trimethyl borate. The same results were obtained when the BCl_3 was allowed to react with equimolar amounts of the two bases thoroughly premixed in the nmr tube and when $S(CH_3)_2$ was allowed to displace the $O(CH_3)_2$ from an equimolar amount of $(CH_3)_2OBCl_3$. The distribution of the adducts was determined through the use of B^{11} nmr.

Homogeneous Displacement Reaction with BF_3. Equimolar amounts of $P(CH_3)_3$ and BF_3 were measured in the vacuum system and distilled into a 15-mm nmr tube containing CH_2Cl_2 solvent and a 5-mm tube containing trimethyl borate to be used as an external standard. The contents were allowed to warm, and the adduct, $(CH_3)_3PBF_3$, formed and went into solution. This solution was quickly frozen and an equimolar amount of $N(CH_3)_3$ was distilled into the cold tube. A typical reaction involved approximately 2 mmoles of all reactants. The nmr tube was then sealed with a torch and the contents were kept frozen until the B^{11} nmr spectrum could be obtained. The tube was then warmed and the spectrum was obtained immediately.

Nuclear Magnetic Spectroscopy. All B^{11} nmr spectra were obtained using a Varian HR-60 high-resolution spectrometer. The spectra were obtained from samples in 15-mm tubes and were calibrated by use of side bands of known frequency separation from a standard resonance signal due to an external reference of

trimethyl borate. Proton spectra were obtained with a Varian A-60 spectrometer. The concentration of adduct in the nmr sample varied with the reference acid. For borane and BF_3 adducts the concentration range was 0.4–1.5 M. For all other acids the concentration range was 0.1–0.2 M.

Infrared Spectroscopy. Infrared spectra were obtained in the gas phase using a cell with windows of Eastman Kodak's infrared transmitting optical material, IRTRAN-4. Spectra were obtained in solution using matched liquid cells with NaCl windows. The Perkin-Elmer 237 recording grating spectrometer was used.

Low-Temperature Boron-11 Nuclear Magnetic Resonance Spectra. The B^{11} nmr spectrum of $(CH_3)_2OBH_3$ was obtained in $(CH_3)_2O$ solvent at temperatures ranging from -25 to $-85°$. An external reference of $(CH_3O)_3B$ was placed in the tube used to obtain the spectrum. The reference signal could not be seen at temperatures below $-30°$ because trimethyl borate is frozen below this temperature. The spectrum of $\overline{OCH_2CH_2OBHN(CH_3)_3}$ was obtained at $-25°$ using $BF_3O(C_2H_5)_2$ as an external reference.

Boron–Nitrogen Chemistry. I. Syntheses and Properties of New Cycloborazanes, $(BH_2NH_2)_n$ [1,2]

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Contribution from the Evans Laboratory of Chemistry, Ohio State University, Columbus, Ohio 43210. Received April 23, 1966

Abstract: Cyclic species, cycloborazanes, of composition $(BH_2NH_2)_n$ have been synthesized by the reaction of $NaNH_2$ with $BH_2(NH_3)_2{}^+BH_4{}^-$ in liquid ammonia. Rings with $n = 2$, 3, and 5 have been isolated; evidence is also cited for the formation in small amounts of $(BH_2NH_2)_4$. Infrared, X-ray powder diffraction, and molecular weight data provide evidence for unique species. The principal cyclic product of the synthesis is $(BH_2NH_2)_5$, while lower members are found in only small per cent yields. Under certain conditions $(BH_2NH_2)_2$ isomerizes to $(BH_2NH_2)_3$. Cycloborazanes are significantly more stable thermally and hydrolytically than chain-like $(BH_2NH_2)_n$ species.[2] Possible mechanisms of formation are considered. Evidence is given for the formation of monomeric BH_2NH_2 upon pyrolysis of cyclodiborazane.

The concept of isosterism between the atom groupings B–N and C–C, when introduced almost 40 years ago, implied the expectation that a relatively extensive "boron–nitrogen system" of compounds which are analogs of hydrocarbons should be forthcoming. With reference to the principal classes of aliphatic hydrocarbons, Wiberg subdivided the boron–nitrogen system into the three groups of amine boranes, empirical composition BH_3NH_3, aminoboranes, BH_2NH_2 (referred to as cycloborazanes when known to be cyclic), and borazines, BHNH.[4] Although most of the known unsubstituted boron–nitrogen compounds are indeed isosteric analogs of hydrocarbons, their number is still small and largely confined to cyclic structures.

The least well-known of the three groups are the unsubstituted aminoboranes of empirical composition

BH_2NH_2. Species of this composition had been encountered from the beginning of research in the boron–nitrogen system, and several reactions producing these materials have been reported.[5–9] The products were usually described as "highly polymeric, amorphous solids which split out hydrogen readily," and the composition of these "inorganic polyethylenes" was more often than not inferred from the stoichiometry of the reactions. Closer investigation of one of these materials[2] has indicated a chain-like structure consisting of three to four aminoborane units with end groups of uncertain nature.

The properties of the first truly characterized aminoborane, cyclotriborazane, $(BH_2NH_2)_3$, contrasted

(1) Presented in part at the 148th National Meeting of the American Chemical Society, Chicago, Ill., Sept 1964.

(2) Part II is concerned with chain-like $(BH_2NH_2)_n$ species. To be published.

(3) To whom inquiries should be directed.

(4) E. Wiberg, IUPAC, 16th Conference, Paris, 1957.

(5) H. I. Schlesinger, D. M. Ritter, and A. B. Burg, *J. Am. Chem. Soc.*, **60**, 2297 (1938).

(6) E. Wiberg, K. Hertwig, and A. Bolz, *Z. Anorg. Allgem. Chem.*, **256**, 177 (1948); E. Wiberg, A. Bolz, and P. Buchheit, *ibid.*, **256**, 285 (1948).

(7) G. W. Schaeffer and L. J. Basile, *J. Am. Chem. Soc.*, **77**, 331 (1955).

(8) G. W. Schaeffer, M. D. Adams, and F. J. Koenig, *ibid.*, **78**, 725 (1956).

(9) A. K. Holliday and N. R. Thompson, *J. Chem. Soc.*, 2695 (1960).

sharply with the earlier descriptions of BH_2NH_2 species. This compound, which was synthesized from borazine and first reported by Dahl and Schaeffer,[10] was subsequently isolated in this laboratory from mixtures obtained on reaction of the diammoniate of diborane with sodium acetylide in liquid ammonia.[11] It is crystalline and does not lose hydrogen unless heated to above 100°.

On the hypothesis that other cyclic aminoboranes (i.e., cycloborazanes) should exist and be well behaved, the reactions of diammoniate of diborane with strong bases in liquid ammonia have been investigated further. The results are presented in this paper.

Experimental Section

The usual precautions for working with moisture- and air-sensitive substances were observed.

Reagents. Sodium amide orginating from three different preparative methods was used: (a) prepared by catalytic action of iron(III) nitrate on a solution of sodium in liquid ammonia;[12] (b) iron-free sodium amide synthesized by reaction of diolefins (isoprene, 1,3-pentadiene) with sodium in liquid ammonia;[13] (c) iron-free sodium amide prepared as above, using 3-heptyne as oxidizing agent.[13]

Synthesis of Cycloborazanes. Two experimental routes were investigated. The apparatus is depicted in Figure 1. (a) Diborane, carried on a stream of N_2,[14] was introduced directly to a suspension of $NaNH_2$ in liquid NH_3, or (b) sodium amide was added after all of the B_2H_6 had been generated and passed into liquid NH_3. The latter procedure produced the most satisfactory yields of cycloborazanes and is described in detail.

In a typical synthesis, 1 mole of $NaNH_2$ (39 g) was placed in the bulb attached to the reaction flask (Figure 1). With stopcock A closed, the system was evacuated on the vacuum line, and about 700 ml of NH_3 was subsequently condensed in the flask at −78°. The diborane generator was charged with 1.5 moles of $LiAlH_4$ (57 g) and 2 lb of anhydrous ether, and 300 ml of $BF_3 \cdot Et_2O$ was introduced into the dropping funnel.

With the vacuum line closed to the pump, and with a slow stream of N_2 entering the dropping funnel, stopcock A was cautiously opened. When the entire system had reached atmospheric pressure the vacuum line was opened to a mineral oil bubbler. Diborane was then produced by the slow addition of $BF_3 \cdot Et_2O$ to the $LiAlH_4$ in the course of about 15 hr.

At increased rates of formation of B_2H_6 (governed by the rate of addition of $BF_3 \cdot E_2O$)[15] it became difficult to control the pressure in the reaction system owing to clogging of the frit by deposits of $BH_2(NH_3)_2{}^+BH_4{}^-$. A simple gas flowmeter of the "floating ball" type (0–2 ft³ of air/hr), situated in the nitrogen line leading to the apparatus, served as both a qualitative indicator for the rate of nitrogen flow and as a pressure gauge, guiding the adjustment of the rate of B_2H_6 generation.

When the preparation and transfer of diborane was complete, stopcock A was closed, and the pressure in the reaction flask was reduced to that of the NH_3 solution. $NaNH_2$ was then added in small portions to the magnetically stirred solution of $BH_2(NH_3)_2{}^+$-$BH_4{}^-$ in liquid NH_3. Throughout the course of addition of $NaNH_2$, the reaction flask and vacuum line remained closed to the pump except for the occasional removal of hydrogen gas produced in the reaction. A total of about 2 l. of H_2 was produced in a 1-mole scale reaction.

The clear solution (indicating that the ammonia-insoluble $NaNH_2$ had reacted) was stored at −78° for 12 hr before NH_3 was removed by vacuum sublimation.[12] When the yield of cyclo-
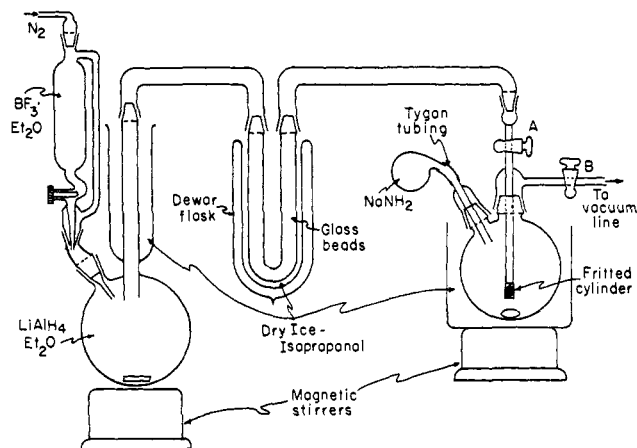
borazanes exceeded about 40%, a precipitate of $(BH_2NH_2)_5$ formed slowly; however, the yields were nearly the same regardless of whether the storage periods were extended.

Separation of the products of the synthesis reaction was carried out in the following manner. First, the mixtures were extracted twice with dry ether to yield from 0.5 to 1 g of material which was separated into two fractions by vacuum sublimation at 80°. In some cases, the residue after sublimation contained a crystalline species which is believed to be cyclotetraborazane; no means for further purification of this species are as yet available. The sublimate consisted of the cyclic species $(BH_2NH_2)_2$ and $(BH_2NH_2)_3$ along with some BH_3NH_3. By heating this mixture to 45° in vacuo $(BH_2NH_2)_2$ and BH_3NH_3 sublimed, and $(BH_2NH_2)_3$ remained behind.

The separation of $(BH_2NH_2)_2$ from BH_3NH_3 is difficult because both substances sublime in vacuo at almost the same temperature in the range of 30 to 35°. By means of repeated fractional microsublimations, $(BH_2NH_2)_2$ could be gradually enriched; however, these attempts were discontinued when it was discovered that relatively larger amounts of $(BH_2NH_2)_2$ of higher purity could be obtained through thermal decomposition of easily accessible $(BH_2NH_2)_5$.

The insoluble residue from the ether extractions was carefully freed of residual ether by subjecting it to high vacuum for 1 day at 50°. $(BH_2NH_2)_5$ was recovered by introducing the mixture in small portions to ice–water, in which the compound is only sparingly soluble while $NaBH_4$ is soluble and the other components are hydrolytically destroyed. The mixture was filtered and the solid portion dried on the vacuum line to yield lumps of material which were powdered and pumped upon again. About 1 l. of ice–water was required for each 3 g of solid material in order to remove completely $NaBH_4$ from the product. Purity was checked by observing the characteristic band of $NaBH_4$ at 2240 cm⁻¹ in the infrared spectrum. *Caution:* The use of contaminated (presumably oxidized) sodium amide leads to explosions. Furthermore, product mixtures of incomplete reactions which contain sizable fractions of unreacted $NaNH_2$ should be abandoned.

Analyses. A weighed sample (30 to 60 mg) was placed in a hydrolysis tube with a break-off tip, and the tube was evacuated on the vacuum line. Aqueous HCl (ca. 5 ml) was distilled into the tube and condensed at −196° in a layer above the analysis sample. The hydrolysis tube was sealed off and removed from the vacuum line, and then brought to a temperature of 160° for extended periods of time (up to 3 weeks in the case of cyclopentaborazane).

Following the hydrolysis period, the tube was cooled to −196° and opened to the vacuum line. Hydrogen was removed by a Töpler system and determined volumetrically. The hydrolysis residue was washed into a volumetric flask from which aliquots were withdrawn for the determination of nitrogen by the Kjeldahl method and of boron by base titration of the mannitol complex of boric acid.

Pyrolysis Experiments. (1) Cyclopentaborazane. On thermal decomposition in vacuo in the temperature range 125 to 145°, $(BH_2NH_2)_5$ lost 68% of its original weight with formation of several boron–nitrogen species. Of particular interest was the production of $(BH_2NH_2)_2$ free of BH_3NH_3, both compounds being formed in the process. The pyrolysis apparatus is shown in Figure

Figure 1. Apparatus for synthesis of cycloborazanes.

(10) G. H. Dahl and R. Schaeffer, *J. Am. Chem. Soc.*, **83**, 3032 (1961).

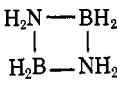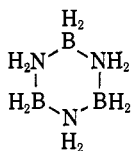(11) S. G. Shore and C. W. Hickam, *Inorg. Chem.*, **2**, 638 (1963).
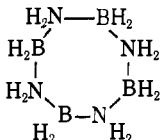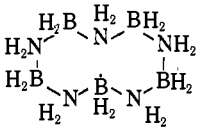
(12) K. W. Greenlee and A. L. Henne, *Inorg. Syn.*, **2**, 128 (1946).

(13) These samples were supplied by K. W. Greenlee, Chemical Samples Co., Columbus, Ohio. Since the synthesis required stoichiometric excess of hydrocarbon and, with diolefins in particular, produced some ammonia-insoluble polymeric material, iron-free sodium amide always contained up to 3% of organic residue.

(14) S. G. Shore and K. W. Böddeker, *Inorg. Chem.*, **3**, 914 (1964); S. G. Shore, K. W. Böddeker, and J. A. Patton, *Inorg. Syn.*, in press.

(15) I. Shapiro, *et al.*, *J. Am. Chem. Soc.*, **74**, 901 (1952).

Table I. Properties of Known Cycloborazanes

	Crystalline solids			
	H_2N-BH_2 $\vert \quad \vert$ H_2B-NH_2	$\underset{B}{\overset{H_2}{}}$ $H_2N{\diagup}\diagdown NH_2$ $\vert \qquad \vert$ $H_2B\diagdown\underset{H_2}{N}\diagup BH_2$	H_2N-BH_2 $H_2B\diagup\diagdown NH_2$ $\vert \qquad\qquad \vert$ $H_2N\diagdown\diagup BH_2$ $\underset{H_2}{B-N}\underset{H_2}{}$	$\underset{H_2B}{}\overset{H_2B}{}\overset{H_2}{N}\overset{BH_2}{}$ $H_2N\diagup\diagdown N \diagup\diagdown NH_2$ $H_2B\diagdown_{\overset{N}{H_2}}\diagup\overset{+}{B}\diagdown_{\overset{N}{H_2}}\diagup BH_2$
Mol wt				
Theory	57.7	86.5	115.4	144.3
Expt	58 ± 3^a	83 ± 1^b	123 ± 3^c	145 ± 4^c
Hydrolytic stability		Not readily attacked by water		
Thermal stability, °C	$>100°$	$>100°$	$>100°$	$>100°$
Solubility	Soluble in DMSO, ethers, NH₃, H₂O, CH₃OH, 1 g in 100 g of dioxane	Similar to (BH₂NH₂)₂	Less soluble in DMSO, NH₃, H₂O than in (BH₂NH₂)₃	Soluble in DMSO, 500 mg in 100 g of NH₃, 100 mg in 100 g of H₂O

ᵃ Cryoscopically in dioxane. ᵇ Cryoscopically in ammonia, also by single-crystal X-ray study (S. G. Shore, unpublished result). ᶜ Cryoscopically in dimethyl sulfoxide.

2. The aluminum foil wrapping effectively established a temperature gradient along which (BH₂NH₂)₂ and BH₃NH₃ were deposited next to each other in such a way that mechanical recovery of relatively pure (BH₂NH₂)₂ was possible. The (BH₂NH₂)₂ formed the first deposit and was recovered in at least 85% purity. About 5 mg was obtained per gram of pyrolyzed (BH₂NH₂)₅.
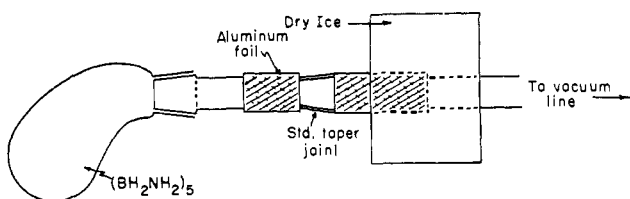

Figure 2. Apparatus for pyrolysis of cyclopentaborazane.

(2) Cyclodiborazane. (BH₂NH₂)₂ was subjected to pyrolysis, and the total mixture of volatile pyrolysis products was examined with the mass spectrometer. The procedure involved vacuum sublimation of (BH₂NH₂)₂ into a zone of elevated temperature and trapping the pyrolysis products at $-196°$ in a U trap connected to the vacuum system. The zone of elevated temperature constituted, in effect, a barrier in the sublimation path of (BH₂NH₂)₂, requiring that the sublimation temperature be raised to a level governed by the temperature of the heat barrier. With the pyrolysis chamber at a temperature of 135°, the substance sublimed at about 80°.

Results

The reaction of diammoniate of diborane with sodium amide in liquid ammonia was found to produce cycloborazanes, cyclic species of composition BH₂NH₂.

$(NH_3)_2BH_2{}^+BH_4{}^- + NaNH_2 \longrightarrow (BH_2NH_2)_n + NaBH_4 + 2NH_3$

Under the various conditions employed, the yields of cycloborazanes and the distribution of products differed widely. When iron-containing NaNH₂ or NaNH₂ synthesized by means of 3-heptyne was introduced to the solution of BH₂(NH₃)₂⁺BH₄⁻ in liquid NH₃, yields of cyclic products of at least 90% with respect to the amount of amide were found. The alternate procedure involving introduction of B₂H₆ to liquid NH₃ suspensions of these types of NaNH₂ gave yields of the order of 20%. The substantially lower yields of cyclic products in the latter procedure are a consequence of the fact that NaNH₂ reacts with the low molecular weight aminoboranes.

The results of experiments which employed NaNH₂ synthesized by means of diolefins proved to be irreproducible from batch to batch of amide, with yields of cyclic (BH₂NH₂)ₙ species ranging from 0 to 50%. However, these were the only experiments in which evidence was obtained for cyclotetraborazane. In all reactions cyclopentaborazane was produced in the largest proportion by far among the cycloborazanes, with yields of the order of 5% of cyclotriborazane and still smaller and varying yields of cyclodiborazane. Sodium borohydride was always a product of the reaction, as were small amounts of ammonia borane, BH₃NH₃, unreacted BH₂(NH₃)₂⁺BH₄⁻, and unidentified, presumably chain-like, aminoboranes.

Characterization of Products. Physical constants and stability data for the known cycloborazanes are summarized in Table I.

Cyclodiborazane. The investigation of cyclodiborazane, the isosteric analog of cyclobutane, was hampered by the fact that only small amounts could be obtained from each preparation, and the product could not be completely freed of BH₃NH₃. A typical 1-mole reaction would yield about 100 mg of (BH₂NH₂)₂, most of which originated from pyrolysis of (BH₂NH₂)₅. The use of smaller quantities of reagents in order to effect about a tenfold dilution proved to increase greatly the percentage yield of (BH₂NH₂)₂, but the capacity of the apparatus precluded this technique as an effective means of preparing the product in large quantity.

Anal. Calcd for (BH₂NH₂)₂: H_{hyd}, 6.99; B, 37.49; N, 48.54. Found: H_{hyd}, 7.7, 7.5; B, 36.6, 37.3; N, 48.8, 48.2.

Cyclodiborazane is apparently thermodynamically unstable with respect to isomerization to the trimeric species, cyclotriborazane. On standing in solution (NH$_3$, CH$_3$OH, Et$_2$O) at room temperature, the dimer slowly transformed to the trimer. Sublimation of the pure dimer (40–45°) also resulted in partial transformation to trimer. The ^{11}B nmr spectrum of a solution of
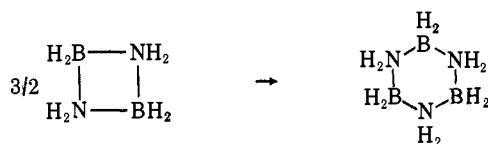
cyclodiborazane in methanol was obtained on a Varian HR-60 spectrometer at 19.25 Mc. The chemical shift of the 1:2:1 triplet for the BH$_2$ boron in the four-membered ring is indistinguishable from that for the boron in the six-membered ring (29.2 ppm relative to (CH$_3$O)$_3$B); however, no new species detectable by nmr spectroscopy developed on standing. Validity of the dimer–trimer transformation was affirmed by X-ray powder diffraction data, which likewise gave no evidence for the formation of other species in detectable quantities.

Cyclotetraborazane. The product believed to be cyclotetraborazane is at present the least well-defined of the cyclic (BH$_2$NH$_2$)$_n$ species. It dissolves in dimethyl sulfoxide; however it cannot be recovered from the solvent in its original form. Since it does not sublime *in vacuo* there are no readily available means for purification of this compound.

Cyclopentaborazane. The principal product of the synthesis, cyclopentaborazane, is a white, microcrystalline solid, which is extremely resistant to hydrolysis. Boiling water attacks it slowly, but complete reaction can be effected only by acid hydrolysis at 160° for an extended period of time. Cyclopentaborazane does not sublime *in vacuo*.

Anal. Calcd for (BH$_2$NH$_2$)$_5$: H$_{hyd}$, 6.99; B, 37.49; N, 48.54. Found: H$_{hyd}$, 7.07; B, 36.3; N, 47.0.

The X-ray powder diffraction patterns of the new cyclic (BH$_2$NH$_2$)$_n$ species are presented in Table II.

Infrared Spectra. Infrared data for the members of the cycloborazane series are recorded in Table III. The spectra 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. The broad absorption band found in the range of 2420 to 2300 cm^{-1} for all cycloborazanes is assigned to the symmetric and asymmetric BH$_2$ stretching modes.[16] This range is sufficiently low to be indicative of quaternary boron. For example the corresponding bands for the quaternary boron in NaBH$_4$ are found in the region of 2380 to 2150 cm^{-1},[17] whereas the symmetric and asymmetric stretching frequencies for the terminal BH$_2$ groups in diborane are at 2614 and 2522 cm^{-1}, respectively.[18] The absorption bands in the region of 1605 to 1558 cm^{-1} are assigned to the NH$_2$ deformation modes and

(16) W. C. Price, R. D. B. Fraser, and T. S. Robinson, *Discussions Faraday Soc.*, 9, 131 (1950).
(17) W. C. Price, *J. Chem. Phys.*, 17, 1044 (1949).
(18) W. C. Price, *ibid.*, 16, 894 (1948).

Table II. X-Ray Powder Diffraction Data for Cycloborazanes[a]

| (BH$_2$NH$_2$)$_2$ | | (BH$_2$NH$_2$)$_4$ | | (BH$_2$NH$_2$)$_5$ | |
d, A	Intensity[b]	d, A	Intensity	d, A	Intensity
6.83	ms	7.08	ms	4.38	m
5.28	s	5.94	s	3.80	vs
4.48	m	5.18	vw	2.87	w
4.39	s	4.48	m	2.188	m
4.08	w	4.20	w	2.108	vw
3.93	w	4.08	s	1.895	w
3.71	vs	3.93	vs	1.668	vw
3.28	mw	3.71	w	1.538	vw
3.14	w	3.52	w	1.433	vw
2.87	ms	3.24	vw	1.258	vw
2.69	m	3.03	m		
2.63	m	2.825	m		
2.520	w	2.347	mw		
2.276	m	2.227	m		
2.198	m	2.108	mw		
2.058	w	2.014	vw		
2.018	w	1.922	vw		
1.864	mw				

[a] Recorded on a Debye–Scherrer camera using Cu Kα radiation. For X-ray diffraction data on cylcotriborazane see ref 11. [b] S, strong; m, medium; w, weak; v, very.

show regularly changing features through the series, from a triplet with an additional shoulder for (BH$_2$NH$_2$)$_2$ to a single absorption band with a shoulder for (BH$_2$NH$_2$)$_5$. All the compounds, with the exception of (BH$_2$NH$_2$)$_3$, show a single absorption at about 1400 cm^{-1} which is tentatively assigned to the B–N stretching frequency.[19] For (BH$_2$NH$_2$)$_3$ an absorption at 1196 cm^{-1} has been assigned to this vibration.[20] None of the cyclic (BH$_2$NH$_2$)$_n$ species show absorptions of significance in the region of 800 to 700 cm^{-1}, which would be indicative of a (single) B–N dative bond.[21]

Table III. Infrared Spectra of Cycloborazanes[a]

| (BH$_2$NH$_2$)$_2$ | | (BH$_2$NH$_2$)$_4$ | | (BH$_2$NH$_2$)$_5$ | |
ν, cm^{-1}	Intensity[b]	ν, cm^{-1}	Intensity	ν, cm^{-1}	Intensity
3310	s	3328	s	3301	s
3264	s	3300	s	3250	s
2380–		3247	s	2420–	
2300	s	2400–		2300	s
1605	m	2345	s	1571	m
1585	m	1587	w	1412	m
1567	s	1558	m	1205	s
1385	s	1405	m	1087	m
1240	s	1241	s	1062	m
1202	s	1202	s	973	w
1140	s	1172	s	845	w
1065	m	1147	m	650	w
1048	m	1125	s		
394	w	1059	m		
820	w	874	w		
721	w	805	w		
693	w				

[a] Taken as KBr pellets on a Beckman IR-9 spectrophotometer. For infrared data on cyclotriborazane see ref 10. [b] S, strong; m, medium; w, weak.
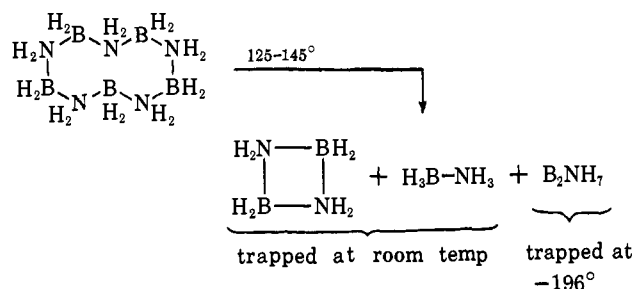
Pyrolysis Products. Thermal decomposition of cyclopentaborazane *in vacuo* proved successful as a

(19) G. E. Coates and J. G. Livingstone, *J. Chem. Soc.*, 1000 (1961).
(20) R. Schaeffer, "Research in Inorganic Polymer Systems," by contract with Wright-Patterson Air Force Base, 1962.
(21) R. C. Taylor, Advances in Chemistry Series, No. 42, American Chemical Society, Washington, D. C., 1964, p 59.

means of obtaining cyclodiborazane. Among other products which were formed, most of which could

$$\underset{\substack{\text{H}_2\text{B} \\ \text{H}_2}}{\overset{\substack{\text{H}_2\text{B} \\ \text{H}_2\text{N}}}{}} \quad \xrightarrow{125\text{-}145°}$$

H₂N—BH₂
| | + H₃B–NH₃ + B₂NH₇
H₂B—NH₂

trapped at room temp · trapped at −196°

not be unequivocally identified, were ammonia borane and a small amount of a highly volatile material trapped at −196°. This substance has a composition corresponding to B_2NH_7. It was found to decompose into diborane and solid aminoboranes in a ratio consistent with this formula in the temperature region of −160 to −140°, i.e., at a far lower temperature than μ-amino-diborane, which has this empirical formula but decomposes slowly into the same components above room temperature.[22]

Two principal species could conceivably be produced on thermal decomposition of cyclodiborazane: the isosteric analog of cyclobutadiene in the boron-nitrogen system, $(BHNH)_2$, through dehydrogenation, and/or monomeric aminoborane, BH_2NH_2, through symmetrical cleavage of the $(BH_2NH_2)_2$ molecule. The mass spectroscopic analysis of the decomposition products indicated formation of monomeric BH_2NH_2.

H₂N—BH₂   HN—BH
| | pyrolysis, 135° | | + 2H₂
H₂B—NH₂   HB—NH

H₂B–NH₂

monomer, trapped at −78°
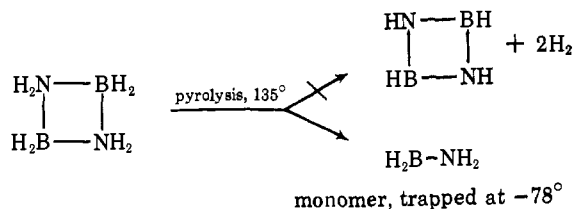
Two mass spectra were taken of the volatile products of thermal decomposition of $(BH_2NH_2)_2$. The spectrum obtained from a sample which had never been subjected to temperatures higher than −78° showed a negligible peak at mass 2 (hydrogen) while the peak of greatest intensity was at mass 28. This peak and those centered about it (27, 29) are readily assigned to the BH_2NH_2 species and its dehydrogenation fragments.

A spectrum taken of the same sample immediately after warming to room temperature showed a considerable amount of hydrogen and a marked decrease in the relative intensities of the peaks near mass 28. The data suggest that monomeric aminoborane, BH_2NH_2, can be obtained through thermal decomposition of $(BH_2NH_2)_2$ but decomposes spontaneously at room temperature with the evolution of hydrogen.

(22) The original reference to aminodiborane[5] discusses its properties and a tentative structure based upon the then accepted structure of diborane, analogous to that of ethane. Aminodiborane is in fact a bridged structure

H₂
H   N   H
 \ / \ /
  B   B
 / \ / \
H   H   H
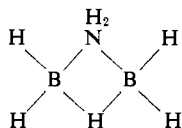
(K. Hedberg and A. J. Stosick, J. Am. Chem. Soc., 74, 952 (1952)).

Discussion

Reaction of Strong Bases with Diammoniate of Diborane. The reaction of diammoniate of diborane with strong bases like sodium amide in liquid ammonia, according to the equation below, is believed to proceed

$$(NH_3)_2BH_2{}^+BH_4{}^- + NaNH_2 \longrightarrow \frac{1}{n}(BH_2NH_2)_n + 2NH_3 + NaBH_4$$
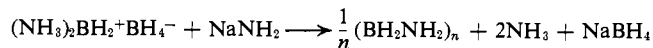
in the following way. The strongly basic amide ion abstracts a proton from the coordinated ammonia molecule of the diamminedihydroboron(1+) cation to form ammonia (N–B)aminoborane, $H_3NBH_2NH_2$. This species may undergo polymerization with loss of ammonia in the following manner
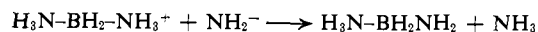
$$H_3N\text{–}BH_2\text{–}NH_3{}^+ + NH_2{}^- \longrightarrow H_3N\text{–}BH_2NH_2 + NH_3$$

cies may undergo polymerization with loss of ammonia in the following manner

H₃N–BH₂NH₂
     ↑   ⟶ H₂NBH₂NH₂BH₂–NH₃ + NH₃
H₂NBH₂–NH₃
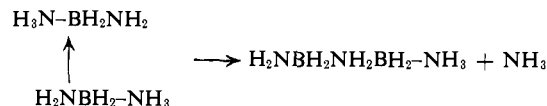
to produce higher ammonia (N–B)aminoboranes which subsequently cyclize with elimination of the remaining ammonia molecule.

$$H_3N(BH_2NH_2)_n \longrightarrow (BH_2NH_2)_n + NH_3$$
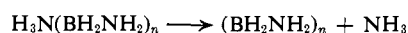
As an alternative to self-association with the loss of the ammonia molecule, the ammonia (N–B)amino-borane may attack the more electrophilic boron atom in the diamminedihydroboron(1+) cation and effect polymer buildup in the following fashion.

H₃N–BH₂–NH₃⁺
     ↑   ⟶ H₃N–BH₂NH₂BH₂–NH₃⁺ + NH₃
H₂NBH₂–NH₃
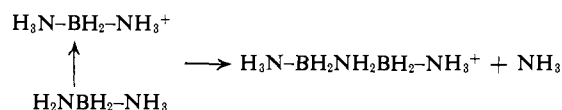
The polymeric cation may next lose a proton to an amide ion and subsequently extend itself via the above reaction or cyclize with the loss of an ammonia molecule.

Some details concerning the reaction sequence may be inferred from these observations: (1) sodium amide, which is insoluble in liquid ammonia, disappears rapidly when added to the ammonia solution of diammoniate of diborane; (2) the main product of all reactions is cyclopentaborazane, with the remaining cyclo-borazanes found in only small per cent yields; (3) the cyclization step precludes further polymerization, as exemplified by the fact that the cycloborazanes are stable entities in liquid ammonia.

This information suggests that the formation and subsequent association of the polymeric units is rapid, producing chains which contain predominately five B–N units. Indeed, a study of the freezing point depression of ammonia solutions of $(NH_3)_2BH_2{}^+Cl^-$ and KNH_2 has confirmed that an apparent molecular weight corresponding to a species of five B–N units is quickly approached.[23] Since cyclotriborazane is a stable species, an expectation of the unusually high yield of pentameric product is not implied by the suggested reaction schemes. Additional subtle factors are undoubtedly operative also. Likewise, there must be an abrupt decline in the stability or probability of forming polymeric chains of higher than five units, or the species must at this point be in an especially favorable situation for cyclization. No evidence for the

(23) J. A. Patton, M.S. Thesis, Ohio State University, 1965.

existence of cycloborazanes higher than the pentamer was found, and it is unlikely that other reactions[2] produce open-chain polymers of higher molecular weight. The precipitation of cyclopentaborazane from the reaction solution is evidently not attendant with the cyclization step, since yields of the pentamer did not differ substantially whether the solvent was removed before or after precipitation was observed.

It is not known why the yields of cyclic aminoboranes were erratic when the reaction was run with sodium amide prepared by the use of diolefins. Even when no cyclic products were found, the amide had reacted completely to form sodium borohydride which indicates that at least the lowest ammonia (N–B)aminoborane had been formed. It seems that the cyclization with elimination of ammonia must be critically dependent upon the absence of certain polymeric or unsaturated organic materials.

Cyclic vs. Open Aminoboranes. In conjunction with other work from this laboratory there appear to be two distinct classes of unsubstituted aminoboranes, the cycloborazanes and the less well-defined, open-chain aminoboranes. The new cycloborazanes $(BH_2NH_2)_2$ and $(BH_2NH_2)_5$ have been characterized, and evidence was obtained that $(BH_2NH_2)_4$ is also formed. Cyclic structures are accepted for the borazanes described here on the basis of the following criteria. The analytical data show ratios of constituents in accordance with the composition BH_2NH_2, which precludes the possibility of end groups such as $-BH_3$. The relatively inert character of these compounds with respect to protolysis, indicating quaternary boron moieties, is also consistent with cyclic structures. In addition, $(BH_2NH_2)_3$ is identical with the product obtained by Dahl and Schaeffer from borazine.[10]

Unique X-ray powder diffraction patterns and infrared spectra have been obtained for each member of the cyclic $(BH_2NH_2)_n$ series. By contrast, the open aminoboranes are amorphous and give no characteristic X-ray pattern, and their infrared spectra do not differentiate samples prepared by several different techniques.[2] The lower cycloborazanes sublime in vacuo at characteristic temperatures, while the amorphous materials of equivalent molecular weight do not sublime but lose hydrogen at room temperature or on slight warming.

The Alcoholysis of Polyphosphoric Acid

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Abstract: The reaction between polyphosphoric acid and several alcohols has been investigated. Product formation is clearly correlated to acid strength, with the fraction of phosphorus remaining as H_3PO_4 equal to $1/\bar{n}$ ($\bar{n}$ = the average chain length). Titrations and P^{31} nmr data indicate that the chains are cleaved randomly with respect to unsubstituted phosphorus.

Condensed phosphoric acid has many uses in organic synthesis[1] and is especially interesting as a phosphorylating agent because of the moderate conditions of the reaction and the relatively mild effects of the reagent compared to phosphorus pentoxide or other phosphorus intermediates. Currently there are available several compositions above 100% H_3PO_4, the properties of which vary as the strength of the acid increases.[2] The utility of these as phosphorylating agents may also be expected to vary. We therefore have explored the reaction between alcohols and condensed phosphoric acids to extend the rather limited information now available.[3,4] We attempt to develop a theoretical explanation for the observed behavior via a statistical approach.

Experimental Section

Reaction Conditions. All reactions were carried out under anhydrous conditions and without solvent. When the alcohol was a liquid, the reactants were mixed at room temperature; otherwise the alcohol was warmed to just above its melting point, and then added rapidly to the acid.

A moderate (10–30°) temperature rise was noted on mixing. When no further heat was evolved, the mixture was heated to temperatures ranging from 50 to 100°, and held there until titration indicated no further change in the relative amounts of the various kinds of phosphorus present.

While a number of esters were prepared, only those having a chain length of eight or more carbon atoms were isolated in pure form. Isolation procedures involved work-up with ether in the usual way.[4] Because of the relatively small influence of the hydrophilic phosphate group in the long-chain esters, some free alcohol was carried through the work-up to the final product. This is reflected in the elemental analyses of all but one of the purified materials (see Table I).

In addition to these purified materials, we have also studied, in greater detail, the reaction between polyphosphoric acid and n- and isobutyl alcohol. t-Butyl alcohol was dehydrated to isobutene on contact with polyphosphoric acid at room temperature.

(1) F. D. Popp and W. E. McEwan, Chem. Rev., 58, 321 (1958).
(2) J. R. Van Wazer, "Phosphorus and Its Compounds," Vol. I, Interscience Publishers, Inc., New York, N. Y., 1958, Chapter 12.
(3) E. Cherbuliez and H. Weniger, Helv. Chim. Acta, 29, 2006 (1946).
(4) A. K. Nelson and A. D. F. Toy, Inorg. Chem., 2, 775 (1953).