystal data checked the experimental powder pattern (Table VII), thus providing an unambiguous indexing for the chloride salt. It was then assumed that a line in the bromide pattern, corresponding to a given line in the chloride pattern would have the same h, k, l values as the chloride line. It was thus necessary to adjust values of a*, b*, and c* for the bromide and iodide salts until the calculated d_c^* values [Eq. (1)] showed the best agreement with the experimental bromide and iodide results obtained from the powder patterns [Eq. (2)].

If a*, b*, and c* are the approximate assumed reciprocal lattice constants from which the indices of each line are determined and Δa^*, Δb^*, and Δc^* are the differences between the actual reciprocal lattice constant and the approximate a*, b*, or c* values then the accurate reciprocal cell parameters can be defined as $a^* + \Delta a^*$, $b^* + \Delta b^*$, and $c^* + \Delta c^*$.

It is then desired to find Δa^*, Δb^*, and Δc^*, all related to Δd^* by the equation:

$$\Delta d^* = \frac{2}{d_c^*} \left(h^2 a^* \Delta a^* + h^2 b^* \Delta b^* + l^2 c^* \Delta c^*\right) \qquad (3)$$

and chosen such that the function F is a minimum (based on least-squares procedures for fitting data).

$$F = \sum \left(|d_o^* - d_c^*| - \Delta d^*\right)^2 = \min \qquad (4)$$

By substituting relation (3) into (4), differentiating with respect to Δa^*, Δb^* and Δc^* and equating to zero, one obtains:

$$0 = \frac{\partial F}{\partial \Delta a^*} = \sum \frac{d_o^* - d_c^*}{d_c^*} h^2 - 2a^* \Delta a^* \sum \frac{h^4}{d_c^{*2}} - 2b^* \Delta b^* \sum \frac{h^2 k^2}{d_c^{*2}} - 2c^* \Delta c^* \sum \frac{h^2 l^2}{d_c^{*2}}$$

$$\frac{\partial F}{\partial \Delta b^*} = \sum \frac{d_o^* - d_c^*}{d_c^*} k^2 - 2a^* \Delta a^* \sum \frac{h^2 k^2}{d_c^{*2}} - 2b^* \Delta b^* \sum \frac{k^4}{d_c^{*2}} - 2c^* \Delta c^* \sum \frac{k^2 l^2}{d_c^{*2}} = 0$$

$$\frac{\partial F}{\Delta c^*} = \sum \frac{d_o^* - d_c^*}{d_c^*} l^2 - 2a^* \Delta a^* \sum \frac{h^2 l^2}{d_c^{*2}} - 2b^* \Delta b^* \sum \frac{k^2 l^2}{d_c^{*2}} - 2c^* \Delta c^* \frac{\sum l^4}{d_c^{*2}} = 0$$

TABLE VII

OBSERVED AND CALCULATED hkl VALUES FOR $[H_2B(NH_3)_2]Cl$

(Indexing of Powder Pattern)

hkl	$\frac{4\sin^2\theta}{\lambda^2}$		d	Intensity
	Observed	Calculated		
200	0.0388	0.0384	5.08	ms
002	0.0524	0.0524	4.36	weak doublet
220	0.0772	0.0772	3.60	m
202	0.0912	0.0908	3.31	vs
131	0.1104	0.1092	3.01	w
222	0.1304	0.1296	2.77	s
113	0.1380	0.1384	2.69	w
321	0.1380	0.1360	2.69	w
400	0.1552	0.1536	2.54	s
420	0.1924	0.1920	2.28	ms
004	0.2104	0.2100	2.18	mw
422	0.2452	0.2448	2.02	ms
521	0.2920	0.2920	1.85	w
440	0.3088	0.3072	1.80	w
115	0.3500	0.3484	1.69	vw
404	0.3628	0.3548	1.66	m
620	0.3848	0.3848	1.61	w
602	0.4004	0.3988	1.58	m
622	0.4384	0.4376	1.51	w

These are three simultaneous equations in three unknowns, Δa^*, Δb^*, and Δc^*. In the case of the bromide salt, since $a^* = b^*$, the system can be reduced to two equations in two unknowns.

Approximate values of a^*, b^*, and c^* were originally obtained in each case from the relation

$$d^* = \sqrt{a^{*2}h^2 + b^{*2}k^2 + c^{*2}l^2}$$

By selecting three of the observed d^* values and their accimpanying h, k, and l values, one could obtain three equations in three unknowns, the unknowns being the approximate a^*, b^*, and c^* values for the lattice. These approximate methods gave very good results since the least-squares treatment indicated corrections of only .003Å, .003A and .006Å for a, b, and c of the iodide salt and a correction of only .002Å for both a and c.

A probable error of ± 0.02Å in each of the cell parameters is suggested on the basis of the following analysis. The relation between a, b, and c and the observed d values can be expressed as: $d^2 = a^2h^2 + b^2h^2 + c^2l^2$
Differentiating, we have:

$$d\delta d = h^2a\delta a + k^2l\delta b + l^2c\delta c$$

The maximum value for the error in a, δa, can be found if one assumes δb and $\delta c = 0$. Then

$$\delta a = \frac{d\delta d}{h^2a}$$

Since $a \geq d$ and $h^2 \geq 1$, we may say that

$$\delta a \leq a/d\ \delta d \approx d\left(\frac{d_o^* - d_c^*}{d_c^*}\right)$$

The above assumes that $\delta d/d \approx \delta d^*/d^*$. The maximum error in a can then be computed as:

$$\delta a = a\sqrt{\frac{\sum\left(\frac{d_o^* - d_c^*}{d_c}\right)^2}{n}}$$

Thus a = ± .012Å for the iodide and ± .014 for the bromide. The assigned error of ± .02Å thus appears to be reasonably conservative.

Tables VII, VIII, and IX give the observed and calculated hkl values for $[H_2B(NH_3)_2]Cl$, $[H_2B(NH_3)_2]Br$, and $[H_2B(NH_3)_2]I$, respectively.

TABLE VIII

OBSERVED AND CALCULATED hkl VALUES FOR $[H_2B(NH_3)_2]Br$

hkl	$\frac{4\sin^2\theta}{\lambda^2}$		d	Intensity
	Observed	Calculated		
200	0.0365	0.0364	5.22	s
002	0.0486	0.0490	4.51	w,D
220	0.0727	0.0728	3.71	ms
202	0.0856	0.0855	3.42	vs
131	0.1036	0.1033	3.10	vw
222	0.1219	0.1219	2.86	s
113	0.1286	0.1286	2.79	vw
400	0.1457	0.1456	2.62	ms
420	0.1822	0.1820	2.34	ms
402	0.1943	0.1947	2.27	ms
422	0.2307	0.2311	2.08	s
143	0.2660	0.2651	1.94	w
440	0.2900	0.2912	1.85	w
343				
503	0.3396	0.3379	1.72	m
620	0.3639	0.3640	1.66	w
602	0.3769	0.3767 *	1.63	m
424	0.3769	0.3782 *	1.63	m
622	0.4117	0.4131	1.56	w
640	0.4728	0.4733		
543	0.4834	0.4835		
363	0.5215	0.5199		
642	0.5215	0.5223		
650	0.5558	0.5552		
703	0.5558	0.5563		
800	0.5807	0.5824		
535	0.6159	0.6160		
830	0.6653	0.6644		
563	0.6653	0.6655		
840	0.7275	0.7281		
383	0.7756	0.7747		
850	0.8108	0.8100		
547	0.7742	0.9741		

*One line observed for both lines calculated.

TABLE IX

OBSERVED AND CALCULATED hkl VALUES FOR $[H_2B(NH_3)_2]I$

Intensity	hkl	$\frac{4\sin^2\theta}{\lambda^2}$		hkl	$\frac{4\sin^2\theta}{\lambda^2}$		hkl	$\frac{4\sin^2\theta}{\lambda^2}$	
		Observed	Calculated		Observed	Calculated		Observed	Calculated
vw	020	0.0330	0.0330	523	0.3475	0.3475	066	0.6883	0.6893
s	200	0.0346	0.0346	602	0.3551	0.3552	901	0.7134	0.7120
w	210	0.0429	0.0429	135	0.3551	0.3554	616	0.7134	0.7122
m	220	0.0678	0.0676	054	0.3802	0.3806	266	0.7236	0.7239
vw	022	0.0761	0.0766	171	0.4227	0.4237	921	0.7449	0.7449
s	202	0.0784	0.0782	270	0.4389	0.4387	391	0.7581	0.7568
m	222	0.117	0.112	640	0.4428	0.4435	672	0.7581	0.7593
vvw	232	0.1532	0.1524	711	0.4428	0.4432	517	0.7581	0.7587
m	420	0.1699	0.1715	036	0.4654	0.4666	636	0.7771	0.7782
vw	004	0.1744	0.1744	462	0.4808	0.4790	0-10-0	0.8255	0.8247
w	133	0.1810	0.1810	272	0.4808	0.4823	537	0.8255	0.8247
w	204	0.2086	0.2090	345	0.4808	0.4824	094	0.8421	0.8424
m	430	0.2124	0.2127	731	0.5089	0.5092	585	0.8421	0.8423
w	250	0.2408	0.2408	703	0.5229	0.5222	2-10-0	0.8583	0.8593
vw	440	0.2704	0.2704	525	0.5229	0.5219	682	0.8817	0.8830
vvw	115	0.2878	0.2894	416	0.5388	0.5391	547	0.8817	0.8824
w	343	0.3084	0.3080	181	0.5479	0.5474	816	0.9563	0.9546
w	442	0.3141	0.3140	355	0.5562	0.5566	286	0.9563	0.9548
	125	0.3141	0.3141	082	0.5705	0.5714	961	1.0098	1.0088
	503	0.3141	0.3145	373	0.5812	0.5801	458	1.0427	1.0423
	620	0.3432	0.3446	274	0.6131	0.6131	096	1.0602	1.0604
	450	0.3432	0.3447	191	0.6883	0.6876	4-10-6	1.3563	1.3556

4. THE NUCLEAR MAGNETIC RESONANCE SPECTRUM OF THE COMPLEX CATION $[H_2B(NH_3)_2]^+$. THE PROTON SPECTRUM

(a) Background

The technique of nuclear magnetic resonance absorption has been exploited in recent years as a tool for structural studies in both organic and inorganic chemistry. Although a number of erroneous structural proposals have resulted from improper interpretation of NMR data by overly enthusiastic workers, NMR data can, if properly interpreted and supported, give useful structural information. In particular, it should be possible to differentiate between different types of hydrogens bound in the complex cation $[H_2B(NH_3)_2]^+$. Thus the resonance of two chemically identical hydrogens bound to the B^{11} nucleus will be split into four bands of equal intensity (I for B = 3/2 $\therefore$ 2I + 1 = 4), while the resonance of the six protons bound to chemically identical nitrogen atoms will be split into three bands of equal intensity (I for N^{14} = 1 $\therefore$ 2I + 1 = 3) if coupling with only nearest atoms is considered to be significant.

For a proton of given chemical environment, we may define the chemical shift, σ, as

$$\sigma = \frac{H_c - H_r}{H_r} \times 10^5$$

where H_c is the magnetic field strength necessary for nuclear magnetic resonance of the proton under consideration and H_r is the corresponding value for a reference compound, usually water. If both values are measured at constant frequency, the frequency dependence of the resonance cancels out and σ may be interpreted as a measure of the diamagnetic shielding of the proton in question. It is of course obvious, then, that the diamagnetic shielding is an indicator of the chemical environment of the proton. Using the definitions above, one finds that more positive values of σ should imply greater shielding and a more hydridic character for the hydrogens while less positive and more negative values of σ imply more protonic character for the hydrogens. As yet, however, no complete correspondence between σ values and chemical acidity can be claimed.(35)

Proton magnetic resonance studies have been very effective in structural studies on organic compounds; unfortunately, their application to boron-nitrogen systems has been much less effective, since the lines for protons bound to boron are split into smaller bands of reduced intensity by the magnetic moment of the boron nucleus. Since the major isotope of carbon has no nuclear moment, the proton magnetic resonance spectrum of an organic compound is usually much simpler than that of its boron counterpart. The limited solubility of the salts of $[H_2B(NH_3)_2^+]$ in various solvents resulted in a weak signal at best and no suitable signal could be obtained from the solid salts of the cation. The fourfold

(35) J D Roberts, Nuclear Magnetic Resonance (McGraw-Hill, N. Y., 1959), p. 24.

splitting by the boron nucleus of the weak signal obtained from solutions gave rise to such weak absorption that identification of peaks was difficult, and assignments as given below are based on the identification of very weak lines which appeared reproducibly in the spectrum. The observations and interpretations can be considered as consistent with the structural data already available on the cation, but one would need to be a real optimist to interpret the very weak lines as direct experimental evidence for the structure. In short, if one knows what pattern is anticipated, it is possible to find all the very weak absorptions expected; but if one were to look at the spectrum without initial prejudice, the separation of certain peaks from the background could well provide a problem. Conditions are still being studied in an attempt to obtain more unequivocal NMR data.

(b) Experimental Results and Discussion

Dihydridodiammion-boron (III) iodide was prepared from the diammoniate of tetraborane as described earlier (see page 26. The deuterated salt $[H_2B(ND_3)_2]I$ was prepared in an analogous fashion using $B_4H_{10}\cdot 2ND_3$ as the starting material. Diethylene dimethyl ether $[CH_3O\text{-}C_2H_4\text{-}O\text{-}C_2H_4\text{-}O\text{-}CH_3]$ (dried over CaH_2) and liquid NH_3 (dried over sodium) served as solvents. $[H_2B(NH_3)_2]I$ dissolved in the polyether (saturated solution) should show a triplet of moderate intensity for the six protons of the two ammonia molecules. The resonance of the six equivalent protons would be split into three peaks by the nitrogen nucleus (I for N = 1 and 2I + 1 = 3). Samples were examined using a Varian High Resolution spectrometer. Three such peaks were clearly recognized for $[H_2B(NH_3)_2]I$ in the polyether solvent with values of σ, the chemical shift, at 0.048, -0.035, and -0.117. The average value for the six hydrogens of the coordinated ammonia molecules is thus -0.04 in the polyether solution with an average separation of peaks equal to 0.08. Ammonium iodide in the same solvent has a δ value of -0.20 and pure liquid ammonia has a δ value of 0.43 with a separation of peaks equal to 0.11. It is of interest that available chemical data indicate increasing acid character for protons in the series $NH_3 < [H_2B(NH_3)_2]^+ < NH_4^+$; the increasing negative character for the δ values of these similar compounds is consistent with the postulate made earlier, namely, that the smaller amount of diamagnetic shielding around the proton would show up as a more negative δ value and a more acidic proton. The identity of the nitrogen-hydrogen peaks was confirmed by running the spectrum of $[H_2B(ND_3)_2]I$ in polyether. Since the precession frequency of the deuterium nucleus is 6.5 megacycles per 10,000 gauss and the oscillator used for the protium nucleus has a frequency of 40 megacycles, deuterium resonance does not appear with the oscillator used. The fact that the lines attributable to N-H absorption did not appear when $[H_2B(ND_3)_2]^+$ was used as solute supports the assignments given. As might be expected, identification of the N-H absorption was impossible when liquid ammonia was used as a solvent for $[H_2B(NH_3)_2]I$.

The B-H resonance was particularly difficult to detect in solutions using polyether as the solvent because of: (1) the low solubility of $[H_2B(NH_3)_2]I$ in the solvent; (2) the fact that only two B-H hydrogens are found per mole as

compared to six N-H hydrogens, and (3) the fourfold splitting of the already weak signal by the boron nucleus. Only one of the four weak B-H absorptions could even be recognized tentatively in the polyether solution. In the liquid ammonia solution the dihydridodiammino-boron (III) iodide is somewhat more soluble than it is in the ether solvent. In this solvent four weak lines, identified as due to B-H absorption, were recognized at σ values of 0.62, 0.37, [0.12 not visible] and -0.13. The average σ value for the B-H proton of $[H_2B(NH_3)_2]I$ is thus 0.24 with a separation of peaks corresponding to 0.25. Sodium borohydride in liquid ammonia showed the expected four peaks at a σ value of 0.52 and a peak separation of 0.20.

The fact that the average absorption of the B-H hydrogens in $NaBH_4$ comes at a more positive value (0.52) than the average absorption of the B-H hydrogens in $[H_2B(NH_3)_2]I$ (0.24) implies greater electronic shielding and thus more hydridic character for the hydrogens of $NaBH_4$ than for the B-H hydrogens of $[H_2B(NH_3)_2]I$. This fact is in agreement with all available chemical information. The foregoing NMR study will be more conclusive if more definitive absorption can be obtained in subsequent work.

5. THE REACTIONS OF THE $[H_2B(NH_3)_2]X$ SALTS WITH SODIUM IN LIQUID AMMONIA

The process expected was:

$$Na + [H_2B(NH_3)_2]X \xrightarrow[NH_3]{liq} H_2BNH_2 + NH_3 + 1/2\ H_2 + NaX$$

Two samples, identified as $[H_2B(NH_3)_2]Cl$ by their X-ray powder pattern, were allowed to react with an excess of sodium in liquid ammonia at -78° using conventional techniques. Values of H_2 liberated prior to a sharp change in rate were: 0.9 and 1.4 equivalents of H/per mole of $[H_2B(NH_3)_2]Cl$. It is to be noted that the two values are in poor agreement even though conditions were formally the same. It is also significant that H_2 evolution did not stop at the points indicated above but merely slowed up. On long standing a value as high as 2 equiv. $H/[H_2B(NH_3)_2]Cl$ was obtained. Since the solid reactant was identified as $[H_2B(NH_3)_2]Cl$ in each case by X-ray methods, it appears that the sodium reaction is not reliable as a means of compound characterization. It appears that these observations support earlier conclusions regarding the identity of $B_2H_6 \cdot 2NH_3$ (I) and $B_2H_6 \cdot 2NH_3$ (II). As noted on page 13, the question of compound purity seems to be a major factor in the rate and stoichiometry of the reaction of Na and the cation $[H_2B(NH_3)_2^+]$. Certainly the diagnostic value assigned to the sodium reaction in earlier studies is subject to serious question in view of current evidence.

D. The Synthesis of "The Diammoniate of Diborane" by Metathesis

Heretofore the diammoniate of diborane has been best prepared by the direct reaction between solid NH_3 and gaseous B_2H_6 under very carefully controlled con-

ditions.[15e] The identification of both cation and anion in the solid suggested an alternative metathetical procedure for synthesis. If appropriate separative procedures were available to purify the products, one could effect synthesis by means of the general equation.

$$[H_2B(NH_3)_2]X + M[BH_4] \longrightarrow MX + [H_2B(NH_3)_2][BH_4]$$

The nature of the separation and purification procedure would of course be determined by the identity of M^+ and X^- and the properties of MX.

1. THE REACTION BETWEEN KBH_4 AND $[H_2B(NH_3)_2]Cl$

If M^+ in the foregoing type of reaction is K^+ and X^- is Cl^-, one may take advantage of the low solubility of KCl in liquid ammonia solution. The following equation then results:

$$[H_2B(NH_3)_2]Cl + KBH_4 \xrightarrow[-78°C]{\text{liq } NH_3} [H_2B(NH_3)_2][BH_4] + \underline{KCl}\downarrow$$

The KCl may be separated from the liquid ammonia solution by vacuum line filtration and the "diammoniate of diborane" should be recoverable from the filtrate.

A sample of $[H_2B(NH_3)_2]Cl$, free from NH_4Cl, was dissolved in liquid ammonia at -78°C along with a stoichiometric amount of pure KBH_4. After 14 hours of stirring at -78°C the solution was filtered (temperature held at -78°C during filtration); the solid retained on the filter was identified as KCl from its X-ray diffraction pattern. The solvent ammonia was removed from the filtrate by sublimation of the solvent, and the solid residue, presumably $[H_2B(NH_3)_2][BH_4]$, was examined by means of X-ray diffraction. In the pattern lines of $[H_2B(NH_3)_2][BH_4]$ were found except that a slight displacement of all lines was noted (see Figs. 11a and b). It was assumed that the displacement resulted from isomorphous substitution of Cl^- for BH_4^- in the $B_2H_6 \cdot 2NH_3$ lattice. The hypothesis was checked by dissolving a mixture of $[H_2B(NH_3)_2]BH_4$ and a small amount of $[H_2B(NH_3)_2]Cl$ in liquid ammonia, and then removing the solvent ammonia by sublimation at -78°C. In the X-ray diffraction pattern of the resulting solid, no lines for $[H_2B(NH_3)_2]Cl$ were found, and the lines for $[H_2B(NH_3)_2][BH_4]$ were somewhat displaced, just as was found in the metathesis product. It is thus concluded that a sample of the "diammoniate of diborane," somewhat contaminated by chloride ion and K^+ had indeed been produced in the metathesis reaction.

2. THE REACTION BETWEEN $LiBH_4$ AND $[H_2B(NH_3)_2]B_3H_8$ IN DIETHYL ETHER

The synthesis, characterization, and structure proof for the compound $[H_2B(NH_3)_2][B_3H_8]$ are described in a subsequent section. Assuming the above structure to be correct, the following reaction would be anticipated:

$$[H_2B(NH_3)_2][B_3H_8] + LiBH_4 \xrightarrow[-78]{Et_2O} [H_2B(NH_3)_2][BH_4]\downarrow + LiB_3H_8$$

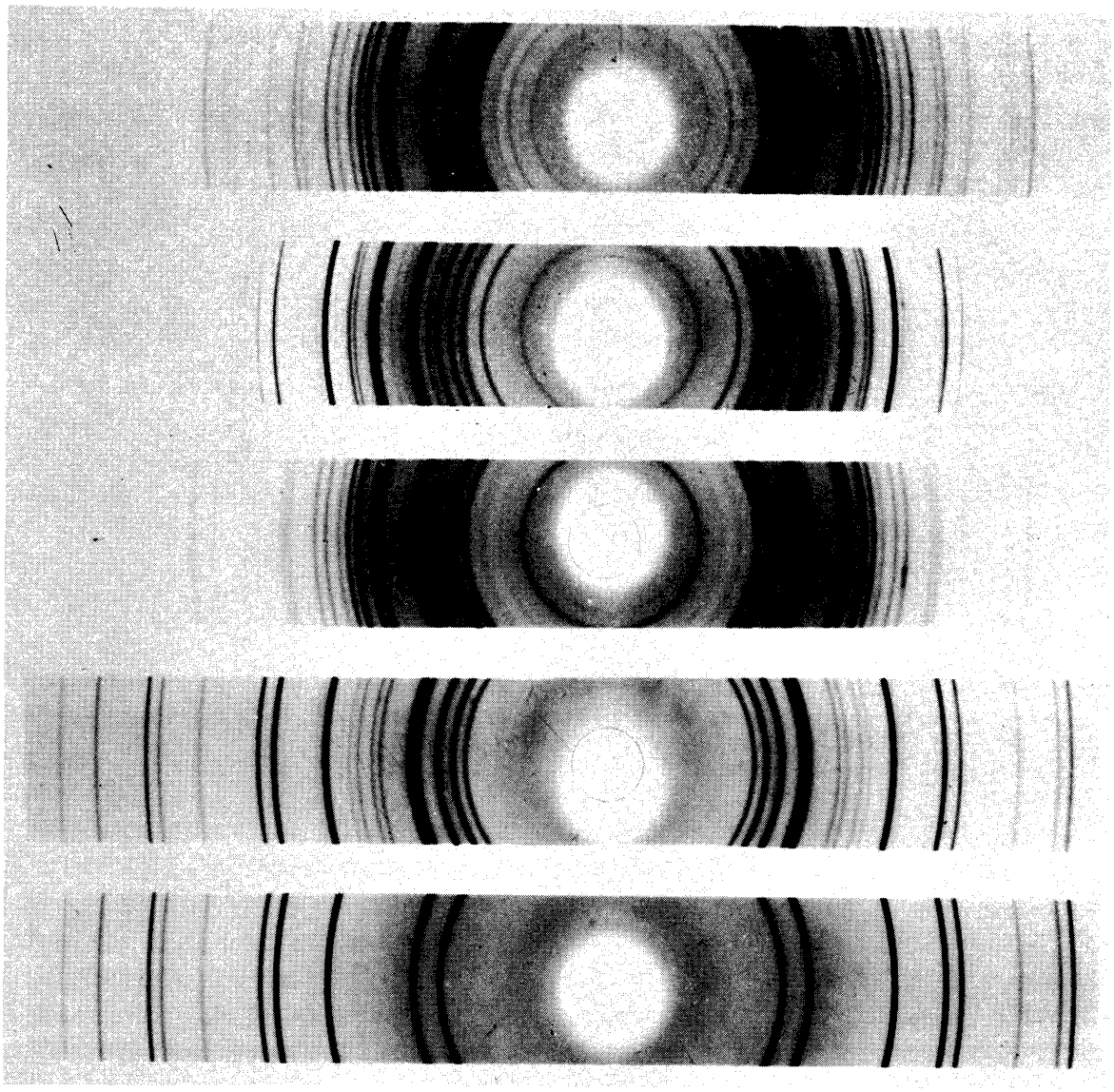

Fig. 11

(a) Powder pattern for $H_2B(NH_3)_2\ BH_4$.

(b) Powder pattern for the ammonia soluble fraction in the reaction between KBH_4 and $H_2B(NH_3)_2\ Cl$.

(c) Powder pattern for a mixture of $H_2B(NH_3)_2\ Cl$ and $H_2B(NH_3)_2\ BH_4$.

(d) Powder pattern for a mixture of KBH_4 and $H_2B(NH_3)_2\ BH_4$.

(e) Powder pattern for KBH_4.

When diethyl ether solutions of $LiBH_4$ and $[H_2B(NH_3)_2]B_3H_8$ were stirred at -78°C for a few minutes, no ether insoluble $B_2H_6 \cdot 2NH_3$ was formed. However, when this cold solution was allowed to warm up slowly, white crystals of pure $B_2H_6 \cdot 2NH_3$ (identified by X-ray pattern) started to form near -23°C. The white precipitate redissolved when the system was cooled to -78°C and reappeared when the temperature was raised slowly. The filtrate obtained by removal of the precipitate gave a white, gluey material when the solvent was removed. The gluey residue contained a microcrystalline solid phase. An X-ray powder pattern of this gluey mass gave evidence for a new crystalline solid phase, presumably LiB_3H_8. The supposed impure LiB_3H_8 residue gave off H_2 slowly at room temperature. The entire study is as yet incomplete. Details of other metathesis reactions for the synthesis of $B_2H_6 \cdot 2NH_3$ will be presented when more certain characterization of reactants has been effected.

E. A Summary of Developments on the Diammoniate of Diborane and Its Derivatives

Arguments to support the structure $[H_2B(NH_3)_2]BH_4$ for the "diammoniate of diborane" have been presented in earlier publications.[15] The following additional information relative to the "diammoniate of diborane" and related structures has been reported in the foregoing pages.

(a) A procedure for preparing $B_2H_6 \cdot 2NH_3$ in one-gram lots has been developed.

(b) A microcrystalline form of $B_2H_6 \cdot 2NH_3$ has been obtained and the powder pattern is tabulated for ready compound identification.

(c) Relatively strong evidence against the structure $[HB(NH_3)_3](BH_4)_2$ has been accumulated. The so-called "diammoniate of diborane II" which was formerly assigned this structure[15] has been shown to consist chiefly of the regular "diammoniate of diborane" with the structure $[H_2B(NH_3)_2]BH_4$. The stoichiometry of the sodium reaction ($B_2H_6 \cdot 2NH_3 + Na \longrightarrow NaX + 1/2\ H_2$) which was formerly a major line of evidence supporting the structure $[HB(NH_3)_3][BH_4]_2$ appears to be very sensitive to compound purity and the structural significance of the earlier data on the sodium reaction is questionable. Molecular weight data which supported the diammoniate (II) data are also subject to re-evaluation.

(d) Improved methods for the synthesis of pure salts of the form $[H_2B(NH_3)_2]X$ have been developed.

(e) A complete single-crystal X-ray crystallographic study which established the structure $[H_2B(NH_3)_2]Cl$ has been completed and the data confirm the above structural assignment in every detail. The structures of the bromide and iodide have also been deduced.

(f) A nuclear magnetic resonance study of $[H_2B(NH_3)_2]I$ can be best interpreted in terms of the accepted structure of the cation $[H_2B(NH_3)_2]^+$.

(g) The "diammoniate of diborane I," $[H_2B(NH_3)_2][BH_4]$, has been prepared by metathesis, a fact which offers final and complete chemical support for the above structure. It is now possible to make the diammoniate of diborane without going through diborane.

II. REACTIONS, STRUCTURES, AND PROPERTIES OF OTHER DIBORANE ADDITION COMPOUNDS

A. Background

The "normal base-borane adducts" have the form Base: BH_3. It was a deviation from this expected pattern which made the previously discussed ammonia addition compounds of diborane anomolous. Trimethylamine-borane, first reported by Burg and Schlesinger,[36] can be prepared by a variety of reactions. These include:

(a) $H_3BCO + (CH_3)_3N \longrightarrow (CH_3)_3NBH_3 + CO$

(b) $B_2H_6 + 2(CH_3)_3N \longrightarrow 2CH_3NBH_3$

(c) $Al(BH_4)_3 + (CH_3)_3N \longrightarrow (CH_3)_3NBH_3$ + other products

(d) $NH_4BH_4 + (CH_3)_3N \longrightarrow (CH_3)_3NBH_3 + H_2$ + other products

The compound is a white, crystalline solid which melts at 94-94.5°C, has a vapor pressure of 77.2 mm at 96.9°C and an extrapolated boiling point of 171°C. It is monomeric in the vapor state and is relatively stable toward thermal decomposition; it is hydrolyzed slowly by water.

Wiberg, Boltz, and Buckheit[37] reported that dimethylamine reacts with diborane to give an unstable product, $(CH_3)_2HNBH_3$, which loses hydrogen at room temperature to give an amine borane, $(CH_3)_2NBH_2$. On the other hand, G. Huff and co-workers at Callery Chemical Company reported that $(CH_3)_2HNBH_3$ (or an isomeric product) could be prepared as a stable, nonhygroscopic solid which did not decompose in alkaline or neutral aqueous solution and which could be distilled without decomposition.[38] Huff and co-workers first prepared the stable product by electrolysis of a solution of borohydride salt dissolved in liquid dimethylamine. No further direct evidence regarding this apparent inconsistency in the properties of $(CH_3)_2HNBH_3$ has been reported in the literature, although Bissot, Campbell, and Parry,[31] working under the sponsorship of WADC, found that the stability of a closely related molecule $HO(CH_3)_2NBH_3$ was very much dependent upon the purity of the sample being studied. The pure compound $HON(CH_3)_2BH_3$ was stable up to 55°C while the impure product evolved

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(36) A. B. Burg and H. I. Schlesinger, J. Am. Chem. Soc. 59, 780 (1937).
(37) E. Wiberg, A. Bolz, and P. Buckheit, Z. anorg. Chem. 256, 285 (1948).
(38) W. H. Schechter, C. B. Jackson and R. M. Adams, Boron Hydrides and Related Compounds, Second Edition, Callery Chemical Co., Callery, Pa., May 1954.

hydrogen easily at room temperature. Such an observation suggested that the instability of Wiberg's compound might be related to impurities present in his sample, while Huff's stable adduct would be a pure form of the same compound.

Monomethylamine-borane was first described by Wiberg[39] as an unstable solid which melted at 5-10°C with evolution of hydrogen. A sample of monomethylamine-borane prepared by Parry, Kodama, and Schultz[15g] using Wiberg's procedure melted just above 0°C with gas evolution and McCoy and Bauer[3] described both Me_2HNBH_3 and MeH_2NBH_3 as unstable solids at 0°C. No stable form of this complex has been reported in current literature.

The properties of ammonia-borane, first reported by Shore and Parry,[31,15c] stand in sharp contrast to the properties reported by Wiberg for monomethyl and dimethylamine-boranes. The compound is a white crystalline solid with a negative temperature coefficient of solubility in diethyl ether from -78° to 25°C. Clear rigorously anhydrous ether solutions are stable at room temperature to the extent that only a small amount of precipitate appears after standing for several days. The precipitate has the empirical composition $(H_3NBH_3)_n$. Trace quantities of hydrogen indicate that small amounts of $(H_2NBH_2)_n$ may contaminate the ether insoluble solid. In the presence of trace quantities of moisture, the ether solution becomes very unstable and solid material is precipitated quite rapidly.

Ammonia-borane is soluble and stable in anhydrous liquid ammonia. On the basis of X-ray powder pattern intensities, there was no detectable conversion to the diammoniate when a sample stood for 30 hours at -78°C and an additional 18 hours at -45°C in liquid ammonia. Reaction of ammonia-borane with sodium in liquid ammonia liberated one equivalent of hydrogen per mole of ammonia-borane. The stoichiometry of the process suggests the reaction:

$$H_3NBH_3 + Na \longrightarrow 1/2\ H_2 + NaH_2NBH_3$$

The sodium amidotrihydridoborate (III) has not been isolated from this process in pure form; its preparation by another procedure has been reported by Schlesinger and Burg[6] but has not yet been verified.

Solid ammonia-borane appears to undergo slow conversion to the "diammoniate of diborane" at room temperature. A sample which stands at 25°C in a dry atmosphere will not redissolve completely in ether. Very slow loss of hydrogen at room temperature occurs also. Its stability is orders of magnitude higher than that reported by Wiberg for $CH_3H_2NBH_3$ and $(CH_3)_2HNBH_3$. Solid ammonia-borane sublimes with difficulty under high vacuum. Its density is 0.74 g/cm³.

The structure of solid H_3BNH_3 was determined independently from powder data by Lippert and Lipscomb[40a] and by Hughes.[40b] The unit cell is tetragonal

(39) E. Wiberg, Naturwissenschaften 35, 182 (1948).

(40) a) E. L. Lippert and W. N. Lipscomb, J. Am. Chem. Soc. 78, 503 (1956);
b) E. W. Hughes, ibid., 78, 502 (1956).

with the C axis differing only slightly in length from the other two. The structure of H_3NBH_3 is shown in Fig. 12. The highly ordered boron-nitrogen arrangement implies a high dipole moment for the molecule.

In addition to the nitrogen bases, many other electron-pair donor molecules can coordinate with the BH_3 group. Even the weak secondary bases CO and PF_3 can form borane adducts.[36,41] Adducts of these weak bases have not been easily justified by the usual theoretical prejudices used to interpret coordination phenomena and a more detailed study of the properties of these materials seemed to be of considerable interest.

B. The Amine-Boranes

1. PREPARATION AND STABILITY OF THE MONO-, DI-, AND TRIMETHYLAMINE-BORANES

(a) Background

As noted in Section IIA, ammonia-borane and trimethylamine-borane have been described as stable, well-characterized solids while monomethylamine-borane was described as an unstable material which loses hydrogen below room temperature. To compound the confusion, stable and unstable forms of dimethylamine-borane have been described, and the possible existence of isomers has been suggested.

During the systematic studies in this laboratory of the amine-boranes, monomethylamine-borane was prepared by the low-temperature interaction of methylamine and diborane in tetrahydrofuran. The resulting product from the reaction:

$$2MeNH_2 + B_2H_6 \xrightarrow{\text{Tetrahydrofuran}} 2MeNH_2BH_3$$

was surprisingly stable at room temperature and even melted sharply at 58°C without observable decomposition. This behavior is reminiscent of an earlier observation made by Bissot[42] in this laboratory to the effect that $HO(CH_3)_2NBH_3$ is a low-melting unstable solid when impure, but is a stable solid melting sharply at 55°C when pure. Physical data obtained on the series of amine-boranes indicated rather clearly that the stable compounds under study are indeed legitimate members of a series and suggest strongly that the unstable samples are simply impure materials resulting from uncontrolled local conditions during compound formation.

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(41) R. W. Parry and T. C. Bissot, J. Am. Chem. Soc. 78, 1524 (1956).

(42) D. H. Campbell, T. C. Bissot, and R. W. Parry, J. Am. Chem. Soc. 80, 1549 (1958).

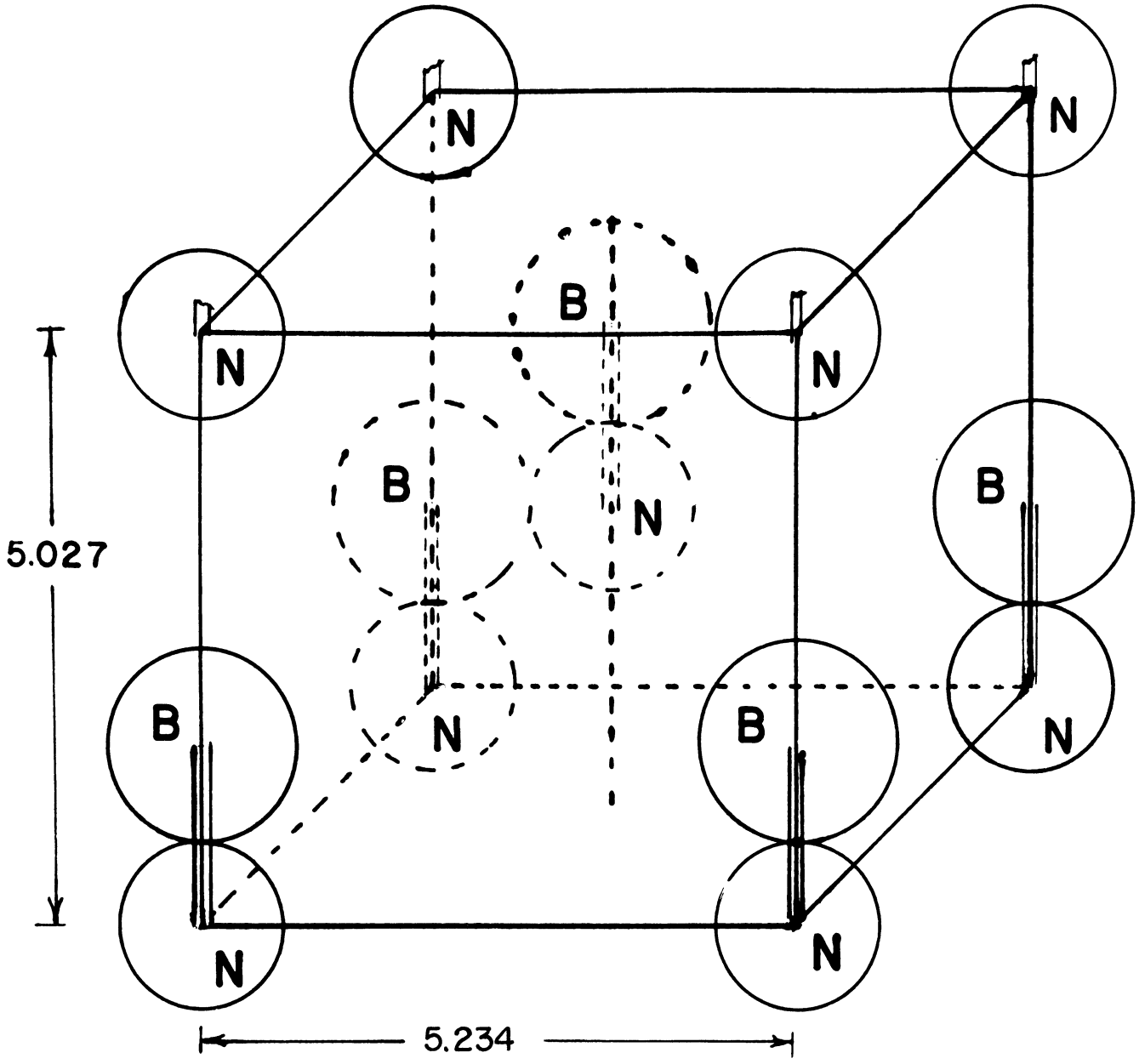


Fig. 12. The structure of H_3NBH_3.

(b) Experimental Procedure for the Preparation of Stable Methylamine-Borane

Diborane was distilled twice at the temperature of methylcyclohexane slush to remove higher hydrides. A 50-millimole sample of B_2H_6 was added slowly at -78°C to 15 ml of liquid tetrahydrofuran (previously dried over $LiAlH_4$). Commercial anhydrous methylamine (Matheson) was dried over sodium and about a 2-ml sample of the liquid was distilled into the reaction tube containing the tetrahydrofuran solution of B_2H_6. A slush bath at -112°C was placed around the reaction tube and the system was allowed to stand. The temperature rose gradually. The solvent and excess amine were removed when the temperature reached -45°C; the system was then allowed to warm to room temperature for a few minutes to aid in solvent removal. Finally the reaction tube was surrounded with ice and the last traces of amine and solvent were removed by pumping on the system with the high-vacuum pump for 10 hours. Trimethylamine-borane and dimethylamine-borane should sublime under these conditions.

A cold finger was then inserted into the reaction tube, the sample was warmed to room temperature, and $MeNH_2BH_3$ was sublimed onto the cold finger as large rectangular crystals. After about half of the product had sublimed, the residue liquified. The sublimation was then discontinued and the residue discarded.

The pure product melts sharply at 58°C. It is soluble in ethyl ether and dioxane, and dissolves with difficulty in benzene. Analysis of the sample showed: hydridic H = 6.64%, B = 23.8%; calculated values for $CH_3NH_2BH_3$ are: hydridic H = 6.68%, B = 24.10%.

2. VAPOR PRESSURES AND HEATS OF VAPORIZATION FOR THE AMINE-BORANES

As part of the program of study of the chemical and physical properties of the amine-boranes, it appeared desirable to obtain vapor-pressure data which could yield values for the heats of sublimation of the compounds. Since the sublimation pressures of the substances are all quite low, below one millimeter of mercury at room temperature, the usual manometric techniques are not suitable. The experimental procedure employed, therefore, was the Knudsen method which involves the measurement of the weight of material effusing through an orifice in a given time. This method, although fairly simple and straightforward experimentally, is subject to numerous sources of error which must be eliminated, or for which a correction must be applied. In particular, it is assumed that a saturated vapor exists in the vaporization chamber, that the vapor molecules effuse through the orifice into a region of zero pressure, that the effusion process is molecular (i.e., the orifice diameter is smaller than the mean-free path), and that the vapor molecules are single molecular units. A correction customarily is applied for the back reflection of molecules from the sides of an orifice of finite thickness. Values of this correction due to Clausing are given by Dushman,[43] who also discussed thoroughly the above and other sources

(43) S. Dushman, Scientific Foundations of Vacuum Technique, (John Wiley and Sons, N. Y., 1949), p. 99.

of error in this experiment. The pressure is calculated from the relationship

$$P(mm) = 17.4 \frac{W}{K A t} \sqrt{\frac{T}{M}}$$

where W is the weight of the substance in grams effusing in time t seconds through an orifice of area A cm^2. M is the molecular mass, T the absolute temperature and K is the correction factor for orifice thickness. The two orifices used had diameters of 0.0374 cm and 0.076 cm and ratios of thickness to radius of 0.163 and 0.314, respectively. The corresponding correction factors were 0.935 and 0.865.

The compounds studied included mono-, di-, and trimethylamine-borane and ammonia triborane, $NH_3B_3H_7$. The preparations of all but the trimethylamine compound are described elsewhere in this report;(44) the preparation of trimethylamine borane is available in the literature. All compounds were purified by vacuum sublimation immediately before use and were handled in a dry atmosphere. They appeared as white crystalline substances with no amine odor and sharply defined melting points. To eliminate the possibility of error from decomposition during the course of a determination, the stability of the compounds was checked under comparable conditions. This test consisted of a hydrogen evolution measurement in vacuum over a period of several days and indicated that no significant loss in weight from this cause occurred.

The data obtained are given in Table X for the four compounds. It should be noted that part of the data listed were determined after the closing date for the termination of the contract covered by this report. They have been included here for the sake of completeness. To calculate the heats of sublimation of the compounds, the data were fitted to the integrated form of the Calusius-Clapeyron equation using least-squares methods. The values obtained from the slopes together with the vapor-pressure equations are given below for the various compounds. In the case of the trimethylamine compound, data determined by conventional manometric techniques are available in the literature(44) for temperatures between room temperature and the melting point. Since these data appeared consistent with those determined in the present investigation, all data were used in determining the constants of the equation.

Methylamine-borane $(CH_3)NH_2{:}BH_3$

$$\text{Log}_{10} P(mm) = -\frac{4114\ (1 \pm 0.053)}{T} + 11.411\ (1 \pm 0.063)$$

range = 0° to 45°C $\Delta H = 18.8 \pm 1.0$ kcal/mole

(44) This report, Section IIB. A. B. Burg and H. I. Schlesinger, J. Am. Chem. Soc. 59, 780 (1937).

TABLE X

VAPOR-PRESSURE DATA FOR SOME AMINE BORANES

Methylamine Borane, $(CH_3)NH_2:BH_3$		Dimethylamine Borane, $(CH_3)_2NH:BH_3$		Trimethylamine Borane, $(CH_3)_3N:BH_3$		Ammonia Triborane,* $NH_3:B_3H_7$	
Temperature, °K	Pressure, mm x 10^3	Temperature, °K	Pressure, mm x 10^2	Temperature, °K	Pressure, mm x 10	Temperature, °K	Pressure, mm x 10^3
273.6	0.239	273.8	0.778	273.4	0.984	303.6	0.776
292.8	1.63	285.7	2.32	274.2	1.04	309.6	1.31
300.0	6.73	285.7	2.52	283.4	3.29	314.2	1.99
300.0	6.60	291.1	4.12	283.4	3.27	319.4	3.15
305.4	8.42	294.0	5.90	289.4	5.15	327.0	5.81
306.9	10.3	295.2	6.64	289.4	5.16		
306.9	8.49	299.2	11.1	296.4	8.96		
309.1	14.1	302.5	18.8	297.5	8.19		
313.2	17.8	306.0	24.9	298.0	7.94		
314.4	19.6	306.0	25.3				

*Ammonia-triborane, although not a legitimate member of this series, was included here to conserve space since the procedure is the same as that already described.

Dimethylamine-borane $(CH_3)_2NH:BH_3$

$$\text{Log}_{10}\ P(\text{mm}) = -\frac{4034\ (1 \pm 0.038)}{T} + 12.544\ (1 \pm 0.042)$$

range = 0° to 35°C $\Delta H = 18.5 \pm 0.7$ kcal/mole

Trimethylamine-borane $(CH_3)_3N:BH_3$

$$\text{Log}_{10}\ P(\text{mm}) = -\frac{2962\ (1 \pm 0.014)}{T} + 9.894\ (1 \pm 0.014)$$

range 0° to 90°C $\Delta H = 13.6 \pm 0.2$ kcal/mole

Ammonia triborane $H_3N:B_3H_7$

$$\text{Log}_{10}\ P(\text{mm}) = -\frac{3739\ (1 \pm 0.0075)}{T} + 9.200\ (1 \pm 0.0096)$$

range = 30° to 55°C $\Delta H = 17.1 \pm 0.1$ kcal/mole

The uncertainties in the constants of the preceding equations represent standard deviations calculated from the residuals of the experimental data.

Inspection of the heats of sublimation shows that the values for the mono- and dimethylamine compounds are approximately the same and are some 5 kcal/mole higher than the value for the trimethylamine compound. This suggests that a single hydrogen bond involving a hydrogen attached to nitrogen is important in the crystal structure of the first two compounds.

3. THE DIPOLE MOMENTS OF THE AMINE-BORANES

(a) The Implications of Dipole Moment Studies

Many writers have made much of the fact that benzene and borazene are isosteric; in fact, borazene, $B_3N_3H_6$, is frequently referred to as "inorganic benzene." The analogy is encouraged by a marked similarity in many of the physical properties of borazene and benzene, but the chemical implications of such an analogy are clearly eliminated by marked differences in the chemical behavior of the two reagents.

After ammonia-borane was first prepared, many workers (i.e., E. Wiberg, E. Hughes, etc.) were quick to note that the molecule was isosteric with ethane and the trivial name "inorganic ethane" began to appear in discussions of H_3NBH_3. Although borazene and benzene have rather similar physical properties, ammonia-borane bears no obvious physical or chemical relationship to ethane. The former is a white crystalline solid which has a barely detectable vapor pressure at 40°C while the latter is a gas with a boiling point of -92°C. The low volatility and highly ordered crystal structure of ammonia-borane suggests a high degree of electrical disymmetry in the molecule, a fact which should show up clearly in the

size of its dipole moment; indeed the measured and published[45] value of 5.9D confirms such expectations.

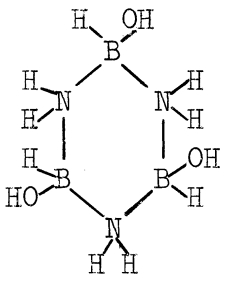
The method of representing in conventional formulae the charge separations which give rise to such a dipole value is rather arbitrary. Two possibilities might be considered. In the first, the fact that the boron atom of the BH_3 group accepts part interest in the electron pair of the nitrogen is frequently used to support the assumption that the boron becomes negative relative to its original state in the borane group, while the nitrogen of the ammonia becomes positive relative to its original state in the ammonia molecule. Charges are then assigned as follows:

$$\overset{\delta+}{H_3N} \longrightarrow \overset{\delta-}{BH_3}$$

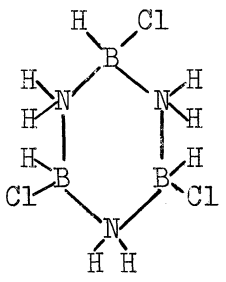
Alternatively, one can try to represent the fact that boron is more electropositive than nitrogen by the structure

$$\overset{\delta-}{H_3N}\overset{\delta+}{BH_3}$$

The latter representation is clearly suggested by the fact that reactions of compounds containing such boron-nitrogen structures usually occur to give products in which the more electropositive portion of the attacking reagent is bound to the nitrogen while the more electronegative portion is bound to the boron, e.g.,



$B_3N_3H_6 \cdot 3H_2O$



$B_3N_3H_6 \cdot 3HCl$

A comparison of the two formulae soon reveals that the difference between the two modes of representation is a result of the reference state chosen in each case. The first case implies that the boron of ammonia-borane is clearly negative when compared to the boron of an uncomplexed borane group, but the line of reasoning from which the formula was developed says nothing which demands that the boron bear either a relatively positive or negative charge in comparison to the nitrogen atom with which it is associated. In this sense the first representation can be misleading, particularly when applied to molecules containing atoms of distinctly different electronegativity values; it is much less misleading in carbon chemistry. This situation can be clearly represented by reference to a molecule such as LiCl. When the coordination compound $Li(NH_3)_x^+ Cl^-$ is

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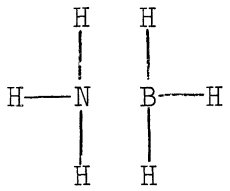
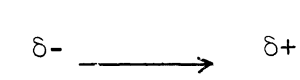
(45) J. R. Weaver, S. G. Shore, and R. W. Parry, J. Chem. Phys. 29, 1 (1958).

formed, the Li^+ ion is in all probability less positive than it was in LiCl, but the donation of electronic charge by each nitrogen does not mean that Li is of necessity negative with reference to either Cl^- or the attached nitrogen atoms. Electronegativity arguments, on the other hand, clearly suggest in agreement with chemical information, that the boron is the relatively positive end of the ammonia-borane molecule. On the basis of the above argument, the representation preferred in this discussion will be

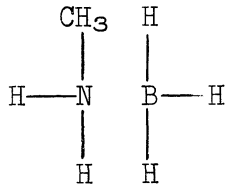
$$\overset{\delta-}{H_3N}\overset{\delta+}{HB_3}$$

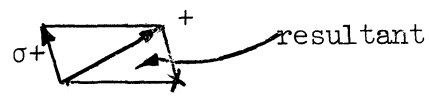
The usual inductive effect arguments of organic chemistry indicate that replacement of a hydrogen atom by a methyl radical should result in donation of relatively more electronic charge to the binding atom. Thus in $CH_3H_2NBH_3$ the methyl group should donate relatively more negative charge to the nitrogen than did the hydrogen of H_3NBH_3.





Simple Dipole Vectors

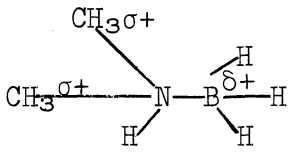


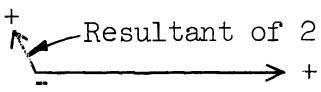


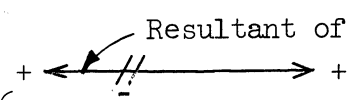
Simple Dipole Vectors

The naive vector model shown above indicates rather clearly that the effect of the electronic shift on the dipole is a most sensitive function of the molecular angles; indeed, with very reasonable assumptions regarding simplified "bond moments" and angles, one can rationalize the experimental fact that MeH_2NBH_3 has about the same moment as H_3NBH_3. The best available values are ammonia-borane 5.01D and methylamine-borane 5.02D. (See experimental subsection of this section.)

With two methyl groups replacing hydrogen as in dimethylamine, the inductive effect of the two methyl groups can be compensated in large degree by the angular orientation of the methyl groups. Thus the argument is not inconsistent with the observed value of 4.95D. Finally, in trimethylamine the fact that the three methyl groups are symmetrically placed about the nitrogen would demand a reduction in the dipole value.







The observed value of 4.69 is consistent with, but does not prove the simple model. The value is also consistent with the greater volatility of the compound Me_3NBH_3.

The above picture does predict, however, something yet to be verified as fact. The compound $H_3NBH_2CH_3$ could well have a moment comparable to that of ammonia borane, but the value for $H_3NB(CH_3)_3$ should indeed be larger than that of ammonia-borane. The measurement of moments for compounds of this type is of interest for the testing of both naive and sophisticated electronic models of the compounds involved. Indeed, dipole moment values for these materials offer a rather valuable testing ground for many theoretical concepts.

Since the amine-boranes are not sufficiently volatile as a group to permit the highly desirable vapor-phase studies, it has been necessary to make measurements in solution and to try to estimate the magnitude of the solvent effect in each recorded value. Unfortunately, methods for establishing these corrections are not well defined, and it is necessary to examine the overall question of dipole moment measurement for this group of compounds to obtain defensible data for the series. Many theoretical approaches to the question are found in the literature; selection of the most appropriate model for the system is still under examination.

(b) The Experimental Measurement of Dipole Moments for the Amine-Boranes

(1) Materials and the Preparation of Solutions for Measurement.

(1.1) Benzene.—Merck Reagent grade benzene, dried by refluxing with $LiAlH_4$, was used to make up the benzene solutions and to standardize the dielectric cell. It was used without drying for rinsing the dielectric cell and as a secondary standard. The dielectric constant of the undried material is only .003 to .004 higher than that of the dried substance. Moderate exposure to air does not affect the dielectric constant of benzene. It is a much more convenient standard than dioxane.

(1.2) Dioxane.—Preliminary purification of best quality commercial dioxane involved refluxing it with dilute HCl for 12 hours, preliminary drying involving storage of the liquid for several days in contact with successive batches of KOH, and finally distilling the liquid from $LiAlH_4$. Even the product obtained from the last step was not completely dry as was shown by a high value for its dielectric constant (2.255 as compared to an accepted value of 2.209). When the final product was refluxed with $LiAlH_4$ for several hours, and then distilled, the measured value of the dielectric constant was in good agreement with the accepted literature value (2.209 ± .003). Dioxane picks up water rapidly from the air and great care is required in its handling. Vacuum techniques were employed in general manipulation of this solvent.

(1.3) Ethyl ether.—Commercial "anhydrous diethyl ether" was dried by refluxing with $LiAlH_4$. Observed values for the dielectric constant were

4.205, 4.209, 4.225, and 4.207 as compared with an accepted value at 25°C of 4.235. This may indicate the presence of a nonpolar impurity but was not regarded as serious, since it should not affect the increment in dielectric constant resulting from the addition of solute.

(1.4) Ammonia-borane.—Samples from laboratory stock (see Ref. 15c for preparation) were placed on a filter in the vacuum line and leached into the solution tube (Fig. 13a) with the solvent. No weights were taken in the ammonia-borane determinations so the concentrations were available only from analysis. Samples for analysis were withdrawn from the solution at the time that it was transferred to the dielectric cell. Although H, B, and N values were obtained, the values for hydridic H were the most consistent with dielectric constant measurements. The boron values were the least reliable of the three. Typical hydridic H/N ratios were 2.93, 2.97, and 3.00. The final run on ammonia-borane was made by weighing out samples in the dry box as described below. The resulting solutions were completely clear, confirming the purity of the sample and the dryness of the solvents.

(1.5) Monomethylamine-borane.—The product resulting from the procedure described in Section IIB1 was used after sublimation. Solution preparation is described below.

(1.6) Dimethylamine-borane.—Samples of dimethylamine-borane, prepared by the method of Huff at Callery Chemical Company, were generously donated by Callery. The authors wish to thank Dr. Huff and Callery Chemical Company for these samples. The product was always sublimed before using. In preparing the solution the product was either sublimed directly into the preparation tube (Fig. 12a) or the sample was weighed out in the dry box. Analysis of representative samples confirmed the identity and purity of the product used. A representative ratio of hydridic hydrogen to nitrogen was 2.96; hydridic hydrogen to boron values of 3.15 and 3.08 were obtained.

(1.7) Trimethylamine-borane.—Trimethylamine was stored above $LiAlH_4$ to remove water and lower amines. It was then used to prepare trimethylamine-borane by conventional procedures. The compound was sublimed several times before use.

(2) Techniques of Measurement.— A rigidly standardized procedure was followed in preparing solutions.* The solution tube (Fig. 13a) was cleaned with nitric and chromic acids, rinsed with tapwater and distilled water until the water film remained continuous, then dried in the oven at 110°C. The tube was then evacuated, filled with dry nitrogen under a slight positive pressure, removed from the vacuum system and capped quickly with a rubber syringe stopper Stopcock grease was removed using a tissue soaked in CCl_4, static electricity was removed by wiping the entire assembly with a barely damp chamois, and the entire assembly was weighed, using as a tare a similarly shaped tube and stopper

*Except the modification for ammonia-borane; see Section IIB3(b).

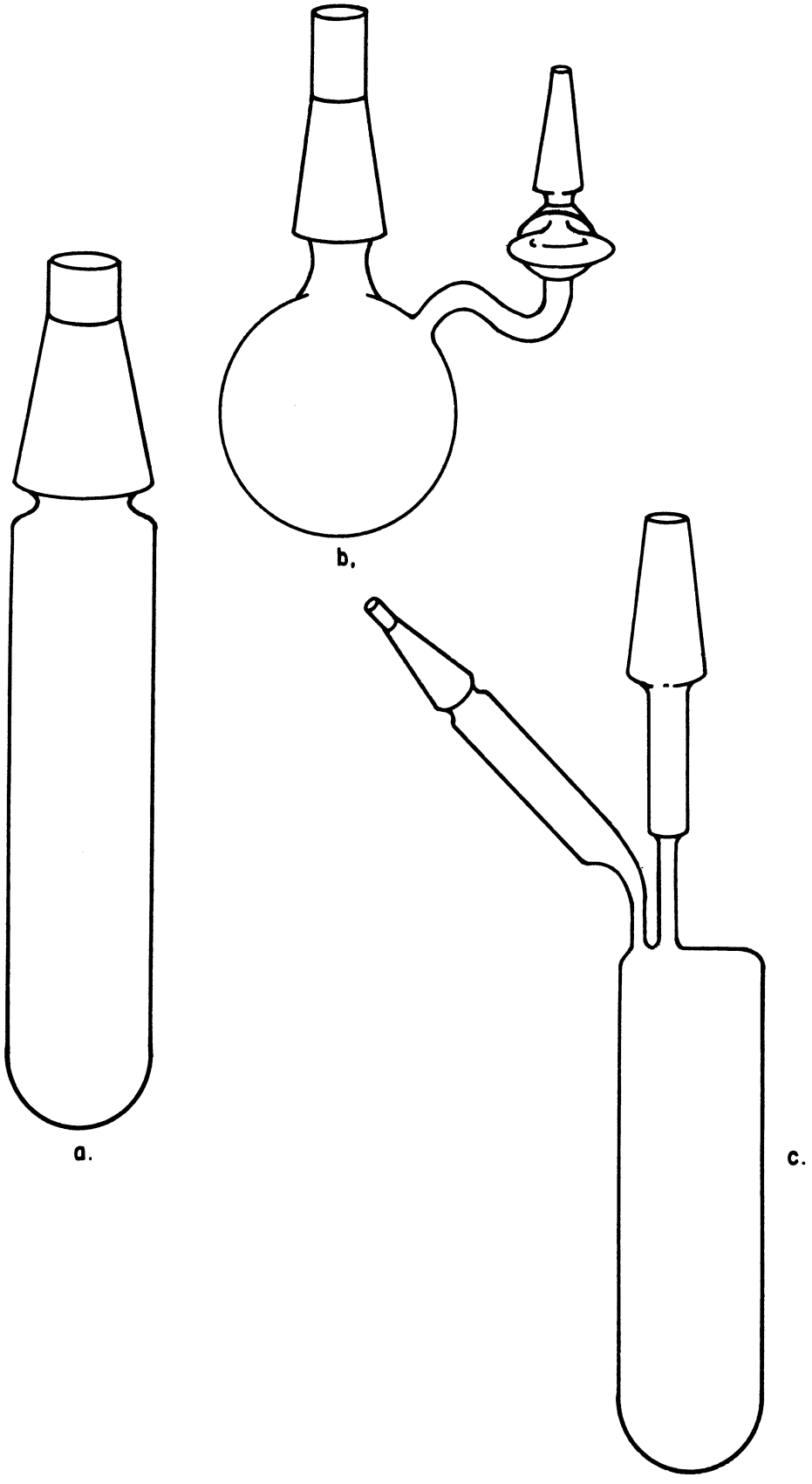


Fig. 13. a) Solution tube for dielectric constant. b) Special vacuum flask. c) Solution density flask.

assembly which had been treated in a similar fashion.

If the solute was to be sublimed into the tube, the lower part of the ground glass joint was lightly greased, the stopper removed and the tube quickly evacuated. After subliming in the solute, the tube was again filled with dry nitrogen, removed and weighed as before. For certain methylamine-borane and ammonia-borane runs, the tube was introduced into the drybox, opened, filled, capped, removed, and weighed as before.

The solvent was distilled from $LiAlH_4$ into the special flask shown in Fig. 13b. Dry nitrogen was admitted through the side arm and the flask was removed from the line and capped using a rubber syringe stopper. Whenever solvent was to be removed from this vessel by means of a hypodermic syringe, N_2 was admitted through the side arm to maintain a positive pressure of dry N_2 above the liquid. Using a 50-ml syringe, solvent could be transferred into the weighed solution tube (Fig. 13a) containing the solute. By reweighing, the quantity of a solvent added could be determined. Discrepancies in density determinations indicate that the rubber caps will absorb as much as 40 mg of benzene.

(2.1) Dielectric constant measurements.—Dielectric constant values were obtained using a precision heterodyne heat apparatus generously donated to The University of Michigan by the Chrysler Corporation. Solutions were introduced into and removed from the cell of the instrument by a syringe. After removal of the solution, the cell was filled twice with benzene, a reading being taken after the second time to check the constancy of the cell and measuring system. After removal of the benzene, dry nitrogen was passed through for five minutes, then solution was again introduced into the cell. The actual measurement required about 5 minutes but no change was detected as a result of longer standing.

(2.2) Determination of the cell constant for the dielectric measurements.—The cell constant is the ratio between condenser reading and dielectric constant for a known standard. Benzene was used as the standard, using the National Bureau of Standards value of 2.274 for its dielectric constant at 25°. The value of the constant was confirmed by reproduction of the accepted value for the dielectric constant of rigorously dried dioxane (2.209 ± .003) using the cell constant obtained from benzene. A new value for the cell constant was needed whenever the cell was resilvered.

(2.3) Refractive index measurements.—Solution remaining in the syringe after filling the dielectric cell was used for the refractive index measurement. Since the contribution of the refractive index term to the dipole moment value is almost negligible for these highly polar solutes, no attempt was made to obtain the dispersion; only the refractive index for the sodium D line, n_D, was obtained. A Bausch and Lomb precision Abbe refractometer was used and the solution was introduced directly between the plates and measurements were made rapidly.

(2.4) Density measurements.—To obtain density measurements on certain solutions, the special solution tube in Fig. 13c was substituted for the tube in Fig. 13a. The solute was sublimed into the tube and glass caps were placed over the joints during weighing. After insertion of the weighed quantity of solute, the solvent was carefully added, by a syringe. The tube capped with a syringe was equilibrated in a thermostat; then the level of solvent in the tube was carefully adjusted to that of a fine scratch on each constriction. The upper parts of the tube were heated with a heat gun to volatilize any excess liquid in that region. The tube was then closed with glass caps and weighed. Because of the extra manipulation and difficulty in mixing, the dielectric constant measurements on these solutions were in general less reproducible than those made on solutions from the tube shown in Fig. 13a.

(3) Results.—A large number (more than 60) of runs have been made. The technique is a difficult one but as procedures were refined, results became both more precise and more accurate (as based on reproduction of accepted values of dielectric constants of solvents, etc.). The values meriting the highest confidence are summarized in Table XI. The orientation polarization was obtained from the Cohen-Henriquez equation:

$$P_{orientation} = \frac{3M_o}{d_o(e+2)^2}\left[\frac{de}{dx} - 2(n_\infty)_o \frac{dn_\infty}{dx}\right]$$

where

$P_{orientation}$ = the molar orientation polarization of the solute

M_o = molecular weight of solvent

d_o = density of solvent

e_o = dielectric constant of pure solvent.

$(n_\infty)_o$ = the refractive index of benzene extrapolated to infinite wave length

and x, e, and n_∞ are the mole fraction, dielectric constant, and index of refraction at infinite wave length for the solution.

The molar orientation polarization of the solute is related to the dipole moment of the solute by the equation:

$$u = \left[\frac{akT\ P_{orientation}}{4\pi\ N_A}\right]^{1/2}$$

TABLE XI

SUMMARY OF DIPOLE MOMENT DATA

A. DIOXANE AS THE SOLVENT

1. Ammonia-borane

Mole % H_3NBH_3 in Solution	Dielectric[+] Constant of Solution	$\left[\frac{\partial e}{\partial x}\right]^{*}$	$\left[\frac{\partial n_D}{\partial x}\right]^{**}$	$\left[\frac{\partial d}{\partial x}\right]^{***}$	Dipole Moment Solute
0	2.209	--	--	--	--
.392	2.346	35.5	--	-.15±.03	--
.293	2.313	35.2	--	--	--
.402	2.351	35.4±.8	--	--	--
.840	2.504	35.1±.4	--	--	--
1.455	2.713	34.6±.2	.04±.005	--	--
1.99	2.89	34.2	.03	--	--
Best value from region of of highest precision (1%)		34.5±.5	.04±.005	-.15±.03	4.94 D
Value extrapolated to infinite solution (Fig. 13)		35.5	--	--	5.01 D

2. Methylamine-borane

Mole % $CH_3H_2NBH_3$ in Solution	Dielectric Constant of Solution	$\left[\frac{\partial e}{\partial x}\right]$	$\left[\frac{\partial n_D}{\partial x}\right]$	$\left[\frac{\partial d}{\partial x}\right]$	Dipole Moment Solute
0	2.215	--	--	--	--
.659	2.2448	35.4±1.0	--	--	--
1.754	2.817	34.3±1.0	--	--	--
0	2.212	--	--	--	--
1.122	2.608	35.3±.4	.02±.005	-.18±.03	--
0	2.208	--	--	--	--
.710	2.458	35.3±.6	--	--	--
1.654	2.787	35.0±.3	.02±.005	-.21±.02	--
Best value (measured)		35.2±.3	.02±.005	-.20±.03	4.99 D
Best value (extrapolated)		35.5	.02±.005	-.20±.03	5.02 D

[+]Values calculated using cell constant obtained with benzene as standard.

*Rate of change dielectric constant of solution with concentration.

**Rate of change refractive index (NaD line) of solution with concentration.

***Rate of change density of solution with concentration.

TABLE XI (Continued)

3. Dimethylamine-borane

Mole of $(CH_3)_2HNBH_3$ in Solution	Dielectric Constant of Solution	$\left[\frac{\partial e}{\partial x}\right]$	$\left[\frac{\partial n_D}{\partial x}\right]$	$\left[\frac{\partial d}{\partial x}\right]$	Dipole Moment Solute
0	2.08	--	--	--	--
.279	2.304	34.5±.8	Value below repeated on 4 solutions:	Value below repeated on 2 solutions	--
.757	2.470	34.5±.4			--
1.464	2.715	34.6±.2	-.005±.005	-.32±.04	--
0	2.12	--	--	--	--
.570	2.409	34.5±.6	--	--	--
1.097	2.594	34.8±.3	-.005±.005	--	--
Best value (measured)		34.6±.3	-.005±.005	.32±.04	4.96
Best value (extrapolated)		34.3	-.005±.005	.32±.04	4.93

4. Trimethylamine-borane

Mole % $(CH_3)_3NBH_3$ in Solution	Dielectric Constant of Solution	$\left[\frac{\partial e}{\partial x}\right]$	$\left[\frac{\partial n_D}{\partial x}\right]$	$\left[\frac{\partial d}{\partial x}\right]$	Dipole Moment Solute
0	2.213	--	--	--	--
.115	2.249	31±4	--	--	--
.315	2.311	31.1±1.5	--	--	--
.650	2.413	31.0±.6	-.02±.005	--	--
.850	2.479	31.3±1.0	--	--	--
.88-	2.490	31±2	-.03±.02	--	--
1.10	--	--	--	-.37	--
2.42	--	--	--	-.43	--
Best value (measured)		31.2±.5	-.02±.005	-.43±.05	4.71
Best value (extrapolated)		31.0	-.02±.005	-.43±.05	4.69

5. Ammonia triborane

0	2.202	--	--	--	--
.262	2.357	59.2±4	--	--	--
.541	2.529	60.4±.2	--	--	--
1.115	2.878	60.6±1	+.09±.02	--	--
Best value (measured)		60.6±1	+.09±.02	--	6.55 D
Best value (extrapolated)		60	+.09±.02	--	--

TABLE XI (Continued)

B. BENZENE AS THE SOLVENT

1. Methylamine-borane

% Solute in Solution	Dielectric Constant of Solution	$\left[\frac{\partial e}{\partial x}\right]$	$\left[\frac{\partial n_D}{\partial x}\right]$	$\left[\frac{\partial d}{\partial x}\right]$	Dipole Moment Solute
0	2.274	--	--	--	--
.404	2.375	25.1	--	--	--
.662	2.426	22.9	-.045	--	--
1.479	2.562	19.4	-.039	--	--

2. Dimethylamine-borane

0	2.274 (std)	--	--	--	--
.359	2.377	28.7	-.07	--	--
.396	2.385	28.0	-.07	--	--
.743	2.474	26.9	--	--	--
.788	2.485	26.8	-.07	-.34	--
1.066	2.550	25.9	-.07	--	--
1.594	2.668	24.7	-.073	--	--
3.356	3.058	23.4	-.066	--	--

3. Trimethylamine-borane

0	2.274 (std)	--	--	--	--
.218	2.341	30.6	-.105	-.22	--
.301	2.363	29.6	-.11	--	--
.343	2.375	29.5	-.10	--	--
.665	2.470	29.4	-.10	--	--
1.275	2.652	29.7	.098	--	--
1.814	2.819	30.0	-.098	--	--
2.245	2.950	30.1	-.097	--	--
Best value (measured)		29.9±3	-.098±.003	-.22±.05	4.64
Best value (extrapolated)		29.7	-.098±.003	-.22±.05	4.62

TABLE XI (Concluded)

C. DIETHYL ETHER AS THE SOLVENT

1. Ammonia-borane

Mole % of Solute in Solution	Dielectric Constant of Soltuion	$\left[\frac{\partial e}{\partial x}\right]$	$\left[\frac{\partial n_D}{\partial x}\right]$	$\left[\frac{\partial d}{\partial x}\right]$	Dipole Moment Solute
0	4.205	--	--	--	--
1.390	4.696	35.2	-.14	--	--

2. Methylamine-borane

0	4.205	--	--	--	--
.709	4.507	42.6	$\pm$.07	--	--

3. Dimethylamine-borane

0	4.205	--	--	--	--
.339	4.347	41.9	+.08	--	--
.730	4.510	41.8	+.08	--	--
1.266	4.730	41.5	+.08	--	--
0	4.225	--	--	--	--
.990	4.645	42.4	+.09	--	--
2.07	5.075	41.0	+.087	--	--

4. Trimethylamine-borane

0	4.209	--	--	--	--
.522	4.398	36.2	+.07	--	--
1.019	4.583	36.7	+.07	--	--

where

T = the absolute temperature = 298°K

k = the Boltzmann constant = 1.38×10^{-16}

N_A = Avogadro's number = 6.02×10^{23}

The most precise dielectric data for each solute-solvent pair are shown in Fig. 14. The rate of change of dielectric constant with concentration, $(\partial e/\partial x)$, is plotted against the mole fraction of solute in the solution. The variation in the $(\partial e/\partial x)$ with mole fraction is a point of some importance and is discussed in the next subsection.

In Table XI the best value (measured) of $(\partial e/\partial x)$ for each solute-solvent pair is the measured value in the neighborhood of 1-2 mole percent where the precision of the data is highest. The entry labeled "best value (extrapolated)" is obtained by extrapolating the appropriate lines of Fig. 14 to infinite dilution.

(4) Discussion.—All the amine-boranes show a high dielectric constant, as was anticipated. As seen in Table XII, the values for ammonia-borane, methylamine-borane, and dimethylamine-borane in dioxane are comparable. The value for trimethylamine-borane in dioxane is significantly lower than the other three.

TABLE XII

THE DIPOLE MOMENT OF THE AMINE-BORANES
IN DIOXANE AS A SOLVENT

Solute	Extrapolated Dipole Moment
Ammonia-borane [H_3NBH_3]	5.01 Debyes
Methylamine-borane [$CH_3H_2NBH_3$]	5.02 Debyes
Dimethylamine-borane [$(CH_3)_2HNBH_3$]	4.93 Debyes
Trimethylamine-borane [$(CH_3)_3NBH_3$]	4.69 Debyes

Several interesting and as yet unresolved points are evident from Fig. 14. These are listed below.

The monomethyl and dimethyl compounds show an abnormal variation of dielectric constant with concentration in benzene. The nature of the variation is what would be expected if the solute exists in both a monomeric and polymeric form.

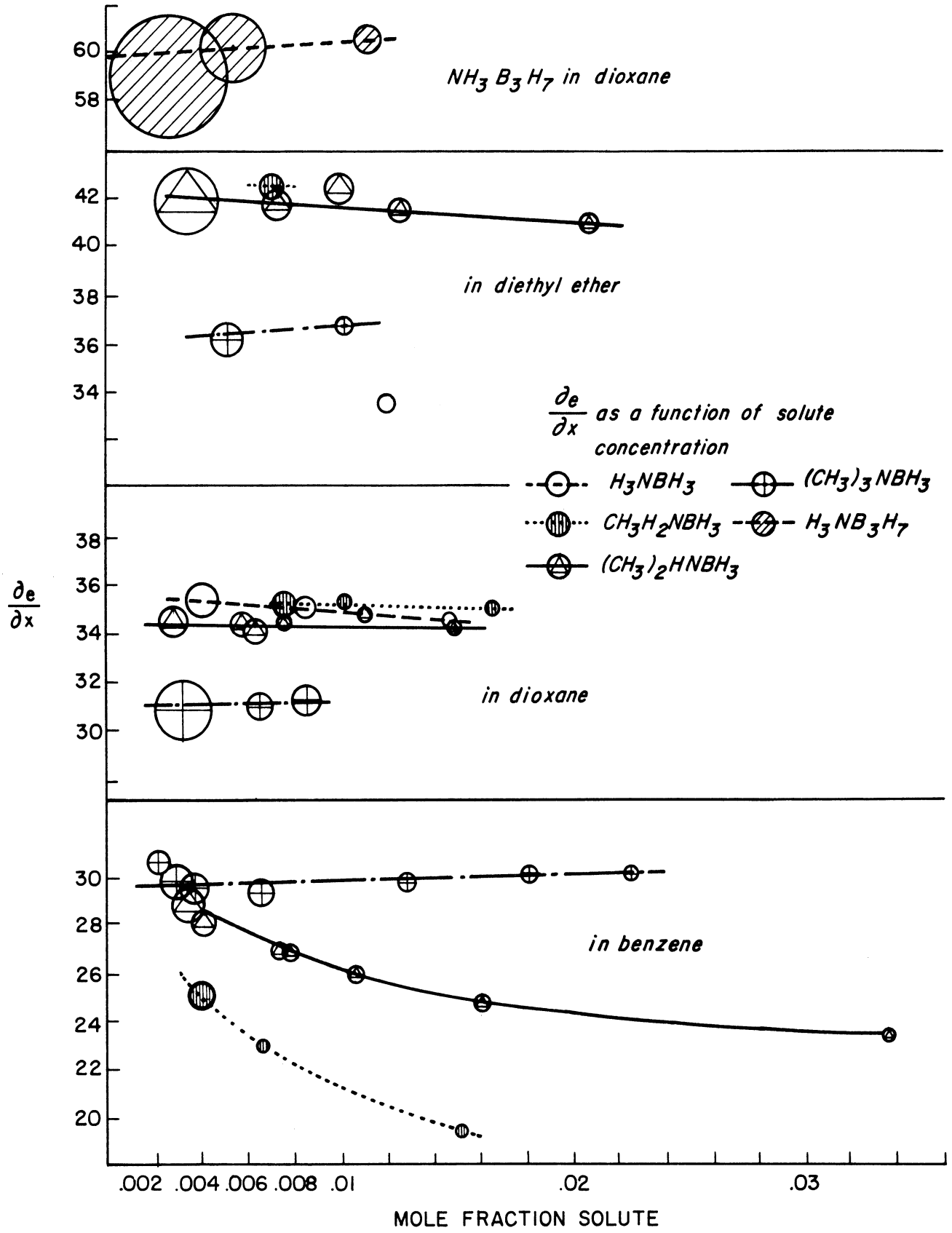


Fig. 14. ∂e/∂x versus mole percent solute.

The slope of the line would indicate that the association is greatest for the monomethyl compound. The low value for the single measurement of ammonia-borane in ether might possibly be due to the same phenomenon. It may be worth noting that the monomethylamine-borane in benzene and the ammonia-borane in ether dissolved with difficulty, while ammonia-borane is insoluble in benzene.

It is interesting and probably significant that the slope of the trimethylamine-borane line appears to be positive in each solvent. A small positive slope is indeed expected from theory for a normal solute. On the other hand, ammonia-borane seems to give a negative slope in dioxane, while the monomethyl and dimethylamine-borane lines are nearly horizontal in the same solvent. Such deviation from theory (if real) might suggest a small amount of association or of solute-solute interaction. Such an interaction was suggested in the solid by the heats of sublimation. The negative slope of dimethylamine in diethyl ether could also suggest solute-solute interaction.

As expected from theory, $(\partial e/\partial x)$ is higher in ether with a dielectric constant of 4.2 than in dioxane with a constant of 2.209. In benzene, however, the value is slightly lower than in dioxane, the reverse of what one would expect from the dielectric constants. Specific solvent-solute interaction is indicated.

4. THE RAMAN SPECTRA OF THE AMINE-BORANES

(a) Background

Despite the rather active chemical interest in boron hydrides and their derivatives, the amount of spectroscopic work which has been carried out on these compounds has been disproportionately small. This disparity is particularly marked if one compares the data available on vibrational frequencies, assignments, force constants, molecular parameters, and so on for the derivatives of simple hydrocarbons with the corresponding data for the various boron-hydride derivatives. Experimental difficulties caused by the high reactivities of the boron compounds are responsible to a large degree for this situation; however, if studies are carried out on condensed phases and at low temperatures, a great deal of spectroscopic information can be obtained which can yield significant values for molecular constants and provide a basis for comparisons of chemical properties. A systematic study of all the amine-boranes is in progress; the data on ammonia-borane are most complete.

(b) Vibrational Frequencies and Assignments of Isotopic Varieties of Ammonia-Borane Having C_{3v} symmetry

(1) Background.—Ammonia-borane is of some interest spectroscopically since it provides a molecule of relative simplicity and high symmetry containing the B-N "dative bond." Since the hydrogen atoms on the boron and nitrogen

atoms are sufficiently dissimilar chemically that exchange does not occur at a measurable rate in solution, it is possible to prepare a number of deuterated derivatives in which the symmetry of the parent molecule is preserved. The possibility of arriving at an unequivocal set of assignments is thus excellent and the results should be of considerable value in the interpretation of spectral results for more complicated boron compounds. In addition, the data provide a basis for the further comparison of the frequencies associated with the BH_3 group as they are modified in complexes with different bases.

(2) Experiment.—Ammonia-borane was prepared by standard methods,[15c] the appropriate deuterated materials being used where necessary to get isotopically substituted molecules. Deutero-ammonia was prepared from Mg_3N_2 and heavy water while B_2D_6 was prepared from BF_3 and $LiAlD_4$ according to standard procedures. All samples were purified before use by removing all material insoluble in diethyl ether.

In view of the nature of the compound, Raman spectroscopy was most suitable for use in the investigation and samples were prepared in liquid ammonia and in dimethyl ether using essentially the same procedure as for the work on the borohydride ion (see page 165). The concentration range customarily employed was between 3 to 5 molar and the samples were maintained at temperatures of approximately -35° during an exposure. Infrared spectra of some of the samples were obtained as Nujol mulls but the compounds proved too soft to mull readily and the spectra obtained were not entirely satisfactory. Details of the spectroscopic equipment are given in Ref. 15h.

(3) Experimental Results.—The Raman frequencies observed for five isotopic varieties of $H_3N{:}BH_3$ dissolved in liquid ammonia or ammonia-d_3 are listed in Table XIII. In some cases where solvent interference prevented observation of a band in the liquid ammonia solution, values obtained from dimethyl ether solutions or from the infrared spectra of Nujol mulls have been substituted. Less information was obtained from the dimethyl ether solutions than the ammonia due to the greater number of solvent bands and consequently greater interference. With one exception, the positions of the observed bands were not shifted significantly on going from one solvent to the other. The exception is the frequency assigned to the B-N stretching vibration which appears at 787 cm^{-1} in liquid ammonia solutions of $N_3H{:}BH_3$. This frequency was found at 755 cm^{-1} in dimethyl ether solution, indicating an appreciable solvent interaction, probably with the ammonia. The exact nature of the interaction is not certain but it seems likely that it involves a weak N-H..N hydrogen bond. Comparison of the solvent effect on the N-H bands would give most direct support to this hypothesis but unfortunately interference by solvent bands in the NH_3 solution was too great to allow the solute bands to be distinguished. However, in molecules containing the ND_3 group, it was possible to distinguish the N-D variations of the complex both in liquid ND_3 solution as well as in dimethyl ether solution and positions of the bands in the two solvents agreed within a few cm^{-1}. The failure of the N-D bands to shift is evidence against the hydrogen bond hypothesis and the exact nature of the interaction remains uncertain. For consistency in the

TABLE XIII

ASSIGNMENT OF FREQUENCIES IN THE SPECTRA OF THE AMMONIA-BORANES

Solutions in Ammonia or Ammonia-d_3

Observed Frequencies, cm^{-1}					Symmetry and No.		Description[a]
H_3NBH_3	D_3NBH_3	H_3NBD_3	D_3NBD_3	$D_3NB^{10}D_3$			
(3185[b])[c]	2323[b]	--	2323[b]	--	a_1	ν_1	ν-NH
2263	(2260[b])	1641	1643	1645	a_1	ν_2	ν-BH
1175	1171	857	840	848	a_1	ν_3	δ-BH_3
1060[d]	--	--	--	--	a_1	ν_4	δ-NH_3
787	754	737	708	712	a_1	ν_5	ν-BN
(3300[b])	(2465[b])	--	(2460[b])	--	e	ν_7	ν-NH
2316	2313	1743	1715	1741	e	ν_8	ν-BH
1600[d]	--	--	--	--	e	ν_9	δ-NH_3
--	--	--	--	--	e	ν_{10}	δ-BH_3
--	1006	917	917	936	e	ν_{11}	ρ-BH_3
--	--	648	574	(570)	e	ν_{12}	ρ-NH_3
		1575?			A_1		$\nu_3+\nu_5$
			1767	1775	E		$\nu_3+\nu_{11}$
		1833	1834	1871	A_1 + E		$2\nu_{11}$
		2319					H contamination on BD group?
2372	2372[b]	1716			A_1		$2\nu_3$
	(2380[b])		2378[b]		A_1 + E		$2\nu_9$
	2163		2162	(2161)			Apparently due to interaction with solvent
3040 to 3100							
	2252		2262	(2260)			

a Symbols sued: ν = stretching, δ = deformation, ρ = rocking.

b Value taken from the Raman spectrum of a dimethyl ether solution of the material.

c Bracket indicates a rather large uncertainty in the value, 5 to 10 cm^{-1}.

d Value taken from the infrared spectrum of a Nujol mull of the material.

discussion of the frequency assignments, values from the liquid ammonia solutions will be used.

(c) Discussion

X-ray studies[40] have shown that $H_3N{:}BH_3$ has an ethane-like structure with C_{3v} symmetry (see Fig. 12). Such a molecule should possess twelve vibrational frequencies classified into five A_1, one A_2 and six E frequencies, the latter being doubly degenerate. The A_1 and E frequencies are allowed in both infrared absorption and the Raman effect but the A_2 is forbidden in both. The notation used in describing the frequencies and an approximate description of the mode of motion is given in Table XIV.

TABLE XIV

DESCRIPTION OF FUNDAMENTAL VIBRATIONS OF $H_3N{:}BH_3$

Frequency	Symmetry	Description
ν_1	A_1	Symmetrical N-H stretch
ν_2	A_1	Symmetrical B-H stretch
ν_3	A_1	Symmetrical H-N-H deformation
ν_4	A_1	Symmetrical H-B-H deformation
ν_5	A_1	B-N stretch
ν_6	A_2	Torsional motion around B-N axis
ν_7	E	Asymmetrical N-H stretch
ν_8	E	Asymmetrical B-H stretch
ν_9	E	Asymmetrical H-N-H deformation
ν_{10}	E	Asymmetrical H-B-H deformation
ν_{11}	E	BH_3 group rock
ν_{12}	E	NH_3 group rock

The isotopic substitution of deuterium for hydrogen should result in a marked lowering of the frequencies involving hydrogen motions, the ratio approaching 1.41. The effect on the other frequencies, while easily discernible, should be much less pronounced. Since a number of the fundamentals have not been observed in the spectra, application of the more rigorous product rule to the isotopic frequencies to confirm assignments does not appear feasible.

The two N-H stretching modes of the normal compound were readily identified as the bands at 3185 and 3300 cm^{-1} in spectra of dimethyl ether solutions, the former being assigned to the symmetric mode on the basis of polarization measurements. These two frequencies shift, respectively, to 2323 and about 2460 cm^{-1} with deuteration on the nitrogen. Deuteration of the boron had virtually no effect on the N-H frequencies, indicating little coupling between the two ends of the molecule. It is of interest to note that both N-H stretching frequencies

are some 100 cm^{-1} lower than the corresponding frequencies of 3304 and 3394 observed for free NH_3 in a dimethyl ether solution of the same concentration.

Boron-hydrogen stretching frequencies occur in the region around 2300 cm^{-1}, but the identification of the fundamentals in the present case was complicated somewhat by the presence of overtones of the bending modes enhanced in intensity by Fermi resonance with the fundamentals. The two bands at 2263 and 2316 cm^{-1} in the spectrum of the normal molecule have been assigned, respectively, to the symmetrical and unsymmetrical modes largely on the basis of their intensities and position. They shift to approximately 1640 and 1740 cm^{-1} upon deuteration. As in the case of the N-H bands, the B-H frequencies are relatively unaffected by deuteration of the other end of the molecule. Both B-H stretching frequencies are relatively low, the position of the symmetrical mode virtually coinciding with the corresponding frequency of the borohydride ion[2] while the unsymmetrical is about 70 cm^{-1} higher than ν_3 of the same ion. Previous work has shown that the position of the B-H stretching frequencies of the BH_3 group is a good index of the strength of the interaction with the Lewis base. In the present molecule, it appears that ammonia is nearly the equal of the hydride ion, H^-, in the extent of its interaction with BH_3.

Due to solvent interference in both solvents, it was not possible to identify either of the N-H or N-D deformation modes in solution. Results from an infrared mull of the normal material indicate that both occur at positions virtually unchanged from their positions in the free ammonia molecule. The symmetrical B-H and B-D deformation fundamentals were identified at about 1175 and 840 cm^{-2}, their expected positions, on the basis of polarization measurements. The unsymmetrical mode was not observed, either because its intensity was too low or because it was accidentally degenerate with the symmetrical frequency.

The remaining symmetrical frequency is ν_5, the B-N stretching vibration, and its position is of particular interest, partly because of the information which it can yield regarding the dative bond and also because there has been some disagreement about its position in related molecules. The situation is particularly favorable for its identification in the present case since the only other fundamentals belonging to the A_1 symmetry class involve hydrogen motions almost exclusively and consequently can be distinguished with little chance of confusion.

The only band which appears as a possible choice for ν_5 occurs at 787 cm^{-1} in the liquid ammonia spectrum of the normal compound. This band is moderately strong and well polarized. Upon deuteration of both ends of the molecule, the band shifts to 708 cm^{-1} giving a frequency ratio of 0.90. If the NH_3 and BH_3 halves of the molecule are considered as approximate point masses, the ratio of isotopic frequencies should be given by the square root of the inverse ratio of reduced masses, $\sqrt{\mu/\mu^*}$. This mass is calculated to be 0.91 for the comparison of the normal and completely deuterated molecules, the difference of only 1% providing excellent support for the correctness of the assignment. Similar comparisons using the frequencies of the partially deuterated species gives agreements of the same order of magnitude. The B-N force constant calculated using

the diatomic approximation is 2.8 millidynes/Ångstrom. The value given for this force constant by Badger's rule using the B-N distance of 1.6 Ångstroms[40] is 2.4 md/Å. The agreement is satisfactory considering the empirical nature of the rule, the large (±0.2 A.U.) uncertainty in the B-N distance, and the other approximations involved. It is of interest to note that the B-N distance in this molecule is the same within limits of error as the B-N distance in the BF_3 amine complexes[46] and that consequently the B-N frequency in these latter compounds should be found in the region near 800 cm^{-1} instead of the region near 1000 cm^{-1} where it has recently been assigned.[47]

Of the three fundamentals remaining to be discussed, one, ν_6, is inactive and no information was obtained as to its position. The other two involve rocking motions of the BH_3 and NH_3 groups and may be expected to have low intensities in the Raman effect. The values assigned to the BH_3 and BD_3 rocking frequencies, 1006 and 917 cm^{-1}, respectively, are somewhat higher than the values assigned to the corresponding motions in the BH_3CO molecule and are not to be considered as final. In particular, the possibility exists that one or the other may be the asymmetric deformation mode which has not been assigned. The NH_3 and ND_3 rocking motions, on the other hand, appear fairly certainly identified as the bands at 648 and 574 cm^{-1} since they are the lowest in the spectra and nitrogen deuteration affects them appreciably while boron deuteration does not.

The least certain of the above assignments are those for the deformation and rocking modes of the BH_3 group. At the present time, the Raman data do not appear adequate to allow a clear decision to be made. Information from the infrared spectra of thin films at low temperatures, if the films can be prepared, may supply the necessary evidence, and it also appears that a normal coordinate treatment will be necessary for final confirmation.

5. THE NUCLEAR MAGNETIC RESONANCE SPECTRUM OF Me_2HNBH_3

The nuclear magnetic resonance spectrum of molten Me_2HNBH_3 was obtained. Three peaks attributable to B-H links and one to the N-H resonance were visible. The study is still incomplete.

C. Phosphorous Trifluoride-Borane

1. BACKGROUND

Phosphorus trifluoride-borane was first prepared in this laboratory under

(46) J. L. Hoard, S. Geller, and W. M. Cashin, Acta. Cryst. 4, 396 (1951).
(47) a) J. Goubeau and H. Mitschelen, Z. phys. Chem. 14, 61 (1958).
b) H. Luther, D. Mootz, and R. Radwitz, J. Pract. Chem. 277, 242 (1958).

sponsorship of WADC.[41] The molecule was of considerable theoretical interest since earlier arguments of Chatt had suggested that boron and aluminum would be incapable of forming coordination compounds with PF_3 because they lacked electrons. Since publication of the original paper, it has been suggested by others, without any experimental or real theoretical support, that the molecule is held together by "π-bonds" involving delocalization of the B-H electrons. Such speculation seems to do little beyond clutter the literature.

Of the more immediate concern is an experimental study of the structure and chemistry of this molecule. Parry and Bissot assumed an ethane-like structure for the molecule. The reaction of the molecule with trimethylamine was that expected from conventional theory. If stoichiometric quantities of F_3PBH_3 and trimethylamine were mixed, the trimethylamine displaced the PF_3 quantitatively to form $(CH_3)_3NBH_3$ and free PF_3. If an excess of trimethylamine were used, the liberated PF_3 reacted in a one-to-one ratio to give gases and a solid which was never fully characterized.

When F_3PBH_3 reacted with excess ammonia over the temperature range -178° to -80°, five molecules of ammonia seemed to be picked up by each molecule of the borane adduct. The reaction with stoichiometric quantities of ammonia was not carried out and the nature of the ammonia reaction product was never established.

2. THE RAMAN SPECTRUM OF PHOSPHORUS TRIFLUORIDE-BORANE AND PHOSPHORUS TRIFLUORIDE-BORANE-d_3

More definitive structural information of F_3PBH_3 and F_3PBD_3 has been obtained from a study of the Raman spectra of these molecules. All observed bands were assigned and the ethane-like model, assumed in the original work was supported. The molecule has C_{3V} symmetry.

The samples prepared as described after fractionation on the vacuum line 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.[48] The spectra of the liquid were obtained at -80°C, qualitative polarization measurements being made on the hydrogen compound only, using the two method and polaroid cylinders. The data reported in Table XV represent the averages from several spectra, the estimated probable error being approximately 1 cm^{-1} except where indicated.

Reference has been made previously[47] to the chemical similarity between PF_3 and carbon monoxide, and to the similarity in properties between phosphorous trifluoride-borane and carbon monoxide-borane. In view of the known structure of H_3BCO,[49] it would therefore be expected that the phosphorous complex would

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(48) G. L. Vidale and R. C. Taylor, J. Am. Chem. Soc. 78, 294 (1956).
(49) Gordy, Ring, and Bury, Phys. Rev. 78, 512 (1950).

TABLE XV

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	ν_{12}	PF_3 rock
370	362	vw	e	ν_{11}	F-P-F deformation
441	421	m, p	a_1	ν_5	F-P-F deformation
607	572	s, p	a_1	ν_4	P-B stretch
697±2	--	vw	e	ν_{10}	BH_3 rock
799		vw			Diborane?
886±5	--	vw, p?	A_1	$2\nu_5$	2x441=882
920	--	w, p	A_1+A_2+E	$\nu_8-\nu_{12}$	1117-197=920
944	944±5	m, p?	a_1	ν_3	P-F stretch
957±3	958±2	m, dp	e	ν_9	P-F stretch
1040±3	--	w, p	A_1	$\nu_4-\nu_5$	441+607=1048
1077	--	w, p	a_1	ν_2	H-B-H deformation
1117	807	s, dp	e	ν_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	$2\nu_2$	2x1077=2154
2247±2	1602	vw	A_1	$2\nu_8$	2x1117=2234
2328±4	--	vvw		$2\nu_3+\nu_5$?	Calc 2329
2385	1717	vs, p	a_1	ν_1	B-H stretch
2455	1845	vs, dp	e	ν_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

have an ethane type configuration with C_{3v} symmetry. 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 H_3BCO which have been determined recently.(50) 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 H_3BCO. Boron-hydrogen deformation bands are observed at 1077 and 1117 cm^{-1} for the a_1 and e modes which 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 944 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_3BH_3 were not observed directly. The position of the first, the symmetrical B-D band, is estimated at 842 cm^{-1} from its first overtone, and the position of the second, the BD_3 rock, is estimated to be close to 600 cm^{-1} from the comparison with the frequencies of D_3BCO. The calculated product rule ratios using these estimated values are 1.98 and 2.53 for the a_1 and e classes, respectively, which may be compared with theoretical values of 1.97 and 2.61. The spectra thus can be interpreted satisfactorily in term of the C_{3v} or ethane-like model.

3. THE REACTION BETWEEN F_3PBH_3 AND AMMONIA

As noted in an earlier section, the reaction between F_3PBH_3 and trimethylamine can be summarized by the equations:

$$Me_3N + F_3PBH_3 \longrightarrow Me_3NBH_3 + PF_3$$

$$PF_3 + ME_3N_{(excess)} \longrightarrow \text{New Products}$$

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(50) R. C. Taylor, J. Chem. Phys. 26, 1131 (1957); this report, p. .

It is tempting to extrapolate the behavior of NMe_3 and to predict that a similar reaction might take place if NH_3 were used in place of NMe_3, but a well-supported axiom of coordination chemistry indicates that the chemistry of ammonia cannot be predicted from observations on other amines. The following studies were undertaken to establish the nature of the F_3PBH_3 - NH_3 reaction.

Addition of one mole of NH_3 to F_3PBH_3 without solvent over a temperature range of -78°C to -170°C did not result in liberation of PF_3 or the isolation of H_3NBH_3. Only NH_4F was formed and 1/4 of the original F_3PBH_3 was recovered from the system. It was also found that PF_3 reacted with ammonia at -111°C to produce NH_4F as one of the products.

The NH_3 + F_3PBH_3 reaction was then tried under somewhat milder conditions using as excess of NH_3. Diethyl ether was used as a solvent and a controlled low temperature, ranging from -111°C to -35°C, was employed. Under these conditions the reaction is best represented as:

$$6NH_3 + F_3PBH_3 \xrightarrow[-111 \text{ to } -35°C]{Et_2O} \downarrow 3NH_4F + (H_2N)_3PBH_3$$

The latter compound, triamido-phosphorus-borane, is a new ether-soluble crystalline solid with a characteristic X-ray diffraction pattern. It is stable when pure but undergoes decomposition when contaminated. Analytical data for characterization show: H_2 = 32.0 mmoles/g; N = 45.5 ± .5 mmoles/g; B = 12.1 mmoles/g. Theoretical values for $(H_2N)_3PBH_3$ are H_2 = 32.3 mmoles/g; N = 45.3 mmoles/g; B = 11.55 mmoles/g.

It has been pointed out by others that the BH_3 group isisoelectronic with the oxygen atom and indeed certain early molecular orbital arguments compared B_2H_6 and the oxygen molecule. While the original arguments were rendered inapplicable by geometric differences, one might extrapolate the above unestablished argument to note a similarity between F_3PO and F_3PBH_3 with ammonia:

$$6H_3N + F_3PBH_3 \longrightarrow 3NH_4F + (NH_2)_3PBH_3$$

$$6H_3N + F_3PO \longrightarrow 3NH_4F + (NH_2)_3\,PO$$

The above formalistic relationsip does not prove the validity of the analogy. A combination of more conventional reaction processes might well account for the observation. For example, one might write

$$NH_3 + F_3PBH_3 \longrightarrow H_3NBH_3 + PF_3 \xrightarrow{NH_3} NH_4F + F_2PNH_2BH_3$$

Such a process could well account for the observations of the one to one reaction. Alternatively, one might write

$$NH_3 + F_3PBH_3 \longrightarrow H_3NBH_3 + PF_3$$

$$PF_3 + 6NH_3 \longrightarrow 3NH_4F + P(NH_2)_3$$

$$H_3BNH_3 + P(NH_2)_3 \longrightarrow (H_2N)_3PBH_3 + NH_3$$

More detailed mechanistic studies are underway, but the formalistic analogy which serves at least as a reaction guide is still of interest and is worthy of more explicit testing. The work is continuing.

D. Raman Spectra, Vibrational Assignments, and Force Constants for H_3BCO and D_3BCO

Spectroscopic studies of compounds such as H_3BCO are of interest since they can provide information not only on the BH_3 group but also on the nature of the acid-base interaction between the BH_3 and the CO. In the present work, the Raman spectrum of H_3BCO, has been obtained, a complete assignment of fundamental frequencies has been made, and a set of valence force constants has been determined which agrees with experimental data for four isotopic combinations.

Only one previous spectroscopic paper on H_3BCO has appeared, a paper by Cowan[51] reporting the infrared spectrum of the vapor. Five fundamentals reported by him agree with the values found in the present work, two he did not observe, and his assignment of the last appears incorrect. No data for the D_3BCO molecule have been found.

1. EXPERIMENTAL

Both H_3BCO and D_3BCO were prepared by reaction of B_2H_6 or B_2D_6, respectively, with CO in a sealed tube at several atmospheres pressure. After several days, the tubes were opened and the contents carefully fractionated at low temperatures on the vacuum line. After fractionation, the sample was distilled into the Raman cell which was then sealed off. To reduce thermal decomposition, the vapors were never allowed to come in contact with surfaces warmer than about -50°C during all transfer operations. The spectra obtained showed no bands attributable to diborane or CO which would be produced as decomposition products. The sample of H_3BCO examined was about 1 ml in volume while the D_3BCO was about 0.2 ml. During the exposures, the samples were maintained at approximately -80°C, at which temperature the decomposition occurring in the liquid is negligible. A general description of the apparatus and spectrograph has been given previously.[48] Exposure times varied from ten minutes to three hours using Eastman 103a-J plates. Measurements were made with a comparator directly on the plates and on enlarged tracings made with a Leeds and Northrup microphotometer. The estimated probable

(51) R. D. Cowan, J. Chem. Phys. 18, 1101 (1950).

error for most lines reported is approximately 1 cm^{-1}.

2. EXPERIMENTAL RESULTS

The experimentally observed frequencies for H_3BCO are listed in Table XVI and those for D_3BCO are listed in Table XVII. Tracings of spectra of the two substances selected to show the fundamentals most clearly are shown in Figs. 15 and 16. The agreement between the frequencies here reported and those found previously in the infrared of the vapor is very satisfactory, the differences at most amounting to a few cm^{-1} and being well within the normal shifts in frequency observed in the transition from vapor to liquid. Several overtones and combinations were observed on some of the longer exposures on H_3BCO which are not shown in the figure. No bands attributable to diborane or CO were observed in any of the spectra indicating a fairly high purity for the compounds. However, a weak band was observed at 2411 cm^{-1} in the spectrum of the deuterated compound which indicates a small amount of hydrogen to be present.

3. ASSIGNMENTS

The H_3BCO molecule has C_{3v} symmetry which predicts eight fundamentals, all active in the Raman effect, which are either totally symmetric (A_1) or doubly degenerate (E). Previous work on boron compounds has shown that B-H stretching frequencies fall in the range between 2000 and 2600 cm^{-1}. Three frequencies appear in this range in the H_3BCO spectrum. Deuterium substitution affects only two, however; and, on the basis of their polarization characteristics, the band at 2380 cm^{-1} is assigned as ν_1 and the band at 2434 cm^{-1} as ν_5. In the D_3BCO spectrum, the asymmetric frequency ν_5 occurs at 1825 cm^{-1} but the position of ν_1 cannot be determined exactly because of Fermi resonance with the overtone of the fundamental at 860 cm^{-1}. The two members of the Fermi doublet occur at 1678 and 1749 cm^{-1}. The latter is assigned as the overtone and the former to the fundamental on the basis of the B^{10} satellite appearing on the high-frequency side of 1749 at 1777 cm^{-1}. Comparison of the intensities of the two bands indicates that the coincidence between the overtone and the fundamental is very close and consequently the unperturbed value of ν_1 probably is not far from 1700 cm^{-1} on the high-frequency side. ν_1 was not observed in the infrared spectrum of the hydrogen compound[51] but its predicted value agrees with that given above. The third band in the 2000 cm^{-1} region is immediately identified as the C-O stretch, both from its nearness to the carbon monoxide frequency at 2143 cm^{-1} and from the fact that deuterium substitution does not shift its position. The assignment of the band is further confirmed by its polarization characteristics.

The situation with regard to the B-H bending modes is somewhat more complicated. In the hydrogen compound, a triplet is observed in the 1100 cm^{-1} region with maxima at 1073, 1101, and 1133 cm^{-1}, the first being the most intense and probably polarized. In the D_3BCO spectrum, two bands of approximately equal intensity appear at 808 and 860 cm^{-1}, the latter having a weak satellite on its high-frequency side at 881 cm^{-1}. Since polarization measurements were not made

TABLE XVI

OBSERVED RAMAN FREQUENCIES OF LIQUID H_3BCO AT -80°C

Band Position (in cm^{-1})	Intensity	Assignment
317	m	ν_8-e fundamental
632	vvw	$2\nu_8$
692	w (pol.)	ν_4-a fundamental
705±2	vw	ν_4'-B^{10} isotopic species
816	w	ν_7-e fundamental
1073	s (pol.?)	ν_3-a_1 fundamental
1101	m	ν_6-e fundamental
1133	w	$\nu_7+\nu_8$
1626	vvw	$2\nu_7$
1761	vvw	$\nu_3+\nu_4$
1887	vvw	$\nu_6+\nu_7$
2129	vw	$2\nu_3$
2169	s (pol.)	ν_2-a_1 fundamental
2380	s (pol.)	ν_1-a_1 fundamental
2434	s	ν_5-e fundamental
2703	vvw	$\nu_1+\nu_8$

TABLE XVII

OBSERVED RAMAN FREQUENCIES OF LIQUID D_3BCO AT -80°C

Band Position (in cm^{-1})	Intensity	Assignment
264	w	ν_8-e fundamental
619	m	ν_4-a_1 fundamental
706	w	ν_7-e fundamental
808	m	ν_6-e fundamental
860	m	ν_3-a_1 fundamental
881	w	ν_3'-B^{10} isotopic species
991	w	?
1678	s	ν_1-a_1 fundamental
1749	s	$2\nu_3$
1777	w	$2\nu_3'$-B^{10} isotopic species
1825	s	ν_5-e fundamental
2169	s	ν_2-a_1 fundamental
2411	w	B-H stretch

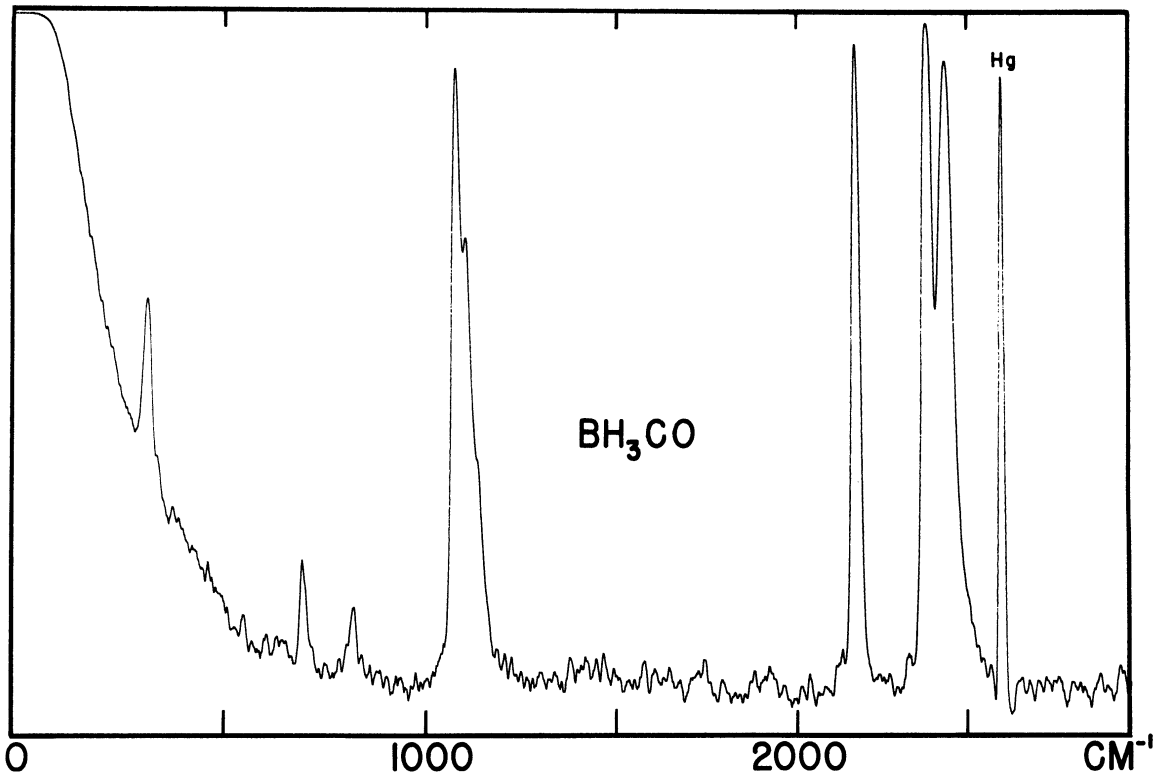

Fig. 15. The Raman spectrum of H_3BCO at -80°C.

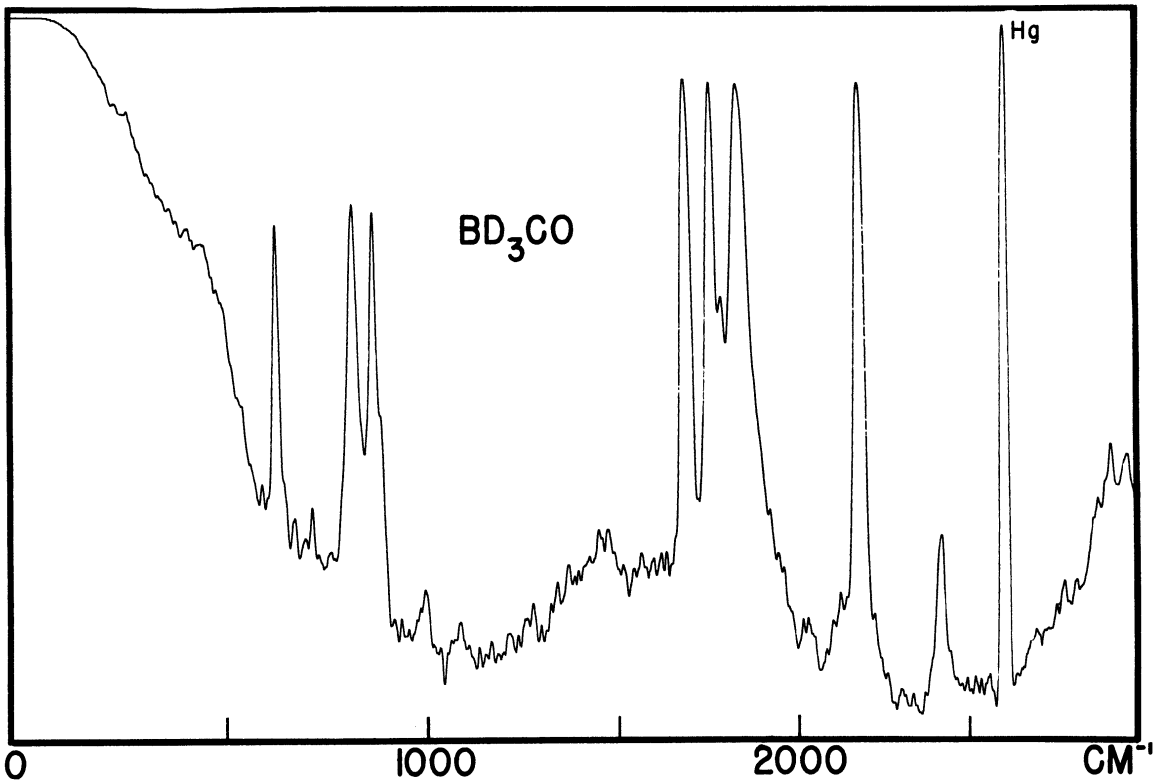

Fig. 16. The Raman spectrum of D_3BCO at -80°C.

on the deuterated spectrum, the product rule plus the results of the normal coordinate treatment were necessary to arrive at a satisfactory assignment. Fortunately, the dimensions and moments of inertia of the four possible isotopic molecules of C_{3v} symmetry, $H_3B^{11}CO$, $D_3B^{11}CO$, $H_3B^{10}CO$, $D_3B^{10}CO$, have been determined from microwave results[49] so that the theoretical product ratios can be calculated with no assumptions. The closest agreement with the theoretical values is obtained by assigning ν_3 to the 1073 cm^{-1} and ν_6 to the 1101 cm^{-1} band in the hydrogen compounds and ν_3 to the 860 cm^{-1} and ν_6 to the 808 cm^{-1} bands of the deuterium species. Confirmation for the interchange in the relative position of the two bands in the deuterium case comes from the normal coordinate calculation of the B^{10} shift. For the A_1 frequency of the deuterated molecule, the calculated shift is 22 cm^{-1}, while for the E frequency it is only 5 cm^{-1}, a separation that would not be resolved by the equipment used. The presence of a weak satellite 21 cm^{-1} higher than 860 cm^{-1} is therefore accepted as additional evidence that the higher band is the A_1 frequency, the satellite being assigned as ν_3 of the B^{10} isotopic species. In the hydrogen compound, the B^{10} isotope shifts are calculated to be +12 and +4 cm^{-1} respectively for ν_3 and ν_6. Since the observed spacings between the members of the observed triplet are 28 and 32 cm^{-1}, it appears that neither can easily be assigned to the B^{10} species. However, the combination of the two E modes at 816 and 317 cm^{-1} has a calculated value of 1133 cm^{-1} and the correct symmetry to resonate with an E fundamental and borrow sufficient intensity to appear as a weak band. The band at 1101 cm^{-1} accordingly is assigned as ν_6. Cowan, in his infrared work,[51] assigned ν_6 to a band at 1392 cm-1. No band at this position was observed in the Raman spectrum, and it appears that the infrared band most likely is $\nu_3 + \nu_8$ which, from the Raman data, is calculated at 1390 cm^{-1}. He assigned ν_3 to a band at 1105 cm^{-1} but comments that this band had some peculiar features which now appear explained.

The remaining fundamentals may all be classed as skeletal modes. The only polarized, fairly intense band left occurs at 692 cm^{-1} in the H_3BCO spectrum and shifts to 619 cm^{-1} upon deuteration. This is assigned to ν_4 in agreement with the infrared results. A satellite was observed at 705 cm^{-1} in the more intense exposures on the hydrogen compound and, on the basis of a calculated shift of +16 cm^{-1} from the force constant treatment, is assigned to ν_4 of $H_3B^{10}CO$. The corresponding shift in the deuterated molecule is calculated to be only 5 cm^{-1} and accounts for the failure to observe a satellite to the 619 cm^{-1} band.

The two fundamentals ν_7 and ν_8 can be considered as bending motions of the axial chain of atoms. The second, ν_8, the B-C-O deformation, is to be expected at a rather low frequency in view of the masses of the atoms involved. It consequently is assigned to the moderately intense depolarized band at 317 cm^{-1} in the H_3BCO spectrum. This fundamental was not observed in the infrared work, but its position was predicted quite accurately. In the deuterated spectrum it appears at 264 cm^{-1}.

The last fundamental, ν_7, which is most simply described as a BH_3 rock, is assigned to 816 cm^{-1} partly by a process of elimination and partly from the infrared evidence. The corresponding band at 706 cm^{-1} in the deuterated compound is rather weak, but the correctness of the assignment is substantiated by the

product rule calculations (Table XX).

4. NORMAL COORDINATE TREATMENT

Cowan[51] carried out a normal coordinate treatment of the H_3BCO molecule based on the results of his infrared study and obtained a set of force constants which produced reasonably satisfactory agreement with his assignments. However, in view of the incorrect assignment for ν_6 and of the fact that data on the deuterated molecule were not available, it would appear that a better approximation can now be obtained. Since his equations did not include interaction force constants, the molecule was reanalyzed using the FG method of Wilson and the following symmetry coordinates:

A_1 species:

$$S_0 = (3 + 3a^2)^{-1/2} \times [\Delta\alpha_{12} + \Delta\alpha_{23} + \Delta\alpha_{31} + a(\Delta\beta_1 + \Delta\beta_2 + \Delta\beta_3)] \equiv 0$$

$$S_1 = \Delta T$$

$$S_2 = \Delta R$$

$$S_3 = 3^{-1/2} (\Delta r_1 + \Delta r_2 + \Delta r_3)$$

$$S_4 = (3 + 3a^2)^{-1/2} [-a(\Delta\alpha_{12} + \Delta\alpha_{23} + \Delta\alpha_{31}) + \Delta\beta_1 + \Delta\beta_2 + \Delta\beta_3]$$

where

$$a = -\frac{\sqrt{3}\cos\beta}{\cos\frac{\alpha}{2}}$$

E species:

$$S_5 = 2^{-1/2} (\Delta r_2 - \Delta r_3)$$

$$S_6 = 2^{-1/2} (\Delta\beta_2 - \Delta\beta_3)$$

$$S_7 = 2^{-1/2} (\Delta\alpha_{31} - \Delta\alpha_{12})$$

$$S_8 = \Delta\delta_X$$

In terms of the molecule parameters, T refers to the C-O bond, R to the B-C bond, r_i to the ith B-H bond, α_{ij} to the H-B-H angle between r_i and r_j, β_i to the ith H-B-C angle and δ_X to the B-C-O angle. The equilibrium values for these parameters taken from the microwave work[49] are as follows: T = 1.131A, R = 1.540A, r = 1.194A, α = 113°52', β = 104°37', δ = 180°.

The elements of the inverse kinetic energy (G) matrix were evaluated from the tables of Decius[52] and the note by Ferigle and Meister.[53] As a check on

(52) J. C. Decius, J. Chem. Phys. 16, 1025 (1948).
(53) S. M. Ferigle and A. G. Meister, J. Chem. Phys. 19, 982 (1951).

the correctness of the equations, the force constants of Cowan were substituted into the secular equation and the roots were found to agree with his calculated values. The present calculations were carried out in terms of the symmetry force constants, F_i and F_{ij}, where the single index indicates principal force constants and the double, interaction constants. It was found that the calculated frequencies were rather insensitive to most of the possible interaction force constants but were quite sensitive to two. It was not necessary to give values to any of the insensitive constants to obtain a satisfactory fit, and the potential energy, therefore, is given adequately by the following expression containing only ten constants:

$$2V = F_1S_1^2 + F_2S_2^2 + F_3S_3^2 + r^2F_4S_4^2 + 2RF_{24}S_2S_4 + F_5S_5^2 + r^2F_6S_6^2 + r^2F_7S_7^2 + RTF_8S_8^2 + 2R^2F_{68}S_6S_8$$

This reproduces the sixteen frequencies of the $H_3B^{11}CO$ and $D_3B^{11}CO$ molecules with a standard deviation from the observed values of 0.3% which undoubtably is less than the error introduced by the harmonic approximation. Since there are four product rule relations among the sixteen fundamental frequencies, twelve independent data exist, and the problem is slightly overdetermined. By inspection of the potential function, it will be seen that the F matrices are nearly diagonal, only one off-diagonal element appearing in each symmetry block. The off-diagonal element in the A_1 block is F_{24} linking the symmetrical bending coordinate and the B-C stretching coordinate, while the off-diagonal element of the E block, F_{68}, links the BH_3 rocking coordinate with the B-C-O deformation. In both cases, the two lowest frequencies in the respective symmetry classes are involved, and considerable mixing of the two motions is indicated.

The valence force potential constants are related to the symmetry force constants through the elements of the F matrix and in principle may be obtained by solving a set of simultaneous equations. Frequently, however, the number of valence force constants exceeds the number of equations available so that a number of constants must remain undetermined. In such circumstances, the practice has been either to tabulate appropriate unresolved combinations of the valence force constants or to make arbitrary but reasonable assumptions regarding the magnitude of certain of the constants which permits the assignment of numerical values for the rest. The usual assumptions involve setting some of the interaction constants equal to zero; the particular ones selected being chosen on the basis of previous experience or other physical arguments. An alternative and perhaps more objective way of introducing enough arbitrary assumptions to allow giving values to all valence force coordinates is to retain the redundant symmetry coordinate, S_0, in the transformation from the $\underline{f}$ matrix to the $\underline{F}$ matrix and then to equate the elements of the $\underline{F}$ matrix involving the redundant coordinate to zero. In the present case, this procedure provides enough equations so that values for all constants can be given. These are tabulated in Table XVIII. It must be emphasized that this method is just as arbitrary as the older procedure; the only justification is that it is objective and can be applied in a consistent manner to molecules of different structures.

TABLE XVIII

FORCE CONSTANTS FOR THE H_3BCO MOLECULE

Symmetry Force Constant	Value (md/Å)	Valence Force Constant	Value (md/Å)
F_1	17.9800	k_T	17.9800
F_2	2.7900	k_R	2.7900
F_3	3.2920	k_r	3.1587
F_4	0.3486	k_α	0.2768
F_{24}	0.1753	k_β	0.2801
		$k\delta$	0.2744
F_5	3.0920	k_{rr}	0.0667
F_6	0.2203	$k_{\alpha\alpha}$	-0.0703
F_7	0.2434	$k_{\beta\beta}$	-0.0339
F_8	0.2744	$k_{\alpha\beta}=k'_{\alpha\beta}$	-0.0567
F_{68}	0.0793	$k_{R\alpha}$	-0.0633
		$k_{R\beta}$	0.0790
		$k_{\beta\delta}$	0.0647

$k_{RT} = k_{rR} = k_{r\alpha} = k'_{r\alpha} = k_{r\beta} = k'_{r\beta} = k_{\alpha\delta} = k_{r\delta} = 0$

The values calculated for the fundamental frequencies of carbon monoxide-borane by the normal coordinate treatment are compared with those observed in Table XIX. Since two frequencies attributed to B^{10} molecules were observed, the calculations were extended to include both boron isotopic species. The calculated values for the B^{10} molecular frequencies are given in Table XIX in the form of the shifts in frequency from the calculated values of the corresponding B^{11} frequencies. As an additional check on the calculations, the B^{11}/B^{10} product rule ratios were calculated using a set of B^{10} frequencies obtained by adding the calculated isotope shifts to the experimentally observed B^{11} frequencies. The agreement as shown by the numerical values in Table XX is quite satisfactory.

Comparisons of force constants from different molecules are not always as meaningful as one would like because published values inevitably depend on such factors as the type of potential function used and the number of interaction constants retained, the closeness of fit secured, the magnitude of the anharmonicity errors, and so on. Bond stretching force constants are the least affected by such variations and when derived by the usual valency force field can be used qualitatively in the same fashion as bond energies and bond lengths to give an indication of the electron density concentrated in a given bond. In the carbon monoxide borane molecule one of the interesting observations is the small effect which the presence of the borane group has on the C-O bond. The force constant of the C-O bond in carbon monoxide gas calculated from the observed infrared frequency of 2143 cm^{-1} is 18.5 md/Å. This is decreased only to 17.98 md/Å

TABLE XIX

COMPARISON OF OBSERVED AND CALCULATED VALUES OF THE FUNDAMENTAL FREQUENCIES FOR THE VARIOUS ISOTOPIC SPECIES OF THE H_3BCO MOLECULE[a]

Fundamental		$H_3B^{11}CO$				$D_3B^{11}CO$				$H_3B^{10}CO$		$D_3B^{10}CO$	
		Obs	Calc	Diff.	%	Obs	Calc	Diff.	%	Calc Shift	Obs	Calc Shift	Obs
A_1	ν_1	2380	2378	-2	0.1	(1700)[b]	1701	--	-	+ 2.5	--	+ 4.3	--
	ν_2	2169	2169	0	0	2169	2169	0	0	0.4	--	0.4	--
	ν_3	1073	1070	-3	0.3	860	863	+3	0.3	12.1	--	22.5	21±2
	ν_4	692	691	-1	0.1	619	621	+2	0.3	16.0	13±2	4.8	
E	ν_5	2434	2431	-3	0.1	1825	1827	+2	0.1	15.0	--	21.3	--
	ν_6	(1101)[b]	1101	--	-	808	805	-3	0.4	3.6	--	5.4	--
	ν_7	816	816	0	0	706	704	-2	0.3	6.3	--	3.2	--
	ν_8	317	315	-2	0.6	264	265	+1	0.4	0.0	--	0.1	--

a Standard deviation for 14 frequencies = 0.3%.

b The data enclosed in parentheses are for fundamentals disturbed by Fermi resonances and are estimated values.

TABLE XX

COMPARISON OF PRODUCT RULE RATIOS FOR VARIOUS ISOTOPIC COMBINATIONS OF THE H_3BCO MOLECULE

Isotope Held Constant	Isotopes Compared	Symmetry Class	Frequency Product Ratio Theoret.[a]	Calc[b]	Dev.
B^{11}	H/D	A_1	1.931	1.953	1.1%
B^{11}	H/D	E	2.513	2.522	0.4
B^{10}	H/D	A_1	1.929	1.951	1.1
B^{10}	H/D	E	2.498	2.507	0.4
H	B^{11}/B^{10}	A_1	1.036	1.036	0.0
H	B^{11}/B^{10}	E	1.017	1.017	0.0
D	B^{11}/B^{10}	A_1	1.037	1.037	0.0
D	B^{11}/B^{10}	E	1.024	1.023	-0.1

a Calculated from moments of inertia of reference 3 and the masses involved.

b The frequencies for the B^{11} molecules were those observed; the frequencies for the B^{10} molecules were obtained by adding the shifts determined in the force constant treatment to the experimental values of the B^{11} frequencies.

in H_3BCO, whereas in nickel carbonyl the C-O force constant is 15.9 md/Å,[54] and in carbon dioxide it is 15.5 md/Å. This small change is consistent with the small (ca 0.001 A) increase in CO bond length and with the chemical instability of the molecule. However, the adjacent B-C bond is not as weak a bond as one might expect from this, its force constant of 2.79 md/Å being only slightly less than the value 2.9 md/Å predicted by Badger's rule. Unfortunately, there appear to be no other data available on B-C bond constants for further comparisons. However, the calculated value for H_3BCO does not seem entirely consistent with the rather large amount of no-bond character which has been proposed[49] for this bond.

The two molecules, perhaps, with which it would be of most interest to compare B-H stretching force constants are diborane and the borohydride ion. A value of 3.42 md/Å has been used in a normal coordinate treatment of diborane;[55] however, this figure was transferred unaltered from an earlier treatment of borazine,[56] and it is of doubtful significance to do more than note that it is of the same magnitude as the value found in the present work. A more reliable

(54) B. L. Crawford and P. C. Cross, J. Chem. Phys. 6, 525 (1938).

(55) R. P. Bell and H. C. Longuet-Higgins, Proc. Roy. Soc. (London) A183, 357 (1945).

(56) B. L. Crawford and J. T. Edsall, J. Chem. Phys. 7, 223 (1939).

value has been calculated recently by Scherer[57] in an investigation of the infrared intensities of the vibrational bands of diborane but this datum has not yet been published.

The value of 3.16 md/Å found for the B-H constant in H_3BCO appears to be significantly greater than the value 2.77 md/Å calculated for the borohydride ion (see page 172). This difference can be interpreted as indicating that the electronic configuration around the boron atom is somewhere intermediate between the trigonal sp^2 hybridization expected for the hypothetical free BH_3 molecule and the tetrahedral sp^3 hybridization in the borohydride ion and as indicating that the lone pair of electrons on the carbon atom have not been utilized fully in forming the boron-carbon bond. The same conclusion, of course, can be drawn from the larger than tetrahedral angle (113°) in H_3BCO.

Finally, it may be pointed out that the experimental product rule ratios for the hydrogen-deuterium substitution listed in Table XX are greater than the theoretical values, even though the differences are not large. Exact agreement, of course, is not to be expected since the observed rather than harmonic values have been used in calculating the ratios. However, the normal effect of anharmonicity is to cause the experimental ratios calculated in this way to be less than the theoretical.[58] In view of the weight of other evidence and of the fact that all experimental ratios are greater than the theoretical, it does not seem probable that there is an error in the assignments. The difference, therefore, may also reflect the specific electronic structure of the molecule or the BH_3 group and, if so, should be found in other molecules containing the borane group.

E. The Structure of the Diammoniate of Borane-Carbonyl

1. BACKGROUND

When borane-carbonyl was first prepared by Burg and Schlesinger,[59] it was noted that the complex reacted with trimethylamine to give trimethylamine-borane and free CO, but the compound appears to react in a different fashion with ammonia. A solid product containing 2 moles of ammonia per mole of borane-carbonyl was formed. The structure of this so-called "diammoniate of borane-carbonyl" remains a mystery, and the mystery is being examined in this laboratory.

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(57) J. Scherer, thesis, Univ. of Minn., April, 1958.
(58) F. Halvorsen, Revs. Modern Phys. 19, 87 (1947).
(59) A. B. Burg and H. I. Schlesinger, J. Am. Chem. Soc. 59, 780 (1937).

2. THE MODEL

In rationalizing the behavior of borane-carbonyl, a formalistic analogy between F_3PO and F_3PBH_3 was noted. The BH_3 group seemed to be serving in a formal sense as a coordinated oxygen. An extrapolation of the above argument would suggest that H_3BCO might be analogous under some circumstances to CO_2 and the diammoniate of borane-carbonyl might well be considered analogous to ammonium carbonate.

$$2H_3N + CO_2 \longrightarrow NH_4^+ \left[\begin{matrix} O \\ | \\ C\text{-}O \\ | \\ NH_2 \end{matrix} \right]^-$$

$$2H_3N + H_3BCO \longrightarrow NH_4^+ \left[H_3B\text{-}C \begin{matrix} \diagup O \\ \diagdown NH_2 \end{matrix} \right]^-$$

The resulting solid $H_3BCO \cdot 2NH_3$ does not easily form a crystalline solid which will yield either a powder pattern or single-crystal photograph. The problem is similar to that encountered in the early studies of $B_2H_6 \cdot 2NH_3$. As in the former case, chemical evidence may well provide the first structural information.

Samples of $H_3BCO \cdot 2NH_3$ have been prepared for study. The diammoniate is much more stable than the parent H_3BCO molecule.

III. THE REACTIONS AND STRUCTURES OF THE AMMONIA ADDITION COMPOUNDS DERIVED FROM TETRABORANE

A. Background

Although the reaction between diborane and ammonia has been studied rather intensively, little work other than the pioneer study of Stock and his colleagues[60] has been carried out on the tetraborane-ammonia reaction. The solution of the structural problem associated with $B_2H_6 \cdot 2NH_3$ increased interest in the ammonia addition compounds of tetraborane, since the possibility of a systematic extension of concepts seemed most challenging. Indeed, as will be shown in the following sections, the chemistry of tetraborane parallels that of diborane rather closely.

B. The Preparation and Structure of the Diammoniate of Tetraborane

1. THE PROBLEM

In their initial study of the reaction between tetraborane and ammonia Stock, Wiberg, Martini, and Nicklas[60] froze excess ammonia and tetraborane together using liquid air; then they held the system at -78°C for one hour. When excess ammonia was removed, the composition of the residue corresponded to the formula $B_4H_{10} \cdot 4NH_3$. The solid decomposed when warmed to room temperature; gaseous boron compounds, hydrogen, and ammonia gas were liberated, and the "salt-like solid turned to a liquid." When excess tetraborane was used in the reaction instead of an excess of ammonia, an unstable solid residue of composition $B_4H_{10} \cdot 2.5NH_3$ resulted.

In a careful study of the same system made in this laboratory, neither the formula $B_4H_{10} \cdot 4NH_3$ nor $B_4H_{10} \cdot 2.5NH_3$ could be verified despite all efforts to reproduce the experimental conditions described in the original study. A modification of the experimental procedures resulted, however, in the isolation of a pure diammoniate of tetraborane $B_4H_{10} \cdot 2NH_3$, which is stable at room

(60) A. Stock, E. Wiberg, and H. Martini, Ber. 63, 2927 (1930); A. Stock, E. Wiberg, H. Martini, and A. Nicklas, ibid., 65B, 1711 (1932).

temperature. A preliminary description of this solid has been given.[61] In this report a more complete account of the investigation is recorded, and evidence is presented in support of the belief that the original "compounds" described by Stock and his co-workers were indeed complex and unstable mixtures.

2. THE PREPARATION AND PROPERTIES OF $B_4H_{10}\cdot 2NH_3$

When ammonia was added slowly to a cold (-78°C) ether solution of tetraborane, the ammonia was absorbed completely. An excess of tetraborane (in relation to ammonia) was always used. If the system was aged at low temperature (4 days at -78, 12 hours at -45), and then the solution filtered and the solvent removed from the filtrate at -45°C, a white, dry, microcrystalline solid identified by analysis as $B_4H_{10}\cdot 2NH_3$ was obtained. The molecular weight of the product as determined by vapor pressure depression in liquid ammonia was 81 (61c). In diethyl ether values obtained by vapor pressure depression ranged from 150 to 250. The theoretical value for $B_4H_{10}\cdot 2NH_3$ is 87. The marked discrepancy between results in liquid ammonia and in ether would suggest that $B_4H_{10}\cdot 2NH_3$ is an ionic type of solid. Ionic solids such as $NaBH_4$, NH_4Br, and $[H_2B(NH_3)_2]BH_4$ exist in liquid ammonia as ion pairs, thus giving a molecular weight in this solvent equal to the normal formula weight.[62] On the other hand, certain ionic or semi-ionic solids which dissolve in ether [e.g., $FeCl_3$, $Na_2HB(CH_3)_2$][63] give ion clusters and high values for the apparent molecular weight.

The compound $B_4H_{10}\cdot 2NH_3$ undergoes no visible decomposition in air at room temperature. It dissolves in cold water with only very slow hydrogen evolution. Acid or platinized platinum accelerates hydrogen evolution markedly in water. The compound is soluble in liquid ammonia and, judging from its X-ray powder pattern, it is unchanged upon recovery from the liquid ammonia solution. If perfectly dry, the compound will dissolve in anhydrous diethyl ether to give a stable solution at room temperature; the compound can be recovered unchanged by evaporation of the solvent. If, however, the solid has been handled in moist air prior to its solution in ether, a precipitate slowly forms. The diammoniate of tetraborane is insoluble in aromatic as well as in aliphatic hydrocarbons.

The crystalline nature of the material is indicated by the X-ray powder data. The interplanar spacings and relative intensities of the reflections are given in Table XXI. A single-crystal X-ray study is being conducted in the laboratory of Dr. C. Nordman of this department.

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(61) a) G. Kodama and R. W. Parry, J. Am. Chem. Soc. 79, 1007 (1957); b) G. Kodama and R. W. Parry, paper presented before the Inorganic Section of the Sixteenth International Congress of Pure and Applied Chemistry, (Paris, 1957), p. 483; c) G. Kodama, Ph.D. dissertation, Univ. of Mich., 1957.

(62) R. W. Parry, G. Kodama, and D. R. Schultz, J. Am. Chem. Soc. 80, 24 (1958).

(63) A. B. Burg and G. W. Campbell, Jr., J. Am. Chem. Soc. 74, 3744 (1952).

TABLE XXI

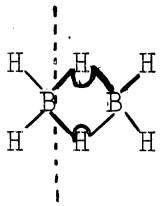
INTERPLANAR SPACINGS AND RELATIVE INTENSITY DATA FOR $B_4H_{10}\cdot 2NH_3$

Intensity*	d(Å)	Intensity	d(Å)
w	6.50	w	2.36
w	6.10	mw	2.29
m	4.63	w	2.18
s	4.10	w	2.03
m	3.69	vw	1.97
w	3.48	vw	1.89
m	3.29	vw	1.84
w	3.06	vw	1.81
ms	2.88	vw	1.78
m	2.78	vw	1.74
w	2.62	vw	1.60
m	2.57	vw	1.54
m	2.52	vvw	1.50
w	2.46		

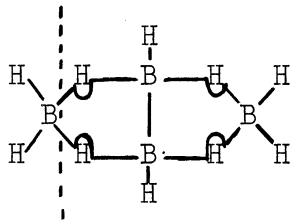
*s = strong, m = medium w = weak, v = very.

3. CHEMICAL EVIDENCE FOR THE STRUCTURE OF $B_4H_{10}\cdot 2NH_3$

Although no unequivocal physical evidence on the structure of $B_4H_{10}\cdot 2NH_3$ is yet available, it is possible to assign a structure with a high degree of certainty on the basis of chemical evidence. The arguments listed earlier supporting an ionic or semi-ionic model are reminiscent of those used in the case of the diammoniate of diborane which has the structure $[H_2B(NH_3)_2][BH_4]$. The structures of diborane and tetraborane can be represented in planar projection as:



and



It is significant that the end borons of tetraborane are bound to the rest of the molecule only by double bridge bonds. This feature resembles rather closely, but is not identical to, the double bridge bond structure of diborane. Nonsymmetrical cleavage of the double bridge bond of diborane by ammonia (see

dotted line on formulas) results in the structure $[H_2B(NH_3)_2^+][BH_4^-]$. An application of the same argument to tetraborane suggests for the diammoniate of tetraborane the structure $[H_2B(NH_3)_2^+][B_3H_8^-]$. Such a model immediately suggests a number of discriminating chemical reactions which should be of structural significance. These are outlined below.

(a) The Reaction of $B_4H_{10}\cdot 2NH_3$ with Sodium

The reaction between sodium and the diammoniate of diborane was one of the basic experimental points upon which proposals for the structure of $B_2H_6\cdot 2NH_3$ were based. The data may be interpreted[64] in terms of the structure $[H_2B(NH_3)_2][BH_4]$ by using the following equation:

$$[H_2B(NH_3)_2][BH_4] + Na \xrightarrow[-78°C]{\text{liq } NH_3} 1/2\ H_2 + NaBH_4 + H_2BNH_2$$

Since the reaction is fundamentally that of the complex cation $[H_2B(NH_3)_2]^+$ and sodium, one would expect the following reaction if the proposed structure for $B_4H_{10}\cdot 2NH_3$ were accepted:

$$[H_2B(NH_3)_2][B_3H_8] + Na \xrightarrow[-78°C]{\text{liq } NH_3} 1/2\ H_2 + NaB_3H_8 + H_2BNH_2$$

The prior isolation and unequivocal characterization of NaB_3H_8 in an excellent independent study by Hough, Edwards, and McElroy[65] provided an easy and meaningful framework for the study of the above reaction.

A solution of $B_4H_{10}\cdot 2NH_3$ in liquid ammonia will react with dissolved metallic sodium at -78°C to liberate one half mole of hydrogen per mole of $B_4H_{10}\cdot 2NH_3$ (see Fig. 17 for related data). This reaction is complete in 20 minutes; further hydrogen evolution proceeds more slowly (Fig. 17). If the reaction is stopped after the initial rapid hydrogen evolution process has been completed, NaB_3H_8 can be extracted in 60 to 70% yield from the solid residues by leaching them with diethyl ether. The NaB_3H_8 was identified by comparing its X-ray powder pattern with that of an authentic pattern for NaB_3H_8 which was kindly furnished by Dr. L. J. Edwards of Callery Chemical Company.

(b) The Reactions of $B_4H_{10}\cdot 2NH_3$ with HCl and HBr

Schlesinger and Brown[66] found that under proper conditions metal borohydrides will react with HCl as indicated by the following equation:

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(64) D. R. Schultz and R. W. Parry, J. Am. Chem. Soc. 80, 4 (1958).
(65) W. V. Hough, L. J. Edwards, and A. D. McElroy, J. Am. Chem. Soc. 78, 689 (1956).
(66) H. I. Schlesinger and H. C. Brown, J. Am. Chem. Soc. 62, 3429 (1940).

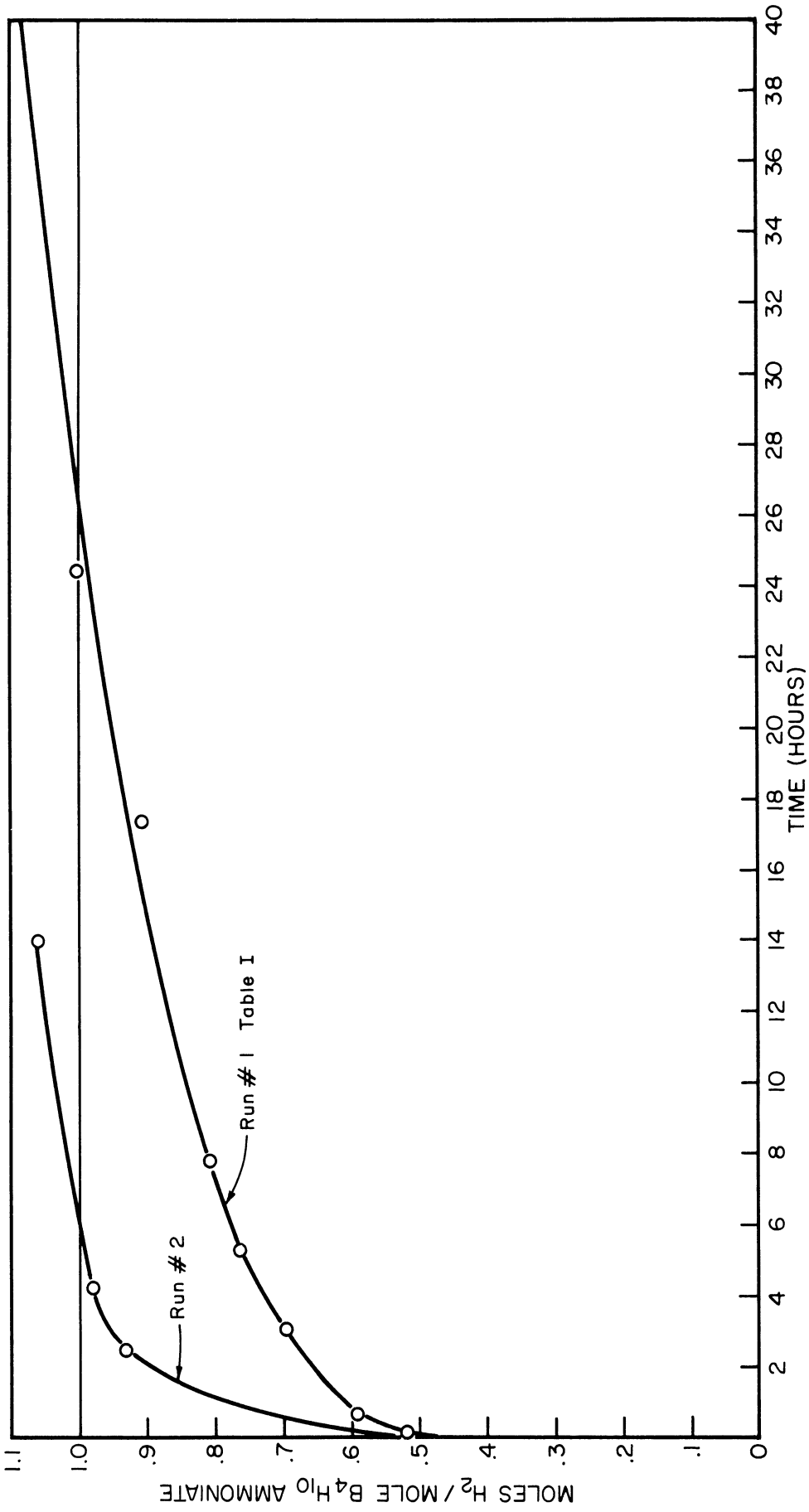


Fig. 17. The rate of H_2 evolution in the reaction between sodium and $B_4H_{10} \cdot 2NH_3$.

$$MBH_4 + HCl \longrightarrow MCl + H_2 + 1/2\ B_2H_6$$

In his early studies on the diammoniate of diborane Stock[67] noted that HCl acts on $B_2H_6 \cdot 2NH_3$ to give significant quantities of B_2H_6. The observation was interpreted by Schultz[64] in this laboratory as evidence for a borohydride ion in $B_2H_6 \cdot 2NH_3$.

$$[H_2B(NH_3)_2][BH_4] + HX \longrightarrow [H_2B(NH_3)_2]X + H_2 + 1/2\ B_2H_6$$

An extrapolation of such an argument to the structure proposed for $B_4H_{10} \cdot 2NH_3$ gives the equation:

$$[H_2B(NH_3)]_2^+[B_3H_8] + HX \longrightarrow [H_2B(NH_3)_2]X + H_2 + B_3H_7$$

$$(X = Cl^- \text{ or } Br^-)$$

The B_3H_7 group would immediately undergo further reaction unless stabilized by coordination with a suitable base used as solvent. The interaction of HCl with a stoichiometric quantity of $B_4H_{10} \cdot 2NH_3$ in diethyl ether solution at -78°C gave rapid liberation of the expected mole of hydrogen and immediate precipitation of the ether insoluble solid $[H_2B(NH_3)_2]X$ where $X = Cl^-$ or Br^- (Fig. 18). The complex chloride and bromide salts were shown to be purer forms of the salts first prepared earlier from the diammoniate of diborane.[64] Indeed, it is

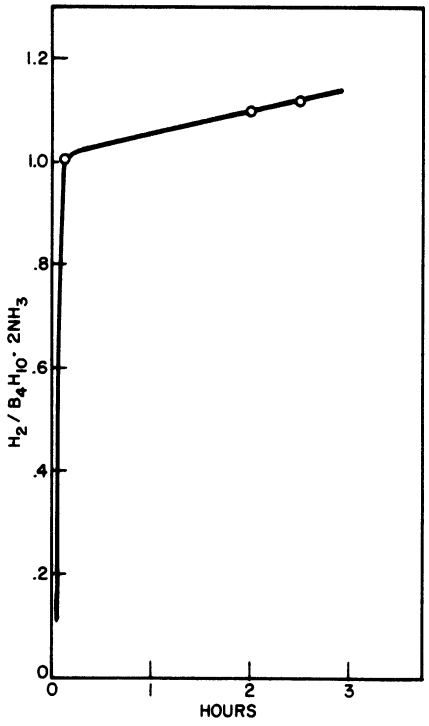


Fig. 18. Evolution of H_2 from the reaction of $B_4H_{10} \cdot 2NH_3$ with excess of HCl.

(67) A. Stock, Hydrides of Boron and Silicon, Cornell Univ. Press, Ithaca, 1933.

proper to note that the reaction between $B_4H_{10}\cdot 2NH_3$ and HCl or HBr in diethyl ether at -78°C is the best method currently available for preparing pure samples of chloride and bromide salts of the dihydride-diammineboron (III) cation.

Analytical values and molecular weight data based on vapor-pressure depression of a liquid ammonia solution are contained in the experimental section, and a single-crystal X-ray study of the chloride salt by Nordman and Peters(68) removes all doubt about the structure of this solid.

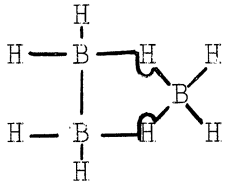
(c) The Preparation of Ammonia-Triborane from $B_4H_{10}\cdot 2NH_3$

When diethyl ether was used as the solvent at -78°C, the B_3H_7 fragment, resulting from the action of HCl on $B_4H_{10}\cdot 2NH_3$, was stabilized at -78°C by formation of the etherate, $(C_2H_5)_2OB_3H_7$. If such a solution is warmed, the etherate dissociates and the B_3H_7 group decomposes. If, however, ammonia is added to the cold (-78°C) ether solution, ammonia, being a stronger base than ether, will displace it to give the stable solid.

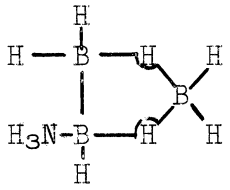
$$NH_3 + (C_2H_5)_2OB_3H_7 \xrightarrow[Et_2O]{-78°C} (C_2H_5)_2O + H_3NB_3H_7$$

The ammonia adduct produced was identical in all respects to the product prepared by other methods and described elsewhere.(69) Yields were about 45%.

In summary, strong evidence has been presented for the cation $[H_2B(NH_3)_2^+]$ and the anion $B_3H_8^-$ in $B_4H_{10}\cdot 2NH_3$. It is suggested that the anion has the general form:



resulting from the original B_4H_{10} geometry. Such a structure is suggested by the known geometries of the parent B_4H_{10} and the daughter compound $H_3NB_3H_7$.(70-71)



(68) C. Nordman and C. Peters, J. Am. Chem. Soc., in press; this report, p. 34.
(69) G. Kodama and R. W. Parry, J. Am. Chem. Soc., in press; this report, p. 120.
(70) C. Nordman and C. Reimann, J. Am. Chem. Soc., in press.
(71) This report, p. 132.

4. THE SYSTEM AMMONIA-TETRABORANE IN ETHER—EXCESS AMMONIA PRESENT

Using excess ammonia in the direct reaction of ammonia and tetraborane instead of excess tetraborane, Stock[60] found the unstable compound $B_4H_{10}\cdot 4NH_3$. The following study in ether was undertaken in an effort to isolate or obtain evidence for a stable form of Stock's tetraammoniate of tetraborane.

A given quantity of tetraborane was dissolved in diethyl ether. Ammonia was then introduced above the liquid at -78°C. The apparent equilibrium pressure (ammonia plus ether) above the solution at -78°C was measured as the ammonia content of the system was increased. Results are summarized in Fig. 19. Although a choice between the formula $B_4H_{10}\cdot 2NH_3$ and the formula $B_4H_{10}\cdot 2.5NH_3$ is arbitrary from the data of Fig. 19, the former composition is preferred in view of previously described observations. It is particularly significant that no evidence suggesting the expected composition $B_4H_{10}\cdot 4NH_3$ is contained in Fig. 19. On the other hand, certain, as yet incomplete, observations suggest the possibility of higher ammoniates. The ether solution remained clear as long as the ratio NH_3/B_4H_{10} did not exceed 2, but a noticeable precipitate formed when the ratio exceeded 2.5. Data on the preparation of $B_4H_{10}\cdot 2NH_3$ indicate that compound formation proceeds very slowly at -78°C. A long aging period was required. Since the entire experiment of Fig. 19 was completed in 5 hours, it is doubtful that the formation of the final compound, $B_4H_{10}\cdot 2NH_3$, was ever completed. Intermediate ammoniates are a more reasonable possibility.[72] The formation of the trace of precipitate suggests the possibility of an ether-insoluble higher ammoniate, but the amount of solid available up to the present time has not permitted characterization.

5. THE SYSTEM AMMONIA-TETRABORANE WITHOUT SOLVENT

The earlier study[60] on the system $B_4H_{10}\cdot NH_3$ involved mixing quantities of B_4H_{10} and NH_3 together and then pumping off the excess ammonia or tetraborane after equilibration for 1 hour at -78°C. Similar experiments conducted in this laboratory indicated that many hours of aging were required for apparent equilibration. This fact alone indicates that the earlier products were in all probability mixtures rather than single solid phases.

In a typical experiment, patterned after that of Stock, an excess of ammonia was frozen with a measured quantity of tetraborane; then the system was equilibrated at -78°C for 5 hours. After 5 hours the reaction vessel was opened to a trap cooled with liquid nitrogen and excess ammonia was removed. The overall composition of the B_4H_{10}-NH_3 adduct was followed as a function of time. Data are shown in Fig. 20. Comparable data of Stock for a sample without the preliminary 5-hour aging period are shown for comparison. Under the conditions

(72) This study was carried out before the preparation of $B_4H_{10}\cdot 2NH_3$, and the observations made herein suggested the procedure which led to the isolation of $B_4H_{10}\cdot 2NH_3$.

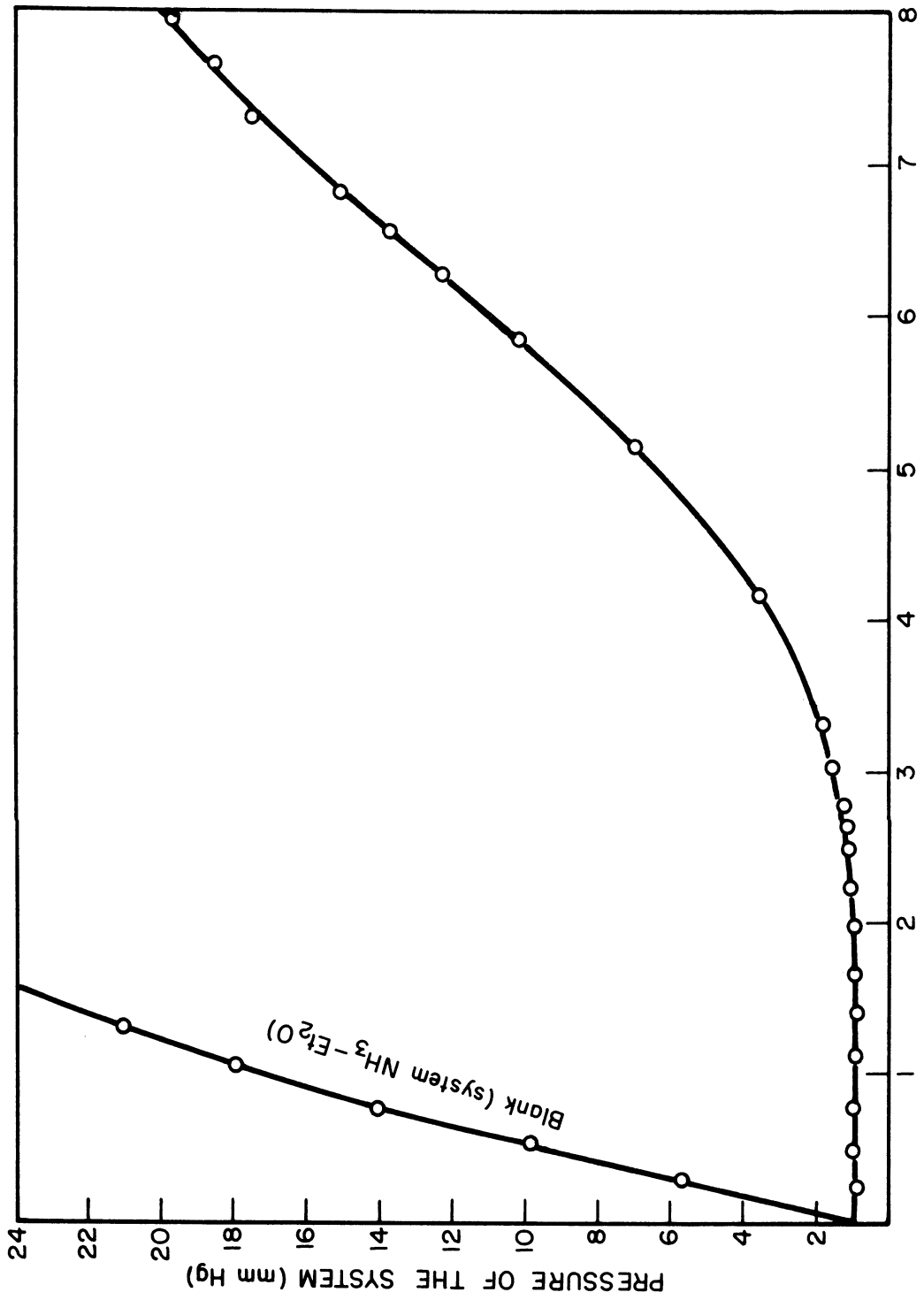


Fig. 19. Ammonia pressure above an ether solution of tetraborane.

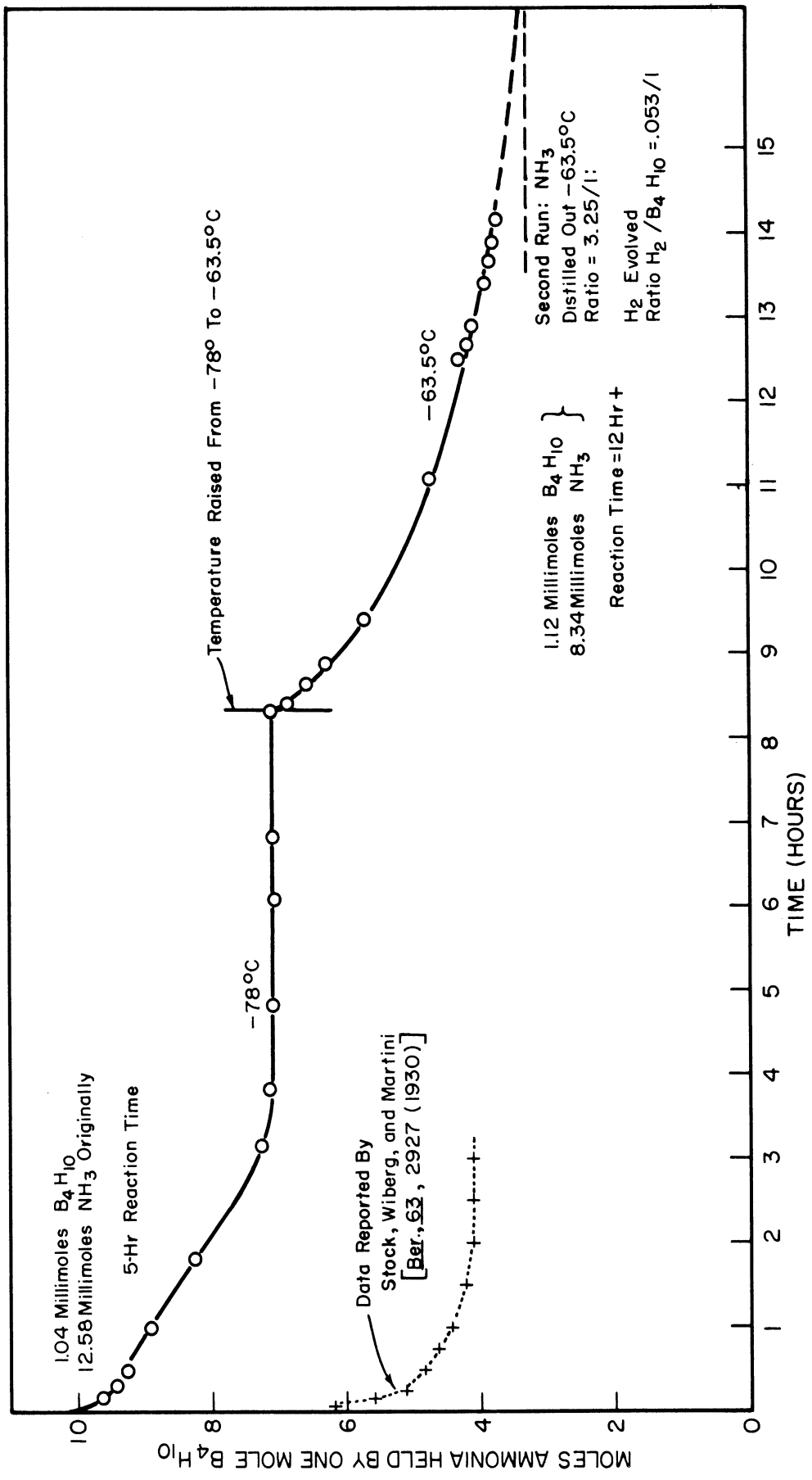


Fig. 20. Composition of system B_4H_{10}—excess NH_3 as a function of time.

described above, the composition of the residue at -78°C corresponds to the formula $B_4H_{10}\cdot 7NH_3$. When no change in composition was detected at -78°C, the temperature was raised to -63.5°C. At this higher temperature, ammonia was lost without significant hydrogen evolution. The composition of the residue appeared to be approaching $B_4H_{10}\cdot 3NH_3$, although the stoichiometry was rather poor (Fig. 20). At temperatures above -63.5°C additional ammonia was evolved and the ratio N/B_4 slowly approached 2. It is significant that in systems of this type H_2 evolution became quite vigorous above 0°C, and the ratio H_2/B_4H_{10} became as large as 0.82 on some samples after several days.

A pressure composition diagram was then constructed for the system B_4H_{10}-NH_3. A sample of ammonia was placed in a tube and a measured excess of ammonia was added. The apparent equilibrium pressure above the solid adduct was measured at -78°C, -63°C, -45°C, and -35°C. Part of the ammonia was removed and the pressure measurements were repeated. Many days were required to reach a steady pressure at each temperature-composition point. Data are presented in Fig. 21. At temperatures above -78°C the highest definite ammoniate appears to be $B_4H_{10}\cdot 6NH_3$. At -78°C the data do not exclude the composition $B_4H_{10}\cdot 7NH_3$ shown in Fig. 20. It is also of interest to note that the data of Fig. 20 are not in conflict with the existence of $B_4H_{10}\cdot 6NH_3$ at -63.5°C, but simply imply that such a hexammoniate has a measurable dissociation pressure at that temperature; thus ammonia can be removed to a trap cooled with liquid nitrogen.

Stock's observations on the instability of the above product at temperatures above -23°C were confirmed. The adduct of B_4H_{10}-NH_3 prepared without solvent evolved ammonia and hydrogen gas and became liquid when warmed to room temperature. In fact, even "stable $B_4H_{10}\cdot 2NH_3$" lost hydrogen and ammonia and turned to a liquid when added to the viscous liquid residues from the above system. Thus even if $B_4H_{10}\cdot 2NH_3$ were formed by the direct reaction of B_4H_{10} and ammonia, the unstable and catalytically active byproducts formed in the same reaction would complicate the isolation of pure $B_4H_{10}\cdot 2NH_3$ at room temperature.

Some evidence for $[H_2B(NH_3)_2][B_3H_8]$ was indeed found in the product resulting from the reaction described by Fig. 20 and in related processes. If B_4H_{10} and ammonia were frozen together with liquid nitrogen and then warmed to -78°C, aged for 3 days at this temperature, dissolved in liquid ammonia, and treated with metallic sodium, hydrogen gas was evolved (Fig. 17) and NaB_3H_8 could be extracted from the solid product in yields up to 60%. Such an observation suggests that the solid product resulting from the prolonged interaction of tetraborane and excess ammonia at -78°C is largely an ammonia addition compound or ammonia solvate of $[H_2B(NH_3)_2][B_3H_8]$; the data would argue against the hypothesis that any major portion of the $B_3H_8^-$ ion has been destroyed through attack of the ammonia on its double bridge bonds. The problem of higher ammoniates is still being studied.

The utilization of a solvent such as ether to moderate the direct reaction between a boron hydride and an electron donor molecule was initiated by Steindler

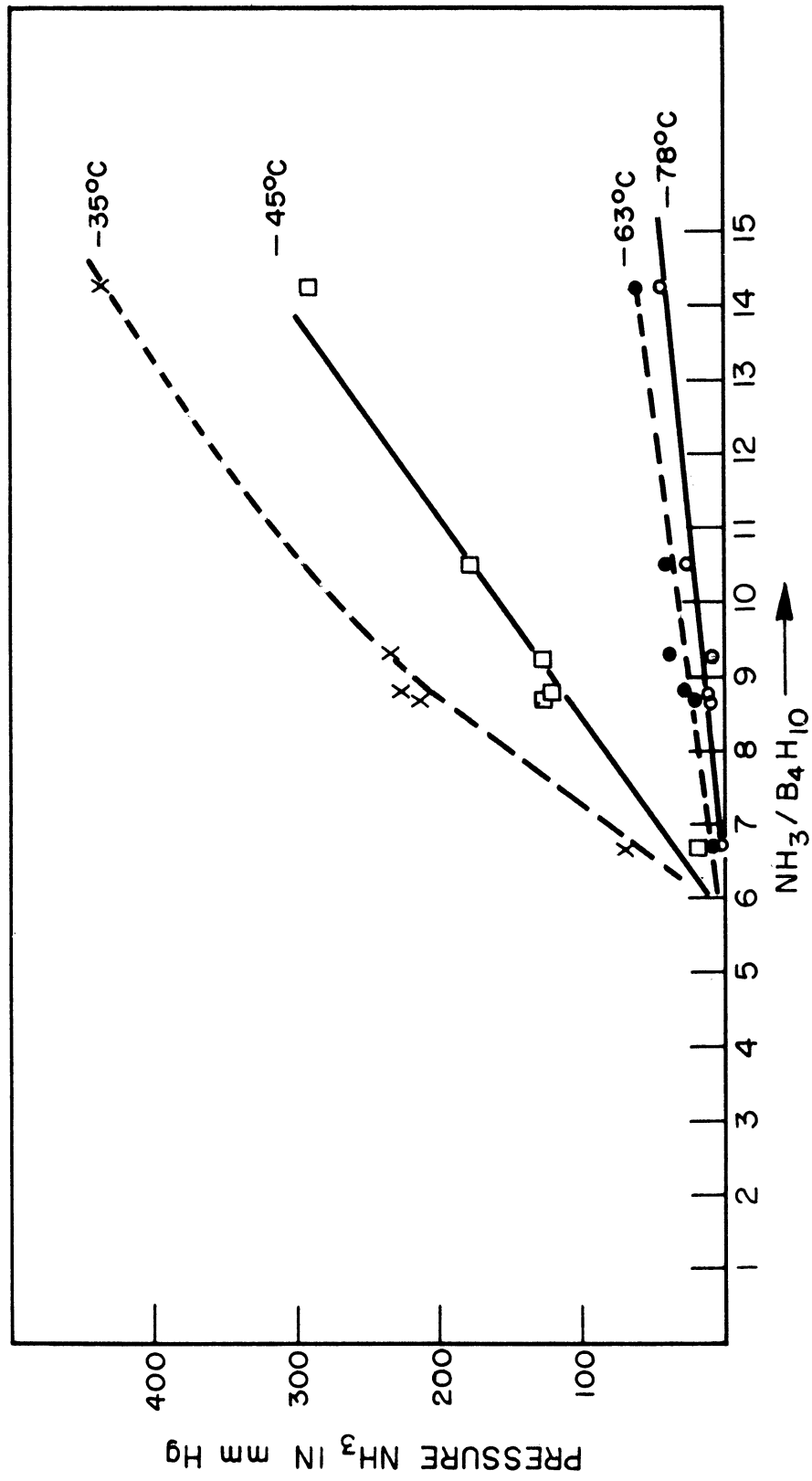


Fig. 21. Pressure composition diagram for system tetraborane ammonia.

and Schlesinger[73] in a study of the reaction between diborane and hydrazine. They obtained excellent stoichiometry in diethyl ether, while Emeleus and Stone[74] failed to isolate well-defined compounds in an earlier investigation involving direct combination of reagents. Similarly, Campbell, Bissot, and Parry[75] were able to moderate the reaction of diborane and hydroxylamine by using ether as a solvent; yet without the solvent the reaction either would not go or resulted in a violent explosion. All available data thus suggest that Stock's earlier direct reaction products (i.e., $B_4H_{10} \cdot 2.5NH_3$ and $B_4H_{10} \cdot 4NH_3$) were in all probability complex and unstable mixtures, which contained some undefined precursors of the structure $[H_2B(NH_3)_2^+][B_3H_8^-]$.

6. DISCUSSION

The foregoing observations suggest that the use of a solvent is important in the isolation of a stable tetraborane-ammonia adduct. It is equally clear that the choice of the solvent ether is of great importance in determining the nature of the product formed. If the ether is a relatively strong electron donor, it will cleave the double bridge bond of the tetraborane molecule symmetrically to give one half mole of B_2H_6 and the etherate of B_3H_7. Addition of ammonia to this system then results in the displacement of the ether by the stronger base to give the compound $H_3NB_3H_7$.[69] On the other hand, if the ether is a weak electron donor and it does not attack the diborane molecule under the conditions used, it will simply serve as a diluent and heat-transfer medium to minimize localized overheating. Under such conditions the ammonia attacks the tetraborane molecule directly in the ether solution and effects nonsymmetrical cleavage of the double bridge bond without further decomposition. It is clear that B_4H_{10} is not attacked by the diethyl ether at low temperature since it was found in this and other laboratories[76] that B_2H_6, the normal decomposition product, is not evolved and B_4H_{10} can be separated unchanged by fractionation.

The resemblance between the chemistry of diborane and the tetraborane is indeed striking. Nearly every diborane reaction finds a predictable and verifiable counterpart in tetraborane chemistry. Such analogies are apparent in this and another section of this report.[69]

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(73) Steindler and H. I. Schlesinger, J. Am. Chem. Soc. 75, 756 (1953).

(74) H. Emeleus and F.G.A. Stone, J. Chem. Soc. 840 (1951).

(75) D. H. Campbell, T. C. Bissot, and R. W. Parry, J. Am. Chem. Soc. 80, 1949 (1958).

(76) H. I. Schlesinger, Univ. of Chicago, Navy Contract No. N173 S-9820, Final Report (1946-47).

7. EXPERIMENTAL

(a) Reagents Used

(1) B_4H_{10}.—The majority of the tetraborane used in this investigation was donated by Professor Thomas Wartik of Pennsylvania State University and by Drs. George Huff and L. J. Edwards of Callery Chemical Company. Some of the product was prepared in this laboratory. The high-pressure storage of B_2H_6 in a stainless-steel cylinder at room temperature was the best preparative method. This method was described to R. W. Parry by Dr. Wartik and Dr. Edwards and will be described in more detail by them. The product was fractionated at -85°C or -95°C and stored at liquid nitrogen temperature. It was again fractionated at -100°C before its use. The vapor pressure of the purified compound was 386 ± 1 mm at 0°C.

(2) Other Reagents.—Commercial NH_3, $(C_2H_5)_2O$, $LiAlH_4$, BF_3, NaH, Na, etc., were used in top quality grade. Customary methods of purification and handling were used and have been described in earlier reports.(77)

(b) The Preparation of $B_4H_{10}\cdot 2NH_3$

The slow addition of ammonia to a cold (-78°) ether solution of B_4H_{10} gave complete ammonia absorption. An excess of B_4H_{10} was always used. After ammonia addition the system was aged for four days at -78° and for twelve hours at -45°. The solution was filtered on a vacuum line filter at -45° to remove a slight turbidity; then the ether was removed at -45° from the clear filtrate. The white solid which was left after removal of the ether was washed with cold dry benzene and transferred to a filter disc. It was then washed through the filter disc with dry ether. Removal of the solvent left a white, dry microcrystalline solid which was characterized as follows. Anal. N, 32.3; B, 49.4; H_2 124.3 mmoles/g. Theory for $B_4H_{10}\cdot 2NH_3$: N, 32.1; B, 49.5; H_2, 125.8 mmoles/g based on the hydrolysis equation

$$B_4H_{10}\cdot 2NH_3 + 8H_2O + 2H^+ \longrightarrow 4HBO_2 + 2NH_4^+ + 11H_2$$

The molecular weight as determined by vapor pressure depression in liquid ammonia was 81. Theoretical for $B_4H_{10}\cdot 2NH_3$ is 87. Yields ran as high as 86% based on the NH_3 used or 78% based on the B_4H_{10} (slight excess used).

In Table XXII a number of reaction conditions and their results are listed.

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(77) R. W. Parry, et al., The Chemistry of Boron Hydrides and Related Hydrides WADC Tech. Report 56-318 (1956).

TABLE XXII

THE REACTION OF B_4H_{10} AND NH_3 IN DIETHYL ETHER

B_4H_{10} (mmoles)	NH_3 (mmoles)	Ether (ml)	NH_3 / B_4H_{10}	Temp. (°C)	Time	Yield of $B_4H_{10}\cdot 2NH_3$ Based on NH_3 (pct.)	Yield of $B_4H_{10}\cdot 2NH_3$ Based on B_4H_{10} (pct.)	Remarks
4.18	7.56	3	1.81	-78 to -70	30 min	0	0	(a)
4.20	1.91	2	0.455	-78 to 0	1 hr	54	12.3	(b)
2.18	3.35	3	1.54	-95	1 hr	low	low	
3.08	5.55	5	1.8	-78	4 hr	40.5	37.4	(c)
2.05	3.84	10	1.88	-78	3 days	54	51	(c)
2.37	4.25	10	1.8	-78 -45	4 days 12 hr	86.5	77.7	(c)

a Product became liquid at room temperature.
b Purity of product in doubt because methods of purification were not well developed at the time of the run.
c Solvent ether removed at room temperature.

(c) The Reaction of $B_4H_{10}\cdot 2NH_3$ with Sodium in Liquid Ammonia

A sample of $B_4H_{10}\cdot 2NH_3$ weighing 74.8 mg (0.856 mmole) was placed in a dried nitrogen-filled tube and an excess of sodium in a bulb was crushed into the tube. The tube was attached to the vacuum line and 2 ml of liquid ammonia was condensed onto the sample. The temperature was rapidly raised to -78°C. In 5 minutes 0.358 mmole of H_2 was liberated. On standing for an additional 15 min at -75°C, 0.101 mmole of H_2 gas was evolved. (Total H_2 = 0.459 mmole = 1.07 equiv $H_2/B_4H_{10}\cdot 2NH_3$.) The excess sodium was eliminated by shaking with mercury and filtering at -35°C. H_2 gas evolved during this operation was 0.027 mmole. Most of the solvent ammonia could be removed at -35°C by distillation. Warming the residue to room temperature resulted in rapid evolution of H_2 gas. (Total H_2 then equaled 1.35 mmoles.) The solid residue was leached with dry diethyl ether at room temperature in the vacuum line extraction system. From the filtrate NaB_3H_8 was obtained by evaporation of the solvent at room temperature. The yield of NaB_3H_8 was 69% based on the equation:

$$[H_2B(NH_3)_2][B_3H_8] + Na \longrightarrow H_2NBH_2 + NH_3 + NaB_3H_8 + 0.5\ H_2$$

(d) The Reactions of $B_4H_{10}\cdot 2NH_3$ with HCl and HBr. The Formation of $[H_2B(NH_3)_2]Cl$ and $[H_2B(NH_3)_2]Br$.

In a typical run 1.84 mmoles of $B_4H_{10}\cdot 2NH_3$ was placed in a reaction tube and dissolved in about 2 ml of diethyl ether. The solution was frozen with liquid nitrogen and 1.78 mmoles of HCl was condensed into the tube. When the temperature was raised to -78°C, hydrogen gas (1.74 mmoles) was evolved in 15 minutes and a white precipitate formed. The precipitate was separated in the vacuum line filtration assembly; the solid was washed through the filter disc with liquid ammonia, and the solvent ammonia was distilled from the filtrate at -45°C. A sample of $H_2B(NH_3)_2]Cl$ weighing 119 mg remained (yield = 79%). Analytical data showed B = 13.2%; N = 33.9%; hydridic H = 2.41%; Cl^- = 42.7%. Theoretical values for $[H_2B(NH_3)_2]Cl$: B = 13.1%; N = 34.0%; hydridic H = 2.43%; Cl^- = 43.05. The molecular weight was determined by vapor pressure depression in liquid ammonia using standard methods[62] (see Fig. 6). The value obtained by extrapolation to infinite dilution was 95. The result is in only fair agreement with the theoretical value of 82.3, but the deviation is in the range of uncertainty of the method. The X-ray powder pattern was the same as that for $[H_2B(NH_3)_2]Cl$ made in an earlier study[64] and is identical to the powder pattern calculated from the single-crystal data of Nordman and Peters.[68]

The compound $[H_2B(NH_3)_2]Br$ could be obtained by a similar procedure if HBr were substituted for HCl. Analysis of the bormide salt gave: B = 8.46%; N = 22.15%; Br^- = 62.5%; hydridic H = 1.56%. Values calculated for $[H_2B(NH_3)_2]Br$ are: B = 8.53%; N = 22.10%; Br^- = 63.02%; hydridic H = 1.58%. The molecular weight in liquid ammonia was about 120 as compared to a theoretical value of 127 (Fig. 6). Detailed powder pattern is given elsewhere.[64]

(e) The Preparation of $H_3NB_3H_7$ from $B_4H_{10}\cdot 2NH_3$

The filtrate obtained from the reaction between $B_4H_{10}\cdot 2NH_3$ and HCl (see previous section) was agitated constantly at -78°C and 1.44 mmoles of ammonia gas was slowly introduced into the system. It was absorbed completely. The solvent ether was removed at room temperature and from the viscous liquid left in the tube $H_3NB_3H_7$ was sublimed in the vacuum sublimation system at 40 to 50°C. The yield was 36.5 mg or 45% on the basis of ammonia added.

(f) The System Ammonia-Tetraborane in Ether—Excess Ammonia Present

A sample of tetraborane (1.02 mmoles) was dissolved in 4 ml of diethyl ether and maintained at -78°C under constant agitation by means of a pulsating magnetic stirrer. Measured amounts of ammonia were introduced into the system. A constant pressure was reached in less than 5 minutes after each addition of NH_3. The pressure above the system was measured using an oil manometer. The blank run was made without B_4H_{10} in the ether. Data are given in Fig. 19.

(g) The System Ammonia-Tetraborane Without Solvent

The stoichiometry obtained for the direct reaction of tetraborane and ammonia without solvent was strongly dependent upon experimental conditions. The two cases differentiated by Stock were reaction systems containing an excess of ammonia and those containing an excess of tetraborane.

(1) Excess Ammonia Present.—A measured amount of B_4H_{10} was condensed by liquid nitrogen at the bottom of a reaction tube and a measured amount of ammonia condensed in a ring above it. The system was allowed to warm slowly to the reaction temperature. Data for a typical run are plotted in Fig. 20 and several runs under different conditions are summarized in Table XXIII. A rapid examination of runs 1 and 3 indicates that the formula approached by the resulting residue is strongly dependent upon the aging period provided at -78°C and upon the temperature of the sample during removal of excess ammonia. It will be noticed that Stock, Wiberg, and Martini used well-specified time and temperature for their initial reaction and well-specified time and temperature for the removal of ammonia to obtain the results reported. The marked time dependence strongly suggests a reaction mixture which had not reached its equilibrium condition.

(2) Excess Tetraborane Present.—The reactants were frozen together as indicated previously. Excess B_4H_{10} was distilled from the mass. Typical data are shown in Table XXIV. In run 2 a small amount of solid, stable at room temperature, appeared on the wall of the tube above the decomposing residue. The X-ray powder pattern of the solid was that of $B_4H_{10}\cdot 2NH_3$.

(h) The System B_4H_{10}-NH_3-$B_4H_{10}\cdot 2NH_3$

About 30 mg (0.3 mmole) of freshly prepared $B_4H_{10}\cdot 2NH_3$ was placed in a reaction tube, and 1.25 mmoles of B_4H_{10} and 7.30 mmoles of NH_3 were condensed above the solid. The system was allowed to warm slowly to -78°C and maintained for 12 hours at this temperature. After the removable ammonia was distilled out at -78°C, the system was allowed to warm to room temperature. The B_4H_{10}-NH_3 adduct formed by the direct interaction became liquid, evolving gas. The crystalline $B_4H_{10}\cdot 2NH_3$ gave off gas as it came into contact with the decomposing liquid. In 4 hours 1.02 mmoles of H_2 was collected and a viscous liquid phase removed in the reaction tube. At this stage the H_2 gas evolution from the system was very slow. At this point more $B_4H_{10}\cdot 2NH_3$ (0.16 mmole) was added to the system. Slow evolution of gas was observed at the solid-liquid interface. In about an hour close to 0.2 mmole of H_2 gas was collected. A small amount of solid phase remaining in the viscous mass was identified as $B_4H_{10}\cdot 2NH_3$ by its X-ray powder pattern.

TABLE XXIII

SUMMARY OF RUNS ON $B_4H_{10}NH_3$

Run No.	Millimoles		Reaction		NH_3 Removal		NH_3/B_4H_{10} Ratio Approached by System	H_2/B_4H_{10}, mmoles
	B_4H_{10}	NH_3 at Start	Temp. (°C)	Time (hr)	Temp. (°C)	Time (hr)		
				Data from This Study				
1	1.04	12.58	-196 to -78	5	-78 -63.5	8.5 6.00	7.05 3 to 3.2	nil nil
2	1.12	8.34	-165 to -65	12+	-63.5	--	3.2	0.053
3	0.325	4.66	- 78	1	-78 -63 -45 -23 0 25	24 6 3 8 25 6	3.2 2.91 2.83 2.34 2.16 2.16	0.15 0.15 0.15 0.17 0.70 0.76
4	0.337	5.17	- 78	24	-23 25 70-80 25	3.3 18 5 24	3.03 2.14 2.14 2.14	0.016 0.72 0.81 0.82
				Comparable Data from Stock, Wiberg, and Martini				
1S	0.445	4.7	- 75	1	-75	Ab.3[a]	4.0	N.R.[b]
2S	0.455	4.8	- 75	1	-75	Ab.3	4.0	N.R.
3S	0.442	4.6	- 75	1	-75	Ab.3	4.0	N.R.

[a] About 3.
[b] Not reported.

TABLE XXIV

THE ADDITION OF EXCESS B_4H_{10} TO AMMONIA

Run	mmoles NH_3	mmoles B_4H_{10}	Temp	Time at Temp Listed (min)	Ratio NH_3/B_4H_{10}	Remarks
1	1.62	5.53	-196 to -126	20		Unstable at room temperature.
			-95°C	30	2.25	
			-78°C	90		
2	2.46	8.37	-196 to -95	20		Mostly unstable at room temperature but some $B_4H_{10}\cdot 2NH_3$ isolated.
			-78°C	30	1.8	
			-35°C	150		

(i) The Reaction Between Sodium and the Solid Product Resulting from the Direct Interaction of B_4H_{10} and Excess NH_3

To the product from run number 1 of Table XXIII 3 ml of liquid ammonia was added; then a bulb containing an excess of sodium metal (0.1 g) was crushed and added to the frozen system. The temperature was permitted to rise to -78°C and then held at this value. H_2 evolution as a function of time is shown in Fig. 17. Similar data for run number 2 are shown on the same figure. In both cases one half mole of H_2 per mole of B_4H_{10} was liberated rapidly, but the rate of the secondary H_2 evolution process varied widely depending apparently on sample purity.

In a second run intended to isolate solid sodium salts before they decomposed in the system, the following procedure was followed. About 3 ml of ammonia was condensed above 1.86 mmoles of B_4H_{10} in a reaction tube. The system was allowed to warm slowly to dry-ice temperature and then was held at -78°C overnight. An excess of sodium was added to the system as described before; then the temperature was raised rapidly to -78°C. After one-half hour, ammonia and evolved hydrogen were removed, and 1.17 equivalents of H_2 per mole of B_4H_{10} were found. The last traces of ammonia were pumped off at room temperature. The solid residue was leached with dry diethyl ether in the vacuum line extraction system. A crystalline compound was isolated by evaporating the ether from the filtrate. The solid was identified as NaB_3H_8 by its powder pattern.

The foregoing experiment was confirmed by a second experiment involving only one significant change in experimental detail. Ammonia was removed from

the system at -78°C but the solid residue was aged for 3 days at -78°C before addition of solvent ammonia and of sodium. After 15 minutes the ratio of hydrogen evolved to B_4H_{10} was 0.51/1.73. A total of 0.725 mmole of H_2 gas was collected in all. The ratio H/B_4H_{10} was 1.06. NaB_3H_8 was again leached from the solid residue and identified by its X-ray powder pattern and by analysis for hydridic hydrogen, and boron. The ratio H/B was 2.96; the theoretical value is 3.00.

Although the yield of NaB_3H_8 was not determined in the above run, yields were good; a third run with a 2-day aging period at -78°C and -50°C gave a 60% yield of recovered NaB_3H_8.

(j) The Reactions of $Mg(AsF_6)_2$ with B_4H_{10}-NH_3 Adducts - A Precipitation Test for the Borohydride Ion

In an earlier study from this laboratory,[6] it was noted that the addition of $Mg(SCN)_2$ to a liquid ammonia solution of a borohydride resulted in the precipitation of $[Mg(NH_3)_6][BH_4]_2$. The process served as a qualitative means of identifying the BH_4^- ion in the liquid ammonia solution. Subsequent study in this laboratory has indicated that $Mg(AsF_6)_2$ is a better reagent than the thiocyanate since it is not as subject to attack by the borohydride ion. The reagent was prepared as follows. $KAsF_6$ was prepared from KH_2AsO_4 using the method of Dess and Parry.[78] The $K(AsF_6)$ was converted to $Mg(AsF_6)_2$ by shaking a water solution with successive portions of a magnesium ion exchange resin. The dried compound dissolved readily in liquid ammonia and was recrystallized once from this solvent before use. The recrystallized solid was stable in open air and had the formula $[Mg(NH_3)_6][AsF_6]_2$. $[Mg(NH_3)_6](AsF_6)_2$ serves as an excellent precipitant for BH_4^- ion in liquid ammonia and as such serves as a discriminating test for this presence of the borohydride ions in the liquid ammonia aolution. $Mg(NH_3)_6^{++}$ does not precipitate the $B_3H_8^-$ ion from liquid ammonia, as was shown by the following experiments. About 20 mg of freshly prepared $B_4H_{10}\cdot 2NH_3$ were mixed with $[Mg(NH_3)_6]$ $(AsF_6)_2$ in a reaction tube, and about 3 ml of liquid ammonia were condensed into the system. A temperature of -78°C was maintained for over 12 hours. No precipitate was formed in the solution. Similarly, a mixture of NaB_3H_8 and $Mg(AsF_6)_2$ gave no precipitate when a liquid ammonia solution was formed by condensing NH_3 on to the solids. In contrast, $B_2H_6\cdot 2NH_3$ and $NaBH_4$ gave precipitates of $[Mg(NH_3)_6](BH_4)_2$ when $[Mg(NH_3)_6]$ $(AsF_6)_2$ was added to their liquid ammonia solutions.

Although properly prepared $B_4H_{10}\cdot 2NH_3$ gave no evidence for the presence of the BH_4^- ion, it was found that the product formed by the direct interaction of B_4H_{10} and excess ammonia without solvent gave some evidence for the BH_4^- ion. It is assumed that this contaminant resulted from the more vigorous reaction conditions in the absence of solvent. A large excess of NH_3 and 0.974 mmole of B_4H_{10} were condensed together in a reaction tube. The tube was then surrounded by dry ice and allowed to react at -78°C for 12 hours. The system was frozen

(78) H. M. Dess and R. W. Parry, J. Am. Chem. Soc. 79, 1589 (1957).

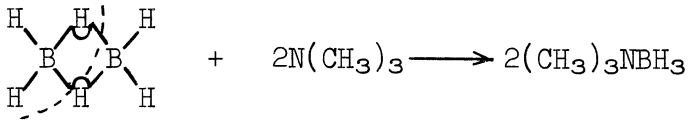
and $[Mg(NH_3)_6][AsF_6]_2$ was introduced onto the frozen product under a dry nitrogen atmosphere. About 3 ml of solution was prepared by condensing more ammonia onto the system. The white precipitate formed was filtered in the vacuum line filtration system. This solid appeared to be reactive in moist air. In its X-ray powder pattern every line of $[Mg(NH_3)_6][BH_4]_2$ was found. No attempt was made to identify or separate the other components.

C. The Preparation and Properties of Ammonia-Triborane, $H_3NB_3H_7$

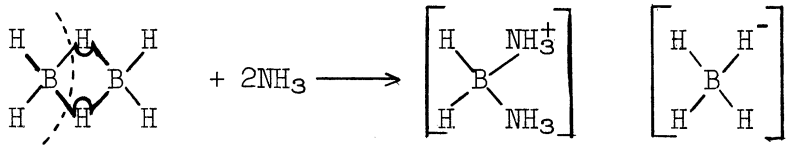
1. EARLIER STUDIES

The initial study of the reaction between tetraborane and trimethylamine by Burg and Stone[79] indicated that the tetraborane molecule can give $3BH_3$ groups which appear as 3 molecules of $H_3BN(CH_3)_3$. A polymeric residue remained in the reaction vessel. The careful and definitive study by Edwards, Hough, and Ford[80] on the system $(CH_3)_2N\text{-}B_4H_{10}$ indicated that under properly controlled reaction conditions $N(CH_3)_3$ and B_4H_{10} will combine to give the new compound $(CH_3)_3NB_3H_7$. The data suggest immediately the possible existence of the compound $H_3NB_3H_7$, which would bear the same relationship to $(CH_3)_3NB_3H_7$ that H_3NBH_3 bears to $(CH_3)_3NBH_3$.

Indeed, one may note a striking parallel between the reactions of tetraborane and diborane with $N(CH_3)_3$ and the reactions of tetraborane and diborane with NH_3. It is known that trimethylamine brings about symmetrical cleavage of the double bridge bonds in diborane to give $(CH_3)_3NBH_3$:



whereas ammonia brings about a nonsymmetrical cleavage of the double bridge bonds to give the diammoniate of diborane:[81]



Similarly, the direct reaction of tetraborane and trimethylamine to produce $(CH_3)NB_3H_7$ can be interpreted as a symmetrical cleavage of the double bridge

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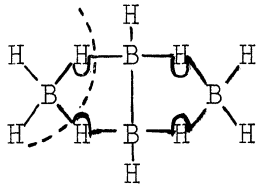
(79) A. B. Burg and F.G.A. Stone, J. Am. Chem. Soc. 75, 228 (1953).

(80) L. J. Edwards, W. V. Hough, and M. D. Ford, to be published.

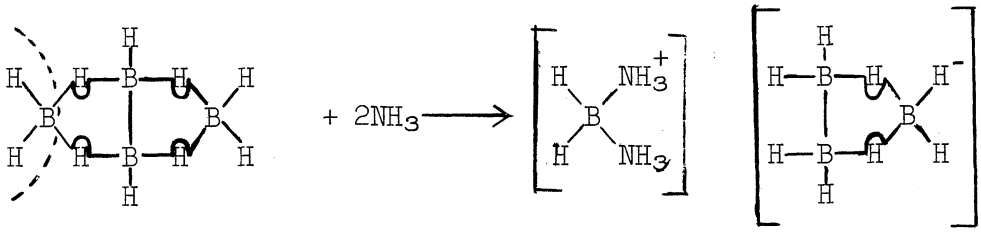
(81) D. R. Schultz, S. G. Shore, R. W. Parry, G. Kodama, P. R. Girardot, R. C. Taylor, and A. R. Emery, J. Am. Chem. Soc. 80, 1-30 (1958).

bonds in tetraborane:[82]



$$+ 2N(CH_3)_3 \longrightarrow (CH_3)_3NBH_3 + (CH_3)_3NB_3H_7$$

and the direct reaction of ammonia with tetraborane can be interpreted as a nonsymmetrical cleavage of the double bridge bonds to give the diammoniate of tetraborane[61] [this report, p.].



Because the direct reaction of ammonia with diborane gives nonsymmetrical cleavage of the double bridge bonds, the synthesis of ammonia-borane, H_3NBH_3, was delayed for a number of years and was achieved only by indirect methods.[83] Similarly, the triborane analog of H_3NBH_3, namely, $H_3NB_3H_7$, cannot be synthesized by direct reaction of NH_3 and B_4H_{10} but can be prepared by indirect routes. Fortunately, the analogy with diborane chemistry is close and comparable reactions are applicable; however, such an analogy was not established at the beginning of this research

2. METHODS FOR SYNTHESIZING $H_3NB_3H_7$

Shore and Parry[83] showed that the interaction of $LiBH_4$ with an ammonium halide salt proceeded as indicated below:

$$LiBH_4 + NH_3Cl \xrightarrow[25°C]{Et_2O} H_2\uparrow + H_3NBH_3 + \underline{LiCl}\downarrow$$

An extension of Shore's reaction to the new compound, NaB_3H_8, described by Hough, Edwards, and McElroy[84] gave a process which can be represented by the equation:

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(82) L. J. Edwards, W. V. Hough, and M. D. Ford, XVIth International Congress of Pure and Applied Chemistry, Section of Inorg. Chem., p. 475, Paris, July, 1957; L. J. Edwards, et al., to be published.

(83) S. G. Shore and R. W. Parry, J. Am. Chem. Soc. 80, 8 (1958).

(84) W. V. Hough, L. J. Edwards, and D. McElroy, J. Am. Chem. Soc. 78, 689 (1956).

$$NaB_3H_8 + NH_4Cl \xrightarrow[25°C]{Et_2O} H_2 + H_3NB_3H_7 + NaCl\downarrow$$

The new compound ammonia-triborane, $H_3NB_3H_7$, was sublimed in vacuum at 40 to 50°C from the solid residues which remained after removal of the solvent ether. The reaction was not as clean-cut as that involving $LiBH_4$. Rather complex side reactions appeared to be taking place. Yields of recovered $H_3NB_3H_7$ ranged from a trace to 38% on the basis of the NaB_3H_8 used. Most yields were in the range of from 20 to 30%.

A second extrapolation of diborane chemistry provided a direct synthesis of $H_3NB_3H_7$ from the diammoniate of tetraborane, $B_4H_{10}\cdot 2NH_3$; this process provided important information in establishing the structure of $B_4H_{10}\cdot 2NH_3$[7] and has been described in Section IIIB of this report.

The most effective method for the synthesis of 10-gram quantities of $H_3NB_3H_7$ is somewhat analogous to the procedure recommended by Shore and Parry[83] for the synthesis of H_3NBH_3 from the dimethyl etherate of borane:

$$B_2H_6 + 2(CH_3)_2O \longrightarrow 2(CH_3)_2OBH_3$$

$$(CH_3)_2OBH_3 + NH_3 \longrightarrow H_3NBH_3$$

Edwards, Hough, and Ford[82] reported that a number of ethers will react directly with tetraborane at room temperature to give diborane and the etherates of the B_3H_7 group. Yields were reported as quantitative when tetrahydrofuran was used. The reaction of such etherates with ammonia might then give $H_3NB_3H_7$. The overall process can be represented as:

$$B_4H_{10} + R_2O \xrightarrow[R_2O]{25°C} 1/2\ B_2H_6 + R_2OB_3H_7$$

$$R_2OB_3H_7 + NH_3 \xrightarrow[-78°C]{\text{Diethyl ether}} H_3NB_3H_7 + R_2O$$

By proper selection of the ether, good yields of $H_3NB_3H_7$ have been obtained.

Certain characteristics of the ether appear to be of major importance. First it should be a strong enough base to react smoothly with B_4H_{10} to give a relatively stable B_3H_7 etherate at room temperature. Diethyl and dimethyl ethers were <u>not</u> suitable because they are too weak as a base and the B_3H_7 group decomposes so rapidly at room temperature that the subsequent low-temperature ammonia reaction cannot be effected. On the other hand, the triborane-etherate, $R_2OB_3H_7$, should not be extremely stable or difficulty might be encountered in

displacing the ether by ammonia at -78°C. It was found that the tetrahydrofuran adduct of B_3H_7, $C_4H_8OB_3H_7$, reacted with ammonia in a solution of diethyl ether at -78°C, but the yields of recovered $H_3NB_3H_7$ were only about 70% and a fair amount of unidentified liquid always contaminated the sublimed product.

It was assumed, although not established with certainty, that the high stability of the tetrahydrofuran adduct contributed to the low yield. According to McLaughlin, Tamres, and Searles,(85) tetrahydropyran is intermediate in base strength between diethyl ether and tetrahydrofuran toward BF_3 as a reference acid; it should thus be suitable for $H_3NB_3H_7$ synthesis. When tetrahydropyran was used as the original ether in small-scale runs, yields of $H_3NB_3H_7$ were as high as 94% on the basis of the original B_4H_{10} used. Yields of 70 to 80% were obtained in larger-scale (20-gram lots) operation.

The product obtained directly from the ether displacement procedure appeared to contain small amounts of impurities which rendered the compound somewhat less stable than the $H_3NB_3H_7$ obtained directly from the reaction between NH_4X and NaB_3H_8. When the ether displacement procedure was utilized in the preparation of 20-gram lots of $H_3NB_3H_7$, the product was crystallized from benzene and then from toluene to obtain a solid of high purity.

3. PROPERTIES OF $H_3NB_3H_7$

Pure ammonia triborane is a white crystalline solid which can be sublimed very slowly under high vacuum. It melts at 73-75°C with slow evolution of hydrogen. It can be handled in air without obvious decomposition. It is surprisingly resistant to complete hydrolysis; periods of several days at 120°C in 6N HCl were used to hydrolyze the product for analysis. It is extremely soluble in diethyl ether; in fact, it picks up ether vapor avidly to give an ether solution. The original compound can be recovered unchanged on vaporization of the ether. It can be dissolved in and recovered unchanged from liquid ammonia at -75°C and from benzene. It is soluble in acetone and alcohol, and very slightly soluble in petroleum ether. X-ray powder data for identification of the solid are presented in Table XXV.

Westrum and Levitin(86) have shown that it undergoes an apparent first-order transition involving an enthalpy increment of 1233 cal/mole and an entropy increment of 4.15 cal/mole x deg at 297.10°K. The crystal structure of the low-temperature form has been worked out by Nordman and Reimann(87) (see page 132 of this report). Details of compound characterization are in the experimental section.

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(85) M. Tamres and D. E. McLaughlin, private communication (1957); D. E. McLaughlin, M. Tamres, and S. Searles, presented at the 133rd meeting of the American Chemical Society, April, 1958.

(86) E. F. Westrum, Jr., and N. E. Levitin, J. Am. Chem. Soc., in press.

(87) C. E. Nordman and C. Reimann, J. Am. Chem. Soc., in press; page 132 of this report.

TABLE XXV

INTERPLANAR SPACINGS AND RELATIVE INTENSITY DATA FOR $H_3NB_3H_7$, HIGH-TEMPERATURE FORM (TETRAGONAL)

Intensity[a]	d(Å)	hkℓ[b]
s	4.48	101
s	4.33	110
m	3.29	002
m	3.06	200
m	2.62	112
m	2.52	211
w	2.24	202
w	2.07	103
w	1.95	301

a s = strong, m = medium, w = weak.

b These indices were assigned and verified on the basis of intensity data from the single-crystal work by Nordman and Reimann.

At -78°C, $H_3NB_3H_7$ was not attacked by trimethylamine, but at room temperature it reacted with an equimolar quantity of the base to give trimethylamine-borane [$(CH_3)_3NBH_3$], and an unidentified solid which decomposed slowly through evolution of hydrogen gas. It was not possible to recover any trimethylamine-triborane, $(CH_3)_3NB_3H_7$, from the products.

Ammonia-triborane in liquid ammonia solution at -78°C reacted with dissolved sodium metal (present in excess) to give one equivalent of hydrogen per mole of $H_3NB_3H_7$ in 20 minutes. Slow hydrogen evolution continued until a total of 1 mole of H_2 per mole of $H_3NB_3H_7$ was obtained. The residue left by removal of the solvent contained $NaBH_4$ on the basis of the X-ray powder pattern. No ether soluble component was detectable in the residue, and no other components were recognized in the mixture. Additional work on the chemistry of $H_3NB_3H_7$ is in progress.

As noted on page 73 of this report, $H_3NB_3H_7$ has a dipole moment of 6.5 Debyes, and its vapor pressure (see pages 63 and 64) is given by the equation

$$\log_{10} P(mm) = \frac{-3739\ (1 \pm .0075)}{T} \times 9.200\ (1 \pm .0096)$$

over the range of 30 to 55°C.

$$\Delta H_{vap} = 17.1 \pm 0.1 \text{ kcal/mol}$$

4. EXPERIMENTAL

Conventional vacuum lines were used for handling volatile and/or air-sensitive reactants and products. Moisture-sensitive solids and nonvolatile liquids were handled in a dry box.

(a) Materials Used

(1) B_2H_6.—Diborane was prepared from BF_3 and $LiAlH_4$ by conventional techniques.(88)

(2) B_4H_{10}.—Most of the tetraborane used in this investigation was donated by Professor Thomas Wartik of the Pennsylvania State University and by the Research Department of Callery Chemical Co. The authors wish to express their sincere appreciation. Some additional supplies of B_4H_{10} were prepared by converting B_2H_6 to B_5H_{11} by the method of Burg and Stone.(79) B_5H_{11} was then converted to B_4H_{10} by heating it in the presence of H_2(89). Tetraborane was also prepared by high pressure storage of B_2H_6 at room temperature.(90)

B_4H_{10} used in small-scale runs was fractionated at -85°C or -95°C and was stored at -196°C until used. It was fractionated at -100°C just before use. The vapor pressure of the purified compound was 386 ± 1 mm at 0°C. Tetraborane used in the larger-scale preparations was distilled from a -95°C bath after initial removal of B_2H_6 at -126°C.

(3) $LiAlH_4$, CaH_2, and NaH.—Commercial products from Metal Hydrides, Inc.

(4) BF_3.—Commercial diethyl etherate from Baker and Adamson. Solution was distilled immediately before use.

(5) NH_3.—Commercial, dried in vacuum line over sodium before use, or stored with dissolved sodium in steel tank and distilled directly into vacuum system.

(6) Ethers.—

(6.1) $(C_2H_5)_2O$.—Reagent grade, stored in vacuum line over $LiAlH_4$ for several days before use. For larger-scale operation anhydrous grade ether was used directly from a fresh can.

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(88) I. Shapiro, H. G. Weiss, M. Schnick, S. Skolnik, and G.B.L. Smith, J. Am. Chem. Soc. 74, 901 (1952).

(89) A. B. Burg and H. I. Schlesinger, J. Am. Chem. Soc., 55, 4009 (1933).

(90) W. H. Schechter, C. B. Jackson, and R. M. Adams, Boron Hydrides and Related Compounds, (Second Edition, Callery Chemical Co., Callery, Pa., 1)54, p. 17.

(6.2) Tetrahydrofuran.—Product of E. I. duPont de Nemours Co., distilled once and stored in vacuum line over $LiAlH_4$.

(6.3) Tetrahydropyran.—Product of E. I. duPont de Nemours Co., distilled once and dried over $LiAlH_4$. For larger-scale operation tetrahydropyran was refluxed for 2 hours over CaH_2 and stored above CaH_2 until used.

(7) Benzene.—Reagent grade benzene was dried and stored over CaH_2.

(8) Toluene.—Reagent grade toluene was dried and stored over CaH_2.

(9) Methylcyclohexane.—Technical grade methylcyclohexane was refluxed over CaH_2, distilled, and stored over CaH_2.

(10) NaB_3H_8.—Sodium triborohydride, first described by Hough, Edwards, and McElroy, was prepared in this laboratory by a new and easier procedure suggested from the work of Hough, Edwards, and McElroy.(91)

(11) All Other Reagents.—These were always the best available commercial product and were always dried by appropriate methods prior to use.

(b) The Preparation of $H_3NB_3H_7$ by the Reaction Between NaB_3H_8 and Ammonium Halides

In a typical run, 1 to 3 millimoles of NaB_3H_8 and an amount of ammonium chloride or bromide salt about 10% larger than the NaB_3H_8 sample (on an equivalent basis) were loaded in a dry box into a special reactor tube. The tube was equipped with an electromagnetically activated hopper type stirrer and consisted of a 25-mm pyrex tube, about 200 mm long and fitted on the top end with a 24/40 inner joint. This joint was sealed into an outer joint with De Khotinskey Cement. The outer joint was fastened through a U-bend to a stopcock which was equipped with a standard type of mercury protection plug to eliminate attack of ether on the stopcock grease.(92) The stopcock assembly was then fastened through a second U-bend to the vacuum system by a greased 24/40 joint. Dry diethyl ether (about 5 ml) was distilled into the reactor. The contents of the system were frozen with liquid nitrogen and the reactor was removed from the line at the greased joint. The mercury plug was put into place by inverting the unit. Then the system was warmed to room temperature. The ether slurry was magnetically stirred at room temperature for periods ranging from 20 to 40 hours. At intervals the mercury plug was removed from the stopcock by a reversal of the above procedure, the system was replaced on the vacuum system, and hydrogen was pumped into a gas burette with a Toepler pump. The reaction was

(91) W. V. Hough, L. J. Edwards, and A. D. McElroy, to be published.

(92) G. Kodama, Ph.D. dissertation Univ. of Mich., 1957, p. 82; see also for related structure R. T. Sanderson, Vacuum Manipulation of Volatile Compounds, (J. Wiley and Sons, N. Y., 1948), p. 69, Type II, Fig. 19.

continued until the ratio between evolved H_2 and NaB_3H_8 used approached one. In general NH_4Cl seemed to react more rapidly than NH_4Br.

The white precipitate which formed in the ether was removed by filtration in the vacuum line filter assembly and was identified by its X-ray powder pattern as a sodium halide and a small amount of unreacted ammonium halide. When the solvent was distilled under vacuum from the filtrate, either a white solid or a viscous liquid was left in the tube. The tube was then transferred to a cold-finger type of vacuum sublimation apparatus. When the outer tube was immersed in a 40 to 50°C water bath, $H_3NB_3H_7$ was sublimed from the residue to the cold-finger condenser wall (10°C). $H_3NB_3H_7$ could be scraped off the cold finger in open air. Yields ranged from a trace to 38%. The microcrystals of $H_3NB_3H_7$ were first characterized on the basis of an elemental analysis and by a molecular weight determination. The observed values were: B = 57.2$_8$, N = 24.4%, H_2 on acid hydrolysis = 141 mmoles/g. Values calculated for $H_3NB_3H_7$ are: B = 57.4%, N = 24.8%, H_2 = 141.5 mmoles/g based on the hydrolysis equation:

$$H_3NB_3H_7 + 9H_2O + H^+ \longrightarrow NH_4^+ + 3B(OH)_3 + 8H_2$$

The molecular weight as determined by vapor pressure depression in diethyl ether at 21°C was 55 in the concentration range of 0.35 to 0.65 molal; the theoretical value for $H_3NB_3H_7$ is 56.6. The molecular weight procedure is the same as that described earlier(93) except for changes necessitated by the change in solvent. Analytical procedures have been described elsewhere.(94)

(c) The Preparation of $H_3NB_3H_7$ by Displacement of an Ether by Ammonia in An Etherate of Triborane

(1) Large-Scale Laboratory Synthesis Involving Displacement of Tetrahydropyran.—The process described below is that which was used in preparing approximately 25-gram samples of ammonia-triborane for calorimetric studies (see Ref. 106 on p. 145) and other investigations. At the present time, it represents a relatively large-scale synthesis for compounds of this type. It is proper to note that the rapid evolution of diborane during the formation of the etherate may be dangerous if uncontrolled, and that localized heating, which may arise in large-scale operation, is a major factor in reducing yields of $H_3NB_3H_7$.

The reactor consisted of a 500-ml three-necked flask. One side neck was fitted with a glass plug and the other neck with a low-temperature reflux condenser, the outlet of which was connected to a manometer and then through a stopcock to the vacuum system. The center neck was equipped with a commercial "Lew" magnetic stirrer (Sci. Glass Apparatus Co., Bloomfield, N. J.). The

(93) R. W. Parry, G. Kodama, and D. R. Schultz, J. Am. Chem. Soc., 80, 24 (1958).
(94) T. C. Bissot, D. H. Campbell, and R. W. Parry, J. Am. Chem. Soc. 80, 1868 (1958).

reactor was evacuated to remove moisture; dry nitrogen was then admitted to the system and the glass plug was removed. A steady stream of dry nitrogen through the system minimized moisture entry while the plug was out. A 100-ml quantity of dry tetrahydropyran was added through the opening, the plug was replaced; the tetrahydropyran was cooled to -196°C and the system was evacuated. A 55-ml sample of liquid tetraborane, measured at 0°C, was condensed into the reactor. The temperature was allowed to rise slowly from -196°C until evolution of gaseous diborane was noted. At this point it was necessary to immerse the flask again in liquid N_2 until the reaction was moderated. CAUTION. B_2H_6 evolution may be sudden and vigorous.

As diborane evolution proceeded, B_2H_6 was removed to the vacuum line where it was purified and stored. After most of the diborane had been evolved, the reaction flask was cooled to -78°C and allowed to stand overnight. The remainder of the diborane, the excess tetrahydropyran, and traces of hydrogen gas were then removed from the reactor over the temperature range of from -78 to 25°C.

The tetrahydropyran-triborane which remained in the reactor melted just below room temperature and was unstable in contact with air. The reactor flask was flooded with dry nitrogen under slight pressure, the glass plug was removed from the side neck, and 200 ml of dry diethyl ether were added. The ethyl ether solution was cooled to -78°C, and the system was evacuated. A 15-ml quantity of anhydrous liquid ammonia (measured at -45°C) was then cooled to -78°C and opened to the reactor. Ammonia, maintained at a constant pressure near 46 mm in the reactor, was thus absorbed slowly by the constantly stirred ether solution. Approximately 12 hours elapsed between the beginning of NH_3 absorption and the beginning of the subsequent step. The flask was next warmed to room temperature and the excess ammonia, displaced tetrahydropyran, and ethyl ether solvent were distilled from the system and discarded.

The white solid remaining in the flask was primarily ammonia-triborane. It was extracted with three 50-ml portions of benzene. Each portion of solution was removed through a fritted filter stick inserted through the neck of the reactor flask. An excess of methylcyclohexane (about 300 ml) was added to the benzene solution, and ammonia triborane separated as a precipitate. The product was filtered out under a stream of dry nitrogen (not in vacuum system) and was dried under vacuum.

Further purification was effected using the special apparatus shown in Fig. 22. After drying the apparatus shown in Fig. 22 by passing dry nitrogen through it, a 6- to 8-gram aliquot of the crude $H_3NB_3H_7$ from the process above was dissolved in about 60 ml of dry benzene and placed in funnel I. Methylcyclohexane from funnel II was introduced into the precipitation vessel and the benzene solution of $H_3NB_3H_7$ was filtered through the frit in the stem of funnel I and allowed to drip into the methylcyclohexane in the precipitation vessel. By adjusting flow rates, methylcyclohexane was maintained in a six to one excess during precipitate formation. After precipitation and filtration the solid was washed with a small aliquot of methylcyclohexane and dried with dry nitrogen.

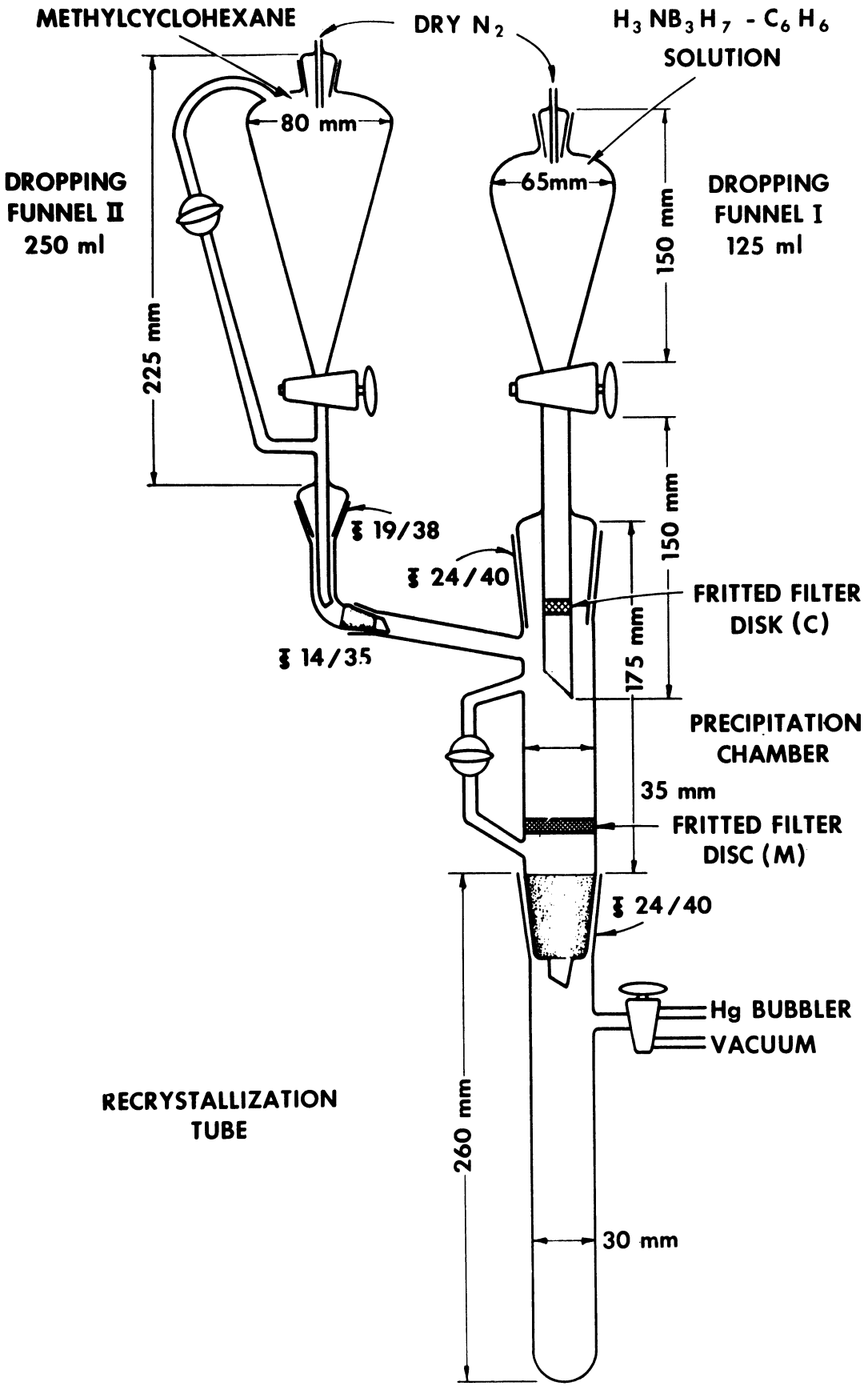


Fig. 22. Apparatus for recrystallization of $H_3NB_3H_7$.

While the dry nitrogen stream passed through the system, the flask used to collect the liquids from the filter was replaced by the recrystallization tube. Funnel I was removed and a 35-ml portion of toluene was added to the precipitate in the precipitation vessel. About 30 minutes were allowed for the toluene to become saturated with $H_3NB_3H_7$; then the toluene solution was pulled through the frit into the recrystallization tube. The tube was removed under an N_2 stream and capped. This clear solution was cooled to -95°C in a toluene slush and the $H_3NB_3H_7$ which crystallized was filtered at -78°C under a dry N_2 atmosphere. All retained toluene was removed from the product under vacuum at 25°C.

The toluene solution which was recovered contained a considerable amount of ammonia-triborane and was used further to extract the precipitate.

The yield of crude ammonia triborane was 70 to 80% based on the tetraborane used. Final purification reduced the overall yield to about 50%. The high purity of the product obtained from the above process was indicated by its stability and by the analysis. Values found were: N = 24.9%; B = 57.2%; H_2 on acid hydrolysis = 141 mmoles/g. Theory: N = 24.8%, B = 57.4%, H_2 = 141.5 mmoles/g.

(2) Small-Scale Laboratory Synthesis Involving Displacement of Tetrahydrofuran.—About 5 ml of tetrahydrofuran and 0.97 mmole of B_4H_{10} were condensed together into a reaction tube; then the temperature was allowed to rise slowly. No reaction was observed up to -23°C but at room temperature 0.46 mmole of B_2H_6 was evolved in half an hour. A trace of H_2 gas (0.027 mmole) was collected. Crystalline tetrahydrofuran-triborane remained in the tube when excess tetrahydrofuran was removed. The solid was dissolved in excess tetrahydrofuran again and 0.96 mmole NH_3 was frozen above the etherate (-196° bath). The system was allowed to warm to room temperature and stirred for half an hour. The solvent was removed at 0°C. From the white solid residue a 42.5-mg sample of $H_3NB_3H_7$ was sublimed (X-ray identification). The yield of still impure product was 79%. Diethyl ether was also used as a solvent for the displacement reaction but neither the yield nor product quality was improved (69%).

(3) Attempted Small-Scale Laboratory Synthesis Using Diethyl Ether.—A sample of B_4H_{10} (1.40 mmole) was dissolved in about 3 ml of diethyl ether and the solution was allowed to warm to ice temperature. A very slow and small vapor pressure rise due to B_2H_6 evolution was observed. The system was maintained at ice temperature for 4 hours. Then to permit continuous B_2H_6 removal, the stopcock was opened very slightly to the fractionation train while the reaction mixture was maintained at room temperature. B_2H_6 which entered the train was carefully fractionated by vacuum distillation (-78 and -126°C traps) until 0.632 mmole of B_2H_6 was obtained. BH_3/B_4H_{10} ratio = 0.975. During the foregoing process less than 0.04 mmole H_2 was liberated.

Then 1.25 mmoles of NH_3 was introduced slowly to the stirred solution at -78°C. A small amount of solid $B_4H_{10}\cdot 2NH_3$ remained in the tube (identified by its X-ray powder pattern) along with a viscous liquid. Only a trace of $H_3NB_3H_7$ could be sublimed from the reaction mixture.

(4) Small-Scale Laboratory Synthesis Using Tetrahydropyran.—A sample of tetraborane (1.69 mmoles) was condensed into 2 ml of tetrahydropyran and the system was warmed to room temperature. At room temperature the reaction was much slower than that with tetrahydrofuran. To minimize attack of the tetrahydropyran on the stopcock grease in the system, the temperature of the reactor was reduced to 0°C and maintained for 15 hours. The B_2H_6 evolved (0.817 mmole) was separated by fractionation. The excess tetrahydropyran was removed at 0°C; 3 ml of diethyl ether was condensed into the system; then a sample of ammonia (3.4 mmoles) was added to the reactor and a temperature of -78°C was maintained for 10 hours. On removal of the ethers a dry solid was left in the system. $H_3NB_3H_7$ was sublimed at 52°C to give an 81% yield (77.8 mg).

In a second run using 4.75 mmoles of B_4H_{10} and 1.5 ml of tetrahydropyran conditions were the same as above except the system was allowed to stand for 24 hours at -78°C after addition of 9.80 mmoles (twofold excess) of ammonia. A 94% yield (.253 g) of $H_3NB_3H_7$ could be sublimed from the solid residue.

(d) The Reactions of $H_3NB_3H_7$

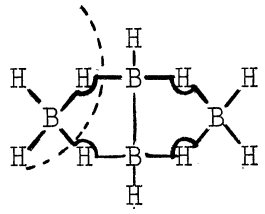
(1) The Reaction of $H_3NB_3H_7$ with Sodium Dissolved in Liquid Ammonia.—A sample of $H_3NB_3H_7$ (.189 mmole) was dissolved in about 1.5 ml of liquid ammonia; sodium metal (0.1 g) in a small glass tube was added in two portions by breaking the tube immediately before addition. After introducing the first portion the solution was warmed to -78°C. The blue color of Na faded rapidly and 0.10 mmole of H_2 was evolved. No more H_2 was evolved at -78°C over 12 hours. The second portion of Na was then added as above. In 20 minutes 0.012 mmole of H_2 was given off. After 5 hours an additional 0.057 mmole appeared. Total H_2 = 0.169 mmole $H_2/H_3NB_3H_7$ = 0.895. Further gas evolution was very slow and the solution remained blue. The excess of Na was removed from solution by amalgamation at -35°C. Additional H_2 (.007 mmole) was given off during the amalgamation. The sodium-free clear solution was filtered from the amalgam, and the solvent ammonia was distilled from the filtrate. In the white solid residue $NaBH_4$ was detected by its X-ray powder pattern, but no component soluble in diethyl ether could be extracted from the residue.

(2) The Reaction of $H_3NB_3H_7$ with Trimethylamine.—A sample of $H_3NB_3H_7$ (.55 mmole) was placed in a tube and trimethylamine (0.565 mmole) was condensed above it. The system was allowed to warm slowly. At -78°C no visible reaction was observed, but as the temperature rose and solid $H_3NB_3H_7$ began to dissolve in liquid trimethylamine, fairly rapid reaction was noted. Without waiting for the completion of the reaction, the noncondensable gas and the volatile components were removed from the system. They were: H_2 = .102 mmole, $(CH_3)_3N$ = .24 mmole, and $(CH_3)_3NBH_3$ about 0.35 mmole. From the solid polymeric residue 0.20 mmole of $H_3NB_3H_7$ was sublimed on warming to 40 to 50°C. No $(CH_3)_3NB_3H_7$ could be detected as a product.

D. The Structure of $H_3NB_3H_7$ from a Single-Crystal X-ray Study

1. EARLIER STRUCTURAL INFORMATION

The cleavage hypothesis used as a basis for correlating the chemistry of diborane and tetraborane [see earlier sections] suggests that the B_3H_7 group arises from symmetrical cleavage of the double bridge bond of tetraborane.



H_3B B_3H_7

Since the structure of B_4H_{10} is accurately known,(95) an accurate determination of the structure of $H_3NB_3H_7$, including the possible identification of B_3H_7 as a fragment of B_4H_{10}, would be a significant contribution to our understanding of the chemistry of these compounds.

2. HIGH-TEMPERATURE FORM

(a) Experimental

Samples of pure $NH_3B_3H_7$ were kindly furnished by Dr. Kodama. The compound is a crystalline solid at room temperature, stable enough to allow recrystallization from a number of common solvents such as acetone, alcohol, and ether.

Powder and single-crystal diffraction patterns showed the crystals to be tetragonal with $\underline{a}$ = 6.11Å and $\underline{c}$ = 6.57Å, giving a calculated density of 0.765 g cm^{-3}, assuming two formula units per cell. Systematic absences observed for $\underline{h}+\underline{k}+\ell$ odd call for a body-centered lattice. These facts require each molecule in the crystal to have fourfold symmetry. This is unreasonable in view of the chemical composition of the molecule. We were therefore led to conclude that the structure is a disordered one with the molecules either axially rotating or having random orientation so as to conform to the fourfold symmetry in a statistical sense.

Diffracted intensities were recorded and visually estimated using powder, Weissenberg and precession techniques. Due to the rapid falloff of the intensities with increasing angle of diffraction, no more than 25 different intensities

(95) M. E. Jones, K. Hedberg, and V. Schomaker, J. Am. Chem. Soc. 75, 4116 (1953); C. E. Nordman and W. N. Lipscomb, ibid., 75, 4116 (1953); J. Chem. Phys. 21, 1856 (1953); E. B. More, R. E. Dickerson and W. N. Lipscomb, J. Chem. Phys. 27, 209 (1957).

($hk\ell$) could be measured.

The presence of disorder led us to investigate the possible existence of a phase transition at lower temperature. A transition was indeed found, but the equilibrium temperature of the transition could not be accurately determined due to considerable supercooling. It was, however, established that the transition point is no lower than -16°C. Single crystals cooled through the phase transition shattered completely.

(b) Structure Determination

Since disorder about the c axis direction was known to exist, the space groups having a complete set of mirror planes parallel to that direction appeared to be the most likely choices. These are C_{4v}^{9} - I4mm and D_{4h}^{17} - I4/mmm. The latter of the two requires an additional disorder with the molecules pointing up or down the c axis at random, barring the chemically very unlikely possibility that the molecules possess a mirror plane perpendicular to their axis of disorder. The high dipole moment of 6.5 Debye units found for ammonia-triborane (see page 73) speaks in favor of the polar space group I4mm, which permits an energetically favorable arrangement of dipoles pointing in the direction of the c axis. This kind of arrangement has previously been found in structures composed of sterically simple or axially disordered molecules with high dipole moments such as hydrogen cyanide[96] and ammonia-borane.[97]

The structure was determined by trial and error. Since only 25 independent intensities have been observed it was essential to keep the number of parameters describing the assumed models as low as possible. The axially disordered molecules were therefore assumed to have cylindrical symmetry about the c axis. The structure factors are then given by:

$$F(hk\ell) = 2\sum_{j=1}^{N/2} f_j J_0\left(2\pi r_j \sqrt{h^2 + k^2}\right)\left(\cos 2\pi \ell z_j + i \sin 2\pi \ell z_j\right)$$

where j ranges over the atoms in one molecule, r_j is the radius, and z_j is the z coordinate of the "doughnut" formed by the jth atom.

The model shown in Fig. 23(a) was first tried. This model has two adjustable parameters, z_M and r_B; the origin is taken as the center of the boron ring. These two parameters, the temperature factor parameter B, and the scale factor were refined by several least-squares cycles, yielding a final value of $R = \Sigma \left| |F_o| - |F_c| \right| / \Sigma |F_o|$ of 0.16. A $\rho(x0z)$ Fourier section computed at this stage revealed an appreciable electron density in the region between the boron ring and the nitrogen atom. This fact and the abnormally long B-N distance in the

(96) W. J. Dulmage and W. N. Lipscomb, Act Cryst. 4, 330 (1951).
(97) E. W. Hughes, J. Am. Chem. Soc. 78, 502 (1956); E. L. Lippert and W. N. Lipscomb, ibid., 73, 503 (1956).

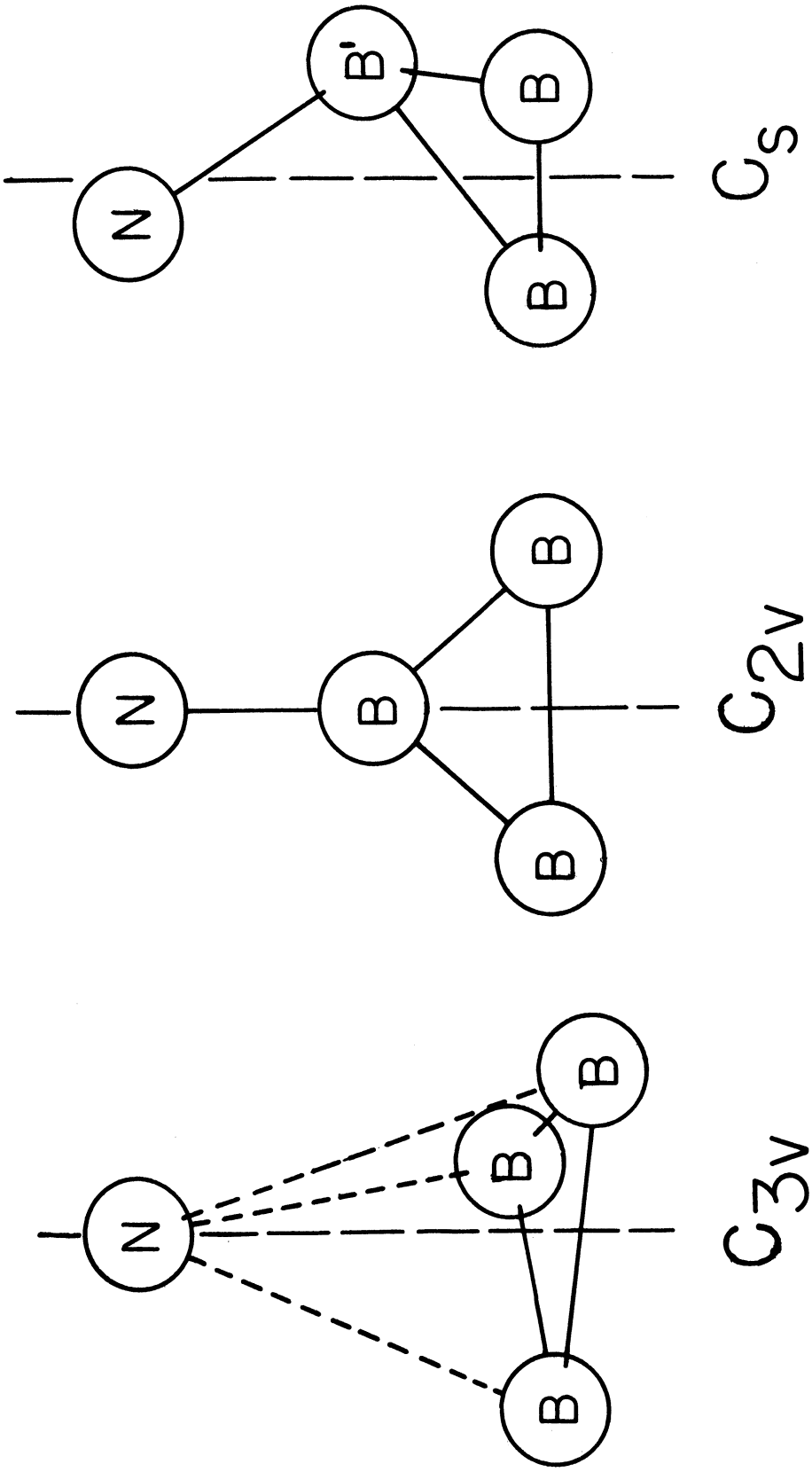


Fig. 23. Trial models of the ammonia-triborane molecule. The z-direction is vertical.

least-squares result led us to try the three-parameter model in Fig. 23(b). Several cycles of least-squares refinement now produced an $\underline{R}$ value of 0.18. A $\rho(\underline{x}0\underline{z})$ electron-density section and the corresponding difference synthesis now showed the distribution of the central boron atom B' to be distinctly disk-shaped, requiring a nonzero $\underline{r}_{B'}$. To a lesser degree the same was found to be true of the nitrogen atom. The two additional parameters $\underline{r}_{B'}$ and $\underline{r}_N$ were therefore introduced [Fig. 23(c)] and a series of least-squares refinements of all seven parameters (including $\underline{B}$ and the scale factor $\underline{K}$) was carried out. The agreement now improved considerably, giving an $\underline{R}$ value of 0.096. An approximate hydrogen contribution with a strong additional temperature factor was now calculated assuming a reasonable distribution of the hydrogen atoms about the nitrogen and boron atoms. Following a final, slight refinement of the seven aforementioned parameters the final $\underline{R}$ factor was 0.074.

The $\rho(\underline{x}0\underline{z})$ electron-density section calculated at this point is shown in Fig. 24. The corresponding $(\underline{F}_o-\underline{F}_c)$ synthesis showed no significant region of disagreement. The observed and final calculated structure factor magnitudes are listed in Table XXVI.

To examine the validity of the assumption that the disordered molecules have cylindrical symmetry, the $\rho(\underline{xy}0)$ and $\rho(\underline{xyz}_{B'})$ sections were computed. Neither one revealed any noticeable departure from cylindrically distributed molecules. This may be due to strong angular motion of the molecules or to poor resolution afforded by the available data, or both. The X-ray data do not warrant any detailed conclusion regarding the angular distribution or the amount of rotational freedom of the disordered molecules.

The final least-squares parameters are $\underline{r}_B = 0.151$, $\underline{r}_{B'} = 0.159$, $\underline{z}_{B'} = 0.190$, $\underline{r}_N = 0.040$ and $\underline{z}_N = 0.408$. The parameter $\underline{B}$ in the temperature factor $\exp(-B \sin^2\theta/\lambda^2)$ is 8.4Å^2. The configuration of the molecule, shown in Fig. 23(c), can be described as a triangle of boron atoms with an out of plane NH_3 group attached to one corner. No bond distances can be deduced unambiguously, but certain limits can be placed on them. The diameter $2\underline{r}_B$ or the two atom boron ring is 1.85 Å; this is the maximum value of the B-B distance. The B-B' distances are approximately 1.8Å, assuming that they are equal and that B-B equals $2\underline{r}_B$. The B'-N distance must be in the range 1.7 ± 0.2Å. These bond lengths agree satisfactorily with values previously found in molecules containing comparable bonds.

3. LOW-TEMPERATURE FORM

(a) Experimental

To prepare crystals of the low-temperature form, a diethyl ether solution of the compound was evaporated while maintained under a slow stream of dry nitrogen in a vial immersed in a chlorobenzene slush bath at -45°C. In this way

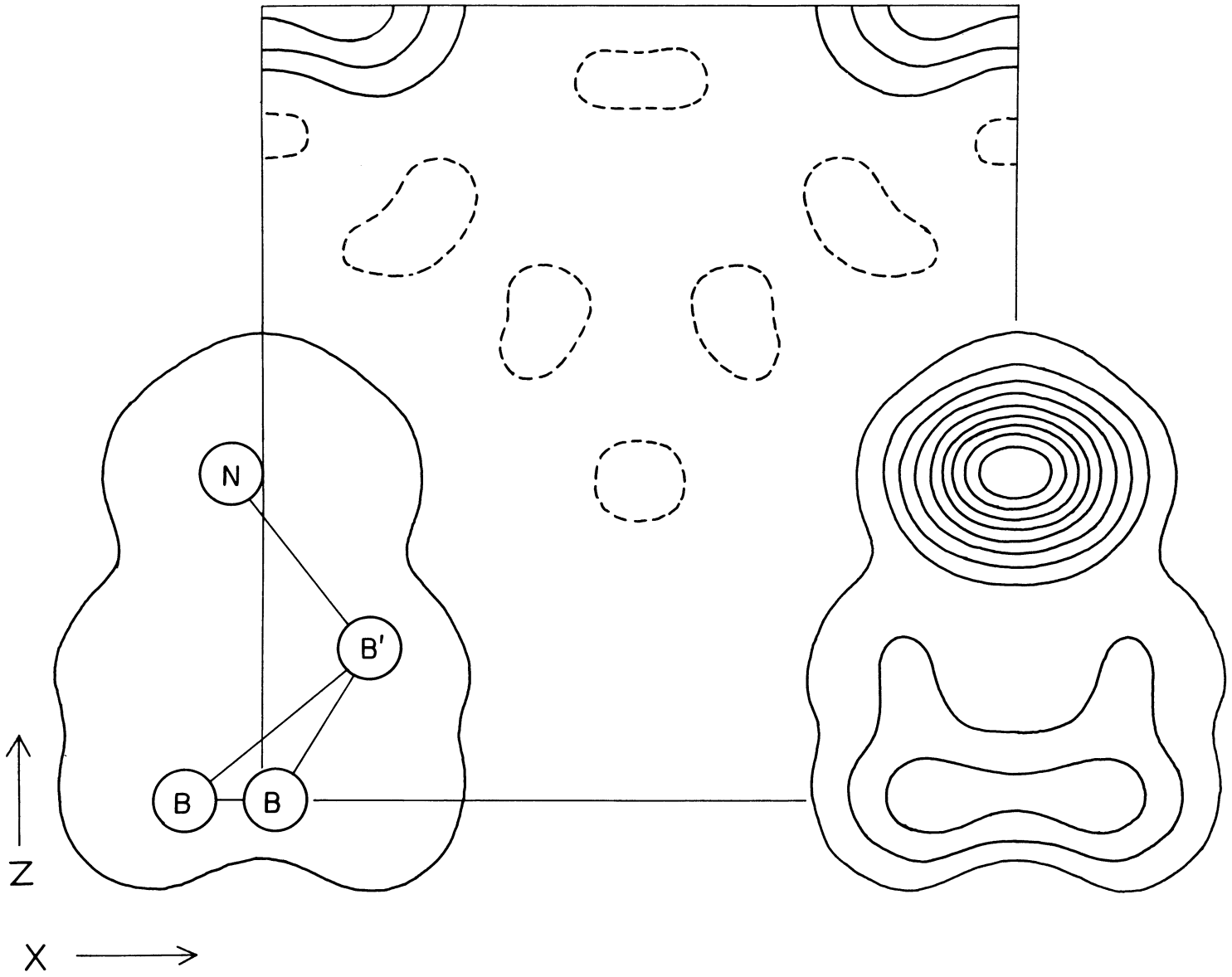


Fig. 24. Electron-density distribution at y = 0 in the unit cell of the disordered, high-temperature structure. Contours are at intervals of 0.4 e Å^{-3}; zero-contour broken

TABLE XXVI

OBSERVED AND CALCULATED STRUCTURE AMPLITUDES (HIGH-TEMPERATURE FORM)

h k ℓ	$\|F_o\|$	$\|F_c\|$	h k ℓ	$\|F_o\|$	$\|F_c\|$	h k ℓ	$\|F_o\|$	$\|F_c\|$
0 0 0	--	64.0	2 1 1	6.3	5.6	3 2 3	1.4	1.5
0 0 2	14.9	15.9	2 1 3	3.1	3.1	3 3 0	<0.8	0.0
0 0 4	4.1	4.4	2 1 5	1.3	1.2	3 3 2	<1.9	1.3
1 0 1	13.1	14.2	2 2 0	3.1	3.1	4 0 0	<0.9	0.1
1 0 3	6.2	5.7	2 2 2	3.2	3.3	4 0 2	<1.8	1.5
1 0 5	3.7	3.5	2 2 4	<1.3	1.3	4 1 1	2.2	2.4
1 1 0	25.5	25.6	3 0 1	4.5	4.2	4 1 3	<1.6	1.0
1 1 2	9.4	8.4	3 0 3	1.9	2.0	4 2 0	<1.2	0.0
1 1 4	2.7	2.6	3 1 0	1.3	1.7	4 2 2	<1.9	1.0
2 0 0	12.6	11.5	3 1 2	2.0	2.7	4 3 1	<1.2	1.1
2 0 2	6.1	5.6	3 1 4	1.3	1.3	5 0 1	1.5	1.1
2 0 4	2.0	1.7	3 2 1	2.7	3.3	5 1 0	<1.3	0.2

satisfactory crystals could be obtained in a few hours. The crystals were mounted and sealed in thin-walled glass capillaries on a simple microscope cold stage. While on the X-ray camera the specimen was maintained at -80 ± 10°C by means of a stream of cold nitrogen gas.

The crystals are monoclinic and belong to the space group $P2_1/n$. The lattice parameters and their estimated standard deviations are

$$\underline{a} = 10.40 \pm 0.015\text{Å}$$

$$\underline{b} = 4.824 \pm 0.006$$

$$\underline{c} = 9.997 \pm 0.012$$

$$\underline{\beta} = 115.2 \pm 0.15°$$

These values were derived from measurements of high-angle reflections on a number of precession patterns of zero-level principal and diagonal nets. With four molecules of $H_3NB_3H_7$ per unit cell the calculated density is 0.827 g cm^{-3}, an increase of 8% over the density of the high-temperature form. No molecular symmetry is demanded.

Data were collected as zero- and upper-level patterns on the Buerger precession camera using MoKα radiation. Reciprocal space was covered systematically to sin θ/λ = 0.572, corresponding to a zero-level precession angle of 24°. Within this range 69% of the diffraction maxima was of measureable magnitude, 25% was unobservably weak and 6% was not evaluated. Including 29 spots observed outside the range, a total of 502 reflections were observed.

Intensities were measured visually by comparison with a scale of timed exposures, and reduced to structure amplitudes in the usual way. The calculation of the Lorentz-polarization factor[98] and all subsequent least-squares refinements and Fourier syntheses were performed on an IBM 650 computer.

(b) Structure Determination

With the knowledge of the structure of the boron-nitrogen skeleton gained from the high-temperature form, approximate boron and nitrogen coordinates were easily found. The $h0\ell$ Patterson projection was readily interpreted; x and z coordinates for the boron and nitrogen atoms were obtained from the corresponding Fourier projection. Approximate y coordinates were found by trial and error.

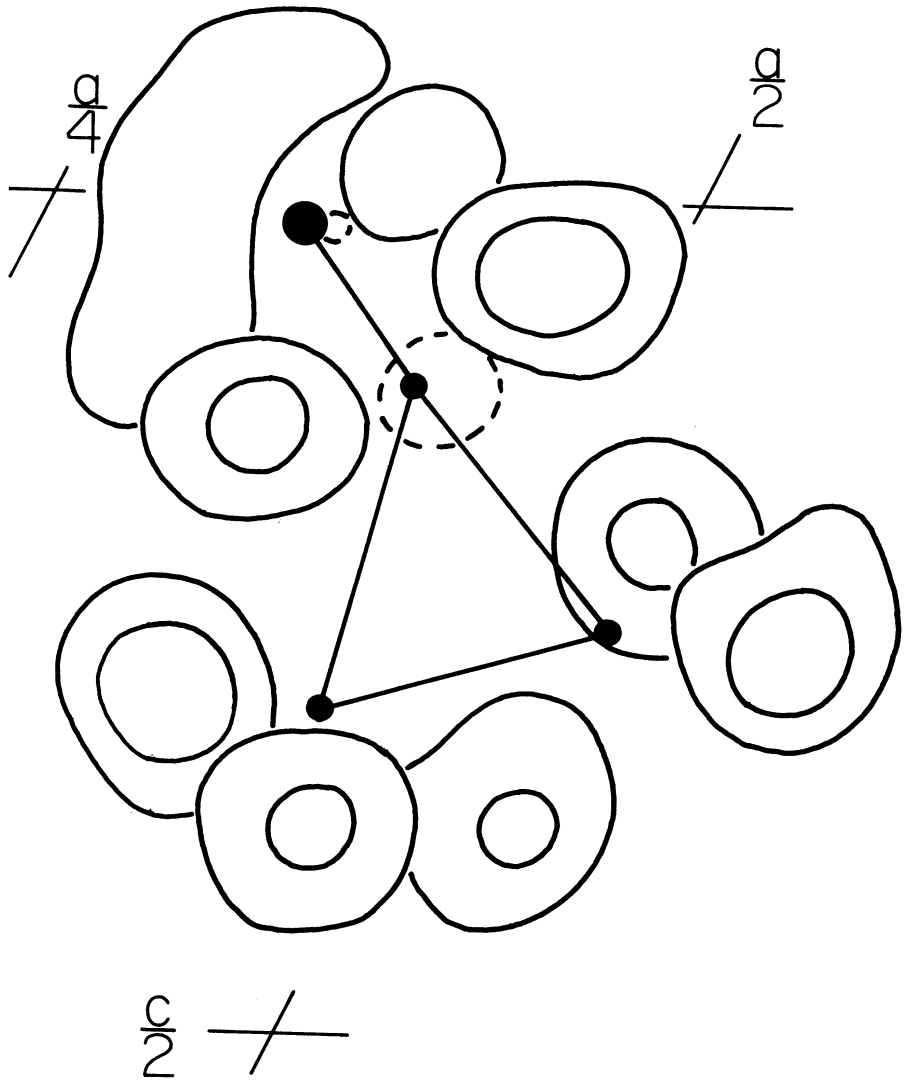
A three-dimensional least-squares refinement of these coordinates and the scale and temperature factors, K and B, was then carried out. The quantity $R' = \Sigma w(KF_o - F_c)^2/\Sigma w K^2F_o^2$ was minimized, taking $w(hk\ell)$ as $3|F_{min}|/|F_o(hk\ell)|$ or unity, whichever was smaller. McWeeny[99] atomic scattering factors were employed; in the case of boron the "average" scattering factor f was used. Toward the end of the refinement a contribution was included for six half-hydrogens forming a ring about the nitrogen atom. This was done to account in an approximate way for the three ammonia hydrogen atoms, whose approximate locations could be inferred. No other assumptions were made regarding hydrogen atoms. An R factor of 0.19 was reached.

The seven hydrogen atoms on the boron skeleton were now located by means of three-dimensional $(KF_o - F_{N,B})$ difference Fourier syntheses. This was done in two steps; only the strongest of the presumptive hydrogen peaks in the first difference synthesis were included in an intermediate model, which was then subjected to further refinement of N and B coordinates. A second $(KF_o - F_{N,B})$ synthesis yielded the rest of the hydrogens. This procedure was probably unnecessarily conservative, since in essence all peaks found in the first difference Fourier were ultimately confirmed as hydrogen atoms.

Anisotropy was observed in the thermal motion of the nitrogen and, to a small extent, boron atoms. This was accounted for in an approximate way by applying two anisotropic temperature corrections, one to f_N and another to f_B, common to all boron atoms. With the hydrogen atoms and the partial anisotropy correction included least-squares refinement of K, overall B, and nitrogen and boron coordinates improved the agreement to $R = 0.117$.

A set of sections of the three-dimensional $(KF_o - F_{N,B})$ synthesis computed at this stage are shown in Fig. 25. All spurious peaks are less than one half the height of the lowest hydrogen peak. This does not include the region of moderately high electron density found in the neighborhood of the nitrogen atom and presumably due to the three unresolved ammonia hydrogens.

(98) J. Waser, Rev. Sci. Instr. 22, 563 (1951); R. D. Burbank, ibid., 23, 321 (1952).
(99) R. McWeeny, Acta Cryst. 4, 513 (1951).



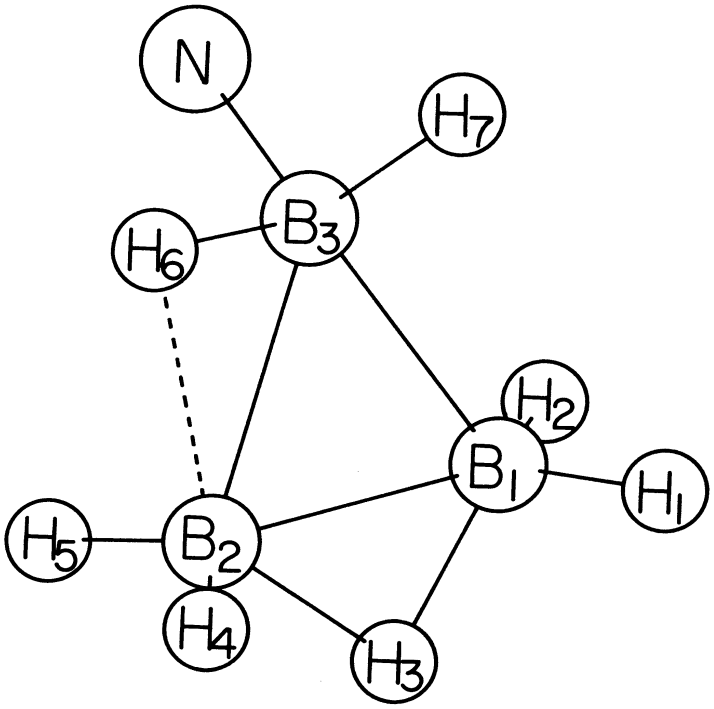


Fig. 25. The structure of the $H_3NB_3H_7$ molecule. Left: The electron density distribution in the $H_3NB_3H_7$ molecule represented by sections near the centers of the hydrogen atoms. The nitrogen and boron atoms have been subtracted out and are indicated schematically. Contours are at -0.25 (broken), +0.25 and +0.50 e $Å^{-3}$. Right: Schematic drawing of the same molecule and key to the numbering of atoms.

The method employed in refining the assumed model structure was now revised to allow all atoms to assume individual, but isotropic, thermal parameters, and several cycles of least-squares refinement of all coordinates and thermal parameters were carried cut. The shifts in coordinates were slight and led to final values of $\underline{R}$ = 0.107 and $\underline{R}'$ = 0.019.

An attempt was now made to find the locations of the three ammonia hydrogens, which had not been found as resolved peaks in any of the difference syntheses. Vaguely suggested maxima in the neighborhood of the nitrogen atom were taken as a starting point for a series of least-squares refinements of all parameters except those relating to the seven hydrogens already found. This refinement failed to improve the agreement previously obtained; in seven cycles the values $\underline{R}$ = 0.113 and $\underline{R}'$ = 0.021 were reached. Perhaps more significantly, the thermal parameters of the three ammonia hydrogens refined to very high values, 5.3, 11.1 and 11.8, suggesting a high degree of rotational freedom. Since, in addition, the H-N and H-H distances in the NH_3 group refined to unconvincing values, we conclude that the three hydrogens cannot be located unambiguously, presumably due to strong angular motion about the B-N bond.

The observed and final calculated structure factors are given in Table XXVII. The values and standard deviations of the atomic coordinates and the thermal parameters are listed in Table XXVIII.

The standard deviations were deduced in the following way: The observed structure factors were divided into six equal sets with the same distribution in sin θ/λ, but otherwise selected at random. Starting with the parameters given in Table XXVIII, each set was separately subjected to least-squares refinement. Usually the refinement was virtually completed in four or five cycles. The resulting six sets of coordinates and thermal parameters constitute, in effect, six independent structure determinations. The standard deviations of the final parameters can be taken as the standard deviations of the means of these quantities as given by

$$(\sum_i r_i^2)^{1/2}/[\underline{n}(\underline{n}-1)]^{1/2}$$

where r_i's are the deviations from the means of the individual values, and $\underline{n}$ = 6 in this case. The difference between the mean of a parameter as obtained from the six sets and the final (Table XXVIII) value was in all cases less than the standard deviation.

4. DISCUSSION

Interatomic distances and bond angles in the ammonia-triborane structure are given in Table XXIX. The standard deviations were obtained from an analysis of the interatomic distances calculated from the six separate sets of coordinates. They include contributions from the standard deviations in the cell parameters, which in the case of the B-N and B-B distances are comparable to

TABLE XXVII

OBSERVED AND CALCULATED STRUCTURE FACTORS (LOW-TEMPERATURE FORM)

h	k	l	KF_o	F_c	h	k	l	KF_o	F_c	h	k	l	KF_o	F_c	h	k	l	KF_o	F_c	h	k	l	KF_o	F_c
0	0	0	--	128.0+	1	3	4-	7.0	6.6-	3	0	7-	6.7	5.2+	4	2	4-	8.9	8.5+	6	1	10-	1.5	2.1-	8	1	1-	1.1	1.4-
0	0	2	2.9	1.4-	1	3	3-	10.0	10.3+	3	0	5-	8.9	9.3-	4	2	3-	1.9	2.4+	6	1	8-	5.6	5.2-	8	1	0	2.7	2.1-
0	0	4	12.4	13.8+	1	3	2-	3.0	2.1-	3	0	3-	17.3	19.7+	4	2	2-	3.7	3.1+	6	1	7-	8.6	8.9-	8	1	1	3.4	3.3-
0	0	8	6.0	5.9+	1	3	1-	6.7	6.4+	3	0	1-	22.3	28.2+	4	2	1-	5.9	4.8+	6	1	6-	6.6	6.4+	8	1	2	2.4	2.3-
0	0	10	2.8	2.6+	1	3	0	4.8	3.9+	3	0	1	16.3	16.3+	4	2	0	6.8	6.0+	6	1	5-	2.5	2.8+	8	1	3	5.6	5.5-
0	1	1	24.8	24.7+	1	3	1	10.5	10.1+	3	0	3	3.1	2.7-	4	2	1	11.3	11.0+	6	1	4-	4.5	5.4-	8	1	4	3.3	4.0+
0	1	2	0.4	0.1+	1	3	3	1.9	1.9+	3	0	5	13.5	12.6+	4	2	2	2.7	2.5+	6	1	3-	2.5	1.5-	8	1	5	1.7	0.9-
0	1	3	21.3	20.0+	1	3	4	3.3	3.9-	3	0	9	7.2	6.4+	4	2	3	9.2	7.1+	6	1	2-	7.4	6.9-	8	2	8-	3.5	3.5-
0	1	4	8.7	8.9-	1	3	5	4.3	4.3+	3	1	9-	3.8	4.1-	4	2	4	8.1	6.9-	6	1	1-	4.7	4.7+	8	2	6-	5.3	5.9+
0	1	5	1.6	1.6+	1	3	8	3.3	2.9-	3	1	8-	2.8	2.7-	4	3	6-	3.6	3.7+	6	1	0	2.6	3.2-	8	2	5-	3.4	4.2+
0	1	6	11.5	10.8+	1	4	4-	5.8	6.9+	3	1	7-	8.1	7.5-	4	3	3-	1.9	2.4-	6	1	1	1.9	1.4-	8	2	4-	4.0	4.0-
0	1	7	5.8	5.8+	1	4	2-	4.9	4.5+	3	1	6-	1.7	1.7-	4	3	2-	9.5	10.7+	6	1	2	2.5	2.4-	8	2	3-	7.9	8.3+
0	1	8	2.4	1.6+	1	4	6	4.4	4.0+	3	1	5-	5.5	4.8+	4	3	1-	14.1	13.5+	6	1	3	4.5	3.6+	8	2	2-	2.7	3.1-
0	1	9	1.7	1.8+	1	5	4-	1.8	1.9+	3	1	4-	5.6	5.7+	4	3	1	4.6	5.2-	6	1	4	3.2	3.6+	8	2	1-	3.8	3.0-
0	1	10	1.1	1.2-	1	5	3-	5.0	5.4+	3	1	3-	6.6	6.1-	4	3	2	7.6	7.9+	6	1	5	3.2	3.1+	8	2	1	2.9	2.0+
0	1	11	2.6	0.6+	1	5	2-	3.0	2.8+	3	1	2-	16.8	18.1+	4	3	4	2.8	1.8+	6	1	6	1.2	1.8-	8	3	8-	2.9	3.2+
0	2	0	5.3	5.8+	1	5	1-	4.0	3.2+	3	1	1-	10.9	11.0-	4	4	7-	3.4	3.5-	6	2	9-	2.7	2.6-	8	3	7-	3.5	3.2+
0	2	1	12.9	13.0-	1	5	0	3.8	4.2-	3	1	0	12.4	10.9+	4	4	5-	5.9	6.3+	6	2	8-	2.8	2.5-	8	3	6-	2.5	2.5+
0	2	2	6.5	6.4+	1	5	1	3.8	4.0+	3	1	1	9.9	8.3-	4	4	3-	4.1	3.9+	6	2	5-	3.1	3.2-	8	3	4-	3.2	3.4+
0	2	3	7.0	6.1+	2	0	10-	6.8	6.2-	3	1	2	11.4	10.1+	4	4	1-	5.0	5.7+	6	2	4-	3.0	2.7-	8	3	1-	4.8	4.9-
0	2	4	12.4	12.7+	2	0	8-	1.4	2.0-	3	1	3	4.6	4.5-	4	5	2-	5.0	6.5+	6	2	3-	3.3	3.2-	8	3	0	3.5	2.9+
0	2	5	3.2	2.7+	2	0	6-	3.3	3.2-	3	1	4	3.9	3.3+	4	5	1-	3.4	4.0-	6	2	2-	3.0	2.4-	8	4	5-	1.5	1.8-
0	2	7	5.5	5.4+	2	0	4-	22.8	24.7-	3	1	5	7.6	7.5+	5	0	11-	2.9	2.4+	6	2	1-	12.0	12.7-	9	0	9-	3.6	4.7-
0	2	8	4.6	4.0+	2	0	2-	40.1	52.6-	3	1	6	7.6	7.7+	5	0	9-	5.2	4.0-	6	2	0	3.2	2.9+	9	0	7-	2.3	2.6-
0	2	9	3.2	2.5+	2	0	0	6.2	6.4+	3	1	8	4.3	3.3+	5	0	7-	7.1	5.8+	6	2	2	4.7	5.9+	9	0	5-	2.1	2.4-
0	3	2	3.8	3.5+	2	0	2	19.1	18.0-	3	2	10-	7.3	5.7-	5	0	5-	18.9	20.2-	6	2	5	1.7	1.5-	9	0	1-	5.3	5.9-
0	3	3	3.5	2.6+	2	0	4	6.2	5.2+	3	2	8-	2.2	2.5-	5	0	3-	7.4	8.9-	6	3	8-	2.3	2.9-	9	0	1	3.1	2.7-
0	3	4	3.8	4.0+	2	0	6	10.7	9.2-	3	2	7-	3.8	3.6+	5	0	1-	9.3	10.5-	6	3	7-	3.3	2.6+	9	0	3	4.1	4.9+
0	3	5	8.6	8.4+	2	0	10	3.9	3.7+	3	2	6-	6.5	6.3-	5	0	1	5.9	5.4-	6	3	6-	4.0	3.9-	9	1	10-	4.1	4.7-
0	3	8	2.8	1.9+	2	1	11-	3.9	4.1-	3	2	3-	8.9	9.0+	5	0	3	9.9	9.2-	6	3	5-	3.7	3.7-	9	1	8-	1.9	2.2-
0	4	1	3.1	2.8+	2	1	10-	6.0	5.2+	3	2	2-	6.3	5.3-	5	0	5	5.3	5.5-	6	3	4-	5.0	6.0-	9	1	7-	4.2	4.4+
0	4	3	6.1	5.8+	2	1	7-	7.6	7.2-	3	2	1-	8.7	8.4-	5	0	7	5.1	4.1-	6	3	3-	5.5	5.5-	9	1	6-	4.0	4.5-
0	4	4	2.7	2.2+	2	1	6-	1.2	1.6-	3	2	0	11.5	11.3-	5	1	11-	5.4	5.1+	6	3	1-	4.4	4.4+	9	1	5-	2.3	2.6-
0	4	5	2.3	1.9-	2	1	5-	6.8	7.4-	3	2	1	16.1	15.5+	5	1	7-	3.2	2.6-	6	3	0	5.9	6.5-	9	1	4-	1.1	0.5+
0	4	7	1.7	3.0+	2	1	4-	2.4	1.4-	3	2	2	3.0	4.1-	5	1	6-	8.6	9.1-	6	3	2	2.2	1.5-	9	1	3-	5.3	5.7-
0	5	2	2.4	2.2+	2	1	3-	23.6	23.7-	3	2	3	5.1	5.2+	5	1	5-	3.8	3.9+	6	3	3	3.1	4.3+	9	1	2-	7.3	7.3-
0	5	4	2.0	2.2+	2	1	2-	7.8	8.7-	3	2	4	4.2	3.9+	5	1	4-	8.3	8.7-	6	4	5-	5.5	5.9-	9	1	1-	1.4	1.5+
1	0	11-	5.8	5.3+	2	1	1-	16.4	16.2-	3	2	5	5.5	4.9+	5	1	3-	1.6	1.0-	6	4	3-	3.2	3.5-	9	1	0	2.0	1.3+
1	0	5-	9.6	9.4+	2	1	0	14.3	13.7+	3	2	8	2.9	2.2+	5	1	2-	12.0	12.8-	6	4	1	2.4	2.2-	9	1	2	2.5	2.5-
1	0	3-	2.6	2.8+	2	1	1	21.2	19.5-	3	3	9-	4.5	3.6-	5	1	1-	8.9	7.9+	7	0	7-	12.1	14.3+	9	1	3	1.2	1.6+
1	0	1	20.1	22.3-	2	1	2	5.6	4.8-	3	3	8-	2.7	2.1-	5	1	0	3.4	2.4-	7	0	3-	8.1	8.7+	9	2	7-	3.5	4.0-
1	0	3	28.1	28.6-	2	1	3	0.7	0.9-	3	3	6-	11.1	9.4+	5	1	1	5.5	4.9-	7	0	1-	2.7	3.4+	9	2	3-	4.3	4.6-
1	0	5	7.2	7.6+	2	1	4	17.4	15.5-	3	3	5-	8.9	8.3-	5	1	2	10.4	9.7-	7	0	1	7.1	6.2+	9	2	2-	4.3	5.7-
1	0	7	11.6	9.5-	2	1	5	9.3	8.4-	3	3	4-	3.5	3.9-	5	1	3	7.2	6.9-	7	0	3	6.8	6.7+	9	2	1-	3.4	2.9+
1	0	9	4.3	3.1-	2	1	7	3.4	3.0+	3	3	1-	5.6	5.4-	5	1	4	5.3	5.1-	7	0	5	1.5	2.0-	9	2	1	2.4	1.6-
1	1	11-	2.8	1.2-	2	1	8	2.2	1.7-	3	3	1	1.7	2.1-	5	1	5	1.7	2.4+	7	1	11-	1.7	1.6+	9	3	7-	3.0	3.8-
1	1	10-	3.8	3.7+	2	1	9	1.7	1.7-	3	3	2	3.0	2.7+	5	1	6	3.7	3.2-	7	1	8-	5.9	7.2+	9	3	6-	6.6	6.5-
1	1	7-	2.0	1.8+	2	2	10-	3.5	3.1-	3	3	4	5.5	5.9+	5	2	8-	5.6	5.0+	7	1	7-	1.1	0.6+	9	3	3-	3.5	3.2-
1	1	6-	5.8	5.9+	2	2	9-	4.1	3.8+	3	3	6	2.5	1.8-	5	2	7-	2.6	2.5-	7	1	6-	2.9	3.3+	10	0	10-	3.4	3.5+
1	1	5-	10.8	10.7+	2	2	6-	12.3	12.9-	3	4	6-	5.1	5.7-	5	2	6-	6.1	4.6-	7	1	5-	2.2	2.7-	10	0	8-	4.3	4.4+
1	1	4-	0.9	0.9-	2	2	5-	5.8	5.5-	3	4	4-	3.9	3.7-	5	2	5-	4.4	3.8-	7	1	4-	9.5	9.6+	10	0	2-	6.4	6.8+
1	1	3-	6.9	6.6+	2	2	3-	4.7	4.6-	3	4	2-	10.2	10.8-	5	2	4-	6.4	6.6+	7	1	3-	4.4	3.8-	10	0	0	2.4	2.1+
1	1	2-	15.8	16.0+	2	2	2-	9.2	8.7-	3	4	0	6.0	6.7+	5	2	2-	6.3	5.9+	7	1	2-	1.0	1.2-	10	0	2	5.7	5.7+
1	1	1-	20.1	19.3-	2	2	1-	4.2	4.3+	3	4	2	3.8	4.3-	5	2	1-	16.9	16.4-	7	1	1-	9.7	9.5+	10	1	7-	3.3	3.9+
1	1	0	30.6	32.5-	2	2	0	10.9	9.6-	3	5	3-	2.8	2.0-	5	2	2	3.2	2.8-	7	1	0	11.6	10.6+	10	1	6-	2.9	3.6-
1	1	1	27.3	28.0+	2	2	1	12.1	10.2-	4	0	12-	5.1	4.5+	5	2	3	7.0	6.6-	7	2	6-	6.2	6.2-	10	1	4-	1.2	1.8-
1	1	2	6.5	5.1+	2	2	2	11.7	9.8-	4	0	10-	1.6	1.2-	5	2	4	2.4	2.3-	7	2	5-	4.6	5.1+	10	1	3-	3.0	3.1+
1	1	3	10.0	8.2+	2	2	3	4.9	3.9-	4	0	8-	3.3	3.7+	5	2	5	3.2	2.0+	7	2	3-	6.4	5.9+	10	1	2-	3.6	4.5+
1	1	4	14.1	13.6-	2	2	4	4.1	3.3-	4	0	6-	13.8	16.4+	5	3	8-	3.2	2.8-	7	2	1-	3.7	3.0+	10	1	1-	2.5	3.1+
1	1	5	5.7	5.0+	2	2	5	10.0	9.0-	4	0	4-	3.7	4.5+	5	3	7-	3.6	2.7+	7	2	0	5.4	5.4+	10	1	1	4.6	4.8+
1	1	7	2.3	1.8-	2	2	8	2.6	2.5+	4	0	2-	11.6	12.9+	5	3	6-	2.5	2.2+	7	2	1	3.8	2.6+	10	2	8-	2.2	3.2-
1	1	8	5.8	5.4-	2	3	9-	3.8	2.6-	4	0	0	3.5	4.3-	5	3	5-	3.0	2.8+	7	2	2	3.3	3.3+	10	2	7-	4.2	4.1-
1	1	9	3.2	2.7-	2	3	7-	6.1	6.1-	4	0	2	1.8	1.9+	5	3	3-	2.2	1.9+	7	3	7-	3.0	3.3-	10	2	2-	3.2	3.3+
1	1	10	3.4	2.8-	2	3	6-	4.1	3.5+	4	0	4	7.8	7.4+	5	3	0	6.3	6.7-	7	3	6-	2.7	2.2-	10	3	3-	4.0	4.7+
1	2	10-	1.6	2.0-	2	3	4-	3.3	3.3-	4	0	6	4.8	4.4-	5	3	1	2.4	0.8-	7	3	5-	2.8	2.5+	11	0	9-	3.5	3.5+
1	2	9-	4.1	3.6+	2	3	3-	3.0	3.3-	4	0	8	4.9	4.1-	5	3	2	3.9	4.4-	7	3	2-	5.7	6.2+	11	0	7-	4.0	3.9-
1	2	8-	3.4	2.7+	2	3	1-	3.2	3.9+	4	1	12-	4.1	3.7-	5	3	4	4.3	4.7+	7	3	1-	2.5	2.1+	11	0	5-	3.9	4.6+
1	2	7-	5.8	5.4+	2	3	0	9.2	7.4-	4	1	10-	2.5	2.3+	5	3	5	4.9	3.5-	7	3	2	2.6	2.5-	11	0	3-	2.0	2.9+
1	2	6-	9.7	9.5+	2	3	1	11.7	9.8-	4	1	9-	7.4	7.1+	5	4	8-	2.1	3.3+	7	3	3	3.6	4.0+	11	0	1	3.7	3.4-
1	2	5-	4.0	3.7-	2	3	2	2.2	1.8-	4	1	6-	8.4	8.1+	5	4	6-	5.5	5.0+	7	4	6-	2.4	2.8+	11	1	7-	3.4	3.8+
1	2	4-	4.4	4.4+	2	3	3	3.1	2.6-	4	1	5-	15.7	17.0+	5	4	4-	2.9	2.6+	8	0	6-	3.9	3.4-	11	1	5-	1.1	1.6+
1	2	3-	2.2	1.1-	2	3	4	4.9	4.5-	4	1	4-	1.4	1.3-	5	4	2-	5.9	6.8-	8	0	4-	7.4	7.2-	11	1	4-	1.7	1.8+
1	2	2-	10.6	10.5+	2	3	5	3.3	2.8+	4	1	3-	1.9	1.5+	5	4	1-	2.9	2.0-	8	0	2-	8.2	7.6+	11	1	3-	1.2	1.3+
1	2	1-	3.0	3.2-	2	3	6	3.4	2.5-	4	1	2-	6.2	4.8-	5	4	0	5.3	5.6+	8	0	0	9.8	11.4-	11	2	3-	3.1	3.7-
1	2	0	10.3	9.4+	2	4	7-	3.2	2.9-	4	1	1-	12.7	11.6+	6	0	12-	1.8	1.0+	8	0	2	1.2	1.6-	12	0	6-	2.1	2.3-
1	2	1	8.7	7.4+	2	4	5-	7.8	7.7+	4	1	0	20.4	18.7+	6	0	10-	5.4	4.5-	8	0	4	8.1	6.6-	12	0	4-	1.4	1.7-
1	2	2	9.5	8.3+	2	4	3-	3.2	3.3-	4	1	1	2.4	2.7-	6	0	8-	7.2	8.0-	8	1	11-	2.1	1.8+	12	0	2-	4.5	5.5-
1	2	3	3.4	2.9-	2	4	1-	5.2	4.8-	4	1	2	8.2	6.5+	6	0	4-	5.8	5.4-	8	1	10-	1.0	0.7-	12	1	8-	3.2	3.7+
1	2	4	12.5	12.2+	2	4	1	4.4	4.1+	4	1	3	5.2	4.3+	6	0	2-	10.4	12.4+	8	1	8-	2.9	2.8-	12	1	7-	1.4	1.2+
1	2	5	7.5	8.0-	2	5	0	5.5	5.9-	4	1	4	2.2	1.6+	6	0	0	8.9	9.2-	8	1	7-	2.7	2.9-	12	1	5-	3.3	4.2-
1	2	6	4.3	4.3-	2	5	1	3.1	3.0+	4	1	5	5.2	4.0-	6	0	2	4.8	4.0+	8	1	6-	4.7	5.6+	12	1	4-	1.3	1.6-
1	2	7	4.0	3.6-	2	5	3	2.5	2.6+	4	2	8-	5.7	4.3+	6	0	4	5.9	4.9+	8	1	4-	1.1	1.1+	12	1	3-	0.9	1.6-
1	3	7-	5.8	5.7+	3	0	11-	5.0	4.7+	4	2	7-	6.6	6.0+	6	0	6	6.7	4.9+	8	1	3-	2.6	2.9-	13	0	7-	3.5	4.8-
1	3	6-	6.1	5.9+	3	0	9-	6.6	5.0-	4	2	6-	2.2	1.5-	6	1	11-	2.9	3.4-	8	1	2-	4.6	4.9+	13	0	5-	1.5	1.5+

TABLE XXVIII

ATOMIC PARAMETERS AND THEIR STANDARD DEVIATIONS

Atom	x	y	z	B
N	0.2007 ± 0.00012	0.4383 ± 0.0003	0.4799 ± 0.00013	2.91 ± 0.13
B_1	-0.0641 ± 0.0005	0.5437 ± 0.0009	0.2441 ± 0.0004	3.18 ± 0.09
B_2	0.0629 ± 0.0003	0.6860 ± 0.0010	0.1935 ± 0.0004	3.14 ± 0.14
B_3	0.1000 ± 0.0002	0.6805 ± 0.0005	0.3868 ± 0.0003	2.62 ± 0.08
H_1	-0.153 ± 0.006	0.678 ± 0.010	0.232 ± 0.005	2.8 ± 1.1
H_2	-0.067 ± 0.004	0.313 ± 0.006	0.283 ± 0.003	3.0 ± 0.7
H_3	-0.063 ± 0.007	0.538 ± 0.008	0.122 ± 0.003	2.3 ± 1.4
H_4	0.042 ± 0.009	0.893 ± 0.016	0.138 ± 0.007	4.4 ± 0.8
H_5	0.148 ± 0.003	0.549 ± 0.011	0.190 ± 0.005	1.8 ± 0.8
H_6	0.169 ± 0.005	0.834 ± 0.007	0.365 ± 0.004	2.0 ± 0.7
H_7	0.052 ± 0.005	0.802 ± 0.011	0.452 ± 0.004	1.6 ± 0.7

TABLE XXIX

INTERATOMIC DISTANCES AND BOND ANGLES

A. Bond lengths

$N-B_3$	1.581 ± 0.003Å
B_1-B_2	1.744 ± 0.005
B_1-B_3	1.820 ± 0.006
B_2-B_3	1.803 ± 0.006
B_1-H_1	1.09 ± 0.03
B_1-H_2	1.18 ± 0.04
B_1-H_3	1.23 ± 0.03
B_2-H_3	1.39 ± 0.05
B_2-H_4	1.12 ± 0.05
B_2-H_5	1.11 ± 0.04
B_2-H_6	1.75 ± 0.03
B_3-H_6	1.12 ± 0.03
B_3-H_7	1.14 ± 0.07

B. Nonbonded intramolecular distances

$N \ldots B_1$	2.806 ± 0.007Å
$N \ldots B_2$	2.861 ± 0.005
$N \ldots H_6$	2.18 ± 0.04
$N \ldots H_7$	2.28 ± 0.07
$B_1 \ldots H_7$	2.28 ± 0.04

C. Bond angles

NB_3B_1	$111.0 \pm 0.5°$
NB_3B_2	$115.3 \pm 0.5°$
NB_3(B plane):	$117.2 \pm 0.5°$

D. Short intermolecular distances

Atom of reference molecule[a]	Atom of neighbor molecule	Molecules related by	Distance
H_7	H_2	Center at (0,1/2,1/2)	2.65Å
H_7	H_7	Center at (0,1,1/2)	2.57
H_6	H_5	2, axis at x=z=1/4	2.43
H_4	H_4	Center at (0,1,0)	2.72

[a]Atomic coordinates of the reference molecule are given in Table XXVIII.

those resulting from the standard deviations in the coordinates. It is clear that standard deviations estimated in this manner fail to reflect any systematic errors in the bond lengths conceivably introduced by incorrectly assumed scattering factor curves.(100)

Topologically, the B_3H_7 group is readily identified with the fragment of tetraborane produced by symmetrical cleavage of the double bridge inferred on chemical grounds (see sections III B and C). A comparison of the detailed geometry with that of tetraborane(101) nevertheless reveals several significant differences. The nonbridged boron-boron distance B_1-B_3 is considerably longer than the value 1.712Å found for its presumptive counterpart in tetraborane. This may be related to the change of the neighboring B_1-H_2 from a bridge to a regular boron-hydrogen bond. On the other hand, the bridged B_1-B_2 distance is much shorter than any of the four bridge B-B distances in tetraborane, all of which lie in the range 1.842 ± 0.007Å. Perhaps the most striking difference is the strong asymmetry of the B_2-H_6-B_3 hydrogen bridge. While the B_3-H_6 distance is indistinguishable from a single B-H bond, the B_2-H_6 distance of 1.75Å is almost 0.4Å longer than the corresponding B-H bridge distances in B_4H_{10} or any other boron hydride. Boron-hydrogen distances approximating this value are found in B_5H_{11}(101) but they are not part of B-H-B bridges of the usual kind.

The overall effect of these distortions from the B_4H_{10} geometry may be interpreted as a tendency toward the structure of a bridge substituted diborane, $(H_3NBH_2)B_2H_5$. The nearly planar configuration of $H_1H_2B_1B_2H_4H_5$ and the closeness of the B_1-B_2 distance to the value 1.770 ± 0.013Å found in diborane(102) would seem to support this interpretation, which presumably would require the free molecule to have a plane of symmetry perpendicular to B_1-B_2. Since B_2-H_6 B_1...H_7 are clearly different, as are N...B_1 and N...B_2, a molecular symmetry plane certainly is not present in the crystal. The H_3NBH_2 group, however, has a plane of symmetry, within experimental error, as shown by its B-H and N...H distances. The violations of the molecular symmetry plane can then largely be accounted for in terms of a tilt of the H_3NBH_2 group with respect to B_2H_5, such as to "crowd" H_6 into B_2. Support for the hypothesis that this might be due to intermolecular repulsions could be sought in the geometry of the close intermolecular contacts involving H_6 and H_7 (Table XXIX). This approach is inconclusive, however, since the H_3NBH_2 group is about equally closely surrounded by neighbors on both sides.

In spite of the above considerations, we feel that the asymmetry of the molecule, which also includes the presumable significant asymmetry of the B_1-H_3-B_2 bridge, is probably too large to be accounted for by mere intermolecular

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(100) F. L. Hirshfeld, K. Eriks, R. E. Dickerson, E. L. Lippert and W. N. Lipscomb, J. Chem. Phys. 28, 56 (1958).

(101) E. B. Moore, R. E. Dickerson and W. N. Lipscomb, J. Chem. Phys. 27, 209 (1957).

(102) K. Hedberg and V. Schomaker, J. Am. Chem. Soc. 73, 1482 (1951).

packing forces. Using the formulation of Eberhardt, Crawford, and Lipscomb[103] our results suggest that the boron triangle in $NH_3B_3H_7$ is held together by two B-H-B bridge bonds and one (B_1-B_3) electron pair bond, but the alternative description in terms of one hydrogen bridge B_1-H_3-B_2 and a central three center bond (B_1-B_2-B_3) cannot be entirely ruled out.

The N-B_3 distance is in satisfactory agreement with other, less accurately determined N-B distances in boron hydride derivatives[104]; it shows particularly close agreement with the more accurately determined boron-nitrogen distances in the addition compounds of boron trifluoride with ammonia and methyl amines.[105]

The packing of molecules in the low-temperature structure viewed down the b axis is shown in the h0ℓ Fourier projection of Fig. 26. As in the high-temperature modification, the end-to-end arrangement is apparent, in this case in the direction of the diagonal glide translation. Molecules in neighboring "chains" lie next to each other rather than staggered as in the high-temperature form; this arrangement amounts to a favorable stacking of dipoles pointing in two opposite directions.

A low-temperature heat-capacity study by Westrum and Levitin,[106] carried out after the completion of the experimental part of the X-ray study, has established the transition temperature as 297.10°K. As pointed out by these authors, the entropy of transition, 4.15 cal. deg.$^{-1}$ mole^{-1}, is approximately equal to Rℓn8. It is interesting to note that the number of equivalent general positions in the space group I4mm is 8, that is, if the only effect of the phase transition were a randomization over these positions of the angular orientation of each molecule, independent of its neighbors, the entropy change would very nearly equal the experimental value.

E. Other Triborane Addition Compounds

1. TRIMETHYLAMINE-TRIBORANE

$(CH_3)_3NB_3H_7$ was first prepared by Edwards and his collaborators at Callery Chemical Company[107] using the reaction between B_4H_{10} and $N(CH_3)_3$. It was

(103) W. H. Eberhardt, B. Crawford and W. N. Lipscomb, J. Chem. Phys. 22, 989 (1954); R. E. Dickerson and W. N. Lipscomb, ibid., 27, 212 (1957).

(104) E. W. Hughes, J. Am. Chem. Soc. 78, 502 (1956); E. L. Lippert and W. N. Lipscomb, ibid., 78, 503 (1956); C. E. Nordman and C. R. Peters, ibid., in press.

(105) J. L. Hoard, S. Geller, and T. B. Owen, Acta Cryst. 4, 405 (1951).

(106) E. F. Westrum, Jr. and N. E. Levintin, J. Am. Chem. Soc., in press.

(107) L. J. Edwards, W. V. Hough, and M. D. Ford, to be published.

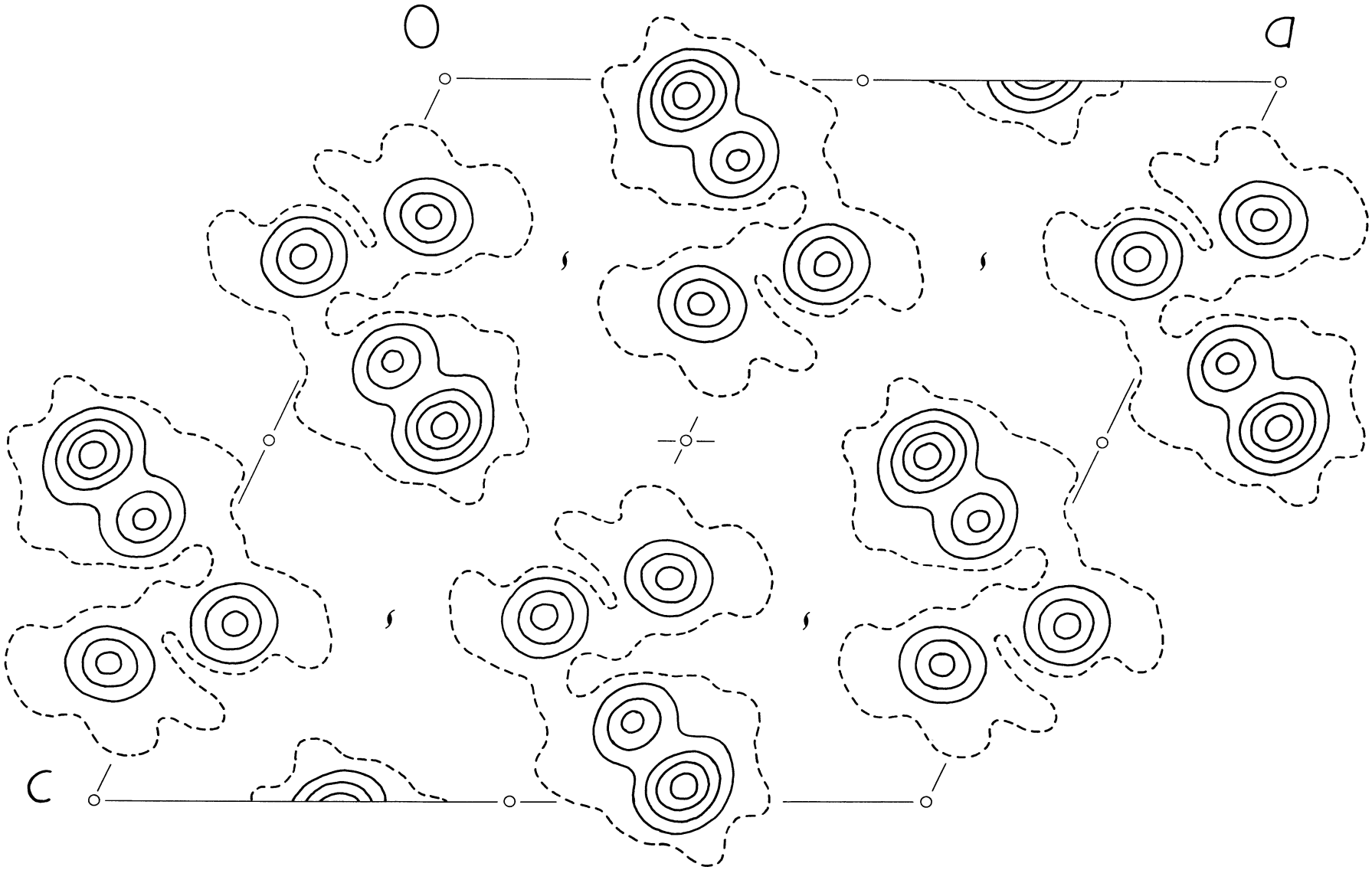


Fig. 26. The packing of molecules in the low-temperature crystal of $H_3NB_3H_7$. Projection onto (010) of the electron density in the low-temperature structure, showing the packing of molecules. Contours are at 1 (broken), 2, 4, 6 and 8 e $Å^{-2}$.

later found that a process involving an initial preparation of a B_3H_7 etherate followed by replacement of the ether by $N(CH_3)_3$ was superior for preparative purposes. Kodama had found that tetrahydropyran is a particularly suitable ether for such a purpose (see page of this report). The following process, modeled after that used by Kodama for the preparation of $H_3NB_3H_7$, was developed in this laboratory by J. C. Carter and G. Kodama under the joint sponsorship of WADC (Kodama) and Callery Chemical Company (Carter). The sample thus prepared was used by Westrum and his collaborators to run the low-temperature heat capacity of $(CH_3)_3NB_3H_7$.

The reactions involved are:

$$(1)\quad 2B_4H_{10} + 2CH_2(CH_2)_4O \longrightarrow 2(CH_2)(CH_2)_4OB_3H_7 + B_2H_6$$

$$(2)\quad CH_2(CH_2)_4OB_3H_7 + (CH_3)_3N \longrightarrow (CH_3)_3NB_3H_7 + CH_2(CH_2)_4O$$

The reaction vessel, a 500-cc three-necked flask, was fitted with an efficient magnetically driven paddle stirrer and a low-temperature reflux condenser attached at the top to a vacuum line and manometer. The third neck of the flask was fitted with a standard taper stopper and used to introduce solvents. One hundred milliliters of tetrahydropyran and one hundred milliliters of toluene were placed in the flask, cooled to -196°C, and the reactor evacuated. The toluene was used to dilute the tetrahydropyran. Fifty milliliters of tetraborane (liquid measured at 0°C) were then distilled into the reactor and the temperature raised slowly, when the first evidence of a reaction occurred, as noted by evolution of diborane, the reactor was immersed in liquid nitrogen. After the reaction had subsided and the pressure had dropped to zero, the reactor was again warmed slowly and the diborane removed. The initial reaction was quite exothermic and very difficult to control, the diborane pressure building up extremely rapidly. After cooling and rewarming, the reaction was generally quite moderate and the diborane could be removed without difficulty. When a 100-cc sample of liquid tetraborane was used, heat-transfer problems and localized heating in the solution resulted in the reaction going out of control for a short period of time.

Unless more efficient methods of heat transfer and temperature control are available, the reaction cannot be recommended for greater than 50 cc of tetraborane and even then only if all precautions of safety are observed.

After the major portion of diborane had been removed, the reaction was cooled to -78°C and allowed to stand overnight. The remainder of the diborane was them removed and the excess tetrahydropyran and toluene were condensed into a tube for removal from the system. The tetrahydropyran-triborane remaining in the reactor melts just below room temperature; it ignites spontaneously when exposed to air in contact with filter paper.

The system was opened under a stream of dry nitrogen and a 200-ml sample of anhydrous ethyl ether was introduced. The reactor was cooled to -78°C and evacuated. It was then necessary to warm the solution again to ice temperature

until the tetrahydropyran triborane had completely dissolved. The solution was cooled to -78°C, and 37 ml of liquid trimethylamine (measured at 0°C) was allowed to distill very slowly into the system. A period of 24 hours was required for the amine to be completely absorbed.

It was necessary to use a stoichiometric amount of trimethylamine because of the possibility of side reactions involving the desired product and excess amine. At this time the reactor was allowed to warm to room temperature and the ethyl ether and liberated tetrahydropyran were distilled from the system and discarded.

The method of recovery and purification of the trimethylamine triborane differed from that used with the ammonia compound. The trimethylamine-triborane could not be precipitated from a benzene solution upon addition of methylcyclohexane. It was recovered and purified by recrystallizing twice from anhydrous toluene at -95°C and filtering through a glass frit cooled to -78°C under a stream of dry nitrogen. The yield of pure product was 65-70%.

The sample was hydrolyzed by heating 100 hours at 150°C with 10% HCl in a sealed tube. Active hydrogen evolved was measured with a Toepler pump and calibrated gas burette. Boron was titrated as boric acid in the presence of mannitol. Trimethylamine was determined by the Kjeldahl procedure. It was necessary to bubble the liberated amine very slowly through a considerable depth of standard acid to obtain efficient absorption. Results of analysis were:

	Found mmoles	Calculated mmoles	% of Calculated
Active Hydrogen	7.28	7.31	99.6
Boron	0.546	0.548	99.6
Trimethylamine	0.181	0.1827	99.0

Ratio:	$(CH_3)_3N$	B	H
	0.994	3.000	7.000

Reagents were the same as those described for $H_3NB_3H_7$ or were the best commercial product.

2. ATTEMPTS TO PREPARE $F_3PB_3H_7$

The isolation in this laboratory of the compound F_3PBH_3, formally analogous to the compounds $(NH_3)_3NBH_3$ and H_3NBH_3, and the isolation of the compounds $H_3NB_3H_7$ and $(CH_3)_3NB_3H_7$ all suggested that it should be possible to prepare the compound $F_3PB_3H_7$ through the reaction of F_3P and tetraborane or one of its derivatives. A number of preparative procedures have been explored but it has not been possible to resolve the resulting reaction mixtures into a fraction identifiable as the desired $F_3PB_3H_7$. Apparently F_3P is such a weak base that it is unable

to stabilize the B_3H_7 fragment long enough to permit compound identification.

Systematic chemical arguments given earlier suggest the following equation to represent the interaction of B_4H_{10} and PF_3

$$B_4H_{10} + PF_{3(excess)} \longrightarrow F_3PBH_3 + F_3PB_3H_7$$

The system was studied by sealing B_4H_{10} and PF_3 in glass tubes equipped with break-off tips. Procedures were analogous to those used for the synthesis of H_3BPF_3.[108] When the PF_3 pressure was 2 atmospheres or less and the reaction time at room temperature was half a day or less, the original PF_3 and B_4H_{10} could be recovered unchanged. If the pressure was above 5 atmospheres and the reaction time at room temperature was 3 days, B_2H_6, F_3PBH_3, and a yellow viscous residue along with very small amounts of fairly volatile, unidentified components were isolated from the reaction mass. Some of the unidentified components had a volatility about the same as or a little less than that of B_4H_{10}; this material decomposed rapidly to PF_3, B_2H_6, and other residues when warmed to room temperature. The very small amount of substance available permitted only crude qualitative identification of products.

The apparent low stability of any $F_3PB_3H_7$ compound at room temperature suggested a low-temperature synthesis in liquid PF_3 which can be represented by the following equation:

$$NaB_3H_7 + HCl + PF_3 \xrightarrow[\substack{PF_3 \\ \text{solvent at} \\ -78°C}]{\text{liquid}} NaCl\downarrow + F_3PB_3H_7 + H_2$$

Because of the very low solubility of NaB_3H_8, the evolution of H_2 was very slow; several days were required to give off one mole of H_2. With a large excess of HCl the reaction proceeded somewhat faster. The resulting reaction mixture was complex and difficult to separate. The material left after the removal of excess PF_3 and HCl decomposed easily when warmed to room temperature. PF_3, B_2H_6, B_4H_{10} and a solid yellow residue were recognized as products.

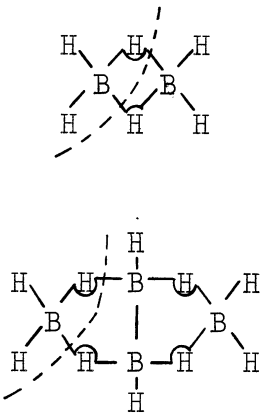
Current data suggest that if $F_3PB_3H_7$ is to be identified, low-temperature techniques will be required for the complete characterization. Further work is in progress.

(108) R. W. Parry and T. C. Bissot, J. Am. Chem. Soc. 78, 1524 (1956).

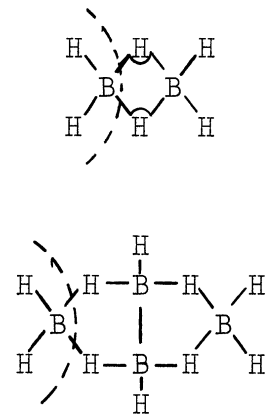
IV. SOME ADDITION COMPOUNDS RELATED TO THE BORANE ADDUCTS

A. Background

Data outlined in earlier sections on the reactions of B_2H_6 and B_4H_{10} have been interpreted in terms of a symmetrical and nonsymmetrical cleavage of the double bridge bonds of these two molecules.



Symmetrical Cleavage
of the Double Bridge Bonds



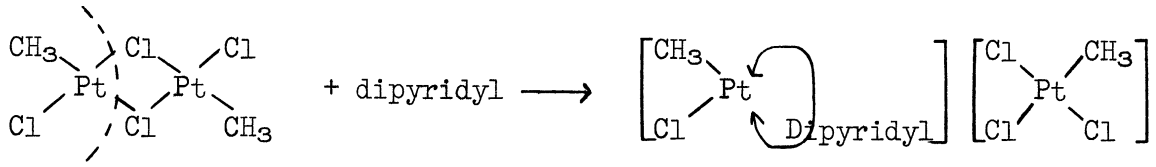
Nonsymmetrical Cleavage
of the Double Bridge Bonds

It has been found that certain reagents such as ammonia promote nonsymmetrical cleavage while others such as trimethylamine and various ethers promote symmetrical cleavage.

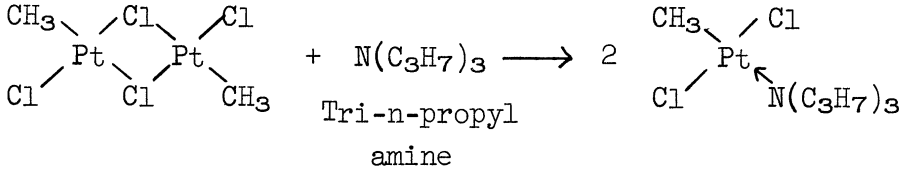
Since the double bridge bond is found in many structures other than the boron hydrides, it is of interest to explore the cleavage reactions as they may apply to compounds such as Al_2Cl_6, $Al_2(CH_3)_6$, and even $[AlH_3]_n$.

Both symmetrical and nonsymmetrical cleavages were reported by Gibson and later by Chatt for certain coordination compounds such as $CH_3ClPtCl_2PtClCH_3$ and $Et_2AuBr_2AuEt_2$.[109]

(109) a) J. Chatt, J. Chem. Soc., 655 (1951). b) Foss and Gibson, J. Chem. Soc., 3093 (1949); ibid., 628 (1951).



Nonsymmetrical Cleavage of Pt Complex



Symmetrical Cleavage of Pt Complex

The current sequence of experiments was undertaken in an effort to gain information on the reactions of the bridge compounds of aluminum. Intelligent correlations between the reactions of such coordination compounds and the electronic configuration of the central metal atom demand more extensive data on the nature of the reaction between bridge molecules and various reagents. Many of the explanations and hypotheses based on π bonding have little basis in experimental fact and the current studies were initiated to establish a more reliable experimental basis for current speculation.

B. The Compound F_3PAlCl_3

1. EARLIER STUDIES

The ability of PF_3 and PCl_3 to form adducts with $PtCl_2$ was first described by Schultzenberger[110] and by Moisson[111] but it remained for Chatt[112] to recognize that the resulting compounds were coordination compounds similar to $Pt(CO)_2Cl_2$ and $[Pt(CO)Cl_2]_2$ described extensively in earlier literature on complex compounds. Chatt pointed out that F_3BPF_3 does not form and he contrasted this with the fact that $[PtCl_2(PF_3)]_2$ can be formed with ease. He attempted to rationalize the experimental difference in terms of the electronic structure of the boron and platinum atoms. He noted that platinum with the electronic configuration $1s^2$, $2s^2$, $2p^6$, $3s^2$, $3p^6$, $3d^{10}$, $4s^2$, $4p^6$, $4d^{10}$, $4f^{14}$, $5s^2$, $5p^6$, $5d^8$, $6s^2$ has 5d electrons which might be donated to the d orbitals of the phosphorus atom and pointed out that the attachment of F to P would lower the d levels of P to a bonding region; thus a "π or dative double bond"

(110) P. Schultzenberger, Bull. Soc. Chim. 17, 482 (1872).
(111) H. Moisson, Bull. Soc. Chim. 5, 454 (1891).
(112) J. Chatt, Nature 165, 637 (1950).

was assumed to be important in the linking of PF_3 to $PtCl_2$. In such a bond, electrons from the metal are donated to the phosphorus atom. Aluminum, with the electronic configuration $1s^2$, $2s^2$, $2p^6$, $3s^2$, $3p^1$, has no such d electrons and would be unable to form a complex with PF_3 by such a mechanism. In support of such an argument, Chatt and Williams[113] noted that no addition compound resulted when PF_3 was passed over sublimed Al_2Cl_6 or Al_2Br_6 at 250°C. More recently Holmes and Brown[114] reported that $AlCl_3$ would not combine with PCl_3 in a low temperature study.

Earlier work in this laboratory[115] indicated that the bridged compound B_2H_6 reacts with PF_3 by symmetrical bridge cleavage to give H_3BPF_3, a molecule which in the earlier arguments of Chatt, cannot be stabilized by π bonding of the type used for platinum complexes. It has since been suggested by Graham and Stone[116] and others that such a complex owes its stability to a delocalization of the B-H electrons to give a "π bond" in a manner comparable to that invoked in the hyperconjugation arguments of organic chemistry. The prime argument for such π bonding was the difference in stability between complexes of borine and BF_3 with bases such as PF_3 and NH_3.

In this laboratory it was suggested that those Lewis acids which are dimeric in the free state would combine with very weak bases such as PF_3 whereas those which are monomeric would not. Thus B_2H_6, Al_2Cl_6, and $Al_2(CH_3)_6$ should combine with PF_3 while BF_3, $B(CH_3)_3$, BBr_3, etc., should not. In an effort to test this prediction, the system Al_2Cl_6-PF_3 has been restudied using the methods employed in the earlier B_2H_6-PF_3 study.

The empirical generalization suggested above can be rationalized by an appropriate combination of steric and electronic arguments which will be presented with a more detailed account of the experimental data in a subsequent publication. The existence of F_3PAlCl_3 and the nonexistence of F_3PBCl_3 are rationalized with more difficulty by "π bonders."

2. THE PREPARATION OF F_3PAlCl_3

Very pure resublimed Al_2Cl_3 (99.9+ % Al_2Cl_6) reacts with PF_3 in a bomb tube under 8 atmospheres pressure in accordance with the following equation:

$$Al_2Cl_6 + 2PF_3 \longrightarrow 2Cl_3AlPF_3 \quad .$$

About 4 hours at room temperature were required for reaction. Shorter periods of time or lower pressures gave no reaction. Longer periods of time permitted group exchange on the complex

(113) J. Chatt and A. A. Williams, J. Chem. Soc., 3061 (1951).
(114) R. R. Holmes and H. C. Brown, Paper No. 70, Div. of Phys. and Inorg. Chemistry, Dallas Meeting of Amer. Chem. Soc., April 12, 1956.
(115) R. W. Parry and T. C. Bissot, J. Am. Chem. Soc. 78, 1524 (1956).
(116) W.A.G. Graham and F.G.A. Stone, J. Inorg. and Nuclear Chem. 3, 175 (1956).

$$n Cl_3AlPF_3 \longrightarrow n PCl_3 + [AlF_3]_n$$

PCl_3 and AlF_3 were recovered as products.

The identity of the complex Cl_3AlPF_3 was established by determining the amount of PF_3 combining with a given amount of Al_2Cl_6. The molecular weight of the solid product was determined by vapor pressure depression in liquid PF_3. An experimental value of 202 as compared to a theoretical value of 221.7 for $AlCl_3PF_3$ supports the proposed monomeric formula. The deviation of almost 10% between the experimental and theoretical values is understandable in terms of experimental difficulties of the method and the slow conversion of Cl_3AlPF_3 to AlF_3 and PCl_3 in liquid PF_3 even at -112°C. It is also appropriate to note that F_3PAlCl_3 is soluble in liquid PF_3 whereas Al_2Cl_6 and PCl_3 are not. Further evidence to support the proposed formula is found in a base displacement reaction. When diethyl ether was added to the solid complex at -112°C, the solid dissolved but no PF_3 was liberated; addition of an equimolar quantity of NMe_3 to the cold solution (-78°C) resulted in liberation of an amount of PF_3 equal to the amount of NMe_3 used. Me_3NAlCl_3 was obtained as a product of the reaction. The process may be summarized by the equation:

$$F_3PAlCl_3 + Me_3N \longrightarrow Me_3NAlCl_3 + PF_3 \quad .$$

The shift of halide groups in the complex is an interesting process. It goes slowly in liquid PF_3 at temperatures as low as -112°C and is rather rapid for the pure solid at temperatures above 0°C. Earlier studies in this laboratory indicated that $CH_3ONHCH_3BH_3$ undergoes a shift of groups to give $B(OCH_3)_3$ and NH_2R as initial products but it was noticed that such a process was always preceded by a loss of H_2. Bissot, Campbell, and Parry[117] interpreted this fact as evidence for the loss of H_2 from N and B, thus opening up a coordination site for group transfer. Since both Al and P can have coordination numbers above 4 rather commonly, it would be expected that the shift of groups would occur even at low temperatures and without initial loss of any coordinated groups. Indeed, such was observed.

3. EXPERIMENTAL

(a) Compound Preparation

Metallic aluminum was burned in a dry chlorine stream in an all-glass system using conventional good techniques (see Fig. 27). The resulting Al_2Cl_6 was sublimed into a small bulb which was then sealed off. Approximately 1 mM of Al_2Cl_6 was trapped in each bulb by means of the glass wool filter A in Fig. 27. The unit B could be weighed before and after subliming in the Al_2Cl_6 and sealing;

(117) T. C. Bissot, D. H. Campbell, and R. W. Parry, J. Am. Chem. Soc. 80, 1870 (1958).

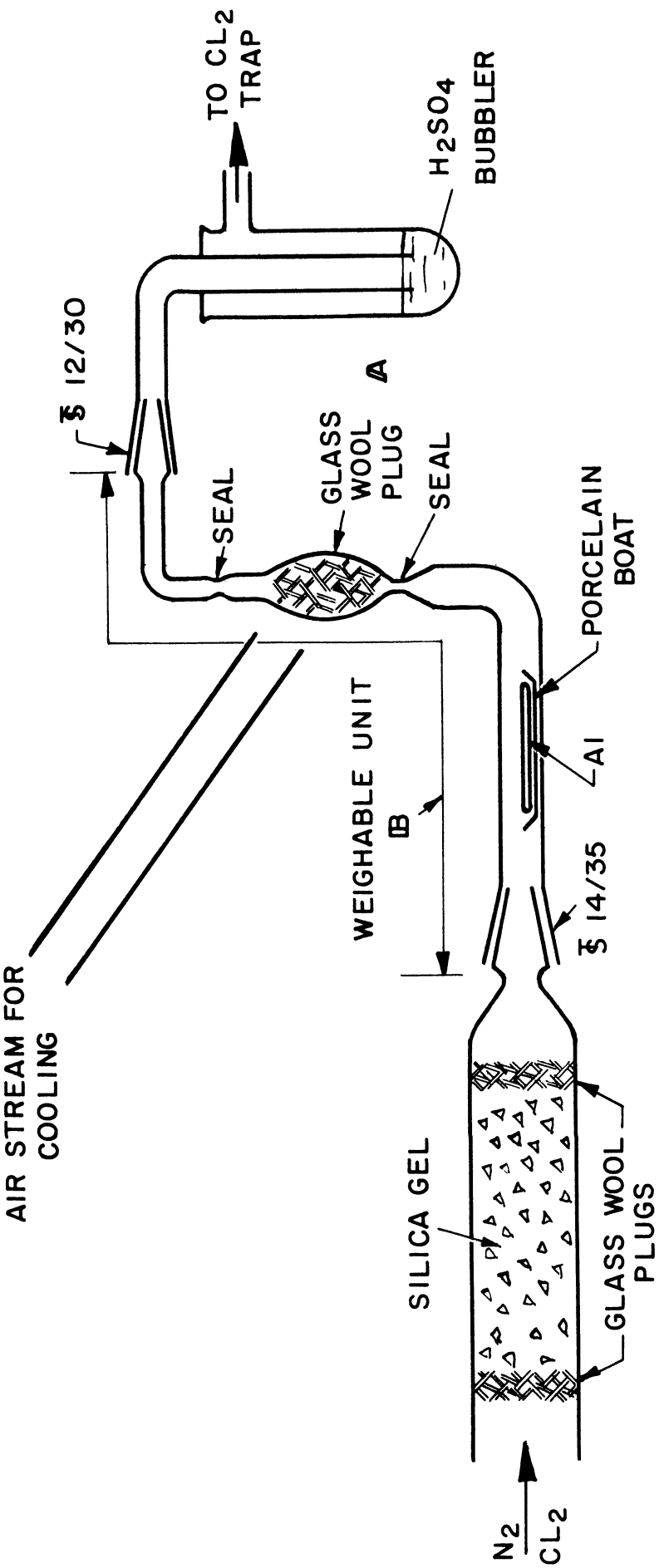


Fig. 27. Apparatus for the preparation of Al_2Cl_6.

thus the weight of Al_2Cl_6 could be accurately determined. The bulb was placed in a heavy-walled glass bomb tube along with a magnet sealed in a glass case (a magnetic hammer). The tube was evacuated and opened to the diffusion pump for several hours prior to use. The tube was also warmed with a flame to aid in drying. The bulb containing the Al_2Cl_6 was then crushed with the magnetic hammer and the dry nitrogen it contained was pumped out (i.e., the magnet inside was picked up by means of an external magnet and dropped on the glass bulb). A measured quantity of PF_3 was condensed into the tube (enough to give a desired pressure of about 8 atmospheres); then the tube was sealed off and transferred to the room-temperature storage area. After standing for the desired length of time, the contents of the tube were frozen with liquid nitrogen, the tube was opened to the vacuum line, and excess PF_3 was removed at -112°C. The amount of PF_3 recovered was measured and the stoichiometry of the reaction between PF_3 and Al_2Cl_6 was determined. Typical data for a number of runs are summarized in Table XXX. The course of the run after product formation was determined by product treatment. A number of separate observations are summarized below.

(b) Decomposition of F_3PAlCl_3 upon Standing

If in the preparation of F_3PAlCl_3 an unusually long time was allowed for the interaction of F_3P and Al_2Cl_6, no evidence for complex formation could be detected, but PCl_3 and AlF_3 could be recovered in stoichiometric quantities. (See runs 1,2,3.) The PCl_3 was identified by its molecular weight which was measured by vapor density. An observed value of 132 compared favorably with the theoretical value of 137. An analysis of the PCl_3 for chloride gave 80.0% Cl^- as compared to a theoretical value of 80.5% Cl^- for PCl_3. The AlF_3 in run 3 was identified after removal of PCl_3, by analyzing for Al by precipitation as 8-hydroxyquinoline. The fluoride was determined on the same sample by precipitation as PbClF. The observed ratio of F^- to Al^{+3} was 2.8 to 1.

In a number of other cases the complex formed and no evidence for PCl_3 was obtainable, but as the solid was allowed to warm up over a relatively long period, PCl_3 appeared (run 6).

(c) The Reaction of the Complex with Trimethylamine, with Dimethyl Ether, and with Diethyl Ether

Trimethylamine (about 0.5 mmole in run 2) was frozen onto the solid complex F_3PAlCl_3 (about 3.20 mmoles) and the system was warmed slowly to -78°C, at which temperature it was allowed to stand for about 1/2 hour. No PF_3 was liberated from this system. As the temperature was allowed to rise, PCl_3 could be separated.

When dimethyl ether was condensed onto the complex (run 14) PF_3 was liberated, but the weaker base, diethyl ether, gave no reaction (runs 10 and 11).

TABLE XXX

DATA FOR THE REACTION OF Al_2Cl_6 AND PF_3

Run	Al_2Cl_6, mM	PF_3, mM			PF_3 Al_2Cl_6	Pressure Atmosphere	Time	Remarks
		Initial	Recovered	Used				
1	0.735	20.46	19.01	1.44	1.96/1	8.1	2 wks	PF_3 was removed at -112°, fractionation at higher temperatures produced PCl_3 (mol. wt. = 132; theo. = 137). Analysis for Cl^- gave 80% vs. 80.5% calc. (see Item 3(b), p. 155).
2	1.60	19.55	16.98	2.67	1.67/1	7.7	4 days	Addition of 0.5 mM $(CH_3)_3N$ gave no PF_3; some PCl_3 was recovered.
3	0.855	20.61	18.91	1.70	1.99/1	8.1	4 days	Recovered 1.68 mM PCl_3 and analyzed for AlF_3 (see Item 3(b) p. 155).
4	1.16	20.05	17.57	2.42	2.08/1	8.0	4.5 hr	No PCl_3 was present originally but some was recovered upon warming to room temperature.
5	0.60	3.30	3.30	--	N.R.	400 mm	7 hr	No reaction with liquid PF_3 in slight excess at -112°.
6	1.03	20.15	18.06	2.09	2.01/1	8.0	3 hr	Addition of $(CH_3)N$ produced no PF_3 but PCl_3 was obtained when tube was warmed to room temperature.
7	1.17	20.33	20.13	0.20	N.R.	8.1	1 hr	Reaction does not go in 1 hr.
10	1.45	20.52	17.40	3.12	2.12/1	8.2	4 hr	Addition of about 2 cc ethyl ether gave no PF_3 at -78°; subsequent addition of about 0.8 mM of trimethylamine gave off about 1 mM material at -78° which had a mol. wt. = 83 (PF_3 mol. wt. = 88).
11	0.91	20.99	19.05	1.94	2.14/1	8.3	4 hr	Addition of 2 cc ethyl ether and 0.603 mM trimethylamine gave 0.606 mM PF_3 (mol. wt. = 87) at -78°.
14	0.855	25.02	22.98	2.04	2.3/1	8.1	4 hr	Prepared for mol. wt. determination but methyl ether solvent displaced PF_3 from the addition compound.
16	1.02	19.49	17.44	2.05	2.00/1	8	4 hr	Molecular weight determination (see Item 3(d) p. 157).
17	0.86	19.71	17.99	1.72	2.00/1	8	4 hr	Molecular weight determination (see Item 3(d) p. 157).

Addition of trimethylamine to the ether solution of the complex resulted in displacement of the PF_3 at -78°C. The most convincing data were obtained in run 11. About 2 ml of diethyl ether was frozen onto the solid complex (about 1.9 millimoles) with liquid nitrogen; then a sample of trimethylamine amounting to 0.603 millimole was frozen on the ether. The system was allowed to warm up to -78°C and 0.606 millimole of PF_3 was liberated. The PF_3 was identified by its molecular weight. The value obtained by vapor density was 87. The theoretical value for PF_3 is 88.

(d) The Determination of the Molecular Weight of F_3PAlCl_3

Molecular weight studies on this solid posed very difficult experimental problems. Conventional solvents such as benzene froze at such a high temperature that halide interchange occurred. Diethyl ether dissolved the solid complex, but because the solvent has two solid phases it is not particularly suitable for freezing point studies and its vapor pressure at suitable temperatures was too low for vapor-pressure depression studies. Dimethyl ether was not suitable as a solvent because it displaced PF_3. Finally, liquid PF_3 was used as a solvent at -112°C. A carbon disulfide slush was used as a thermostat at -112°C. The sample bulbs were immersed directly in the slush; otherwise the procedure was the same as that previously described.[15g] In a typical run the sample weighing some .454 gm was prepared directly in the molecular weight tube. The empty tube was weighed first and the tube was weighed again after the completion of the molecular weight measurement since exposure of the sample to room temperatures during weighing would result in halogen shift. About 23.0 millimoles of PF_3 was used as a solvent. Typical data at about -112°C showed:

P_{mm}	ΔP_{mm}	$\Delta P/P$	Mol. Wt.
446	43.5	0.0975	202
540	52.8	0.0977	201

Theory for F_3PAlCl_3 = 221.4

When more PF_3 was added to get another point, a precipitate formed and ΔP dropped to zero. It is significant that the decomposition of F_3PAlCl_3 in liquid PF_3 at -112°C was confirmed in subsequent studies. It is also noteworthy that AlF_3, PCl_3, and Al_2Cl_6 are all insoluble in liquid PF_3.

A duplicate run on a second sample (0.381 g) also gave a value of 202 for the molecular weight.

The entire area of aluminum complexes is still under active investigation. More will be given in subsequent reports.

C. The Compound $H_3Al[N(CH_3)_3]_2$

One of the procedures used to dry trimethylamine in this laboratory involved the storage of the liquid above lithium aluminum hydride. After the trimethylamine was removed from above the lithium aluminum hydride, a white volatile solid with a sharp melting point of 94°C could be sublimed from the reaction residues. The solid decomposed slowly at room temperature, evolving trimethylamine and other residues. When heated in glass, the solid left an aluminum mirror. Analysis of the solid showed the following: Al = 18.1%, N = 18.9%, H^- = 2.07%. These values support the formula $H_3Al[N(CH_3)_3]_2$ for which analytical values are: Al = 18.1%, N = 18.8%, H^- = 2.03%.

The formula immediately suggested that yields could be improved if AlH_3 were made first and treated with trimethylamine.

Two new preparative processes were then tried. They are described by the equations listed below:

Process 1

$$AlCl_3 + 3LiAlH_4 \xrightarrow{\text{ether}} 4H_3Al\text{-etherate} + 3LiCl$$

$$H_3Al\text{-etherate} + 2N(CH_3)_3 \longrightarrow H_3Al\text{-}2N(CH_3)_3 + \text{ether}$$

Process 2

$$LiAlH_4 + HCl \xrightarrow{\text{ether}} H_3Al\text{-etherate} + H_2 + LiCl$$

$$H_3Al\text{-etherate} + 2N(CH_3)_3 \longrightarrow H_3Al\text{-}2N(CH_3)_3 + \text{ether}$$

The second process gave recoverable yields of more than 65% based on the $LiAlH_4$ used. It also offered an explanation for the original preparative process in which HOH replaced the HCl. Yields were poor when the water content of the amine was low. The molecular weight of the solid was measured by vapor-pressure depression in dimethyl ether solution over a temperature range from -38 to -28°C. The result of 143 ± 8 clearly indicates a monomer.

Shortly after complete characterization of the solid it was found that Wiberg and his collaborators[118] had prepared and characterized the same compound. His melting point of 95°C and monomeric nature of the complex in ether were thus verified independently.

The coordination number of 5 for Al^{+3} in this complex suggested interesting coordination problems which are now being explored by detailed structural investigations.

(118) E. Wiberg et al., Z. Naturforsch., 7b, 578 (1952); Z. anorg. u. allgem. Chem., 272, 221 (1953).

V. PHYSICAL AND CHEMICAL STUDIES ON PURE BORON HYDRIDES AND BOROHYDRIDES

A. The Raman Spectra of Four Isotopic Varieties of Diborane in the Gas Phase[119]

The compounds $^{11}B_2H_6$, $^{11}B_2D_6$, $^{10}B_2H_6$ and $^{10}B_2D_6$ were prepared during the course of a spectroscopic investigation of the borohydride ion and aluminum borohydride. Since the Raman spectra of only the first and last of the above isotopic varieties have been reported in detail, and those only for the liquid state, it was deemed of interest to obtain the gaseous Raman spectra for the complete series.

1. EXPERIMENTAL

The starting material in the preparation of the compounds was the diethyl ether complex of BF_3. This was converted to the appropriate diborane by means of lithium aluminum hydride or deuteride essentially according to standard methods. The boron-11 compounds contained approximately 81% of the ^{11}B isotope, the normal isotopic abundance, while the boron-10 compounds* contained 96% of the desired isotope. The hydrogen content of the deuterated compounds was estimated at less than 2% from the spectral evidence. Purification was accomplished by repeated fractionation on the vacuum line until a constant and reproducible vapor pressure was reached. The values observed for ordinary diborane agreed with those in the literature. The use of BF_3 etherate as a starting material eliminates possible contamination with SiF_4, which is difficult to remove by fractionation.

The spectra were recorded photographically, using the spectrograph and light source described previously.[120] The Raman tubes had an outside diameter of 25mm with an illuminated length of 150 mm and contained the gases at approximately 4 atmospheres pressure. Collimating baffles largely eliminated light scattered from the walls and window. Saturated sodium nitrite solution served as a filter for all exposures; an isopropyl alcohol solution of rhodamine 5 GDN Extra and paranitrotoluene was utilized as an additional filter for a few of the spectra. Exposure times varied from 12 to 72 hr with Eastman 103a-J plates. The resolution of the spectrograph was quite adequate to resolve clearly the isotopic triplet of ordinary diborane at about 800 cm^{-1}. Wavelength measurements were

*Boron-10 was obtained as the $CaF_2 \cdot BF_3$ complex from Union Carbide and Carbon, Oak Ridge National Laboratory.

(119) R. C. Taylor and A. R. Emery, Spectrochemica Acta 10, 419 (1958).

(120) G. L. Vidale and R. C. Taylor, J. Am. Chem. Soc. 78, 294 (1956).

made both on the plates and on enlarged tracings made by a Leeds and Northrup microphotometer. Estimated probable errors accompany the averaged values listed for the frequencies.

2. RESULTS

Observed frequencies, estimated intensities, and assignments for the hydrogen and deuterium compounds, respectively, are shown in Tables XXXI and XXXII. Tracings of typical spectra of the deuterated compounds are shown in Fig. 28. No difficulty was met in identifying the A_g fundamentals, since the characteristic sharp appearance of totally symmetric bands in the Raman spectrum of gaseous compounds is at least as conclusive as depolarization measurements. The other Raman-active fundamentals were typically broad and diffuse and lower in intensity so that frequently they could not be distinguished from the background. In some cases, they were obscured by A_g fundamentals or overtones. This appears to be the reason for the great breadth of the band near 700 cm^{-1} in the deuterated compounds.

Assignment of the overtones and combination bands was made with the help of the infrared active fundamentals of the gas listed by Lord and Nielsen;[121] where Raman-active fundamentals could not be identified from the present work, liquid values from the same paper were used. Frequently alternate possibilities existed for the assignment of weak bands. In such cases, the assignment with A_g symmetry if one existed, was preferred on the grounds that bands of this class would likely be more intense in the Raman effect. Several cases in which the intensity of the overtone or combination was enhanced by Fermi resonance were noted, the most pronounced case occurring in the deuterated compounds and involving $2\nu_3$ and ν_1. The doublet appearing at the position of $2\nu_3$ in the spectrum of $^{11}B_2D_6$ is attributed to the presence of roughly 30% of ^{11}B-^{10}B molecules. The unexpectedly high intensity of the isotopic satellite at 1824 cm^{-1} above that expected from the ratio of isotopic molecules arises from a closer resonance with the ν_1 fundamental in the lighter molecules.

The fundamentals derived from the present work are collected in Table XXXIII. Since they agree quite well with those given by Lord and Nielsen[121], who have considered all previous work, they will not be discussed in detail. It may be pointed out that the general agreement found here supports the essential correctness of the assignments made by these authors.

The application of the Teller-Redlich product rule and also one of the isotopic sum rules to the frequencies of the A_g class is shown in Table XXXIV. The data are satisfactory considering the lack of knowledge of the anharmonicities and the number of fundamentals involved in Fermi resonances.

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(121) R. C. Lord and E. Nielsen, J. Chem. Phys. 19, 1 (1951).

TABLE XXXI

OBSERVED RAMAN FREQUENCIES OF GASEOUS $^{11}B_2H_6$ AND $^{10}B_2H_6$

$^{11}B_2H_6$		$^{10}B_2H_6$		Intensity	Shape	Symmetry	Assignment
Frequency (cm^{-1})	$\pm\ \delta$	Frequency (cm^{-1})	$\pm\ \delta$				
--	-	683	3	vw	sh	A_g	$\nu_9-\nu_{10}$
--	-	786	2	vw	br		$\nu_4(^{11}B-^{11}B)$
788	1	--	-	s	sh	A_g	$\nu_4(^{11}B-^{10}B)$
802	1	--	-	m	sh	A_g	$\nu_4(^{10}B-^{10}B)$
818	2	816	1	s	sh	A_g	?
--	-	832	3	vvw	sh		$\nu_7?,\nu_{15}?$
1026	6	1025	5	w	br		ν_3
1184	1	1186	1	m	sh	A_g	$\nu_9+\nu_{10}$
1310	5	1318	2	w-vw	sh	A_g	ν_6
1755	5	1768	8	w	br	B_{1g}	$2\nu_{15}?$
2011	2	--	-	vw	sh	A_g	ν_2
2109	1	2110	1	s	sh	A_g	$2\nu_3,2\nu_{18}$
--	-	2352	2	w	sh	A_g	$\nu_4+2\nu_5?$
2485	7	--	-	vvw		A_g	ν_1
2532	1	2537	1	vs	sh	A_g	ν_{11}
(2600)	10	2640	10	w	br	B_{2g}	

δ = probable error; s = strong, m = medium, w = weak, sh = sharp, br = broad; frequencies enclosed in parentheses are estimated; assignments followed by a question mark are based on fundamental frequencies obtained indirectly.(121)

TABLE XXXII

OBSERVED RAMAN FREQUENCIES OF GASEOUS $^{11}B_2D_6$ AND $^{10}B_2D_6$

$^{11}B_2D_6$		$^{10}B_2D_6$		Intensity	Shape	Symmetry	Assignment
Frequency (cm^{-1})	$\pm\ \delta$	Frequency (cm^{-1})	$\pm\ \delta$				
712	1	721	1	s	sh	A_g	ν_4
--	-	748	5	w	br		$\nu_7, \nu_{12}, \nu_{15}$?
912	1	928	1	m	sh	A_g	ν_3
971	3	962	3	vw	sh	A_g	$\nu_{16}-\nu_{18}$?
1287	4	1285	5	w	br	B_{1g}	ν_6
1414	3	1446	3	vw	sh	A_g	$2\nu_4$
1438	3	--	-	vw	sh	A_g	$2\nu_{14}$
1459	3	--	-	vw	sh	A_g	$2\nu_7, 2\nu_{12}$?
1488	4	--	-	vw	sh	A_g	$2\nu_{15}$?
1515	1	1515	1	vs	sh	A_g	ν_2
1748	2	1758	3	vw	sh	A_g	$2\nu_{18}$
1809	1	1836	1	s	sh	A_g	$2\nu_3$
1824	1	--	-	m	sh	A_g	$2\nu_3(^{11}B-^{10}B)$
1867	1	1883	1	vs	sh	A_g	ν_1
1912	2	1924	2	w	sh	A_g	$\nu_4+2\nu_4$
1968	2	1990	2	m	br	B_{2g}	ν_{11}

δ = estimated probable error; s = strong, m = medium, w = weak, sh = sharp, br = broad; assignments accompanied by a question mark are based on fundamental frequencies obtained indirectly.[121]

TABLE XXXIII

RAMAN ACTIVE FUNDAMENTALS OF GASEOUS DIBORANE

		$^{11}B_2H_6$	$^{10}B_2H_6$	$^{11}B_2D_6$	$^{10}B_2D_6$
A_g	ν_1	2532	2537	(1860)	(1870)
	ν_2	2109	2110	(1512)	(1514)
	ν_3	1184	1186	(912)	(928)
	ν_4	788	816	712	721
B_{1g}	ν_6	1755	1768	1287	1285
	ν_7	--	--	--	--
B_{2g}	ν_{11}	2600	2640	1968	1990
	ν_{12}	--	--	--	--
B_{3g}	ν_{15}	--	--	--	--

Frequencies enclosed in parentheses are involved in Fermi resonances and have been corrected by an estimated shift.

TABLE XXXIV

PRODUCT AND SUM RULES FOR THE A_g CLASS FREQUENCIES OF GASEOUS DIBORANES

Product Ratio	Calculated	Theoretical
$(^{11}B_2H_6/^{11}B_2D_6)$	2.73	2.825
$(^{10}B_2H_6/^{10}B_2D_6)$	2.74	2.825
$(^{10}B_2H_6/^{11}B_2H_6)$	1.04	1.049
$(^{10}B_2D_6/^{11}B_2D_6)$	1.04	1.049

Sum difference $\sum [\nu_i^2(^{10}B_2H_6) - \nu_2^2(^{11}B_2H_6)] = 7.9 \times 10^4$

$\sum [\nu_i^2(^{10}B_2D_6) - \nu_2^2(^{11}B_2D_6)] = 8.6 \times 10^4$

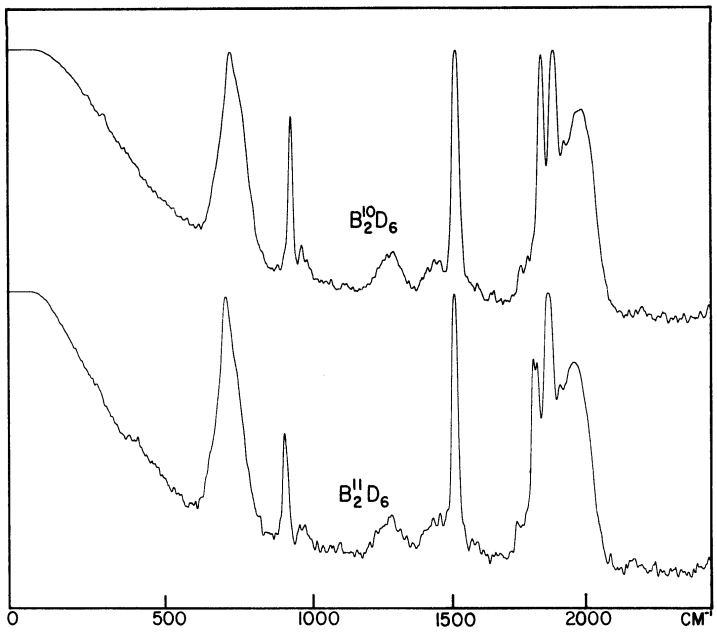

Fig. 28. Raman spectra of ^{10}B and ^{11}B deuteroboranes in the gas phase.

B. Raman Spectroscopy in Liquid Ammonia Solutions. Vibrational Frequencies and Force Constants for Isotopic Species of the Borohydride Ion Having Tetrahedral Symmetry

1. INTRODUCTION

In a previous article[122] the Raman spectra and assignments of the $^{11}BH_4^-$ and $^{11}BD_4^-$ ions dissolved in liquid ammonia were reported. However, solvent interference prevented the observation of one fundamental of the borohydride ion and confused the interpretation of the B-D stretching region of the borodeuteride spectrum. Since this ion is one of the simplest boron hydride structures, it is desirable to have a complete and unequivocal assignment of fundamentals, and consequently the work has been extended making further use of isotopic substitution for both hydrogen and boron. In particular, employment of the isotopic solvent, ND_3, has successfully eliminated interference by solvent bands and has made possible the observation of all the fundamentals of the various isotopically substituted ions. The use of ammonia as a solvent was dictated by solubility considerations, the fact that hydrolysis occurs in aqueous solution and the desirability of a simple solvent spectrum. Since chemical exchange of

(122) Taylor, Schultz, and Emery, J. Am. Chem. Soc. 80, 27 (1958); WADC Technical Report 56-318 (Univ. of Mich. Project No. 1966, Final Rept. June 1956).

hydrogen between the borohydride ion and ammonia occurs extremely slowly, if at all, the two isotopic solvents could be used interchangeably depending on the spectral region of interest.

The final assignment which has been made agrees with all available data and confirms the tetrahedral structure of the ion. The values of the fundamentals have been used to evaluate the force constants of a complete valence force potential function.

2. EXPERIMENTAL

Sodium and lithium borohydrides containing boron-11 in its natural abundance of 81% were obtained from Metal Hydrides, Inc., and purified before use by removing all ammonia insoluble material. Potassium borohydride was prepared by metathesis between $NaBH_4$ and KOH according to a recently described procedure.(123) Borodeuterides and all compounds containing boron-10 were prepared by one of two procedures depending on the alkali metal. Lithium compounds were obtained by reacting an ether slurry of lithium hydride or deuteride with the appropriate diborane in a sealed reaction tube. Sodium and potassium salts were prepared by the reaction of the appropriate diborane with sodium or potassium tetramethoxyborate. The reactions involved have been reported by Schlesinger *et al.*(124) All compounds were purified to remove ammonia insoluble material before use. Boron-10 was obtained in 96% enrichment as the calcium fluoride-boron trifluoride complex from Union Carbide and Carbon Corporation, Oak Ridge, Tennessee. The BF_3 was converted to diborane by reaction of its etherate with lithium aluminum hydride or deuteride. Although a small amount of hydrogen was introduced in the synthesis of the deuterated compounds, its amount was estimated at not more than 2-3% of the total deuterium present and no difficulty was met in the interpretation of the spectra because of the presence of a small percentage of isotopically mixed ions. Deuterated ammonia was prepared in a small steel cylinder by the reaction of D_2O with freshly prepared Mg_3N_2. Its spectrum showed insignificant amounts of hydrogen to be present.

The preparation of the samples has been described previously.(122) In most cases they consisted of 1-2 ml of solution whose concentration lay in the range between 2-4 molar. No significant changes of the spectra with concentration were noted. Reference to the spectroscopic equipment has been given in the earlier paper.(122)

3. EXPERIMENTAL RESULTS AND DISCUSSION

The observed frequencies, assignments, and polarization characteristics of the bands of the alkali metal borohydrides in ammonia solution are listed in Table XXXV, while the corresponding data for the alkali metal borodeuterides are given in Table XXXVI. The values tabulated are averages obtained from several

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(123) Banus, Bragdon, and Hinckley, J. Am. Chem. Soc. 76, 3848 (1954).
(124) Schlesinger *et al.*, J. Am. Chem. Soc. 75, 186-224 (1953).

TABLE XXXV

VIBRATIONAL FREQUENCIES AND ASSIGNMENTS FOR THE BOROHYDRIDE ION IN LIQUID AMMONIA SOLUTION

(in cm^{-1})

$Li^{11}BH_4$	$Na^{11}BH_4$	$K^{11}BH_4$	$Li^{10}BH_4$	$Na^{10}BH_4$	Assignments
1082±2[a]	1080±2	1084±2	1085±2	1093±2	ν_4
1202±3	1210±3	1213±3	1206±5	1208±3	ν_2
2146±5	2146±3	2154±3	2150±3	2161±3	$2\nu_4$
	2244±5			2250±15	ν_3
2265±2	2264±2	2266±3	2268±2	2270±2	ν_1
2402±3	2398±3	2404±3	2409±5	2405±5	$2\nu_2$

[a]Estimated standard deviations.

TABLE XXXVI

VIBRATIONAL FREQUENCIES AND ASSIGNMENTS FOR THE BORODEUTERIDE ION IN LIQUID AMMONIA AND DEUTEROAMMONIA SOLUTIONS

(in cm^{-1})

$Li^{11}BD_4$	$Na^{11}BD_4$	$K^{11}BD_4$	$Li^{10}BD_4$	$Na^{10}BD_4$	Assignments
822±2[a]	823±2	827±2	833±3	834±2	ν_4
854±2	855±2	864±3		858±4	ν_2
1569±3	1570±3	1572±3	1570±2	1571±2	ν_1
1636±4	1636±4	1636±4	1645±3	1650±5	$2\nu_4(E \text{ or } F_2)$
1668±3	1668±3	1670±5	1683±3	1680±2	$2\nu_4(A_1)$
1698±3	1696±5	1694±3	1704±3	1706±4	ν_3
2240±3	2238±4	2238±5	2243±3	2245±2	BD_3H^- ion

[a]Estimated standard deviations.

plates, no distinction having been made between NH_3 and ND_3 solutions.* A small but real shift in band position with cation was apparent and data accordingly have been given for each salt. Data obtained from the sodium salt have been used for purposes of the discussion and in the force constant calculations, since they form the most complete set and are roughly intermediate between the values for the other two alkali metals. Some of the previously published frequencies of the boron-11 compounds[122] have been revised on the basis of a larger number of better quality spectra; these changes are largely within the experimental uncertainty of the previous values.

Satisfactory assignments have been made assuming a tetrahedral configuration for the ion belonging to the T_d point group. This model predicts one A_1, one E, and two F_2 fundamentals, all Raman active. Isotopic substitution of deuterium for hydrogen should result in a marked shift in all frequencies while isotopic substitution of the central boron atom should not affect the A_1 and E frequencies but shift the F_2 fundamentals by a small amount.

The A_1 stretching frequency is easily identified as the 2264 cm^{-1} band in the hydrogen compounds and the 1570 cm^{-1} band in the deuterium from intensity and polarization characteristics. A shift in the apparent position of this fundamental in the borohydride ion on substitution of ^{10}B for ^{11}B probably is due to the fact that ν_1 is superimposed on ν_3 making the observed band maximum sensitive to shifts in the latter. In the borodeuteride ion, a Fermi resonance occurs between ν_1 and the overtone of the band at 823 cm^{-1} which shifts the fundamental some 30 cm^{-1} from its unperturbed value.

The assignment of ν_2, the doubly degenerate bending vibration, to the band at 1210 cm^{-1} in the hydrogen ion and 855 cm^{-1} in the deuterium is confirmed in the present work by the absence of a ^{10}B isotope shift. The other bending fundamental, the triply degenerate ν_4, was not observed previously because of interference by a solvent band; its position was inferred to be near 1080 cm^{-1} from the assignment of a band near 2150 cm^{-1} as its first overtone. When ND_3 is used in place of NH_3, no solvent bands occur from about 900 to 1175 cm^{-1}. The spectrum of BH_4^- in this solvent showed the expected fundamental as a band of moderately low intensity with a maximum at 1080 cm^{-1}. The corresponding band of BD_4^- appeared at 823 cm^{-1}. Confirmation of the assignment was obtained from the ^{10}B isotope shifts of 13 and 11 cm^{-1}, respectively.

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*Evidence suggesting small systematic differences in band position between the two solvents was obtained in the case of one or two of the fundamentals. The specific nature of solute-solvent interaction which this suggests is supported by the observation that the maximum of the symmetrical stretching frequency of BH_4^- differs by about 25 cm^{-1} between NH_3 and H_2O as solvents, and by the fact that the alkali metal borohydrides form stable ammoniates. For most of the bands, however, the differences, if real, between NH_3 and ND_3 solutions were less than the associated probable error in the band positions and have not been considered significant.

The remaining triply degenerate fundamental, ν_3, was the most difficult of the four to identify because of near superposition by ν_1 or overtones in both the hydrogen and deuterium cases. In Fig. 29, ν_3, appears as a shoulder on the low-frequency side of the 2264 cm^{-1} band of the BH_4^- ion. Confirmation of its presence and a better measurement of its position was obtained by polarizing the incident light so that the intensity of ν_1 was greatly reduced. In theory, the A_1 mode of a tetrahedral XY_4 molecule is completely polarized in the Raman effect but because of convergence error in the incident light, this is difficult to demonstrate. In Fig. 30 a spectrum taken with the electric vector of the incident light polarized parallel to the observation direction shows ν_3 as a weak but distinct maximum. Solvent interference necessitated the use of ND_3 for the BD_4^- ion, and again a satisfactory assignment of the four bands observed in the B-D stretching region could not be attained without the help of polarized spectra. The two polarized bands shown in Fig. 31 at 1570 and 1668 cm^{-1} are assigned to the ν_1 and the A_1 component of $2\nu_4$, respectively. They both have been shifted from their expected positions by Fermi resonance. Of the other two bands at 1636 and 1696 cm^{-1}, the latter is assigned to ν_3 since it gives better agreement with the product rule and is more intense. It shifts 10 cm^{-1} on ^{10}B-substitution. The apparent position and breadth of this band may have been influenced by some contribution from $2\nu_2$ which falls at approximately this position but does not have the correct symmetry to resonate. The remaining band at 1636 cm^{-1} is assigned to the E and/or F_2 components of $2\nu_4$, the F_2 component perhaps being enhanced in intensity by resonance with ν_3. It is also possible that this band may involve a B-D stretching motion of the BD_3H^- species which was present in small amounts.

Comparison of the observed frequency product ratios of the four isotopic ions with those predicted by the product rule is shown in Table XXXVII. The agreement in general is satisfactory with the exception of the A_1 class where some of the fundamentals are shifted by resonance. The normal effect of anharmonicity is to cause the observed product ratios as written to be somewhat less than the theoretical. Also included in Table XXXVII are data for the isotopic sum rule applied to the F_2 class frequencies.

4. NORMAL COORDINATE TREATMENT

The vibrational analysis was carried out by means of symmetry factored F and G matrices as described by Wilson.[125] Specific details of the application of this method to a five atom tetrahedral molecule have been given[125,126] previously and will not be repeated here. The B-H bond length in the borohydride ion is not known with a high degree of certainty but it is certainly longer than

(125) Wilson, Decius, and Cross, Molecular Vibrations, McGraw-Hill Book Company, Inc., New York, 1955.

(126) A. G. Meister and F. F. Cleveland, Am. J. Phys. 14, (1946).

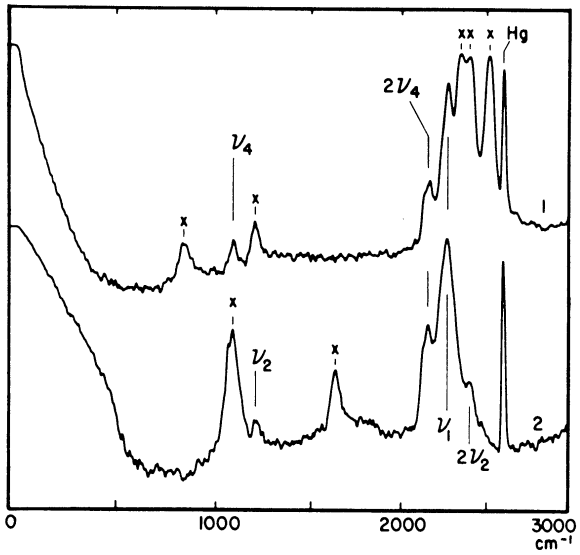

Fig. 29. Raman spectrum of $Na^{10}BH_4$ dissolved in liquid ND_3 (1) or liquid NH_3 (2). Solvent bands indicated by (x).

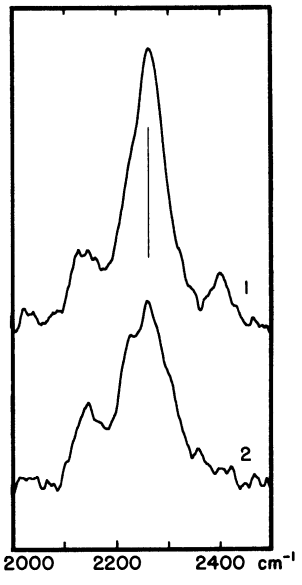

Fig. 30. The B-H stretching region in the Raman spectrum of $^{11}BH_4^-$. 1, perpendicularly polarized incident light; 2, parallel polarized incident light.

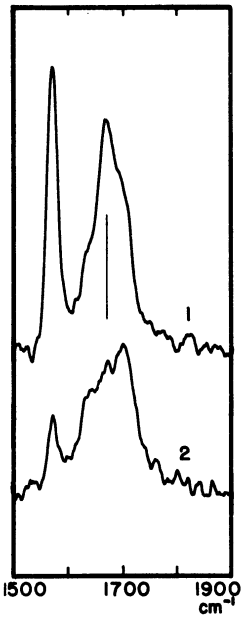

Fig. 31. The B-D stretching region in the Raman spectrum of $^{11}BD_4^-$ dissolved in liquid ND_3. 1, perpendicularly polarized incident light; 2, parallel polarized incident light.

TABLE XXXVII

APPLICATION OF THE TELLER-REDLICH PRODUCT RULE TO THE BOROHYDRIDE ION

Ratio	Class	Frequency Theoretical	Product Ratio Observed	Deviation
$\frac{^{11}BD_4^-}{^{11}BH_4^-}$	A_1	1.414	1.443	+2.1%
	E	1.414	1.414	0
	F_2	1.776	1.736	-2.3
$\frac{^{10}BD_4^-}{^{10}BH_4^-}$	A_1	1.414	1.445	+2.2
	E	1.414	1.408	-0.4
	F_2	1.761	1.727	-1.9
Sum difference: (F_2 class)		$\sum[\nu_i^2(^{10}BH_4^-) - \nu_i^2(^{11}BH_4^-)]$	= 5.52 x 10^4	
		$\sum[\nu_i^2(^{10}BD_4^-) - \nu_i^2(^{11}BD_4^-)]$	= 5.23 x 10^4	

the 1.19 A value found[127] in BH_3CO since the bond in the latter molecule retains an appreciable amount of sp2 character. Price[128] has suggested 1.26 A for $NaBH_4$ from empirical relationships between vibrational frequency and internuclear distance, while Ford and Richards[129] have calculated a distance of 1.255 A from measurements involving line breadths in nuclear magnetic resonance spectra of the same compound. The value of 1.25 A used in the calculations thus probably is not seriously in error, and in any case the force constants are not particularly sensitive functions of this parameter.

The potential function in terms of the symmetry coordinates employed[126] can be written as

$$2V = F_1S_1^2 + r^2F_2S_2^2 + F_3S_3^2 + rF_{34}S_3S_4 + r^2F_4S_4^2$$

where S_1 is the nonredundant symmetry coordinate belonging to the A_1 class, S_2 the symmetry coordinate of the E class, and S_3 and S_4 the stretching and bending coordinates, respectively, of the F_2 class. Principal force constants are indicated by a single subscript and interaction by a double; r represents the assumed equilibrium value of the internuclear distance. Comparison of the calculated with experimental values of the fundamentals of the four isotopic molecules is made in Table XXXVIII. The standard deviation between the two sets (excluding the two A_1 frequencies involved in Fermi resonances) is 0.5% with no deviation exceeding 0.9%. Since this agreement probably is better than the uncertainty in the data caused by experimental error and the neglect of anharmonicity

(127) Gordy, Ring, and Burg, Phys. Rev. 78, 512 (1950).
(128) W. C. Price, J. Chem. Phys. 17, 1044 (1949).
(129) P. T. Ford and R. E. Richards, Discussions Faraday Soc. 19, 230 (1955).

TABLE XXXVIII

COMPARISON OF OBSERVED AND CALCULATED FUNDAMENTAL VIBRATIONAL FREQUENCIES OF THE VARIOUS ISOTOPIC SPECIES OF THE BOROHYDRIDE ION

Fundamental		$^{11}BH_4^-$			$^{10}BH_4^-$			$^{11}BD_4^-$			$^{10}BD_4^-$		
		Obs	Calc	Dev	Obs	Calc	Dev	Obs	Calc	Dev	Obs	Calc	Dev
A_1	ν_1	2264	2267	+0.1	2270	2267	-0.1	(1570)[a]	1604	--	(1571)	1604	--
E	ν_2	1210	1210	0	1208	1210	+0.2	855	856	+0.1	858	856	-0.2
F_2	ν_3	2244	2252	+0.4	2250	2265	+0.7	1696	1688	-0.5	1706	1707	+0.1
	ν_4	1080	1089	+0.9	1093	1097	+0.3	823	823	0	834	827	-0.9

[a]Those values enclosed in parentheses are fundamentals shifted by Fermi resonance.

other approaches using more refined potential functions such as the orbital valency type were considered unnecessary. The symmetry force constants yielding the best fit are given in Table XXXIX. By employing the defining equations for the symmetry coordinates, these data may be used to calculate values for the more common valence force constants. However, since seven valence force constants can be defined in the complete quadratic potential function whereas only five symmetry force constants are available, it is not possible to give a unique set of values for all of the valence force constants. One can, of course, introduce two arbitrary but reasonable assumptions and so obtain numbers for all the constants, but rather than introduce this artificiality, the unresolved combinations of valence force constants have been listed as such in Table XXXIX. The notation employed is largely self-explanatory, the primed constants being used for interactions between coordinates having only one atom in common.

TABLE XXXIX

FORCE CONSTANTS FOR THE BOROHYDRIDE ION

Symmetry Force Constant	Value (10^5 dynes/cm)	Valence Force Constant	Value (10^5 dynes/cm)
F_1	3.0511	k_r	2.768
F_2	0.2897	k_{rr}	0.094
F_3	2.6737	$k\alpha$-$k_{\alpha\alpha}$	0.290
F_4	0.2905	$k\alpha$-$k_{\alpha\alpha'}$	0.291
F_{34}	0.0150	$k_{r\alpha}$-$k_{r\alpha'}$	0.011

C. The Dipole Moment of Tetraborane

1. THE PROBLEM

By a molecular orbital treatment of boron hydride structures using a three-center bond approximation, Eberhardt, Crawford, and Lipscomb[130] were able to rationalize the known dipole moment values of 2.13D for B_5H_9[131] and 3.52D for $B_{10}H_{14}$.[132] Their treatment also predicted a zero dipole moment for B_4H_{10} if the boron skeleton, without moments due to attached hydrogens, were considered. We have measured the dipole moment of tetraborane in benzene solution using a heterodyne beat method and have obtained the relatively small value of 0.56 ± .10 Debye units. The small value could easily imply slight protonic character

(130) W. Eberhardt, B. Crawford, and W. N. Lipscomb, J. Chem. Phys. 22, 989 (1954).

(131) H. J. Hrostowski, R. J. Myers, and G. C. Pimentel, J. Chem. Phys. 20, 518 (1952).

(132) A. W. Laubengayer and R. Bottei, J. Am. Chem. Soc. 74, 1618 (1952).

in the bridge hydrogens and slight negative character in the hydrogens attached to the single bonded borons; these low moments were neglected in the earlier theoretical treatment, and hence the theoretical arguments are not in serious disagreement with the dipole information.

2. EXPERIMENTAL

Tetraborane from laboratory stock was purified by low-temperature fractionation on the vacuum line. The purified product had a vapor pressure of 388 ± 1 mm at 0°C. When the sample was allowed to stand at 0°C for more than a few minutes, decomposition was indicated by a slow buildup in pressure.

Reagent-grade benzene was dried by refluxing with calcium hydride and distilling on the vacuum line.

Solutions were prepared by condensing benzene and a measured volume of tetraborane vapor into a special weighing cell. Transfer to the dielectric cell was made under an atmosphere of dry nitrogen, since it was considered undesirable to evacuate the cell because of damage to the silvered surfaces. The cell was of a conventional design[133] with a capacitance of about 30 micromicrofarads. The measuring circuit has been previously described.[134] It was necessary to make the capacitance measurements rapidly because decomposition of the solute in the dielectric cell produced a slow rise in the apparent dielectric constant value.

Measurements of the refractive index of the solutions were made with a Bausch and Lomb precision Abbe Refractometer. No difficulty was encountered in obtaining reproducible readings before appreciable decomposition took place. The refractive index of each solution was measured using light of three wavelengths (4358Å, 5416Å, 5893Å). A plot of the refractive index for each solution against $1/\lambda^2$ permitted evaluation of the index of refraction for light of infinite wavelength. A plot of n_∞^* against mole fraction permitted evaluation of $(\partial n_\infty^*/\partial x)_0$.

3. RESULTS AND DISCUSSION

Results of the dielectric constant and index of refraction measurements are shown in Tables XL and XLI, respectively. The value of the dielectric constant of pure benzene was obtained from a Bureau of Standards publication[135] and was used to calibrate the dielectric cell.

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(133) LeFevre, Dipole Moments (Methuen and Co., Ltd., London), p. 36.
(134) J. R. Weaver, S. G. Shore, and R. W. Parry, J. Chem. Phys. 29, 1 (1958).
(135) A. A. Maryott and E. R. Smith, Table of Dielectric Constants of Pure Liquids, National Bureau of Standards Circular 514, 1951.

TABLE XL

THE DIELECTRIC PROPERTIES OF TETRABORANE

Mole Fraction	Dielectric Constant at 25°C	n_D^{25} (5893)
0.000	2.274 (135)	1.4971
0.024	2.277	1.4943
0.044	2.278	1.4918
0.088	2.286	--

$\partial e/\partial x = .136 \pm .01$

TABLE XLI

THE INDEX OF REFRACTION OF TETRABORANE

Mole Fraction	Refractive Index			
	5893Å	5461Å	4358Å	λ_∞
0.000	1.4975	1.5015	1.5191	1.4716
0.036	1.4933	1.4973	1.5146	1.4678
0.057	1.4907	1.4949	1.5118	1.4653

$T = 25°C$

$M_o = 78.1$

$d_o = .879$

$e_o = 2.274$

$n_o = 1.472$

$\frac{\partial n_\infty}{\partial x} = - .107 \pm .01$

$P_d = 6.5 \pm .7$ cm3

It is of interest to note that the addition of tetraborane to benzene produces very little change in the dielectric constant, but a considerable decrease in the refractive index, indicating that the contribution of the electronic polarization of tetraborane to the total polarization of the solution is somewhat less than that of the benzene that it displaces, but that the orientation polarization effectively makes up this difference.

Because of the instability of the solutions, no attempt was made to obtain the time-consuming volume measurements necessary for determining the density of the solution. To calculate the apparent dipole moment, use was made of the extrapolation method of Cohen-Henriquez as given by Bottcher.(136) In this method the "orientation polarization" is obtained directly from the dielectric constant and index of refraction measurements without use of the density. The equation used for the calculation was:

$$[P_o]_d^o = \frac{3M_o}{d_o(e_o+2)^2}\left\{\frac{\partial e}{\partial x} - 2(n_\infty^*)_o\left(\frac{\partial n_\infty^*}{\partial x}\right)_o\right\}$$

where $[P_o]_d^o$ is the molar orientation polarization of the solute, M_o, d_o, and e_o are the molecular weight, density, and dielectric constant of benzene, n_o is the refractive index of benzene extrapolated to infinite wavelength, x, e, and n are the mole fraction, dielectric constant, and index of refraction of the solution. This equation differs somewhat from the one given by Bottcher, having been obtained, not by neglecting the effect of the atomic polarization of the solvent, but by using Guggenheim's approximation(137) that the atomic polarization of the solute and solvent are proportional to their partial molar volumes. Since there is no reliable way of estimating the atomic polarization of the solute, this is probably as good an approximation as any.

D. Exchange Studies on Decaborane-14

1. BACKGROUND

Chemical experiments at Callery Chemical Co.(138) have demonstrated that four of the hydrogen atoms in decaborane, $B_{10}H_{14}$, are much more acidic in character than the rest. Inasmuch as structure studies have shown the presence of four three-center or bridge-type bonds in the molecule, identification of the acidic hydrogens with the bridge locations appears logical. To obtain evidence on the validity of such a hypothesis, advantage may be taken of the fact that

(136) C.J.F. Bottcher, Theory of Electric Polarization (Elsevier Publishing Company, Amsterdam, 1952), p. 303.
(137) Ibid., p. 305.
(138) L. J. Edwards, private communication, January, 1957.

boron-hydrogen vibrational stretching frequencies fall into two well-defined and well-separated regions of the spectrum according to the nature of the bond. In general, bands occurring in the region from about 2300 to 2600 cm^{-1} are associated with the presence of terminal hydrogen atoms while bridge hydrogens are indicated by bands in the region of 1400 to 2000 cm^{-1}. Chemical exchange of the active hydrogens with deuterium from heavy water followed by spectroscopic examination should indicate the location of the substituted atoms from the shift of the appropriate bands.

2. EXPERIMENTAL

The exchange of $B_{10}H_{14}$ with D_2O was carried out in the presence of small amounts of CH_3COOD and ethyl acetate since the pure decarborane did not exchange readily. To insure that the compound had not been altered by its treatment, the deuterated sample was re-exchanged with ordinary water after its spectrum had been obtained and the spectrum of the resultant material compared to that of the starting material. The identity of the two spectra showed that the procedure was suitable.

The infrared spectra of the compounds were obtained as nearly saturated solutions in CCl_4 using a Perkin-Elmer Model 21 spectrometer equipped with a rock salt prism. The concentration of these solutions is estimated to be in the neighborhood of 0.3 molar.

3. RESULTS

The bands observed in the spectrum of the original $B_{10}H_{14}$ agreed quite well with those in the infrared spectrum of a CS_2 solution reported by Keller and Johnston.(139) Those differences which were noted were minor and were confined to a few very weak bands in the skeletal region. In the hydrogen stretching region, three bands were observed, each undoubtably containing several unresolved or partially resolved molecular frequencies. The most intense band showed no structure and extended from about 2500 to 2640 cm^{-1}; to it are assigned the several terminal hydrogen stretching frequencies. The next most intense band exhibited a principal maximum at 1515 cm^{-1} with secondary maxima of moderate intensity at 1475 and 1580 cm^{-1}. The third band consisted chiefly of two rather weak maxima at 1890 and 1942 cm^{-1} together with two or three very weak frequencies on either side. The latter two bands are assigned to motions of the bridge hydrogen atoms.

The shape and position of band I in the 2500 cm^{-1} region was not altered significantly after exchange with deuterium. Both band II and band III, however, were shifted to lower frequencies but without change of shape or relative intensity. The principal maximum of band II was found at 1169 cm^{-1} and the secondary maxima at 1140 and 1185 cm^{-1}. The two principal peaks in band III appeared

(139) W. E. Keller and H. L. Johnston, J. Chem. Phys. 20, 1749 (1952).

at 1398 and 1423 cm^{-1}. The ratios of the hydrogen frequencies to those of the deuterium compound thus fall between 1.30 and 1.35 and are quite comparable to the ratios observed for the analogous bands in, for example, diborane and deuterodiborane.

In addition to these frequencies, a fourth band was present in the spectrum of the deuterated sample. This fourth band showed a remarkable similarity in appearance to band II but had only about half the intensity or less. It principal maximum was at 1724 cm^{-1} with the secondary maxima at 1710 and 1742 cm^{-1}. The origin of this band is not clear. Since it appears some 200 cm^{-1} higher than band II in the original (undeuterated) sample, it cannot be attributed to incompletely exchanged material, and similarly it does not seem likely that it arises from "nonexchangeable" bridge hydrogens. It also does not appear to be due to the replacement of terminal hydrogens by deuterium since the ratio of any of the terminal hydrogen frequencies to any of those in band IV is larger than the limiting square root of two. It is possible that it represents a combination of the frequencies in band II with a frequency in the region of 550 cm^{-1} which was beyond the range of the spectrometer in the present investigation. This suggestion is not entirely satisfactory but appears to be the only reasonable one.

Despite the uncertainty in the assignment of this last band, the spectroscopic evidence seems to indicate quite conclusively that it is the bridge hydrogen atoms which can be replaced by deuterium exchange in heavy water and not the terminal, and that these, therefore, are acidic in nature.

Several subsequent studies(140) which have been published since the termination of this work confirm that the bridge hydrogens exchange most rapidly but indicate also that the terminal hydrogens will exchange slowly in a secondary step. The foregoing preliminary study was completed prior to the other more detailed investigations.(141)

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(140) R. W. Parry and L. J. Edwards, J. Am. Chem. Soc., in press (April, 1959).
(141) M. F. Hawthorne and J. J. Miller, J. Am. Chem. Soc. 80, 754 (1958); I. Shapiro, M. Lustig, and R. E. Williams, ibid., 81, 838 (1959).

VI. CHEMICAL CORRELATIONS

The foregoing data together with data available in the Research Division of Callery Chemical Company and in the literature of boron suggest a number of systematic generalizations covering the reactions of the boron hydrides. Such generalizations were made by one of the senior authors (RWP) in collaboration with Dr. L. J. Edwards of Callery Chemical Company. The results are summarized in a paper entitled "Systematics of the Boron Hydrides."(140) While the preparation of this paper was not done directly under this project, part of the data used was a result of these investigations and the assistance of the Wright Air Development Center in providing data for the summary paper is hereby gratefully acknowledged.