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SYNTHESIS AND CHARACTERIZATION OF A NEW
CLASS OF CYCLOBORAZANES

DISSERTATION

Presented in Partial Fulfillment of the Requirements for
the Degree Doctor of Philosophy in the Graduate
School of The Ohio State University

By

Karl Wilhelm Böddeker, cand.chem., M.Sc.

The Ohio State University
1965

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I. INTRODUCTION

A. Background

1. Introduction

It is well known that the "renaissance of inorganic chemistry" is due to no small degree to the pioneering work of Alfred Stock and his school in the field of boron chemistry. The unique character from the standpoint of normal valendy relationships of many boron-containing substances prepared and identified by Stock has stimulated ever increasing research activity in both experimental and theoretical chemistry. The development by Stock's group of new apparatus and techniques was of equally far-reaching importance; in particular, the chemical vacuum line has made possible the investigation of substances not capable of existence outside the thermally and atmospherically controlled environment of the vacuum system.

The chemistry of the element boron is distinguished not only by the unique series of boron-hydrides, but also by the system of boron-nitrogen compounds. It was one of Stock's pupils, Egon Wiberg, who began the systematic investigation of these compounds. He introduced the concept of isosterism to interpret similarities in physical properties between molecules or atom groupings having the same number of atoms and electrons and the
same total nuclear charge. The groups B-N and C-C represent such an isosteric pair and, indeed, many boron–nitrogen compounds are known which are isosteric analogs of hydrocarbons. The fact that Stock discovered the perhaps most striking example for this similarity, borazine, "inorganic benzene" (1), resulted for a time in an overemphasis of the existing analogies and in misappraisal of the differences, as well as difficulties, involved. Deceptive, too, was the early belief that boron, being a neighbor of carbon in the periodic table, should have an extensive chemistry resembling organic chemistry. Even today, almost forty years after the first synthesis of borazine, the number of boron–nitrogen compounds containing only the elements boron, nitrogen, and hydrogen is small, although many organic derivatives are known. The present investigation represents a contribution to the chemistry of unsubstituted isosteric analogs of hydrocarbons in the boron–nitrogen system.

2. Nomenclature

At present, no generally accepted system for the nomenclature of boron-containing substances exists. In 1955, an "Advisory Committee on the Nomenclature of Organic Boron Compounds" was established within the American Chemical Society which, in 1957 and 1958, produced a "Preliminary Report" (2) containing recommendations approved by the Chemical Abstracts Service. These recommendations are followed in this dissertation, except that the well-known designation "diammoniate of diborane"
for the compound \([\text{BH}_2(\text{NH}_3)_2][\text{BH}_4]\) is used, rather than "diammine—dihydroboron(1⁺)hydroborate" as recommended. The other designations are as follows:

Amine—boranes are addition compounds of amines with borane, \(\text{BH}_3\), or substituted boranes.

Aminoboranes are compounds which have a normal covalent bond between boron and nitrogen atoms and in which the free electron pair of the nitrogen can participate in the B—N bond.

Cycloborazanes are cyclic aminoboranes containing alternating B—N bonds. If it is not known whether a compound has a cyclic or chain-like structure, the compound is referred to as an aminoborane, and the degree of polymerization is noted.

Borazines (formerly called borazoles) are the isosteric analogs of cyclic aromatic hydrocarbons.

3. The boron—nitrogen system

Modern boron—nitrogen chemistry may be said to begin with the first synthesis of the diammoniate of diborane by Stock and Kuss in 1923 (3). Much of the subsequent work was done by Wiberg, who developed the basic concepts of the more modern approaches to this system. He classified the boron—nitrogen derivatives into the three major groups of amine—boranes, aminoboranes, and borazines, according to the nature of the bond and in reference to the principal classes of aliphatic hydrocarbons (4). The diammoniate of diborane itself, the true nature of which was not recognized until 1958 (5), has no place in this classification,
as have a number of other boron-nitrogen compounds discovered since. Nevertheless, it must be considered the parent compound for most any of the unsubstituted boron-nitrogen species known, not only historically, but also by way of definite synthetic relationships, as outlined below.

In the following table are summarized the boron-nitrogen species under consideration, including some which have recently been identified in this laboratory. Not included are the hydrazinoboranes and the amine-substituted derivatives of some of the species, which also consist of the elements boron, nitrogen, and hydrogen only.

**TABLE 1**

THE BORON-NITROGEN SYSTEM

<table>
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<th>I</th>
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<th>III</th>
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<tr>
<td>( \text{BH}_3 \text{NH}_3 ) ((=\text{BH}_2 \text{NH}_2^-))</td>
<td>( \text{BH}_2 \text{NH}_2 ) ((\text{BH}_2 \text{NH}_2^2))</td>
<td>( \text{B}_3 \text{N}_3 \text{H}_6 )</td>
<td>([\text{BH}_2 (\text{NH}<em>2^2)</em>{2}] [\text{BH}_4] )</td>
</tr>
<tr>
<td>( \text{H}_3 \text{NBH}_2 \text{NH} ) ((?)</td>
<td>( \text{BH}_2 \text{NH}_2 ) ((\text{BH}_2 \text{NH}<em>2^2)</em>{3})</td>
<td>( \text{B}_9 \text{N}<em>9 \text{H}</em>{14} )</td>
<td>( \text{B}_2 \text{H}_5 \text{NH}_2 )</td>
</tr>
<tr>
<td>( \text{BH}_2 \text{NH}_2 \text{BH}_3 ) ((?)</td>
<td>( \text{BH}_2 \text{NH}_2 ) ((\text{BH}_2 \text{NH}<em>2^2)</em>{4})</td>
<td>( \text{B}_5 \text{N}_5 \text{H}_8 )</td>
<td>( \text{H}_3 \text{NBH}_2 \text{HBH}_3 ) ((?)</td>
</tr>
<tr>
<td>( \text{BH}_2 \text{NH}_2 \text{BH}_3 ) ((?)</td>
<td>( \text{BH}_2 \text{NH}_2 ) ((\text{BH}_2 \text{NH}<em>2^2)</em>{5})</td>
<td>( \text{B}_7 \text{N}<em>7 \text{H}</em>{10} )</td>
<td>( \text{BH}_4 \text{NH}_4 )</td>
</tr>
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Compounds followed by a question mark have not been identified; however, their existence under certain conditions appears to be possible.

The species in the first three columns of Table 1 can be identified with Wiberg's classes of boron-nitrogen compounds,
i.e. are analogs of hydrocarbons. A survey of the table indicates that the B–N unit apparently does not possess the ability for catenation which characterizes the isosteric C–C grouping. Cyclic structures appear to be preferred and are also known to be more stable than chains of corresponding size (6). This observation applies for the numerous organic derivatives of these compounds as well. Indeed, only one chain which is truly the analog of a higher alkane has been reported (7), the compound \( \text{BH}_3\text{NHMe}_2\text{BH}_2\text{NH}_3 \). In other boron–nitrogen chains which are presently under study, the nature of the endgroups is still uncertain.

The cyclic boron–nitrogen compounds can be grouped into three homologous series of species: the cycloborazanes, shown in column II of Table 1, and two groups of borazines representing the boron–nitrogen analogs of non-condensed (benzene, diphenyl, terphenyl) and condensed (benzene, naphthalene, anthracene and phenanthrene) aromatic systems, listed in column III. The cycloborazanes are the subject of this dissertation.

As mentioned above, almost all unsubstituted compounds of the boron–nitrogen system are interrelated through their common descent from the diammoniate of diborane, as follows. Closed tube pyrolysis of the diammoniate yields the simplest borazine, \( \text{B}_3\text{N}_3\text{H}_6 \) (1,8), as well as small amounts of the higher borazines (9), some of which are also found as decomposition products of liquid borazine (10). Cyclotriborazane (hexahydroborazine), \( (\text{BH}_2\text{NH}_2)_3 \), can be synthesized from borazine (11) or from the diammoniate of diborane directly through reaction with
strong bases in liquid ammonia (12). This latter reaction produces all known cycloborazanes in various proportions, presumably under intermediate formation of ammonia(N-B)aminoborane, $H_2NBH_2NH_2$ (see section III.B.). Ammonia–borane, $BH_3NH_3$, is found on reaction of the diammoniate with ammonium chloride in ether (13); both ammonia–borane and diammoniate of diborane are formed in the reaction of tetrahydrofuran–borane with ammonia (14). Reaction of the diammoniate with excess diborane yields ammnodiborane, $B_2H_5NH_2$ (15), which decomposes to give, apparently, aminoboranes. Finally, ammonium hydroborate, $NH_4BH_4$, belongs indirectly to this scheme, because its decomposition leads to the diammoniate of diborane (16).

This outline obviously does not bear much resemblance to the chemistry of carbon, nor does it reveal any underlying principle as to the mechanism of these reactions. The most important difference between the groupings B–N and C–C is, of course, the polarity of the boron–nitrogen bond. In all boron–nitrogen compounds the nitrogen atom bears a larger negative net charge than the boron atom. This is true even for compounds with single dative nitrogen-to-boron bonds, in which the nitrogen still remains negative at the expense of its neighbors (17). In turn, the hydrogen atoms bonded to boron and nitrogen carry opposite partial charges. All unsubstituted boron–nitrogen compounds lose hydrogen more or less readily under formation of mostly ill-defined products or product mixtures. In a few instances, controlled dehydrogenation has been utilized successfully for synthetic purposes. The ease
with which hydrogen is split out can usually be taken as a criterion for the general stability of a boron-nitrogen molecule. For example, open-chain aminoboranes generally seem to lose hydrogen much more readily than cycloborazanes.

4. Aminoboranes

Species of empirical composition \( \text{BH}_2\text{NH}_2 \) have been encountered from the very beginning of research in the boron-nitrogen system. They were described as "white, non-volatile, highly polymeric, amorphous materials which split out hydrogen easily," and their composition was more often than not inferred from the stoichiometry of the reactions (1,18). Burg, in a review article in 1960 (19), stated that "the polyethylene analogue \( (\text{H}_2\text{NBH}_2)_x \) forms crosslinks very easily, with spontaneous loss of hydrogen."

It appears now that most of the reported reactions produced chains or polymers of unknown nature, and in only rare cases cyclic species of the same empirical composition. The following reactions have been reported:

a) Aminodiborane decomposes spontaneously at room temperature (15), according to the over-all equation

\[
\text{B}_2\text{H}_2\text{NH}_2 \rightarrow \frac{1}{n} (\text{BH}_2\text{NH}_2)_n + \frac{1}{2} \text{B}_2\text{H}_6
\]

The aminoborane produced is described as a solid of approximately the volatility of borazine which loses hydrogen to form still higher polymeric material (20).

b) The gas-phase reaction of diborane with ammonia at elevated temperature yields aminoboranes,
B₂H₆ + 2 NH₃ → \frac{1}{n} (BH₂NH₂)ₙ + H₂,

in addition to several borazines and unidentified materials (21, 22). The distribution and nature of the species formed vary with the relative amounts of reactants used, with temperature, and with pressure. The reaction mixtures conceivably contained, at least intermediately, cyclic aminoboranes.

c) The reaction of lithium amide with diborane in diethyl ether produces aminoborane (23) through the reaction

\[
\begin{align*}
\text{Et}_2\text{O} \\
B₂H₆ + \text{LiNH}_2 &\rightarrow \frac{1}{n} (BH₂NH₂)ₙ + \text{LiBH}_4
\end{align*}
\]

This reaction has been re-examined in this laboratory (6), and it was found that the product is neither highly polymeric nor unique, most likely consisting of chains of three to four boron-nitrogen units with endgroups of uncertain nature.

d) The reaction of the diammoniate of diborane with alkali metals in liquid ammonia according to

\[
\begin{align*}
[\text{BH}_₂(\text{NH}_₃)₂][\text{BH}_4] + \text{Na} \rightarrow \frac{1}{n} (\text{BH}_₂\text{NH}_₂)ₙ + \text{NH}_₃ \\
+ \frac{1}{2} \text{H}_₂ + \text{NaBH}_₄
\end{align*}
\]

gives aminoboranes (24), the composition of which is reported to be curiously dependent on the reaction conditions. The analytical data point to the possibility that the aminoborane from this reaction loses hydrogen even more readily than do the before-mentioned species.

e) The reaction of potassium amidotrimethylborate(1⁻) with diborane, according to the overall equation

\[
\text{Et}_2\text{O} \\
\text{KH}_₂\text{NBMe}_₃ + \frac{3}{2} \text{B}_₂\text{H}_₆ \rightarrow \frac{1}{n} (\text{BH}_₂\text{NH}_₂)ₙ + \text{B}_₂\text{H}_₃\text{Me}_₃ + \text{KBH}_₄
\]
yields aminoboranes (25), reportedly resembling those of the previous reaction (24). The related reaction of aminodimethylborane with diborane also gives aminoboranes (25). As in all instances cited so far, the aminoborane products from these reactions were not characterized; however, the authors found evidence for the existence of at least two types of aminoboranes which differ in their stability toward ammonolysis and possibly represent different degrees of polymerization.

f) The reaction of diammoniate of diborane with sodium acetylide in liquid ammonia, proceeding according to

\[
[BH_2(NH_3)_2][BH_4]^+ + NaC_2H_2 \xrightarrow{NH_3(l)} \frac{1}{n} (BH_2NH_2)_n + C_2H_2
\]

was the first reaction recognized to produce cyclic aminoboranes (12). Although in small yield, cyclotriborazane was isolated from the reaction mixture.

g) The first and to date only synthetic procedure for a specific cycloborazene was reported by Dahl and R. Schaeffer (11), who prepared cyclotriborazane by addition of hydrogen chloride to borazine, followed by reduction with sodium hydroborate in diglyme according to the equation

\[
2 B_3N_3H_6·3 HCl + 6 NaBH_4 \xrightarrow{} 2 (BH_2NH_2)_3 + 3 B_2H_6 + 6 NaCl
\]

Significantly, the aminoboranes obtained from the last two reactions do not lose hydrogen unless heated to above 100°C.

With the exception of the synthesis of cyclotriborazane from borazine, all above reactions producing so-called "highly
polymeric" aminoboranes are based, presumably, on the preparation of BH₂NH₂ units which undergo association. The resulting species appear to have well-defined properties only if the association process leads to cyclic structures, that is, to the formation of cycloborazanes.

B. Statement of the problem

As is apparent from the previous discussion, species of empirical or assumed composition BH₂NH₂ are among the less familiar compounds in the boron-nitrogen system. It has not been established that the aminoboranes from most of the above reactions are identical, nor has it been shown that the products are not mixtures of several forms of BH₂NH₂, representing different degrees of association. In principle, the association process of BH₂NH₂ could lead to the formation of a variety of species which have not been reported previously in the boron-nitrogen system.

Consequently, the objectives of the present investigation were:

1. The development of simple methods for generating BH₂NH₂ units.

2. The isolation and identification of associated species formed.

3. The improvement of a synthetic route to the diammoniate of diborane as starting material for this investigation, allowing the preparation of larger amounts than was hitherto possible (26).
4. The accumulation of information to aid eventually in the development of a theoretical understanding of the system. The experiments are described in part II, the results obtained are discussed in part III of this dissertation.
II. EXPERIMENTAL

A. Apparatus

1. Vacuum system

For some of the reactions and separations involved, as well as for drying and storage of reagents and products, a standard vacuum apparatus was used, consisting of a pumping section, a main manifold, a reaction train, and a calibrated Töpler pumping system. Separated from the main manifold, but connected to the reaction train through a stopcock, was a second reaction line, designed to handle large-scale operations and equipped with its own pumping section. The reaction trains contained several reaction stations, each consisting of a stopcock connected to a standard taper joint and, in some cases, to a mercury "blowout." In addition, the auxiliary reaction train contained a large volume trap (27), leading to a horizontal spherical joint station in the arrangement shown in Figure 1, which also shows a typical reaction station with mercury "blowout." A bypath provided direct connection between the horizontal station and the reaction line.

The pumping system for the main manifold consisted of a Duoseal forepump and a mercury diffusion pump, which could be bypassed when necessary to avoid oxidation and contamination of the mercury. The pumping section for the auxiliary reaction train
Figure 1. Reaction station and large volume trap of the auxiliary reaction train.
consisted of a Duoseal forepump and a two-stage metal oil diffusion pump with Dow Corning 703 silicone oil as pump fluid.

Cold traps cooled with liquid nitrogen preceded the diffusion pumps. Since the two reaction trains were interconnected, the whole vacuum apparatus could be evacuated by either one of the pumping sections when required, or both parts could be treated as separate units. For many operations, the vacuum produced by the forepumps alone was sufficient.

2. Reaction apparatus

The reactions with diborane were carried out in the apparatus shown in Figure 2, consisting of a diborane generator (A), connected via a U-trap to the reaction vessel (B). Several sizes of this apparatus were used, according to the scale of the desired reaction. The diborane generator consisted of a pressure equalizing dropping funnel, a round bottom flask, and a reflux condenser filled with glass helices. The reaction vessel, a tube or round bottom flask of appropriate size, was equipped with a gas dispersion frit and a horizontal side arm terminating in a spherical joint corresponding to the spherical joint on the auxiliary vacuum line. Vacuum stopcocks preceded both entrances to the reaction vessel, allowing it to be closed for transportation. Both the diborane generator and the reaction vessel were equipped with a magnetic stirring assembly. Dry Ice-isopropanol slush served as cooling medium for reflux condenser and U-trap, as well as for the reaction vessel. Large scale reactions required
A $18/9$ spherical joint corresponding to the joint on B is provided on the vacuum line.

Figure 2. Reaction apparatus.
cooling of the diborane generator flask with ice water.

The reactions were carried out under a continuous flow of dry nitrogen. Diborane, generated as described in section II.C., was transported by the gas flow into the respective reaction solution through the gas dispersion frit. The carrier gas left the apparatus through the side arm of the reaction vessel, to which a mineral oil bubbler was attached.

3. Handling of substances

Whenever necessary, reagents and products were transported under vacuum or under nitrogen gas and handled under a nitrogen atmosphere in a dry-box.

4. Sublimations

In addition to conventional cold-finger instruments, the apparatus shown in Figure 3 was used for micro-sublimations and separations by fractional vacuum sublimation. A glass tube of 20 to 25 cm length and 8 to 10 mm diameter was closed and slightly bent down at one end. The substance was placed into the closed end of the tube by means of a long-stemmed powder funnel. A short piece of heavy wall Tygon R-3603 tubing, attached to the open end of the sublimation tube, served as a flexible adapter to the vacuum line. To provide uniform thermal contact between the heating bath and the sublimation tube, the lower end of the tube was covered with aluminum foil, as indicated in Figure 3. Cooling was provided by crushed Dry Ice, placed into a card board
Figure 3. Apparatus for fractional micro-sublimation.

box surrounding the sublimation tube at a distance of about 10 cm from the aluminum foil cover. On warming, substance was deposited both along the temperature gradient preceding the Dry Ice box and in the region of lowest temperature at the position of the cold box. The fractions were recovered by cutting the glass tube between the regions of deposited material and scraping the substances out of the sections. Complete separation of substances which sublime at only slightly different temperatures was not effected by this procedure, which, therefore, had to be repeated
several times. As described later, the separation of ammonia-borane and cyclodiborazane by fractional micro-sublimation according to this method proved to be particularly difficult.

Crude separations of volatile solids from non-volatile material were accomplished by using a sublimation technique described by Behrens (28). The mixture was placed to the bottom of a vertical glass tube, about 25 cm in length, connected to the vacuum line. A piece of brass pipe was slipped over the sublimation tube, covering its whole length. By heating the lower end of the metal pipe by means of some heating tape, and cooling the upper portion with tap water running through a few coils of copper tubing, a temperature gradient was established along which the volatile substances were deposited on the wall of the sublimation tube.

A variation of this sublimator, allowing the treatment of larger amounts of substance, was also used. It consisted of a straight glass tube of 25 cm length and 2 cm diameter, furnished with 24/40 inner standard taper joints on both sides. To the lower of these joints the substance holding flask was connected, the seal being provided by a heat resistant Viton O-ring in the joint, rather than vacuum grease. Connection to the vacuum line was made through a stopcock adapter. The flask, including most of the joint, was immersed in an electrically heated sand bath. Provisions for cooling were not required for the substances under consideration which deposited along the lower part of the glass tube. An advantageous feature of this design was that
certain reactions could be conducted in the flask, followed by sublimation, all while the apparatus remained connected to the vacuum line.

5. Thermal decompositions

The thermal decomposition of cyclopentaborazane and cyclo-diborazane is described in sections II.G. and II.H., respectively. The apparatus employed are shown in Figures 9 to 11, along with the description of their respective functions, in the sections cited.

6. Molecular weights

Molecular weights were determined by cryoscopic methods; a conventional Beckmann molecular weight cell equipped with an electro-magnetic stirring mechanism was used. For details consult reference (6).

7. X-ray measurements

X-ray powder diffraction patterns were used for identification and comparison of compounds. A Debye-Scherrer camera of 11.46 cm effective diameter was used with a North American Philips (Norelco) X-ray instrument. Patterns were obtained using Cu$_{\alpha}$ radiation. Exposure times were between 15 and 30 hours at 12 mA and 32 kV. Moisture sensitive samples were sealed into glass
capillaries under a dry nitrogen atmosphere in the dry-box.

8. Infrared spectra

A Perkin Elmer Model 337 double beam grating spectrophotometer was used to obtain infrared spectra. Most spectra were taken on solid samples as KBr pellets. A gas cell with Irtran II (Kodak) windows was used to obtain spectra in the gas phase. The final spectra used to establish the absorption frequencies recorded in section II.F.3. were taken on a Beckman IR 9 instrument.1

9. Mass spectra

A Consolidated Engineering mass spectrometer, Model 21-620, was used for qualitative identification of volatile materials by comparing the relative intensities of peaks obtained with published data.

The mass spectra of the products of thermal decomposition of cyclodiborazane (section II.H.) were taken by the Battelle Memorial Institute, Columbus, Ohio.

B. Reagents and solvents

1. Diborane

Diborane was generated in appropriate quantities for each reaction and was transported by a flow of nitrogen into the respective reaction medium at the rate it was produced. Of the

1I would like to thank Mr. Jay H. Worrell for obtaining these spectra.
several laboratory methods available for generating diborane
(29, 30, 31), a procedure adapted from the method of Shapiro and
co-workers (29) was used and is described in section II.C.

The reagents used were lithium aluminum hydride, obtained
from Metal Hydrides, Inc., Beverly, Mass.; boron trifluoride-
etherate, commercially obtained (Matheson) and purified by
distillation at normal pressure (bp. around 125°C); and com-
mercial anhydrous diethyl ether, which was used as such.

Boron trifluoride-etherate deteriorates even under anhydrous
conditions. However, as long as it does not appear excessively
discolored it can be used for this reaction. When it is stored
in the freezer compartment of a refrigerator, it seems to be stable
over prolonged periods of time.

2. Sodium amide

The following types of sodium amide were used for the syn-
thesis of cycloborazanes: (a) sodium amide prepared according to
Greenlee and Henne (32) by catalytic action of iron(III) nitrate
on a solution of sodium in liquid ammonia; (b) iron-free sodium
amide synthesized by reaction of diolefins (isoprene, 1,3-penta-
diene) with sodium in liquid ammonia (33), according to

\[
C_5H_8 + 2 \text{Na} + 2 \text{NH}_3 + \text{NH}_2(\ell) \rightarrow C_5H_{10} + 2 \text{NaNH}_2
\]

(c) iron-free sodium amide prepared as above, using acetylenic
hydrocarbons (3-heptyne) as oxidizing agent; (d) commercial iron
containing sodium amide.

The iron-free samples were supplied by K. W. Greenlee,
Chemical Samples Co., Columbus, Ohio. Since the syntheses required stoichiometric excess of hydrocarbon and, with diolefins in particular, produced some ammonia insoluble polymeric material, the sodium amide produced always contained about 3 per cent of organic residue.

Results obtained by using the various types of sodium amide differed widely, as described in section II.F.1.

3. Ammonia

Ammonia from a commercial cylinder was dried by condensing it onto sodium metal in a previously evacuated flask on the vacuum line. The time-consuming task of distilling large amounts of ammonia from the storage flask into the reaction vessel was facilitated by directing a stream of air at room temperature against the storage flask.

4. Dimethyl sulfoxide

Dimethyl sulfoxide was supplied by the Crown Zellerbach Corporation and was dried according to recommendations given by the supplier by heating the liquid with sodium hydroxide to 120°C for one hour, followed by distillation under reduced pressure. The substance was stored under a dry nitrogen atmosphere.

The cryoscopic constant of dimethyl sulfoxide, reported erroneously in 1958 (33), was re-determined in this laboratory (6) to 3.59°C/molar.

Because of its low volatility, it is difficult to handle
dimethyl sulfoxide in vacuum systems with narrow openings such as stopcocks.

5. Tetrahydrofuran

Reagent grade tetrahydrofuran was dried with lithium aluminum hydride in the vacuum system and then distilled into the reaction tube.

6. Dioxane

Reagent grade p-dioxane was dried over lithium aluminum hydride on the vacuum line. Amounts needed were distilled into a storage flask and kept under a nitrogen atmosphere.

C. Generation of diborane

As mentioned above, diborane was generated for each reaction by a procedure adapted from the method of Shapiro et al. (29). The reaction, which proceeds according to the overall equation

\[ 4 \text{BF}_3 + 3 \text{LiAlH}_4 \xrightarrow{\text{Et}_2\text{O}} 2 \text{B}_2\text{H}_6 + 3 \text{LiF} + 3\text{AlF}_3 \]

was carried out by dropping boron trifluoride–etherate into a stirred suspension of lithium aluminum hydride in ether. Yields of diborane were based on the amount of hydride used, an excess of boron trifluoride being applied.

The following procedure was used, cf. Figure 2. While the reaction vessel (B) was still connected to the vacuum line, the diborane generator (A) and the attached U-trap were flushed thoroughly with dry nitrogen. After the cooling jacket and the
Dewar vessel had subsequently been filled with Dry Ice-isopropanol slush, the required amount of powdered lithium aluminum hydride and anhydrous ether was introduced into the generator bulb, for which purpose the dropping funnel was temporarily removed. A quantity of boron trifluoride-etherate representing a stoichiometric excess with respect to the amount of hydride used was poured into the dropping funnel, and the system was again flushed with nitrogen. In order to connect the reaction vessel to the diborane generator it was necessary to interrupt the nitrogen flow. After the connection had been made, the stopcocks on B were opened carefully. Stopcock I was opened first, while the nitrogen cylinder valve was still closed. The resulting decrease in pressure in the system was compensated with nitrogen by carefully reopening the valve before stopcock II was opened. Thereafter, the nitrogen flow was adjusted in such a way as to result in a moderate rate of bubbling through the mineral oil in the attached flask. Boron trifluoride-etherate was then allowed to drop slowly into the stirred suspension of lithium aluminum hydride in ether. At the same time, the liquid in the reaction vessel was stirred with a magnetic stirring assembly. From a half to one hour, depending on the scale of the reaction, after the last drop of etherate had been added to the diborane generator, the reaction vessel, with stopcocks closed, was removed for further treatment as described under the respective synthesis products.

The above reaction proceeds in two distinct steps (29).
Until a ratio of borontrifluoride to lithium aluminum hydride of unity is reached, the reaction is exothermic in nature, producing a gelatinous precipitate, but little diborane. When the ratio exceeds one, diborane is evolved in proportion to the amount of borontrifluoride added, in a much less vigorous reaction. For practical purposes, this mechanism implies, in particular for large scale reactions, that the generator bulb must be cooled to the ice point, and that a sufficient amount of ether must be present in order to enable the stirring assembly to cope with the gelatinous precipitate formed. It was found that at least 15 ml of ether per gram of lithium aluminum hydride should be used. According to the two-step mechanism of this reaction it is possible to add at least part of the borontrifluoride-etherate which is required to complete the first half-reaction at a relatively rapid rate, before a reaction apparatus is connected to the diborane generator.

It may be worth while to point out that the advantage of the in situ generation of diborane for reactions on a large scale lies in the fact that the concentration of this material at any time is small and can be controlled. Quantities exceeding one mole of diborane at a time have been prepared by this reaction. A round bottom flask of two liters capacity served as generator flask, and the following amounts of reagents were used: LiAlH₄, 70 g; BF₃·Et₂O, 350 ml; Et₂O, 2 lbs. A plastic bucket, not interfering with the magnetic stirring, filled with ice water was
used to cool the generator bulb. Reactions in which use is made of the large scale synthesis of diborane are described in section II.F.1.

D. **Analytical procedure**

The analytical procedure for the determination of boron, nitrogen, and hydrogen involved the following steps.

A weighed sample of the substance was transferred to the bottom of a hydrolysis tube, using a weighing pig attached to a glass rod of appropriate length. The tube was connected to the vacuum line, evacuated, and 6 N hydrochloric acid was distilled into the tube at \(-196^\circ\text{C}\). Only after the tube had been sealed off was the acid allowed to contact the substance. To complete the hydrolysis, the closed tubes were kept for several days in an oven at 110°C. In the case of cyclopentaborazane it was necessary to heat the hydrolysis tube for several weeks to about 170°C in order to effect complete hydrolysis.

The amount of hydridic hydrogen produced on hydrolysis was measured volumetrically in the Töpler pumping system. For this purpose the tube was returned to the vacuum line, placed in liquid nitrogen, and opened by snapping off its break-off tip allowing the hydrogen to enter the vacuum system.

For further analysis the acidic solution was rinsed into a volumetric flask, and aliquots were taken for the determination of boron and nitrogen. In the case of cyclopentaborazane it was found to be necessary to keep the acidic solution at room
temperature for about two weeks before analysing for boron; if this waiting period was not observed the boron values were found lower than the theoretical values.

Aliquots of the solution were analyzed for boron by titrating boric acid in the presence of mannitol with standard sodium hydroxide. Nitrogen was determined by standard micro Kjeldahl methods. The titrations were carried out using a Beckman Model G pH meter.

E. Diammoniate of diborane and ammonia-borane

1. Preparation

a) The reaction of diborane with ammonia.—Diammoniate of diborane, [(BH₂(NH₃)₂][BH₄], was found to be the sole reaction product on introduction of gaseous diborane, diluted with nitrogen, into liquid ammonia at -78°C. The apparatus shown in Figure 2, and the procedure for generating diborane described above were used. Liquid ammonia, dried over sodium metal, was distilled into the evacuated reaction vessel, which was maintained at -78°C (Dry Ice-isopropanol slush) throughout the reaction. The vessel was then connected to the diborane generator, and diborane was introduced into the stirred liquid as described. After the reaction was completed, the vessel, with stopcocks closed, was disconnected and placed into a Dewar vessel containing liquid nitrogen in order to freeze the clear reaction solution. The vessel was then connected via the side arm to the large volume trap of the vacuum system, again surrounded by a Dry Ice bath, and
the excess ammonia was removed by vacuum sublimation into the trap which was cooled by liquid nitrogen. The last traces of ammonia were expelled by allowing the vessel to warm to room temperature while pumping through the cooled trap. The remaining solid, non-volatile product was transferred into appropriate vials inside a dry-box.

Since no side products were found, this reaction represents effectively a test for the yield of the diborane generating process and, by implication, for the "active content" of the lithium aluminum hydride used. Using fresh samples of hydride, which are rated at 95+ % LiAlH₄, a maximum yield of 97 per cent was obtained.

b) The reaction of tetrahydrofuran–borane with ammonia.—The compounds ammonia–borane, BH₃NH₃, and diammoniate of diborane were synthesized simultaneously in about equi-molar amounts by the reaction of ammonia with tetrahydrofuran–borane in tetrahydrofuran at -78°C. The same apparatus and technique as described for the preparation of diammoniate of diborane was employed. After the introduction of diborane into tetrahydrofuran was completed, the reaction vessel was connected to the vacuum system via the side arm and evacuated while still being surrounded by a Dry Ice bath. Under magnetic stirring dry ammonia was distilled out of a graduated storage vessel onto the reaction solution, forming a liquid layer on top of the tetrahydrofuran phase; the two liquids do not mix. The mixture was stirred for about half an hour, during which period a transitory white precipitate
appeared in the tetrahydrofuran phase. The excess of ammonia and the solvent were removed by distillation into the cooled trap, for which purpose the temperature of the reaction solution was raised to \(-45^\circ C\), using a chlorobenzene slush as cooling medium. After the last trace of solvent had been expelled by pumping at room temperature, the solid product mixture was transferred onto the fritted disk of an extraction apparatus of the type described by Parry and co-workers (16). The apparatus was evacuated, and ammonia-borane was extracted from the reaction mixture with dry ether. Diammoniate of diborane remained behind.

The corresponding deuterated compounds were prepared in an analogous manner.

2. Properties

The compounds were identified by their X-ray powder diffraction patterns, which are reported elsewhere (14,13).

The diammoniate of diborane obtained by the reaction of diborane with ammonia is a white, free-flowing, micro-crystalline powder which is soluble in liquid ammonia. It is readily attacked by moisture. Even under rigorously anhydrous conditions at room temperature it undergoes slow self-decomposition accompanied by evolution of hydrogen, resulting in a pressure increase in storage vessels. Stored at \(-78^\circ C\), however, it appears to be stable over prolonged periods of time. Although it can be handled for short intervals in the open air, dry-box operations are to be preferred. Above \(75^\circ C\) it decomposes rapidly in vacuo. The compound as
obtained by the reaction of tetrahydrofuran-borane with ammonia has the same characteristics, however, the nature of the process renders it somewhat more bulky.

Ammonia-borane is more volatile than the diammoniate, its stoichiometric dimer, and, in contrast to the latter, is soluble in diethyl ether. It sublimes readily in vacuo, beginning at about 30°C. Hydrolytically, it is far more stable than the diammoniate and, indeed, can be dissolved in neutral water with only slight evolution of hydrogen. Under ordinary conditions, there is no interconversion between the two species, however, the diammoniate has been used as starting material for the preparation of ammonia-borane (13).

Reactions of the compounds, structural arguments, and other properties can be found in the pertinent literature (5).

Analysis of \([\text{BH}_2(\text{NH}_3)_2][\text{BH}_4]\). Calc.: hydr. H, 9.79; B, 35.04; N, 45.37. Found: hydr. H, 9.74; B, 34.5; N, 45.7.

F. Cycloborazanes

1. Synthesis

Earlier results obtained in this laboratory (12) had indicated that the reaction of the diammoniate of diborane with strong bases in liquid ammonia provides a suitable access to aminoboranes which are relatively stable towards loss of hydrogen. For the present investigation, sodium amide was used as the base because, aside from the fact that it is reasonably easy to handle, it was hoped that the uncomplicated over-all stoichiometry of the process
would preclude side reactions. Diammoniate of diborane was used in form of its ammonia solutions, prepared as described in section II.E.1. by introducing diborane into liquid ammonia. Thus the process under consideration could be represented by the following over-all equation:

\[
B_2H_6 + NaNH_2 \xrightarrow{NH_2(\ell)} \frac{1}{n} (BH_2NH_2)_n + NaBH_4
\]

Two experimental routes were followed. In one set of experiments, diborane was introduced directly into a suspension of sodium amide in liquid ammonia; in this case, the amide was present in stoichiometric excess during most of the reaction. In another set of experiments, the amide was added after the solution of diammoniate of diborane had been prepared; in this case, the diammoniate was present in excess throughout the reaction.

Since some of the aminoborane species produced by these reactions are formed in only small yields, it was desirable to use relatively large amounts of reactants. Most of the experiments were run on a one mole scale with respect to sodium amide, with an excess of diammoniate of diborane. The procedure for one mole scale reactions is described below.

The apparatus shown in Figure 2 was again employed, modified for these reactions as follows. A flask of two liters capacity was used for the generation of diborane, and a one liter round bottom flask served as reaction vessel. An extra coarse frit was required for dispersion of the gas mixture in the reaction liquid. The dropping funnel on the diborane generator was designed to allow observation of the dropping rate outside the generator.
flask. In addition, a simple gas flow-meter of the "floating ball" type, standardized to a flow of up to two cubic feet of air per hour, was situated in the nitrogen line leading to the apparatus. This instrument which, by its nature, indicates a gas flow as long as the pressure underneath the ball is larger than on the exit side, i.e., in the system, served as both a qualitative indicator for the rate of nitrogen flow and as a pressure gauge. The readjustments in the rate of nitrogen flow, made necessary by the pressure increase inside the apparatus during the experiments, were guided by this indicator, as was the adjustment of the dropping rate of borontrifluoride-etherate into the diborane generator, the ultimate cause of the pressure increase. Because of this pressure, all joints had to be carefully secured. Figure 4 shows the reaction apparatus in use.
during a reaction. The diborane generator is at left, submerged in a bucket of ice-water; the reaction vessel is contained in the second plastic bucket, buried in crushed Dry Ice. Nitrogen gas, coming from the cylinder at right, passes through the flowmeter and a coil of copper tubing in a cold trap before entering the system at the head of the pressure-equalizing dropping funnel visible at left.

For the generation of in excess of one mole of diborane as described in section II.C., the generator was charged with 70 g of lithium aluminum hydride, powdered in a glove-box under nitrogen, and two pounds of commercial anhydrous ether out of freshly opened cans. About 350 ml of boron trifluoride-etherate were used, of which 150 ml were stoichiometrically required to complete the first half-reaction without producing much diborane yet (29).

Depending on the experimental route followed, diborane was introduced either into a suspension of 39 g (one mole) of sodium amide in about 700 ml of liquid ammonia or into this amount of liquid ammonia alone. The reaction time was about 15 hours at a dropping rate of boron trifluoride-etherate into the diborane generator of about one drop every five seconds. At higher dropping rates it became difficult to control the pressure inside the reaction system caused by clogging of the gas dispersion frit, probably due to a deposit of diammoniate of diborane in the frit. If, toward the end of a run, this pressure exceeded tolerable limits, the frit was cleared by forcing ammonia solution
into the stem, through application of a sufficiently large nitrogen pressure onto the surface of the reaction solution; the mineral oil bubbler was temporarily removed for this purpose. The solubility of diborane in ether increases markedly with pressure.

In experiments in which sodium amide was already present, the reaction could be followed by observing the disappearance of the amide, which is only slightly soluble in liquid ammonia. Sometimes, depending on the yield of the reaction and the amount of ammonia present, a precipitate of what proved to be cyclopentaborazane formed slowly, becoming noticeable usually only several hours after the disappearance of the amide. The distribution of products found, however, was nearly the same, regardless of whether the reaction medium was removed before or after precipitation had been observed. The important criterion for a successful reaction, at this stage, was the disappearance of sodium amide, i.e. the formation of a clear solution. Ammonia was removed by vacuum sublimation, following, essentially, the same procedure as described for the synthesis of diammoniate of diborane (section II.E.1.), except that the frozen solution was connected directly to a Duoseal pump equipped with an exhaust line which extended out of a window. Complete removal of ammonia required three days, during which period the Dry Ice bath surrounding the reaction flask was gradually lowered. In order to avoid pressure build-up due to trapped ammonia in the stem of the gas dispersion frit, a rubber stopper was placed into the joint
preceding stopcock I (Figure 2), and the stopcock was opened.

In experiments in which sodium amide was added after introduction of diborane into ammonia had been completed, the procedure was continued as follows. The reaction flask was disconnected from the diborane generator, and the head with gas dispersion frit and stopcocks was removed and quickly replaced by one which, in place of frit and stopcock I (Figure 2), had a length of open glass tubing terminating above the surface of the reaction solution. To the outer end of the glass tube a vessel containing the sodium amide was connected by a short length of heavy wall Tygon R-3603 tubing. The amide had been weighed into the vessel under a nitrogen atmosphere and was protected from the open air by closing the Tygon tubing with a pinch clamp. Only after the apparatus had been connected to the auxiliary vacuum line through the side arm and stopcock II, and the pressure had subsequently been lowered to that of the ammonia solution, was the pinch clamp released. Sodium amide was added in small portions to the magnetically stirred solution in the course of about three hours, each addition being made after the previous one had reacted as indicated by its disappearance in the solution. During this operation, stopcock II remained open to the vacuum line which itself was closed to the pump. A total of about two liters of a non-condensable gas, presumably hydrogen, was evolved during the reaction, which was pumped off from time to time. This experimental procedure always yielded a precipitate in the initially
clear solution within a few hours. Ammonia was removed as described above.

Several grades of sodium amide from various sources have been used for this reaction in both experimental versions, with widely divergent results. The sodium amide varieties are identified as to their origin in section II.B.2., labeled (a) through (d); in reporting the results, reference is made to this classification. In general, the procedure in which sodium amide was added to a diammoniate of diborane solution gave the highest yields in cycloborazanes. By using type (a) and (c) sodium amide, a nearly quantitative yield in cyclopenta­
borazane was realized, with about three per cent cyclotriborazane as the principal side product. Reactions carried out by introduction of diborane into sodium amide suspensions in ammonia produced, at most, about 50 per cent yields, usually less. However, these reactions did produce all known cycloborazanes, in particular when type (b) sodium amide was employed. The separation of such a reaction mixture into its components is described in the following section, II.F.2. Unfortunately, the reactions with this type sodium amide proved to be irreproducible from batch to batch of amide, with yields in cycloborazanes ranging from essentially zero to about 50 per cent with respect to the amount of amide used in this experimental procedure. The only reaction in which type (d) sodium amide was used did not yield cycloborazanes.

Whenever cyclic products were formed at all, cyclopenta­
borazane was found in by far the largest proportion, regardless
of procedure or reactants used. The major side product, found in varying proportions, was always cyclotriborazane. No change was found in the total yield of cycloborazanes or in the distribution of species when the reaction solutions were allowed to stand at \(-78^\circ C\) for extended periods of time before ammonia was removed. Usually, the solutions were kept for about 12 hours, however, in some experiments this period was extended to one week. In one experiment, the dried reaction mixture was re-immersed in liquid ammonia and stored at \(-78^\circ C\) for one week; no change was detected.

Attempts were also made to use elemental sodium instead of sodium amide (24), introducing diborane into a solution of the metal in liquid ammonia. Cycloborazanes were found in small yields, however, the experiments had to be abandoned because of technical difficulties. The gas dispersion frit gradually closed up and could not be "washed" in the manner described above; also, the sodium tends to leave the ammonia solution by creeping up along container walls and the stem of the frit. While these difficulties could be overcome in experiments on small scales, they proved to be uncontrollable in large scale runs.

2. Separation of products

X-ray powder diffraction patterns of freeze-dried reaction mixtures always showed the presence of sodium hydroborate, NaBH4, confirming the observation that sodium amide had indeed reacted, even in runs which did not produce any cycloborazanes; in such cases, additional lines were not detected. When cycloborazanes
were formed, powder photographs showed the strongest line (at 3.80 Å) of cyclopentaborazane, and, in rare cases, the strong lines of cyclotriborazane. Small amounts of material could not be traced by the X-ray technique, nor, of course, could amorphous species be observed.

In a typical experiment, performed on a one mole scale, which produced a favorable yield in low-molecular weight cycloborazanes, the following compounds were encountered in the approximate amounts given: sodium hydroborate, 38 g; cyclopentaborazane, 14 g; unidentified material, presumably containing chain-like aminoboranes, 11 g; a total of about 1 g of cyclodi-, tri-, and tetraborazane, and ammonia-borane; and the excess of diammoniate of diborane not used up in the reaction.

The following steps were used to separate the mixture. First, the mixture was extracted twice with dry ether, each time allowing the solvent to act upon the substance for about one hour before it was filtered through a large Buchner funnel with fritted disk. The whole operation was conducted under nitrogen in a large glove-box.

The residue of this filtration, consisting of cyclopentaborazane, sodium hydroborate, the aminoborane chains, and a small amount of diammoniate of diborane, was introduced into a flask which was connected to the large volume trap of the auxiliary vacuum system. The ether was removed by pumping on the substance through the nitrogen cooled trap, first carefully at room
temperature, then for a day at about 50°C. Cyclopentaborazane was recovered by introducing the mixture into ice water, in which the substance is only sparingly soluble, while sodium hydroborate is soluble and the other components are hydrolytically destroyed. The precipitate was filtered and dried on the vacuum line, yielding lumps of material which were powdered and pumped upon again. About one liter of ice water for every two to three grams of solid mixture was required in order to remove completely sodium hydroborate from the product. Purity was checked by observing the characteristic band of sodium hydroborate at 2240 cm\(^{-1}\) in the infrared spectrum. When cyclopentaborazane was to be used for pyrolysis experiments, the presence of sodium hydroborate was not critical; therefore, less water was then used in this operation in order to repress loss of product due to the small but noticeable solubility of cyclopentaborazane in water.

About one gram of material was obtained from the filtrate of the ether extraction. It was separated into two fractions by vacuum sublimation at 80°C. The residue seems to be cyclotetaborazane. No means for further purification of this fraction are as yet available.

The sublimate consisted of cyclotriborazane, cyclodiborazane, and ammonia-borane. It was further separated by vacuum sublimation at about 45°C, at which temperature cyclotriborazane remains behind.

The separation of cyclodiborazane from ammonia-borane presented problems which have not yet been completely solved.
The substances sublime in vacuo at only slightly different temperatures in the range of 30 to 35°C, and no discriminating solvent has been found yet. The following attempts were made:

(a) Through repeated fractional micro-sublimation as described in section II.A.4., cyclodiborazane was gradually enriched in the fractions deposited along the temperature gradient preceding the cooled section of the sublimation tube (Figure 3). The deposits in the region of lowest temperature, in turn, contained relatively more ammonia-borane. Since this procedure is necessarily wasteful, and only very small amounts of material were available, pure cyclodiborazane was not obtained, although this method appears to be the only potentially useful one.

(b) Micro-sublimations along extended temperature gradients, by several techniques adapted from published accounts (35, 36, 37), did not effect separation. In particular, attempts to sublime the mixture under low nitrogen pressures or in evacuated, sealed tubes rotating in a temperature gradient, resulted in decomposition of the material.

(c) Attempts to separate the mixture by vapor phase gas-chromatography failed, because the working temperature of conventional columns exceeds the temperature at which these compounds decompose.

(e) Unsuccessful, too, was the attempt to remove ammonia-borane through the reaction

$$\text{NH}_3 \text{(g)} \rightarrow \text{NaNH}_2 \text{BH}_3 + \text{NH}_3,$$

carried out by slowly introducing sodium amide into a solution of the mixture in liquid ammonia. It turned out that both compounds
react with sodium amide. When less than the stoichiometric amount of amide was used, pure ammonia-borane could be sublimed out of the reaction mixture.

In view of these difficulties, the reaction of the diammoniate of diborane with sodium amide cannot be considered to be a practical source of cyclodiborazane. A better source was found when it was discovered that cyclodiborazane is formed on thermal decomposition of cyclopentaborazane and can be obtained in at least 85 per cent purity by a technique described in section II.G.1.; the contaminant again was ammonia-borane.

3. Characterization

a) Cyclodiborazane.—This compound, the isosteric analog of cyclobutane, is a white, crystalline solid, which is stable in air and has a limited solubility in most common organic solvents. The solubility in $\beta$-dioxane is about 1 g in 100 g solvent. It is soluble in liquid ammonia. There is no apparent protolysis by water.

The analytical data are summarized in Table 2.

| TABLE 2 |
| ANALYSIS OF $\left(\text{BH}_2\text{NH}_2\right)_2$ |

<table>
<thead>
<tr>
<th></th>
<th>H</th>
<th>B</th>
<th>N</th>
<th>Ratio H:B:N</th>
</tr>
</thead>
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<td>37.49</td>
<td>48.54</td>
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<td>1</td>
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<td>36.6</td>
<td>48.8</td>
<td>2.26:1:1.03</td>
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<td>7.5</td>
<td>37.3</td>
<td>48.2</td>
<td>2.16:1:1.00</td>
</tr>
</tbody>
</table>

$^a$Hydridic hydrogen. $^b$B = 1.00 as reference.
The high ratios of hydrogen to boron and nitrogen reflect the fact that the samples were contaminated with ammonia-borane, as was also shown in the X-ray powder diffraction patterns of long exposure time of the samples.

The apparent molecular weight, determined by freezing point depression of 2-dioxane, was found to be $58 \pm 3$, an average of four values of two independent determinations. The theoretical value for cyclodiborazane is 57.7.

The X-ray powder diffraction data are given in Table 3.

**TABLE 3**

**X-RAY POWDER DIFFRACTION PATTERN OF (BH₂NH₂)₂**

<table>
<thead>
<tr>
<th>Intensity</th>
<th>d, Å</th>
<th>Intensity</th>
<th>d, Å</th>
</tr>
</thead>
<tbody>
<tr>
<td>MS</td>
<td>6.83</td>
<td>MS</td>
<td>2.87</td>
</tr>
<tr>
<td>S</td>
<td>5.28</td>
<td>M</td>
<td>2.69</td>
</tr>
<tr>
<td>M</td>
<td>4.48</td>
<td>M</td>
<td>2.63</td>
</tr>
<tr>
<td>S</td>
<td>4.39</td>
<td>W</td>
<td>2.520</td>
</tr>
<tr>
<td>W</td>
<td>4.08</td>
<td>M</td>
<td>2.276</td>
</tr>
<tr>
<td>W</td>
<td>3.93</td>
<td>M</td>
<td>2.198</td>
</tr>
<tr>
<td>V S</td>
<td>3.71</td>
<td>W</td>
<td>2.058</td>
</tr>
<tr>
<td>WM</td>
<td>3.28</td>
<td>W</td>
<td>2.018</td>
</tr>
<tr>
<td>W</td>
<td>3.14</td>
<td>WM</td>
<td>1.864</td>
</tr>
</tbody>
</table>

*Intensities: S = strong; M = medium; W = weak; V = very.*

CuKα radiation.
The infrared spectrum is shown in Figure 5 and summarized in Table 4.

**TABLE 4**

INFRARED SPECTRUM OF (BH$_2$NH$_2$)$_2$

<table>
<thead>
<tr>
<th>Frequency, cm$^{-1}$</th>
<th>Intensity$^a$</th>
<th>Frequency, cm$^{-1}$</th>
<th>Intensity</th>
</tr>
</thead>
<tbody>
<tr>
<td>3310</td>
<td>S, sp</td>
<td>1202</td>
<td>S, sp</td>
</tr>
<tr>
<td>3264</td>
<td>S, sp</td>
<td>1140</td>
<td>S, sp</td>
</tr>
<tr>
<td>2380–2300</td>
<td>S, br</td>
<td>1065</td>
<td>M, sp</td>
</tr>
<tr>
<td>1605</td>
<td>M, sp</td>
<td>1048</td>
<td>M, sp</td>
</tr>
<tr>
<td>1585</td>
<td>M, sp</td>
<td>894</td>
<td>W, sp</td>
</tr>
<tr>
<td>1567</td>
<td>S, sp</td>
<td>820</td>
<td>W, sp</td>
</tr>
<tr>
<td>1385</td>
<td>S, sp</td>
<td>721</td>
<td>W, sp</td>
</tr>
<tr>
<td>1240</td>
<td>S, sp</td>
<td>693</td>
<td>W, sp</td>
</tr>
</tbody>
</table>

$^a$Intensities: S = strong; M = medium; W = weak; sp = sharp; br = broad.

The B$^{11}$ nuclear magnetic resonance spectrum in dioxane solution showed weakly the expected triplet. However, because of the limited solubility of cyclodiborazane in organic solvents, a sufficiently concentrated solution was not available for this purpose.

The substance sublimes in vacuo beginning at about 30°C. On thermal decomposition in a closed system up to 225°C, somewhat more than two moles of hydrogen per mole of substance was found, the excess being due partially to the inevitable contamination by ammonia–borane. A small amount of borazine, identified by its mass spectrum, was found in the gas phase. The thermal decomposition of cyclodiborazane in an "open" system is described in section II.H.
Figure 5
Infrared spectrum of \( (\text{BH}_2\text{NH}_2)_2 \)
There is evidence, as yet unconfirmed, that the reaction of the compound with sodium amide in liquid ammonia leads to a sodium salt of cyclodiborazane. This species seems to be extremely moisture sensitive and is, at least partially, reconverted to cyclodiborazane on exposure to air. This information was obtained in the course of experiments to react selectively ammonia-borane, in the mixture with cyclodiborazane, with sodium amide (see section II.F.2.).

The investigation of cyclodiborazane was greatly hampered by the circumstance that only small amounts could be obtained which, in addition, could not be completely freed of contamination. A successful experiment performed on a one mole scale yielded a total amount of about 100 mg of enriched cyclodiborazane, most of which originated from the pyrolysis of cyclopentaborazane.

b) Cyclotriborazane.—The properties of this compound have been described in the literature (11, 12). It was found, in addition, that cyclotriborazane begins to sublime under high vacuum at 40°C.

c) Cyclotetaborazane.—This species, at present the least well defined of the cycloborazanes, is a white, crystalline solid which is stable in air. It is insoluble, or of low solubility, in most common organic solvents. It is soluble in dimethyl sulfoxide, from which it cannot be recovered in its original state. It is not attacked by water and highly resistant to acid hydrolysis. Since it does not sublime in vacuo and no
suitable solvent is known, there are as yet no means for purification of this compound, which is obtained as the residue upon sublimation of the ether extract.

The apparent molecular weight, determined by freezing point depression of dimethyl sulfoxide, was found to be $123 \pm 3$; the theoretical value for $(\text{BH}_2\text{NH}_2)_4$ is $115.4$.

The X-ray powder diffraction data are given in Table 5.

The infrared spectrum is shown in Figure 6 and summarized in Table 6.

### TABLE 5

**X-RAY POWDER DIFFRACTION PATTERN OF $(\text{BH}_2\text{NH}_2)_4$**

<table>
<thead>
<tr>
<th>Intensity</th>
<th>d, Å</th>
<th>Intensity</th>
<th>d, Å</th>
</tr>
</thead>
<tbody>
<tr>
<td>MS</td>
<td>7.08</td>
<td>VW</td>
<td>3.24</td>
</tr>
<tr>
<td>S</td>
<td>5.94</td>
<td>M</td>
<td>3.03</td>
</tr>
<tr>
<td>VW</td>
<td>5.18</td>
<td>M</td>
<td>2.825</td>
</tr>
<tr>
<td>M</td>
<td>4.48</td>
<td>WM</td>
<td>2.347</td>
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<tr>
<td>W</td>
<td>4.20</td>
<td>M</td>
<td>2.227</td>
</tr>
<tr>
<td>S</td>
<td>4.08</td>
<td>WM</td>
<td>2.108</td>
</tr>
<tr>
<td>VS</td>
<td>3.93</td>
<td>VW</td>
<td>2.014</td>
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<tr>
<td>W</td>
<td>3.71</td>
<td>VW</td>
<td>1.922</td>
</tr>
<tr>
<td>W</td>
<td>3.52</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

*Intensities: S = strong; M = medium; W = weak; V = very. CuK$_\alpha$ radiation.*
Figure 6  Infrared spectrum of $\left(\text{BH}_2\text{NH}_2\right)_4$
TABLE 6
INFRARED SPECTRUM OF (BH₂NH₂)₄

<table>
<thead>
<tr>
<th>Frequency, cm⁻¹</th>
<th>Intensity</th>
<th>Frequency, cm⁻¹</th>
<th>Intensity</th>
</tr>
</thead>
<tbody>
<tr>
<td>3328</td>
<td>S, sp</td>
<td>1202</td>
<td>S, sp</td>
</tr>
<tr>
<td>3300</td>
<td>S, sp</td>
<td>1172</td>
<td>S, sp</td>
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<tr>
<td>3247</td>
<td>S, sp</td>
<td>1147</td>
<td>M, sp</td>
</tr>
<tr>
<td>2400-2345</td>
<td>S, br</td>
<td>1125</td>
<td>S, sp</td>
</tr>
<tr>
<td>1587</td>
<td>W, sp</td>
<td>1059</td>
<td>M, sp</td>
</tr>
<tr>
<td>1558</td>
<td>M, sp</td>
<td>874</td>
<td>W, sp</td>
</tr>
<tr>
<td>1405</td>
<td>M, br</td>
<td>805</td>
<td>W, br</td>
</tr>
<tr>
<td>1241</td>
<td>S, sp</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

*Intensities: S = strong; M = medium; W = weak; sp = sharp; br = broad.

Cyclotetraborazane is thermally stable in vacuo to about 120°C. Thermal decomposition yields cyclotriborazane and a small amount of cyclodiborazane as the main products.

d) Cyclopentaborazane.—This compound, the principal product of the syntheses, is a white, micro-crystalline solid, insoluble in all common organic solvents. It is soluble in dimethyl sulfoxide, N-methyl-2-pyrrolidone, and, to a limited degree, in dimethyl formamide. It is stable in water. The order of magnitude of solubility in water is 100 mg in 100 g water, in liquid ammonia 500 mg in 100 g ammonia. It is extremely resistant to hydrolysis; boiling water attacks it slowly, and complete hydrolysis can only be effected by acid hydrolysis at 170°C for an extended period of time.

The analytical data are summarized in Table 7.
TABLE 7
ANALYSIS OF (BH$_2$NH$_2$)$_5$

<table>
<thead>
<tr>
<th></th>
<th>H$^a$</th>
<th>H$^b$</th>
<th>B</th>
<th>N</th>
<th>Ratio H:B:N$^c$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Theory</td>
<td>6.985</td>
<td>13.97</td>
<td>37.49</td>
<td>48.54</td>
<td>2:0.95:1.00</td>
</tr>
<tr>
<td>1</td>
<td>6.75</td>
<td>34.5</td>
<td>47.1</td>
<td></td>
<td>2:0.99:1.01</td>
</tr>
<tr>
<td>2</td>
<td>6.72</td>
<td>35.6</td>
<td>47.0</td>
<td></td>
<td>2:1.00:0.99</td>
</tr>
<tr>
<td>3</td>
<td>6.83</td>
<td>36.5</td>
<td>47.0</td>
<td></td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>14.30</td>
<td>38.9</td>
<td>44.2</td>
<td></td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>13.83</td>
<td>36.2</td>
<td>44.7</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

$^a$Hydridic hydrogen by acid hydrolysis.

$^b$Total hydrogen by commercial organic micro-analysis.

$^c$H = 2.00 as reference.

The data reflect the hydrolytic stability of the compound. In the best analysis a degree of hydrolyzation of about 97 per cent was attained. Commercial micro-analysis also revealed the presence of about one half per cent carbon, originating from the organic impurity of the sodium amide used for the synthesis, which amounts to about 3 per cent there.

The apparent molecular weight, determined by freezing point depression of dimethyl sulfoxide, was found to be $145 \pm 4$, as the average of ten values of five independent determinations. The theoretical value for cyclopentaborazane is $144.3$.

The X-ray powder diffraction data are given in Table 8.
TABLE 8
X-RAY POWDER DIFFRACTION PATTERN OF \((\text{BH}_2\text{NH}_2)_5\)

<table>
<thead>
<tr>
<th>Intensity</th>
<th>d, Å</th>
<th>Intensity</th>
<th>d, Å</th>
</tr>
</thead>
<tbody>
<tr>
<td>M</td>
<td>4.38</td>
<td>W</td>
<td>1.895</td>
</tr>
<tr>
<td>VS</td>
<td>3.80</td>
<td>VW</td>
<td>1.668</td>
</tr>
<tr>
<td>W</td>
<td>2.87</td>
<td>VW</td>
<td>1.538</td>
</tr>
<tr>
<td>M</td>
<td>2.188</td>
<td>VW</td>
<td>1.433</td>
</tr>
<tr>
<td>VW</td>
<td>2.108</td>
<td>VW</td>
<td>1.258</td>
</tr>
</tbody>
</table>

*aIntensities: S = strong; M = medium; W = weak; V = very. CuK\(\alpha\) radiation.

Samples recovered from water suspension showed broadened lines in the X-ray powder diffraction diagrams. After recrystallization from dimethyl sulfoxide, sharp lines were observed.

The infrared spectrum of the compound is shown in Figure 7 and is summarized in Table 9.

TABLE 9
INFRARED SPECTRUM OF \((\text{BH}_2\text{NH}_2)_5\)

<table>
<thead>
<tr>
<th>Frequency, cm(^{-1})</th>
<th>Intensity(^a)</th>
<th>Frequency, cm(^{-1})</th>
<th>Intensity</th>
</tr>
</thead>
<tbody>
<tr>
<td>3301</td>
<td>S, sp</td>
<td>1087</td>
<td>M, sp</td>
</tr>
<tr>
<td>3250</td>
<td>S, sp</td>
<td>1062</td>
<td>M, sp</td>
</tr>
<tr>
<td>2420–2300</td>
<td>S, br</td>
<td>973</td>
<td>W, sp</td>
</tr>
<tr>
<td>1571</td>
<td>M, sp</td>
<td>845</td>
<td>W, sp</td>
</tr>
<tr>
<td>1412</td>
<td>M, sp</td>
<td>650</td>
<td>W, br</td>
</tr>
<tr>
<td>1205</td>
<td>S, br</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

*aIntensities: S = strong; M = medium; W = weak; sp = sharp; br = broad.
Figure 7
Infrared spectrum of \((\text{BH}_2\text{NH}_2)_5\)
Cyclopentaborazane does not sublime and is stable in vacuo to about 125°C. The thermal decomposition, which leads to a variety of products, has been studied in detail and is dealt with in section II.G.

e) Comparative summary.—The four unsubstituted cycloborazanes are stable, crystalline compounds which do not lose hydrogen unless heated. The variations in weight-dependent properties, such as volatility, show the expected trends through the series.

The infrared spectra of the members of the series show common features as well as some characteristic differences. For all species, the symmetric and asymmetric NH$_2$ stretching frequencies are found in the region of 3300 to 3250 cm$^{-1}$, with slight variations in position and fine structure of the bands for the individual members. All species show a broad absorption band in the frequency range of 2420 to 2300 cm$^{-1}$, assigned to the symmetric and asymmetric BH$_2$ stretching modes (38). This range is sufficiently low to be indicative of quaternary boron. For example, the corresponding bands for the quaternary boron in sodium hydroborate are found in the region of 2380 to 2150 cm$^{-1}$ (39), whereas the symmetric and asymmetric stretching frequencies for the terminal BH$_2$ groups in diborane are at 2614 and 2522 cm$^{-1}$, respectively (40). The absorption bands in the region of 1605 to 1558 cm$^{-1}$ are assigned to the NH$_2$ deformation modes and show regularly changing features through the series, from a triplet
with an additional shoulder for cyclodiborazane to a single absorption band with a shoulder for cyclopentaborazane. All cycloborazanes with the exception of cyclotriborazane show a single absorption band at about 1400 cm\(^{-1}\), which is tentatively assigned to the B–N stretching frequency (41); for cyclotriborazane, the absorption at 1196 cm\(^{-1}\) has been assigned to this vibration (42). In the range of 800 to 700 cm\(^{-1}\), which is the normal range for the stretching frequency of the (single) B–N dative bond (43), none of the cycloborazanes show absorptions of significance. Further assignments were not made because of considerable structure in the spectra below 1300 cm\(^{-1}\).

A graphical comparison of the X-ray powder diffraction patterns of the four cycloborazanes is shown in Figure 8, along with the pattern of ammonia-borane, which is the closest "monomeric" relative to the series and the contaminant of cycloborazane. The exposure time required to produce a pattern of certain over-all intensity increases with increasing molecular weight; consequently, it becomes more difficult in this order to detect the species in mixtures by means of the X-ray powder diffraction technique.

The relative yields of the cycloborazanes suggest that cyclopentaborazane is thermodynamically the most stable species of the series; cyclotriborazane, which is reported to be stable up to 150°C (11), shows the highest thermal stability in vacuo.
Figure 8. Comparison of X-ray powder diffraction patterns.
G. Pyrolysis of cyclopentaborazane

1. Procedure

On thermal decomposition in vacuo in the temperature range of 125 to 145°C, cyclopentaborazane lost 68 per cent of its original weight with formation of several boron-nitrogen species.

Two types of apparatus, shown in Figures 9 and 10, were used. In the first apparatus, cyclopentaborazane was contained in a glass vial which was placed on the bottom of the pyrolysis tube. The tube, furnished with a cooling jacket containing Dry Ice-isopropanol slush as coolant, was connected to the vacuum line through a U-trap cooled with liquid nitrogen. In the second apparatus, designed for pyrolysis of relatively larger amounts of cyclopentaborazane, the substance was contained in a flask of 50 ml capacity, which was connected to the large volume trap of the auxiliary vacuum line through a length of horizontal glass tubing. The trap was cooled with liquid nitrogen; a cardboard box containing crushed Dry Ice surrounded the horizontal portion of the apparatus.

The procedure simply involved heating the substance to 120°C, followed by very slow increase of the temperature through the decomposition range while pumping through the series of cooled zones. By using the second apparatus, in which eight grams of cyclopentaborazane at a time were pyrolyzed, the gradual temperature increase was extended over a period of 24 hours.

The pyrolysis products were deposited in the apparatus in three fractions which, for one gram of decomposed
Figure 9. Pyrolysis apparatus.

Figure 10. Pyrolysis apparatus.
cyclopentaborazane, consisted of the following materials in the approximate amounts given: (a) a deposit consisting of cyclo-
diborazane, cyclotriborazane, ammonia-borane, and a trace amount of an unknown species, found in the region preceding the Dry Ice cooled part of the apparatus, 30 mg; (b) a fraction of transparent, brittle material, referred to as "glass" in the following, which formed a coat along the Dry Ice cooled portion of the apparatus, 450 mg; (c) a fraction deposited in the liquid nitrogen trap, consisting of a mixture of a volatile and a non-volatile substance, 120 mg. In addition, hydrogen was evolved, and an amount of 320 mg of residue remained behind.

By using the apparatus shown in Figure 9, the first deposit was found in form of a narrow ring while the "glass", separated from this deposit, was spread out evenly over the zone which was cooled uniformly by the Dry Ice-isopropanol slush. By using the second apparatus, on the other hand, the substance mixture of the first deposit was spread out along the temperature gradient between the heated vessel and the cardboard box containing Dry Ice. By covering this apparatus with aluminum foil in such a way that only the central portion of the standard taper joint remained without cover, it was possible to single out a fraction rich in cyclodiborazane, which was deposited in the joint. Accordingly, the first apparatus, Figure 9, was employed to obtain the "glass" and to establish the material balance, while the thermal
decomposition of cyclopentaborazane in the second assembly, Figure 10, provided access to relatively pure cyclodiborazane.

When the temperature was raised more rapidly through the decomposition range of cyclopentaborazane, an increased yield of cyclotriborazane was found among the products. The pyrolysis of "diluted" cyclopentaborazane, using a sample in mixture with sand, resulted in a decrease of the relative proportion of low molecular weight species.

2. Products

The fractions obtained on pyrolysis of cyclopentaborazane were separated and recovered as follows.

First, the volatile substance trapped at -196°C was transferred on the vacuum line into another liquid nitrogen trap by removing the coolant from the original trap. The information obtained as to the nature of this substance lead to the tentative formulation of aminoborane(N-B)borane, $BH_2NH_2BH_3$. The substance decomposed into diborane and solid aminoboranes in a ratio consistent with this formula in the temperature region of -160 to $-140°C$, i.e. at a far lower temperature than aminodiborane which decomposes into the same components at room temperature (15). Mass spectra taken of samples which were kept at $-140°C$ showed, in addition to the dominant presence of diborane, several groups of peaks of low intensity which may be assigned to the monomeric, dimeric, and trimeric aminoborane species. The solid residue obtained from samples which were allowed to decompose at room
temperature appeared to consist of a mixture of open-chain aminoboranes and a small proportion of cyclopentaborazane. The infrared spectrum conformed to that displayed by open aminoboranes (section III.C.), while the X-ray powder diffraction pattern, as well as the fact that part of the substance was stable and insoluble in water, indicated the presence of cyclopentaborazane.

The "glass", as produced with the apparatus shown in Figure 9, appeared to be homogeneous and free of contamination by other pyrolysis products. The nature of this substance is not yet understood. In appearance, it resembles a material described by Wiberg et al. (21) as having the "leaflet structure of naphthalene". It is possible that this material is not a true chemical compound, because the analytical ratios of constituents are not whole-numbered, although they approach the ratios of BH_2NH_2. The analytical data found are: hydridic hydrogen, 6.47; boron, 35.8; nitrogen, 49.7. The ratios of constituents, based on the boron content, are: H_{hydr.}:B:N = 1.97:1.00:1.08. The substance is insoluble in most common organic solvents, soluble in dimethyl sulfoxide. The apparent molecular weight, determined by freezing point depression of dimethyl sulfoxide, is 217 ± 7, as average of four values of two independent determinations. This value is not a whole-numbered multiple of the formula weight of the BH_2NH_2 unit, which is 28.86. The X-ray powder diffraction photograph of the substance showed diffuse, weak bands; however, when recovered from dimethyl sulfoxide, it has precisely the same powder pattern as cyclopentaborazane. The substance is thermally
stable in vacuo to about 170°C; at this temperature it begins to lose hydrogen and attains a slightly yellow color.

The mixture of the lower cycloborazanes, ammonia-borane, and the unknown species was separated by a series of vacuum sublimations, following the same procedure and facing the same difficulties as described in section II.F.2. for the separation of the essentially same mixtures obtained in the course of the synthesis of cycloborazanes. The fraction of enriched cyclodiborazane obtained by the technique described was mechanically separated from the other deposits by carefully scraping the substance out of the glass joint. Cyclodiborazane adheres loosely to the glass wall, while ammonia-borane adheres much more tenaciously. The yield of cyclodiborazane (of at least 85 per cent purity) was about five milligram per gram of pyrolized cyclopentaborazane. The contaminant was ammonia-borane.

The amount of the unknown crystalline substance formed was so small that recovery seems to be out of the question at present. By comparing the relative intensities of lines in the X-ray powder diffraction photographs of sublimed samples it was found, however, that this species is more volatile in vacuo than ammonia-borane. The smallest molecular entity conforming to this observation would be ammonia(N-B)aminoborane, $\text{H}_2\text{NBH}_2\text{NH}_2$, which, on account of its lower dipole moment, would be expected to be of higher volatility than ammonia-borane. Monomeric aminoborane, $\text{BH}_2\text{NH}_2$, is unstable at room temperature (section II.H.). The characteristic lines of the unknown substance in the X-ray
The residues of the pyrolysis experiments, and the non-volatile fractions collected in the liquid nitrogen trap were not investigated.

H. Pyrolysis of cyclodiborazane

The purpose of these experiments were to find out whether the isosteric analog of cyclobutadiene in the boron-nitrogen system, \((\text{BHNH})_2\), can be obtained by dehydrogenation of cyclodiborazane, \((\text{BH}_2\text{NH}_2)_2\), which itself represents the inorganic analog of cyclobutane. Because only small amounts of material were available for this investigation, the results must be considered
of an indicative nature only. No evidence for the existence of the cyclobutadiene analog was found; instead, the mass-spectroscopic analysis of the decomposition products strongly indicated formation of the unstable monomeric aminoborane, BH₂NH₂, with symmetrical cleavage of the cyclodiborazane molecule.

The apparatus shown in Figure 11 was used. Cyclodiborazane, placed in the bent-down end at the left hand side of the apparatus, was sublimed in vacuo into a zone of elevated temperature. The decomposition products were trapped at liquid nitrogen temperature in a U-trap connecting the apparatus to the vacuum system. Both the sublimation temperature and the temperature of the pyrolysis chamber were found to be mutually dependent, because the region of elevated temperature constituted, in effect, a barrier in the sublimation path of cyclodiborazane. In order for the compound to sublime against this barrier, the sublimation temperature had to be raised to a level governed by the temperature of the heat barrier. With a temperature of the pyrolysis chamber of 135°C, cyclodiborazane sublimed at about 80°C. When the temperature of the heat barrier was raised to 170°C, cyclodiborazane did not sublime, but decomposed at about 95°C without leaving the sublimation tube.

Accordingly, the procedure was as follows, cf. Figure 11. First, the temperature of the sand bath heating the pyrolysis chamber was raised to about 130°C, keeping the sublimation tube containing the substance cool with a bath of ice water. When the pyrolysis chamber had attained the desired temperature, the trap
was filled with liquid nitrogen, and the ice water was replaced by a glycerin heating bath. The temperature of the glycerin bath was adjusted to about 80°C, that of the pyrolysis chamber to 135°C. A window in the aluminum foil cover at the position of the substance allowed observation of the rate of disappearance of cyclodiborazane. An amount of 20 mg of cyclodiborazane was pyrolyzed in the course of two hours. Ammonia-borane, contaminating the sample, was not decomposed under these conditions. It was deposited, in pure form, in the glass tubing leading from the hot chamber to the liquid nitrogen trap.

Two mass spectra, recorded in Table 10, were taken of the volatile products of thermal decomposition of cyclodiborazane. The first spectrum, shown in column I of Table 10, was obtained from a sample which had never been subjected to a temperature higher than —78°C. The second spectrum, shown in column II, was obtained from the same sample immediately after it had been allowed to reach room temperature.

Although not all peaks of significant intensity could be assigned, some peaks and their change with temperature provided important clues. The peaks at mass number 2 show that little hydrogen was present in the cooled sample, but that a considerable amount of this gas was produced on warming. The peaks centered around mass number 28, which is the peak of highest relative intensity in both spectra, are readily assigned to the monomeric aminoborane species, BH₂NH₂, and its dehydrogenated fragments. As expected, the relative intensity of these peaks
TABLE 10

MASS SPECTRA OF PYROLYSIS PRODUCTS OF \((BH_2NH_2)_2\)

<table>
<thead>
<tr>
<th>Mass</th>
<th>I</th>
<th>II</th>
<th>Type of peak</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>0.53</td>
<td>30.7</td>
<td>H_2</td>
</tr>
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</table>

Sensitivity for base peak, in divisions per micron: 28, 171.0.
decreases on warming to room temperature. The relatively intense peak at mass number 45 can be interpreted as originating from the opened cyclodiborazane ring after abstraction of a BH$_2$ group.

From these observations it is concluded that monomeric aminoborane, BH$_2$NH$_2$, is obtained as one of the major products of thermal decomposition of cyclodiborazane, and that this compound is stable at -78°C, but decomposes spontaneously at room temperature with evolution of hydrogen.
III. DISCUSSION

A. Cleavage of diborane

The reactions of diborane with Lewis bases have been divided into two classes involving symmetrical (I) and unsymmetrical (II) cleavage, respectively, of the diborane molecule (44).

(I) \[ \text{H}_2\text{B} - \text{BH}_2 \rightarrow \text{BH}_3 + \text{BH}_3 \]

(II) \[ \text{H}_2\text{B} - \text{BH}_2 \rightarrow \text{BH}_2^+ + \text{BH}_4^- \]

Unsymmetrical cleavage of diborane was first recognized in the reactions with ammonia to give diammoniate of diborane (5), and with lithium amide to give aminoborane (23), and was then considered anomalous. More examples of unsymmetrical cleavage are now known: dimethyl sulfoxide (45), monomethylamine, and, to a lesser degree, dimethylamine (46), also split diborane unsymmetrically. The cycloborazanes are indirectly products of the non-symmetrical cleavage of diborane, since they are derived from the diammoniate of diborane. It should be emphasized that this classification is based solely on the nature of the products found and does not imply information as to the mechanism of these reactions which is still, to some degree, a matter of
speculation. Although the nature of the "electron deficient" hydrogen bridge bond is theoretically understood, an operational concept for the interpretation of reactions involving such bonds is still lacking.

It is believed that the reactions of diborane with Lewis bases proceed in two steps, with successive cleavage of the two hydrogen bridges (26, 47). The first step leads to the intermediate formation of species containing a single hydrogen bridge, according to

$$B_2H_6 + :X \rightarrow H^+_2B-H-BH_3 \quad X$$

The existence of single-bridged structures of this kind has been demonstrated for the one-to-one adducts of pyridine and triethylamine (= X) with diborane (48). Cleavage of the bridge in this intermediate structure is expected to be governed by inductive and steric effects. Depending on the nature of the base, two limiting situations with respect to the distribution of the two electrons in the remaining bridge can be visualized: (a) the electrons are distributed symmetrically between the boron atoms; in this limit the attack of the second base molecule would be directed by steric circumstances only, leading most likely to symmetrical cleavage of the diborane molecule. (b) the electrons are localized between the bridge hydrogen and the borane (3) group, whereby, in effect, the ion pair $[BH_2(base)]^+[BH_4]^-\text{ is approached;}$ in this case, the second base molecule is expected to complete the quarternization of the cationic boron species with
formation of the base coordinated dihydroboron(1\(^+\)) ion

\[ \text{[BH}_2\text{.(base)}\text{]}^+ \]

The influence of steric effects is illustrated by the recent observation (46) that the reaction of diborane with monomethylamine leads almost exclusively to unsymmetrical cleavage of diborane, whereas in the reaction with dimethylamine products of both symmetrical and unsymmetrical cleavage are found. While ammonia cleaves diborane unsymmetrically, the reaction with tetrahydrofuran leads to symmetrical cleavage only (49, 50).

The diammoniate of diborane probably owes its exclusive formation in the reaction between diborane and ammonia to the particular stability of the diamminedihydroboron(1\(^+\)) ion, \[ \text{[BH}_2\text{(NH}_3\text{)]}_2^+ \], and other reactions between diborane and Lewis bases may also be discussed in terms of the relative stability of the respective base coordinated dihydroboron(1\(^+\)) ions involved. This is illustrated by the observation that tetrahydrofuranylborane, which has been shown to have the symmetrical constitution \[ \text{THF\cdotBH}_3 \] (49, 50), reacts with ammonia with formation of products of both symmetrical (ammonia-borane) and unsymmetrical (diammoniate of diborane) cleavage of diborane (section II.E.). To account for the formation of the diammoniate under these conditions it is thought that the hypothetical reaction intermediate (\(\text{NH}_3\text{\cdotBH}_3\text{\cdotTHF}\)) releases a hydridic hydrogen to form the base coordinated dihydroboron(1\(^+\)) ion \[ \text{[NH}_3\text{BH}_2\text{THF]}^+ \], which leads to the diammoniate cation on substitution of tetrahydrofuran by ammonia. For an essentially similar transition state,
(py**BH**OHR), encountered on solvolysis of pyridine–borane with 1-propanol, a certain relative stability has been postulated (51).

The unexpected appearance of diammoniate of diborane on decomposition of ammonium hydroborate, formed as the main product from the solid (16), and in about 50 per cent yield in ether solution (13), lends further support to the view that the base coordinated dihydroboron(1+) ion plays a preferred role in these systems.

Finally, it is of interest to note that the strongest band in the infrared spectrum of diborane is attributed to the vibrational mode, at about 1600 cm⁻¹, arising from a large change in dipole moment of the molecule; in the limits of this vibration the species BH₂BH⁻ and BH⁻BH₂⁺ are approached, indicating that "these structures can no doubt make a considerable contribution to the state of a suitably distorted molecule" (40).

B. The reaction of sodium amide with diammoniate of diborane

The reaction between diammoniate of diborane and strong bases like sodium amide in liquid ammonia, according to the overall equation

\[ [\text{BH}_2(\text{NH}_3)_2][\text{BH}_4] + \text{NaNH}_2 \rightarrow \frac{\text{NH}_3}{l} (\text{BH}_2\text{NH}_2)_n + 2 \text{NH}_3 + \text{NaBH}_4, \]

is believed to proceed as follows. The strongly basic amide ion abstracts a proton from the coordinated ammonia molecule of
the diamminedihydroboron(1+) cation to form ammonia(N-B)aminoborane, \( \text{H}_3\text{NBH}_2\text{NH}_2 \):

\[
\text{H}_3\text{NBH}_2\text{NH}^+ + \text{NH}_2^- \rightarrow \text{H}_3\text{NBH}_2\text{NH}_2 + \text{NH}_3
\]

This species undergoes polymerization with loss of ammonia in the following manner:

\[
\begin{align*}
\text{H}_3\text{N-BH}_2\text{NH}_2 & \quad \text{t} \\
\text{H}_2\text{N-BH}_2\text{NH}_3 & \rightarrow \text{NH}_2\text{BH}_2\text{NH}_2\text{BH}_2\text{NH}_3 + \text{NH}_3,
\end{align*}
\]

producing higher ammonia(N-B)aminoboranes which subsequently cyclize with elimination of the remaining ammonia molecule:

\[
\text{H}_3\text{N(BH}_2\text{NH}_2)_n \rightarrow (\text{BH}_2\text{NH}_2)_n + \text{NH}_3
\]

Some details about this mechanism can be deduced from the following observations. The main product from all reactions is cyclopentaborazane, with the remaining cycloborazanes formed in only a few per cent yield. The cyclization step precludes further polymerization, as exemplified by the fact that the cycloborazanes are stable entities in liquid ammonia. Cyclopentaborazane, which is only slightly soluble in liquid ammonia, precipitates slowly from the reaction solutions, becoming noticeable only after several hours. Sodium amide, which is insoluble in liquid ammonia, disappears rapidly when added to the ammonia solution of diammoniate of diborane. This information suggests that the formation and subsequent association of ammonia(N-B)aminoborane in liquid ammonia is rapid, producing chains which contain predominantly five aminoborane units, whereas the cyclization with elimination of ammonia must be a relatively slow step.
Prolonged waiting periods, on the other hand, did not increase the yield of cycloborazanes, regardless of whether precipitation of cyclopentaborazane had occurred or not. Some experiments indicated a somewhat higher yield of cyclotriborazane in reaction mixtures which were recovered from the clear ammonia solutions within a few hours after introduction of diborane had been completed. Generally, the reaction solutions were kept at -78°C for about 12 hours before they were frozen for the removal of ammonia by vacuum sublimation (section II.F.1).

A study undertaken in this laboratory (52), in which the reaction

\[ \text{KNH}_2 + [\text{BH}_2(\text{NH}_3)_2]\text{Cl} \xrightarrow{\text{NH}_3(t)} \text{BH}_2\text{NH}_2 + \text{KCl} + \text{NH}_3 \]

was followed by measuring the freezing point depression of the liquid ammonia solution as a function of time, confirmed these views and showed, in particular, that the molecular weight approaches the value for the pentameric aminoborane long before precipitation of cyclopentaborazane is observed.

If it is assumed that the slow cyclization of pentameric aminoborane with elimination of ammonia precedes the visible formation of precipitate, then an abrupt decline in stability or probability of formation of higher ammonia(N–B)aminoboranes than those containing five units must be concluded, since, according to this mechanism, there should be ample opportunity for further chain build-up. No indication for the existence of cycloborazanes higher than cyclopentaborazane was found, and it
is unlikely that other reactions produce open-chain aminoboranes of higher molecular weight (6).

The low over-all yield of cycloborazanes found on introduction of diborane into a suspension of sodium amide in liquid ammonia (section II.F.1.) can be rationalized by taking into consideration the fact that sodium amide reacts with low molecular weight aminoboranes. This has been shown for the cases of cyclodiborazane and ammonia-borane (section II.F.2.). Cyclopentaborazane is stable in the presence of sodium amide, as was found in experiments in which an excess of amide was maintained throughout the reaction. The fact that the yield of low molecular weight cycloborazanes was always small, regardless of reaction conditions, may be due to this side reaction.

It is not known why the yields of cyclic aminoboranes, found in experiments in which sodium amide prepared with the use of diolefins (section II.B.2.) was used, were erratic. Even when no cyclic products were found, the amide had quantitatively reacted to form sodium hydroborate, indicating that at least the lowest ammonia(N-B)aminoborane had been formed. Since the products of such reactions displayed the general characteristics of open-chain aminoboranes (section III.C.), it is assumed that the process of association to higher ammonia(N-B)aminoboranes, too, was not inhibited in these reactions. It must, therefore, be concluded that the last step, cyclization with elimination of ammonia, is not only slow, but also critically dependent on the absence of certain polymeric or unsaturated organic materials.
C. Cyclic versus open aminoboranes

The information available through earlier work (discussed in section I.A.4.) and this investigation indicates the existence of two distinct classes of unsubstituted aminoboranes, the cycloborazanes and the less well defined open-chain aminoboranes.

Cyclic structures are accepted for the cycloborazanes described in the body of this dissertation on the basis of the following criteria. The analytical data show ratios of constituents in accordance with the composition BH₂NH₂, precluding the possibility of endgroups such as -BH₃. Preliminary B¹¹-NMR studies indicate equivalent boron atoms. The relatively inert character of these compounds with respect to protolysis, indicating quarternary boron moieties, and the absence of further polymerization once the species are formed, are also consistent with cyclic structures.

In addition, the cycloborazanes are crystalline solids which display characteristic X-ray powder diffraction patterns and infrared spectra. The lower members sublime in vacuo at characteristic temperatures.

In contrast to the characteristics of these compounds, the open aminoboranes are amorphous substances, yielding no X-ray powder diffraction patterns, which do not sublime and lose hydrogen at room temperature or on slight warming. The latter property is consistently mentioned in the older literature, testifying to the presumption that the reported substances belong to this class of aminoboranes. Chemical analyses and molecular
weight determinations do not give unambiguous results, because it has, apparently, never been possible to isolate a pure aminoborane chain for identification. The data available show, however, that these compounds are not highly polymeric, as has been assumed widely in the literature, but consist of the order of four aminoborane units (6). The compounds are easily protolized by water and methanol, and are hygroscopic.

That the open aminoboranes produced by various reported reactions do indeed belong to one class of related substances is suggested by the observation that the infrared spectra of three non-crystalline aminoboranes of independent origin were found to be essentially identical. The aminoboranes under consideration originated from: (a) the reaction of diborane with lithium amide in ether (6); (b) the reaction of diammoniate of diborane with certain types of sodium amide in liquid ammonia (section II.F.1.); (c) the decomposition of the substance tentatively identified as aminoborane(N-B)borane, BH₂NH₂BH₃ (section II.G.2.). The infrared absorption bands are listed in Table 11.
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<th>Frequency, cm⁻¹</th>
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<td>S</td>
</tr>
<tr>
<td>2380-2280</td>
<td>S, br</td>
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<tr>
<td>1575</td>
<td>M</td>
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<tr>
<td>1405</td>
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<td>S, br</td>
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<tr>
<td>1050</td>
<td>sh</td>
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<tr>
<td>880</td>
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</tbody>
</table>

\(^a\)Intensities: S = strong; M = medium; W = weak; br = broad; sh = shoulder.

Generally, the spectrum is not as sharp as are those of the cycloborazanes. The absorption band in the region of 2380 to 2280 cm⁻¹, representing the unresolved symmetric and asymmetric BH₂ stretching frequencies, is identical with the corresponding band observed in the spectra of cycloborazanes.

In conclusion, it is of interest to note that recent work in the related field of borazynes of empirical composition XB = NY also lead to the discovery of both well-defined cyclic compounds and less well characterized polymeric, presumably linear (53) species. In addition to the well-known cyclic trimers, that is, borazines, derivatives of cyclic dimeric (54) and tetrameric (55) borazynes have been reported recently. A pentameric cycloborazyne is still unknown.
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