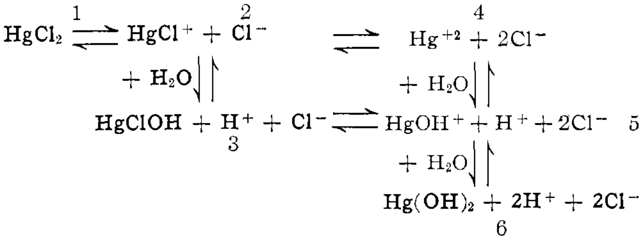
TABLE II

VALUES OF THE SPECIFIC RATE k_R FOR $HgCl^+ + Cl^- \rightarrow HgCl_2$ CALCULATED FROM THE DATA IN TABLE I AND EQ. 11

c_0, mole/l.	k_R, M^{-1} sec.$^{-1}$ ($K_1 = 3.3 \times 10^{-7}$)
9.8×10^{-3}	7.7×10^9
7.9×10^{-3}	7.6×10^9
3.9×10^{-3}	4.4×10^9

$K_1 = 3.3 \times 10^{-7}$ M, a value that follows directly from eq. 4 and 5. This value was not corrected for zero ionic strength. However, it may be more realistic than the corrected "thermodynamic" equilibrium constant,[8] which should be somewhat low due to neglect of HgOHCl in the determination of K (literature value). The values of k_R in Table II agree well with rate constants for similar reactions of Hg^{+2} compounds as well as with those for reactions of Pb^{+2} and Ba^{+2}, which were determined by means of other relaxation methods.[16] The most reliable values seem to be around 7×10^9 M^{-1} sec.$^{-1}$. The rate constants obtained from the above evaluation still may include some systematic errors as a consequence of the very approximative evaluation. The true reaction mechanism is not so simple that it can be represented by eq. 1. There is a coupling of reaction 1 with the hydrolysis steps, which may be represented by the scheme



Only the species indicated by bold types are present in appreciable concentrations. We may consider two limiting cases

(1) The major part of hydrolysis products is present in the form of $Hg(OH)_2$ rather than HgOHCl ($HgOH^+$ and Hg^{+2} are negligible anyway). Then the only step we have to consider is the equilibrium 1–2, as was done in the above evaluation. (The hydrolysis steps do not show an appreciable effect, since the stages 3, 4, and 5 are only present at negligible concentrations and there is no other coupling from 2 to 6.) The results for this single step equilibrium 1–2 are given in Table II.

(2) For the other limiting case we assume that the major part of hydrolysis products is present in the form of HgOHCl. Then we have $[H^+] = [HgOHCl]$. We get a coupling between 1–2 and 2–3, represented by a spectrum of two relaxation times which are related to the normal modes of the coupled system. From the rate equations and conservation conditions we obtain these relaxation times[17] as roots of the characteristic equation

$$\frac{1}{\tau_{1,2}} = -\frac{\alpha_{11} + \alpha_{22}}{2}\left[1 \pm \sqrt{1 - \frac{4(\alpha_{11}\alpha_{22} - \alpha_{12}\alpha_{21})}{(\alpha_{11} + \alpha_{22})^2}}\right] \quad (12)$$

with

$$\alpha_{11} = -\{k_{12} + k_{21}([HgCl^+] + [Cl^-])\}$$
$$\alpha_{22} = -\{k_{23} + k_{32}([HgClOH] + [H^+])\}$$
$$\alpha_{12} = -k_{21}[Cl^-]; \quad \alpha_{21} = -k_{23}$$

Only a relatively small fraction of the total field effect will be related to τ_1, which is governed by the hydrolytic rate constant k_{23} (as the largest quantity in $\alpha_{11} + \alpha_{22}$). The observed dispersion of the relatively large fraction of the field effect ($\tau \approx 10^{-6}$ sec.) is more likely to be associated with τ_2, which can be expressed simply as $-[\alpha_{11} - \alpha_{12}]$, since $\alpha_{22} \approx \alpha_{21}$ (both given by k_{23}) and $\alpha_{22}, \alpha_{21} \gg \alpha_{12}, \alpha_{11}$.

The quantity $-(\alpha_{11} - \alpha_{12}) = k_{12} + k_{21}[HgCl^+]$ is very similar to the relaxation time of the one-step system (eq. 1), as calculated above. In this case, however, we should expect two dispersion steps (of which the second at shorter times is relatively small). This seems to be indicated by the experimental value for $\omega\tau \approx 10$ in Fig. 1. As a consequence the relaxation time would be somewhat longer since the relative decrease of the amplitude in the first step occurs then at lower frequencies. This effect, however, compensates almost completely with shortening of the relaxation time $\tau = (k_{12} + k_{21}[HgCl^+])^{-1}$ as compared with eq. 2, $\tau = [k_{12} + k_{21}([HgCl^+] + [Cl^-])]^{-1}$, so that from both limiting cases almost the same rate constants result. Therefore a figure of 5×10^9 to 1×10^{10} M^{-1} sec.$^{-1}$ should be quite reliable for the rate constant of reaction 1. As mentioned above this figure agrees with values found for Pb^{+2} and Ba^{+2}. It is higher than for smaller divalent cations like Mn^{+2}, Co^{+2}, Mg^{+2}, but is about an order of magnitude lower than those found for protolytic or hydrolytic reactions (*i.e.*, reactions involving H^+ or OH^-) also determined from the dispersion of the dissociation field effect[5,18,19] found in those systems.

Acknowledgment.—E. M. E. is grateful to the National Science Foundation for a postdoctoral fellowship held in the course of this work.

---

[16] M. Eigen, G. Maass, and W. Kruse, unpublished data.

[17] *Cf.* M. Eigen and L. De Maeyer, in A. Weissberger, "Techniques of Organic Chemistry," 2nd Ed., Vol. VIII, Interscience Publ., New York, N. Y.

[18] M. Eigen and K. Kustin, *J. Am. Chem. Soc.*, **82**, 5952 (1960).

[19] M. Eigen and E. M. Eyring, *ibid.*, **84**, 3254 (1962).

CONTRIBUTION FROM THE EVANS LABORATORY OF CHEMISTRY,
THE OHIO STATE UNIVERSITY, COLUMBUS 10, OHIO

The Molecular Weight and Stability of Cyclotriborazane, $B_3H_6N_3H_6$, in Liquid Ammonia[1]

BY S. G. SHORE AND C. W. HICKAM

Received August 23, 1962

Dahl and Schaeffer[2] have reported the preparation of the analog of cyclohexane in the boron–nitrogen system, $B_3H_6N_3H_6$. This is the first compound of empirical

---

[1] Presented before the Inorganic Division at the 141st National Meeting of the American Chemical Society, Washington, D. C., March, 1962.

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

TABLE I

X-RAY POWDER DIFFRACTION DATA FOR CYCLOTRIBORAZANE[a, b]

Relative intensities[c]	d, Å.
s	6.14
s	5.57
w	4.42
vs	3.90
w	3.05
vw	2.80
vw	2.68
w	2.55
w	2.34
w	2.21
vw	2.15
vvw	1.80

[a] CuKα radiation was used. [b] These data were obtained from our samples and from a sample which was generously provided by Professor R. Schaeffer. The patterns were identical in every respect. However, agreement with the published pattern of Dahl and Schaeffer[2] was poor. Owing to systematic error, the values presented above supersede the published data. [c] v, very; w, weak; s, strong.

composition BH_2NH_2 to be studied in detail. In general species of such composition have been considered to be highly polymeric substances[3] and have not been well characterized. Although Dahl and Schaeffer were able to show that their compound was cyclic, their molecular weight data, from tensiometric techniques in liquid ammonia, were of unsatisfactory precision, giving a value of 83.5 ± 14; the possibility was considered that at the temperature of the molecular weight measurements the compound was unstable. An earlier investigation by Hornig, Jolly, and Schaeffer[4] had shown that a material of composition BH_2NH_2, apparently a trimer, would undergo polymerization in liquid ammonia to form an ammonia-insoluble substance.

We found that the reaction of the diammoniate of diborane with sodium acetylide in liquid ammonia produced two crystalline compounds of empirical composition BH_2NH_2.

$$BH_2(NH_3)_2BH_4 + NaC{\equiv}CH \longrightarrow BH_2NH_2 + NaBH_4 + HC{\equiv}CH + NH_3$$

One of these compounds was identical with Dahl and Schaeffer's as determined through comparison of X-ray powder diffraction photographs, Table I. However, this compound could not be obtained in greater than 15% yield. The second crystalline species of composition BH_2NH_2 was the predominant product. It proved to be less volatile than cyclotriborazane and was insoluble in ammonia, glyme, and diglyme. It was undoubtedly of higher molecular weight, though it was not necessarily highly polymeric.[5]

TABLE II

APPARENT MOLECULAR WEIGHT IN LIQUID AMMONIA

Solution	Molality (based on formula of $B_3H_6N_3H_6$)	Mol. wt.
1	0.140	83 ± 1
2	0.235	84 ± 2

It is of interest to note that in Dahl and Schaeffer's synthesis of cyclotriborazane they started with the six-membered borazine ring and assumed that it remained intact throughout the steps required to produce the desired product. On the other hand, in our study BH_2NH_2 units were produced which underwent self-association rapidly to produce the two different crystalline species.

In view of the low yield of cyclotriborazane which we obtained through the self-association of BH_2NH_2 units, and in view of the questions which were raised by Dahl and Schaeffer concerning the molecular weight and stability of their compound, we have supplemented their original observations through a study of the molecular weight and stability of cyclotriborazane in liquid ammonia.

Using a cryoscopic technique, we found the apparent molecular weight of cyclotriborazane to be in good agreement with the formula weight of 86.5.

As a test of the stability of this compound in the solid state, solution 1, Table II, was prepared from $B_3H_6N_3H_6$ which had been allowed to stand at room temperature under a dry nitrogen atmosphere for a period of 1 month. Solution 2, Table II, was prepared from a fresh sample of $B_3H_6N_3H_6$.

As a test of the stability of this compound in liquid ammonia, freezing point measurements were made on the freshly prepared ammonia solutions which were maintained at $-75°$ or lower, and on the same solutions after they had been allowed to stand for about 30 hr. at $-45°$. The molecular weights agreed, for each solution, within the precision cited above. Additional evidence for the stability of $B_3H_6N_3H_6$ is given by the fact that an ammonia solution which was allowed to stand at room temperature for 4 days showed no sign of a precipitate. Cyclotriborazane was the only crystalline species observed in the recovered solute.

Under the conditions of the observations cited above, it is apparent that cyclotriborazane is a stable entity; there is little or no tendency for this compound to be converted to another substance, either in the solid state or in solution, over an extended period of time. Therefore, it is concluded that the low yields of cyclotriborazane from our diammoniate of diborane–sodium acetylide reactions were not due to the conversion of this compound to ammonia-insoluble BH_2NH_2. It is further concluded that the apparent BH_2NH_2 trimer of Hornig, Jolly, and Schaeffer[4] which underwent polymerization in liquid ammonia was not cyclotriborazane.

Experimental

Preparation of $B_3H_6N_3H_6$ from $BH_2(NH_3)_2BH_4$.—Three moles of

---

(3) E. Wiberg and P. Buchheit, *Z. anorg. Chem.*, **256**, 285 (1948); H. I. Schlesinger, D. M. Ritter, and A. B. Burg, *J. Am. Chem. Soc.*, **60**, 2297 (1938); G. W. Schaeffer and L. J. Basile, *ibid.*, **77**, 331 (1955); G. W. Schaeffer, M. D. Adams, and F. J. Koenig, *ibid.*, **78**, 725 (1956).

(4) H. C. Horning, W. L. Jolly, and G. W. Schaeffer, Abstracts of Papers presented at the 131st National Meeting of the American Chemical Society, Miami, Florida, April, 1957, p. 4-R; W. Jolly, "Synthetic Inorganic Chemistry," Prentice-Hall, Inc., Englewood Cliffs, N. J., 1960, pp. 62–63.

(5) The properties of this compound and the reaction of $BH_2(NH_3)_2BH_4$ with strongly basic anions will be given in a future publication.

$BH_2(NH_3)_2BH_4$ was prepared[6] in a 25 × 300 mm. circular tube. To the tube was added 3 mmoles of $NaC{\equiv}CH$[7] under an atmosphere of dry nitrogen. The system then was evacuated and 15 ml. of liquid ammonia was distilled into the tube. The solution then was stirred, by means of a solenoid actuated spiral, for approximately 1 hr. at $-78°$. The appearance of ammonia-insoluble BH_2NH_2 was immediate. There seemed to be no slow induction period preceding the formation of this material. Ammonia then was distilled from the mixture onto sodium metal. The presence of $HC{\equiv}CH$ in the ammonia was demonstrated through the formation of $NaC{\equiv}CH$, which was identified through its X-ray powder diffraction pattern. The presence of $B_3H_6N_3H_6$, $NaBH_4$, and ammonia-insoluble BH_2NH_2 remaining in the reaction tube also was demonstrated through X-ray powder analysis. Cyclotriborazane was isolated from this reaction mixture through a sublimation procedure *in vacuo* at 120°. The yield of $B_3H_6N_3H_6$ was 15% of theory.

Anal. Calcd. for $B_3H_6N_3H_6$: B, 37.6; N, 48.6; H (hydridic), 7.00. Found: B, 37.9; N, 49.8; H (hydridic), 7.01.

Preparation of $B_3H_6N_3H_6$ from $B_3H_3N_3H_3$.—In order to obtain sufficiently large samples for the molecular weight studies, $B_3H_6N_3H_6$ was prepared through modification of the procedure of Dahl and Schaeffer.[2] $B_3H_3Cl_3N_3H_6$ was formed by bubbling excess HCl into a solution containing 10 moles of borazine[8] in diethyl ether at $-78°$. The ether was distilled away, leaving behind the solid hydrochloride adduct to which 35 mmoles of $LiBH_4$ was added. About 50 ml. of anhydrous ether, containing 5 ml. of glyme, was distilled into the flask. The system then was stirred at room temperature until B_2H_6 evolution ceased. Volatile materials then were distilled away, leaving behind the dry ether-free residue, which was placed on a frit and washed with ice-cold water. Cyclotriborazane is insoluble in water, and is unaffected by ice-cold water, *provided ether is absent*. A 90% yield of crude cyclotriborazane was obtained. It was purified for the molecular weight studies through extraction with liquid ammonia at $-75°$.

Molecular Weight Studies.—Molecular weights were determined cryoscopically. The apparatus used has been described briefly elsewhere.[9] Each molecular weight reported in Table II represents an average of eight separate cooling curves; four cooling curves were taken from the freshly prepared solutions and four curves were taken from the solutions which were aged at $-45°$.

Acknowledgment.—We wish to acknowledge, gratefully, the support of this work by the National Science Foundation.

---

(6) R. W. Parry and S. G. Shore, *J. Am. Chem. Soc.*, **80**, 15 (1958).

(7) K. W. Greenlee and A. L. Henne, *Inorg. Syn.*, **2**, 75 (1946).

(8) G. Dahl and R. Schaeffer, *J. Inorg. Nucl. Chem.*, **12**, 380 (1960).

(9) B. Z. Egan and S. G. Shore, *J. Am. Chem. Soc.*, **83**, 4717 (1961).

CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
GENEVA COLLEGE, BEAVER FALLS, PENNSYLVANIA

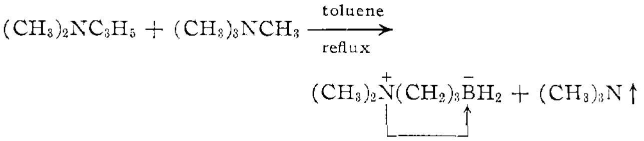
A New Type of Boron–Nitrogen Heterocycle

BY ROY M. ADAMS AND FRANK D. POHOLSKY

Received September 17, 1962

A recent review[1] on heterocyclic boron compounds includes no mention of a five-membered ring with one boron and one nitrogen. Initial attempts to prepare this type of heterocycle by the hydroboration[2] of allylamine resulted in polymer formation. Such a compound has now been prepared from N,N-dimethylallylamine.

The synthesis was successfully carried out by refluxing dimethylallylamine with trimethylamineborane in toluene.[3]



$$(CH_3)_2NC_3H_5 + (CH_3)_3NCH_3 \xrightarrow[\text{reflux}]{\text{toluene}} (CH_3)_2\overset{+}{N}(CH_2)_3\overset{-}{B}H_2 + (CH_3)_3N\uparrow$$

The toluene was removed at atmospheric pressure and the residue was distilled under vacuum. The fraction collected between 80 and 100° at 25 mm. was redistilled to give approximately 25% yields of 1,1-dimethyl-1,2-azaborolidine or cyclo-(N-B)-dimethylaminopropylborane; b.p. 85° (25 mm.).

Anal. Calcd. for $(CH_3)_2N(CH_2)_3BH_2$: C, 60.6; H, 14.2; N, 14.2; B, 11.0. Found: C, 60.6, H, 14.3; N, 14.6; B, 11.1.

The product is a colorless liquid with a boiling point of 185° at 745 mm. and a calculated heat of vaporization of 112 cal./g., indicating very strong intermolecular forces. Molecular weight determinations in benzene, cyclohexanol, and camphene indicated extensive association. This has been found to be characteristic of amineboranes and is attributed to the high dipole moments of such substances due to the formal charges on the nitrogen and boron.[4] However, the mass spectrum shows a cut-off at mass number 99 and the largest peak at mass number 98 which is in good agreement with the formula weight of 98.98. The infrared spectrum indicates a N–B bond and absence of C–C double bonds. The density at 25° is 0.8161 g./ml. and the index of refraction at 25° is 1.4538, leading to a molar refractivity of 32.84. This leads to a calculated value for the atomic refractivity of quaternary boron of 2.5, a value which has not been available previously. The freezing point is approximately $-25°$. The product is immiscible with water and miscible with ether and with toluene.

Attempts to carry out the hydroboration by the direct reaction of diborane with the amine in ethyl ether resulted in the initial formation of a colorless solid, which we were unable to isolate and purify and which we assume is the amineborane. When the ether was evaporated and the product warmed to approximately 120°, an uncontrolled reaction occurred which we believe involved internal hydroboration. Bennett and Skinner[5] have shown that the hydroboration reaction is very exothermic, evolving 136 kcal./mole of

---

(1) P. M. Maitlis, *Chem. Rev.*, **62**, 223 (1962).

(2) H. C. Brown, "Hydroboration," W. A. Benjamin, Inc., New York, N. Y., 1961.

(3) E. C. Ashby, *J. Am. Chem. Soc.*, **81**, 4991 (1959).

(4) H. Noth and H. Beyer, *Chem. Ber.*, **93**, 928 (1960). A referee has pointed out that the cyclic aminoborane trimers behave normally by cryoscopy (*cf.* T. C. Bissot and R. W. Parry, *J. Am. Chem. Soc.*, **77**, 3481 (1955); G. W. Campbell and L. Johnson, *ibid.*, **81**, 3800 (1959). These also have nitrogen and boron carrying formal charges, but due to symmetry have no net dipole moment such as would be expected for our compound.

(5) J. E. Bennett and H. A. Skinner, *J. Chem. Soc.*, 2472 (1961).