In the PAR molecule, the hydrogen atom of the 3-hydroxy group is bonded to the azo group, thereby forming a planar system in which there is maximum conjugation between the azo group and the resorcinol ring. The azo group therefore can exert its large electron-withdrawing effect on the 1-hydroxy group and increase its acid strength considerably. This is demonstrated by the comparison of the pK value of the 1-hydroxy group in the free PAR molecule (7.0) with that of the 1-hydroxy group in 4-(2-pyridylazo)-1-naphthol (p$K' = 10.7$).[12] In the latter compound there is less conjugation in the system and the azo group has a relatively small electron-withdrawing effect on the 1-hydroxy group.

The apparently anomalous position of the hydrogen chelate of PAR (p$K' = 7.0$) in the chelate-acidity series (Table I) may now be understood to arise from these considerations. The especially large acid-strengthening effect on the hydroxy group in the 1:1 Cu(II) chelate of PAR as well as on the hydroxy groups of the 1:2 cobalt PAR chelate may be caused by the excess positive charge on the chelates.

Acknowledgment.—The authors are grateful to the U. S. Atomic Energy Commission for financial assistance.

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CONTRIBUTION FROM THE
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Evidence for the Open Chain Structure of Ethane 1,2-Diamineborane[1]

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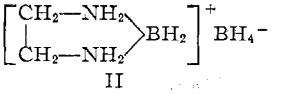
In a previous publication,[2] various aspects of the chemistry of a white crystalline compound, obtained by the reaction of diborane with ethylenediamine, were described. This product was named ethane 1,2-diamineborane on the assumption that the structure was represented by the open chain configuration (I). In view of the fact that Parry and co-workers[3] have shown that the "diammoniate of diborane" has an ionic structure, $[(NH_3)_2BH_2]^+BH_4^-$, structure II also was considered possible.

$H_3BNH_2CH_2CH_2NH_2BH_3$

I



$$\left[\begin{matrix}CH_2-NH_2\\ |\\ CH_2-NH_2\end{matrix}\!\!>\!BH_2\right]^+ BH_4^-$$

II

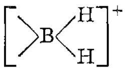
Structure I was favored on the basis of dehydrogenation data and solubility characteristics.

More recently, Goubeau and Schneider[4] reported the preparation of a compound from the reaction of ethylenediamine dihydrochloride with sodium borohydride in tetrahydrofuran. They postulated the "electrolyte" structure (II) for this product largely on the basis of its infrared spectrum.

We now report evidence which indicates that the compound prepared from diborane and ethylenediamine is identical with that obtained by the reaction of ethylenediamine dihydrochloride with sodium borohydride, and that this compound has the structure represented by configuration I.

Results and Discussion

The open chain structure of ethane 1,2-diamineborane has been confirmed by cryoscopic studies in water, and by means of the B^{11} nuclear magnetic resonance (n.m.r.) spectrum. The experimental value of 88 ± 7 molecular weight units is consistent with a monomeric species (I). The B^{11} n.m.r. spectrum, obtained in dimethoxyethane solution,[5] consists of a single boron resonance line split into a quadruplet having peaks of relative intensity 1:3:3:1. Thus, the two boron atoms are equivalent and each is bonded to three hydrogen atoms. The coupling constant of 88 c.p.s. agrees with J_{B-H} values reported for other amineboranes.[6] The B^{11} spectrum of a compound represented by structure II would consist of two boron resonance lines. One of these would be split into a triplet due to spin coupling between boron and two terminal hydrogens in the boronium species



$$\left[>B\begin{matrix}H\\ \\ H\end{matrix}\right]^+$$

The second would be split into a quintuplet due to the coupling of four hydrogen atoms with boron in the borohydride ion. The product of the ethylenediamine–diborane reaction is, clearly, ethane 1,2-diamineborane (I).

This assignment is consistent with solubility data, dehydrogenation data, and results obtained with thallium(I) salts. For example, the high solubility of ethane 1,2-diamineborane in tetrahydrofuran (46–47 g./l. of solution at 25°), 1,2-dimethoxyethane (90–91 g./l. at 27°), and bis-(2-methoxyethyl) ether (98–99 g./l. at 27°) relative to its solubility in water (8–9 g./l. at 27°) is in contrast to the solubility characteristics of the ionic compounds sodium and potassium borohydride.[7]

In addition, the liberation of two moles of hydrogen on thermal decomposition of one mole of starting material is consistent with the known dehydrogenation of

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[1] Taken from the Ph.D. thesis submitted by H. C. K. to Brown University, September, 1961.

[2] H. C. Kelly and J. O. Edwards, *J. Am. Chem. Soc.*, **82**, 4842 (1960).

[3] D. R. Schultz and R. W. Parry, *ibid.*, **80**, 4 (1958), and subsequent papers in this series.

[4] J. Goubeau and H. Schneider, *Ber.*, **94**, 816 (1961).

[5] E. L. Muetterties, personal communications, September 7, 1960; January 30, 1961.

[6] W. D. Phillips, H. C. Miller, and E. L. Muetterties, *J. Am. Chem. Soc.*, **81**, 4496 (1959).

[7] "Sodium Borohydride, Potassium Borohydride," Metal Hydrides, Inc., Beverly, Mass., March, 1958.

primary amineboranes to aminoborines,[8] and with the presence of two $-NH_2BH_3$ groups in the molecule.

Further, Waddington[9] has shown that the reaction of thallium(I) salts with aqueous alkaline borohydride solutions results in the precipitation of insoluble thallium(I) borohydride. The fact that this precipitate was not obtained on treatment of thallous acetate with ethane 1,2-diamineborane under comparable conditions is consistent with the absence of the borohydride ion in the latter compound.

The similarity in the chemical and physical properties and in the infrared spectra of ethane 1,2-diamineborane and the product of Goubeau and Schneider suggested that the two compounds were identical. Proof of the identity was obtained by synthesizing their compound from sodium borohydride and ethylenediamine dihydrochloride in tetrahydrofuran. The infrared spectrum of this compound could be superimposed on the spectrum of ethane 1,2-diamineborane. Also, the B^{11} n.m.r. spectrum of a sample of their compound in 1,2-dimethoxyethane solution consisted of a single line split into a quadruplet having peaks of relative intensity 1:3:3:1.[10] The two reported compounds are, therefore, one and the same, namely, ethane 1,2-diamineborane.

The synthesis of amineboranes by the reaction of borohydrides with amine salts has been known for some time,[11] and the formation of ethane 1,2-diamineborane by this method is not surprising. If, as Goubeau and Schneider imply, the infrared spectrum is indicative of a "gauche" conformation, then ethane 1,2-diamineborane exists in a "gauche" conformation in the solid at room temperature.

Experimental

Materials.—Ethylenediamine dihydrochloride was obtained from Eastman Kodak Company. Sodium borohydride of 98+% purity was obtained from Metal Hydrides, Inc. Tetrahydrofuran, obtained from Matheson, Coleman and Bell, was boiled under reflux over potassium hydroxide, following which it was refluxed over lithium aluminum hydride and distilled using a Widmer column, b.p. 65.5°. A commercial grade of 1,2-dimethoxyethane (Matheson, Coleman and Bell) was purified in the same manner, b.p. 85°.

Preparation of Ethane 1,2-Diamineborane.—The preparation from ethylenediamine and diborane has been described previously.[2] Preparation by the method of Goubeau and Schneider[4] involved stirring a suspension of 2.90 g. of sodium borohydride and 4.87 g. of ethylenediamine dihydrochloride in 500 ml. of tetrahydrofuran at room temperature under a stream of dry nitrogen. After 40 hr., the insoluble matter was removed by filtration, and the solvent removed from the filtrate to give 2.34 g. (73% of theory) of crude product. Purification by aqueous extraction and subsequent analysis of the product were carried out as previously described[2]; yield (purified), 1.63 g. (55% of theory).

Anal. Calcd. for $H_3BNH_2CH_2CH_2NH_2BH_3$ (87.9): H (hydridic), 6.89; B, 24.6; N, 31.9; pK_{enH_2}, 7.31. Found: H (hydridic), 6.76; B, 24.1; N, 32.1; pK_{enH_2}, 7.30.

Solubility Studies.—The solubility of ethane 1,2-diamineborane in various solvents was obtained by determining (by hydrolytic analysis) the hydridic hydrogen content of the amineborane contained in the corresponding saturated solutions.

Cryoscopic Measurements.—These were carried out by the method described by Daniels and co-workers.[12] Following a given determination of Δt_f, a 10-ml. sample of the aqueous solution was analyzed for hydridic hydrogen. The amount of ethane 1,2-diamineborane contained was calculated using the equation

$$\text{g. of en}(BH_3)_2 = \text{g. of H (hydridic)}/0.0689 \qquad (1)$$

For the product of the ethylenediamine–diborane reaction, molecular weight values obtained were 95, 83, 87; av. = 88. For the sodium borohydride–ethylenediamine dihydrochloride reaction product: 93, 88, 86; av. = 89. Calculated for ethane 1,2-diamineborane: 87.9.

Infrared Spectra.—Samples were prepared by compressing mixtures of the diamineborane and anhydrous potassium bromide into wafers. Spectra were obtained using a Perkin-Elmer, Model 137, Infracord T. M. spectrophotometer.

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