[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, CORNELL UNIVERSITY]

A Study of Dihydroxy-*n*-butylborane and its Anhydride[1]

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Physical and chemical properties of dihydroxy-*n*-butylborane ($C_4H_9B(OH)_2$), and its anhydride, 2,4,6-tri-*n*-butylboroxine ($(C_4H_9BO)_3$), have been studied. Data are included on molecular weight in solution, vapor density, vapor pressure, density, refractive index, and, for the latter only, viscosity, surface tension and freezing point. The equilibrium between the dihydroxyborane, boroxine and water is discussed.

Introduction

This study of dihydroxy-*n*-butylborane and 2,4,6-tri-*n*-butylboroxine[2] was undertaken because we felt that a more extensive investigation of the physical and chemical properties of such monoalkyl boranes was needed. Burg did somewhat similar work with the relatively volatile $CH_3B(OH)_2$ and $(CH_3BO)_3$.[3] The synthesis, characterization and general chemical behavior of dihydroxyalkylboranes have been discussed by Johnson, *et al.*[4,5] We chose to study $C_4H_9B(OH)_2$ and $(C_4H_9BO)_3$ because they seemed to represent a balance of properties: they are sufficiently non-volatile to be handled easily, are not difficult to protect from oxidation, and appear to be typical compounds of their respective classes.

Experimental

Preparation and Analysis.—Dihydroxy-*n*-butylborane was prepared, by the method of Snyder, Kuck and Johnson,[4] from methyl borate and *n*-butylmagnesium bromide.

For most purposes $C_4H_9B(OH)_2$ was purified by recrystallization from toluene, followed by washing with petroleum ether and drying in a vacuum desiccator. Further purification for vapor pressure measurements was accomplished by sublimation. Dehydration beyond the formula $C_4H_9B(OH)_2$ was avoided by keeping the subliming crystals at room temperature and condensing the sublimate at the temperature of laboratory cooling water.

Oxidation of $C_4H_9B(OH)_2$ was avoided during storage by immersing the crystals in water. Crystals which had been sucked dry and allowed to stand in laboratory air were slowly oxidized during a period of a week.

Analysis for carbon and hydrogen was done in a microtrain. It was necessary to cover the sample with CuO and to heat cautiously in order to avoid flashing. For boron analysis the best results were obtained with a modification of the peroxide method of Snyder, Kuck and Johnson.[6] It was found possible to omit the step in which the boron-containing sample was heated in a nickel crucible. As judged by repeated analysis of $C_4H_9B(OH)_2$, the standard deviation was about 0.04 in 10.6% boron.

The "content" of hydroxyl groups and boron oxide linkages was determined by titration with Karl Fischer reagent.[7] The esterification reactions

$$C_4H_9B(OH)_2 + 2CH_3OH = C_4H_9B(OCH_3)_2 + 2H_2O$$

$$(C_4H_9BO)_3 + 6CH_3OH = 3C_4H_9B(OCH_3)_2 + 3H_2O$$

are driven to the right by Karl Fischer reagent because the water which is liberated reacts quantitatively with the reagent. The "hydroxyl equivalent" is calculated as millimoles of water liberated per gram of sample.

Anal. Calcd. for $C_4H_9B(OH)_2$: C, 47.12; H, 10.88; B, 10.61; hydroxyl equiv., 19.6 mmoles/g. Found: C, 46.3, 46.4, 46.7, 46.8; H, 9.7, 10.1, 10.1, 10.0; B, 10.58, 10.55, 10.57; hydroxyl equiv., 19.6, 19.6.

2,4,6-Tri-*n*-butylboroxine was prepared by thermal dehydration of the dihydroxyborane. One method involved heating the latter in a bulb which could be opened to an evacuated system. At 120–140° the equilibrium in the bulb was largely in favor of the boroxine and water. By opening the connecting stopcock, most of the water was flash-distilled into the vacuum, leaving behind the relatively non-volatile boroxine. This process was repeated several times until the $(C_4H_9BO)_3$ which remained was pure.

Better yields were obtained by melting $C_4H_9B(OH)_2$ in the still-pot of a fractionating column under a pressure of 300–400 mm. of nitrogen. The temperature was maintained at 100–110° while the pressure was slowly reduced during an hour to about 10 mm. Water was drawn off, and some $C_4H_9B(OH)_2$ condensed in the still-head. The solid was washed out and the dehydration was completed by refluxing $(C_4H_9BO)_3$ for an hour at 130° and 10 mm. The yield was essentially quantitative.

Anal. Calcd. for $(C_4H_9BO)_3$: C, 57.24; H, 10.81; B, 12.89; hydroxyl equiv., 11.91 mmoles/g. Found: C, 57.1, 57.0; H, 10.8, 11.1; B, 12.8, 12.8; hydroxyl equiv., 11.93 (an infrared pattern of one preparation showed no trace of hydroxyl).

Since $(C_4H_9BO)_3$ reacted with oxygen and was rapidly attacked by water, it was vacuum distilled and sealed in breakable glass bulbs for storage until needed. When adequately protected it was stable indefinitely.

Molecular Weight in Solution.—For cryoscopic measurements an all-glass apparatus was used, similar to that described by Billings.[8] The Beckmann thermometer was inserted in a thin-walled well which was immersed in the solution. Stirring was accomplished by using an electromagnet intermittently to raise and lower a coil of steel wire. If desired the cell could be evacuated and then filled with a dry, inert atmosphere.

Three determinations of the molecular weight of $C_4H_9B(OH)_2$ in 0.074, 0.049 and 0.037 molal aqueous solutions gave values of 114.6, 111.0 and 106.7, respectively. The theoretical value is 101.9. Three approximately 0.02 molal solutions in benzene gave molecular weights of 106, 107 and 104.

Two measurements of the molecular weight of $(C_4H_9BO)_3$ in benzene gave values of 254 and 264, compared with the theoretical value of 252.

Vapor Density of $(C_4H_9BO)_3$.—The apparatus used was similar to that described later for the measurement of vapor pressure. On account of the high temperature needed for complete vaporization, an air furnace was used for heating the sample cell. In the temperature range 231–284° the molecular weight ranged between 247 and 256, compared with 252, the theoretical value. The lower values were obtained after cooling from 284°, which probably indicates some sort of slow, irreversible decomposition at this high temperature.

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[1] Based largely on theses submitted by Harold C. Mattraw (1950) and Charles E. Erickson (1953) in partial fulfillment of the requirements for the degree of Doctor of Philosophy. The major portion of the work was supported by the Office of Naval Research.

[2] The nomenclature used in this paper is essentially that recommended in a preliminary report on boron nomenclature (*Chem. Eng. News*, 560, Feb. 6 (1956)) replacing the terms "butaneboronic acid" and "butaneboronic oxide" which have been used in the past. "Boroxine" refers to a six-membered boron–oxygen ring believed to be characteristic of the trimeric dehydration products of dihydroxyboranes.

[3] A. B. Burg, THIS JOURNAL, **62**, 2228 (1940).

[4] H. R. Snyder, J. A. Kuck and J. R. Johnson, *ibid.*, **60**, 105 (1938).

[5] J. R. Johnson, M. G. Van Campen, Jr., and O. Grummitt, *ibid.*, **60**, 111 (1938).

[6] Ref. 4, p. 110.

[7] J. Mitchell, Jr., and D. M. Smith, "Aquametry," Interscience Publishers, Inc., New York, N. Y., 1948, pp. 256–258.

[8] O. B. Billings, Ph.D. Thesis, Cornell University, 1942.

X-Ray Measurements on $C_4H_9B(OH)_2$.—X-Ray powder diffraction patterns were taken using nickel-filtered Cu Kα radiation. Table I gives the spacings that were found.

TABLE I

$C_4H_9B(OH)_2$—POWDER PATTERN

Spacing (Å.)	Intensity	Spacing (Å.)	Intensity
12.08	s	3.23	w (diffuse)
5.14	w	3.02	mw
4.86	ms	2.81	ms
4.63	ms	2.68	w
4.18	vs	2.61	w
3.94	s	2.39	ms
3.73	ms	2.29	mw
3.47	w	2.15	w

The three strongest lines are 4.18, 12.08 and 3.94 Å., decreasing in this order. The powder pattern of orthoboric acid is quite different and can be used for detecting the presence of this substance in partially oxidized and hydrolyzed samples of $C_4H_9B(OH)_2$.

A single crystal of $C_4H_9B(OH)_2$ was grown from a saturated aqueous solution during a period of 4–5 weeks. It was then mounted in a thin-walled Pyrex tube which was filled with silicone oil. The Laue X-ray pattern showed the crystal to be monoclinic. Oscillation about the b-axis gave a pattern from which the dimensions of the unit cell were calculated. The dimension b was obtained from the layer lines while a, c and β were obtained from the zero layer line. Two experiments gave results agreeing within 0.04 Å., so that the unit cell dimensions recorded here are believed to be accurate to within 0.1 Å.; a = 7.38 Å., b = 5.96 Å., c = 7.86 Å., β = 80°. Unit cell volume = 341.5 Å.³.

Choosing two as the number of molecules per cell and $C_4H_9B(OH)_2$ as the formula leads to a calculated density, 0.991_3 g./cc.

Optical Crystallography of $C_4H_9B(OH)_2$.—As crystallized from water by evaporation at room temperature the crystals commonly exhibit rectangular "prismatic" habit with ends shaded. Occasional crystals are found on edge, and their ends show pairs of faces meeting in an angle of 124°. Both of these views give parallel extinction, so the crystals must be assigned to the monoclinic or orthorhombic systems.

The rectangular views yield a biaxial (−) interference figure, $2V$ = 70°, with the axial plane crosswise. The acute bisectrix is inclined less than 10° to the plane of the crystals, and the optic axes are unsymmetrically dispersed (inclined dispersion), thus limiting the crystal system to monoclinic.

The long direction of the crystal is the b-axis; the axial plane is the ac-plane. Refractive indices: $\beta \| b = 1.459$; $\alpha' = 1.450$; $\gamma' = 1.471$.

Sublimed crystals, as well as those crystallized from toluene, had identical optical properties.

Density.—The density of $C_4H_9B(OH)_2$ was determined by a pycnometric method. A batch of crystals which had grown slowly from aqueous solution was used. Silicone oil was chosen as the inert immersion liquid, since $C_4H_9B(OH)_2$ was found to be less soluble in this oil than in other liquids tried. Duplicate determinations gave 1.033 and 1.017 g./cc.

The density of the boroxine was determined by the use of a magnetic densitometer similar to that described by Richards,[9] but modified for use on a vacuum train. The method measures the coil current necessary to move an iron-tailed glass float in the liquid. It had a precision of ±0.0006 density unit in the range of 0.8 to 1.0, and a probable accuracy of ±0.001 density unit. The amount of sample required was less than 2 ml. and this could be recovered after the measurement was made. The apparatus was thermostated by circulating liquids at various temperatures through the jacket. It was calibrated in the desired range by using various liquids of known density.

The density of $(C_4H_9BO)_3$ was found to be represented between −52 and +56° by

$$d_t = 0.906 - 9.6 \times 10^{-4}t(°\text{C.})$$

Vapor Pressure.—The vapor pressure measurements were made in Pyrex cells having a Bourdon-tube type of pressure indicator, essentially as described by Laubengayer and Schirmer.[10] Freshly sublimed $C_4H_9B(OH)_2$ was transferred to stoppered glass tubes under an atmosphere of nitrogen; the stoppers were removed at the moment the sample tube was introduced into the nitrogen-filled cell, prior to evacuating and sealing. The vapor pressures for a typical run are recorded in Table II in the order in which they were obtained. After the first set of five measurements the cell was heated to 160° to effect complete conversion to $(C_4H_9BO)_3$ and H_2O. The apparatus was then cooled below 70° and the pressure of the reformed $C_4H_9B(OH)_2$ was measured at successively lower temperatures.

TABLE II

VAPOR PRESSURE OF SOLID $C_4H_9B(OH)_2$

Temp., °C.	Obsd. pressure, mm. ±0.15	Calcd. pressure, mm.	Temp., °C.	Obsd. pressure, mm. ±0.15	Calcd. pressure, mm.
31.2	1.9	1.8	65.6	30.0	29.9
45.4	6.2	6.2	55.7	14.4	14.1
53.2	11.4	11.6	45.5	6.4	6.2
59.6	19.0	19.0	31.0	2.0	1.8
66.7	32.5	32.4			

The data for the heating cycle are fitted by the equation

$$\log P(\text{mm.}) = \frac{-3660}{T} + 12.281$$

from which the calculated values of the table were obtained. The heat of sublimation is 16.7 ± 0.2 kcal. per mole. The vapor pressure measurement was repeated several times on other samples of $C_4H_9B(OH)_2$; all the results agree closely with the data reported here.

The vapor pressure of liquid $(C_4H_9BO)_3$ was measured in a similar fashion. For temperatures above 180° it was necessary to use an air-bath similar to that described by Broge.[11] The temperature was measured with a chromel–alumel thermocouple. Fragile glass bulbs containing samples of the boroxine were introduced into the cell; they were then broken and any inert gas was pumped off before the cell was sealed.

Table III shows the data that were obtained on two separate samples. For temperatures up to 196° the data are fitted by the equation

$$\log P(\text{mm.}) = \frac{-2906}{T} + 8.342$$

The extrapolated boiling point is 259°. The heat of vaporization in the range 80 to 200° is 13.3 ± 0.3 kcal. per mole.

TABLE III

VAPOR PRESSURE OF $(C_4H_9BO)_3$

Temp., °C.	P(obsd.), mm. ±0.2	P(calcd.), mm.	Temp., °C.	P(obsd.), mm. ±0.2	P(calcd.), mm.
	Sample 1			Sample 2	
92.5	2.2	2.4	108.1	5.6	5.2
113.0	6.6	6.6	148.0	28.1	27.7
137.5	17.1	18.4	174.0	70.8	69.8
150.5	30.9	30.4	196.2	140.4	141.6
168.0	57.4	57.0	201.8	172.2	167.5
173.1	70.0	67.8	159.6	41.1	42.5
180.4	84.9	86.1	136.7	16.9	17.9
159.0	42.0	41.5	82.3	1.6	1.4
146.5	27.0	26.2			
130.0	13.6	13.6			
97.5	2.9	3.1			

Index of Refraction.—A sample of $(C_4H_9BO)_3$ was distilled into a break-seal tube which in turn was sealed to the prism of a Pulfrich refractometer with fish glue. After purging the cell with dry nitrogen, the tip of the tube was broken; $n^{25}\text{D}$ was found to be 1.4193. The molar refraction, R^{25} = 72.11, was calculated from the Lorentz–Lorenz equation.

The B–O bond refractivity was calculated from the measured molar refraction, using 1.73, 1.705 and 1.209, respectively, for the B–C, C–H and C–C bond refractivities. The value obtained was 1.17.

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(9) A. R. Richards, *Ind. Eng. Chem.*, *Anal. Ed.*, **14**, 595 (1942).

(10) A. W. Laubengayer and F. B. Schirmer, THIS JOURNAL, **62**, 1578 (1940).

(11) E. C. Broge, Ph.D. Thesis, Cornell University, 1948.

Viscosity of $(C_4H_9BO)_3$.—A vacuum viscometer was used, the sample being distilled into the viscometer from the vacuum train. The liquid was forced into the upper bulb with dry nitrogen, and the time of downflow was measured as usual. The instrument was calibrated with benzene at 25° and with water at various temperatures between 0 and 50°.

The viscosity of $(C_4H_9BO)_3$ between 0 and 50° is represented by

$$\log \eta(\text{cp.}) = -3.130 + \frac{1055}{T(°\text{K.})}$$

At 20° the viscosity is 2.94 cp. The standard deviation of the differences between the observed values and those calculated from this equation is 0.05 cp.

Surface Tension of $(C_4H_9BO)_3$.—The surface tension was measured by the maximum bubble pressure method described by Sidgwick and Laubengayer.[12] Dried hydrogen gas was used in the apparatus rather than air. The sample of $(C_4H_9BO)_3$ was introduced by distillation through a side arm which was then sealed off. Difficulty was experienced with contamination by traces of moisture. Any $C_4H_9B(OH)_2$ which was formed was insoluble and tended to plug the small capillary. For this reason the results in Table IV show somewhat greater variation than is desired. Three series of runs were carried out, each with a different sample.

TABLE IV

SURFACE TENSION OF $(C_4H_9BO)_3$

Series	Temp., °C.	Surface tension, dyne/cm.	Series	Temp., °C.	Surface tension, dyne/cm.
2	0.4	27.79	1	25.0	25.18
3	0.4	27.87	1	30.0	24.82
3	10.3	26.88	2	30.0	25.10
1	20.0	25.79	3	30.1	24.98
3	20.2	25.97			

A least squares method was used to fit the data by the equation

$$\gamma(\text{dyne/cm.}) = 27.86 - 0.098_3t\ (°\text{C.})$$

The standard deviation of the experimental values, as compared with those calculated from this equation, is 0.13 dyne cm.$^{-1}$, or roughly 0.5%.

Freezing Point of $(C_4H_9BO)_3$.—The freezing point was difficult to determine because of undercooling. The best results were obtained by freezing the liquid and then partially melting it until the stirrer was free. The crystals which remained served as seeds. Two determinations gave −50 ± 1°.

Dihydroxyborane–Boroxine Equilibrium.—The vapor density of volatilized $C_4H_9B(OH)_2$ was measured in the range 70–160°, using the apparatus and the procedure described for vapor pressure measurement. The vapor pressure of the condensed borane was measured at the beginning and the end of each run; at the beginning to make certain that no excess volatile matter was present, and at the end to prove that no gross changes had occurred. By approaching the measured temperature from above and from below, the same pressure–temperature curve was obtained. Thus it was certain that equilibrium was established even though the reaction was very slow, sometimes requiring many hours.

The over-all equation for the reaction is

$$3C_4H_9B(OH)_2 = (C_4H_9BO)_3 + 3H_2O \qquad (1)$$

In order to prevent the condensation of the boroxine that was formed, the total pressure in the system had to be kept under 25 mm. at 70°. The relative error of measurement was quite large for this reason. Several runs were made; the one reported here is typical. Table V shows the data that were obtained. The pressures in the second column are those which would have been observed if there had been no reaction, or if reaction involved no change in the number of molecules, while the pressures in the fourth column were calculated on the assumption that the reaction was complete according to eq. 1.

At the low end of the temperature range the observed pressure was near that calculated for pure $C_4H_9B(OH)_2$, but it tended to be 3% or more too high. This difference is well outside the experimental error. At temperatures above 140° the calculated pressure corresponded to that expected for complete reaction. Since the vapor pressure of $C_4H_9B(OH)_2$ could be reproduced when this mixture was cooled below 70°, a 3:1 molar mixture of H_2O and $(C_4H_9BO)_3$ was probably present at high temperatures. If one assumes that eq. 1 represents the only reaction occurring, about 6% of the acid was decomposed at 68°, 24% at 90° and 92% at 125°.

TABLE V

DEHYDRATION OF $C_4H_9(OH)_2$ (55.6 MG. IN 584 CC. VOL.)

Temp., °C.	Calcd. $BuB(OH)_2$ pressure, mm.	Obsd. pressure, mm.	Calcd. $(BuBO)_3 + H_2O$ pressure, mm.
68.3	19.9	20.5	
74.9	20.3	21.2	
79.0	20.5	21.5	
81.4	20.6	21.7	
89.8	21.1	22.8	
96.8	21.6	24.1	
102.1	21.9	25.1	
106.1	22.1	26.1	29.5
113.3	22.5	27.9	30.0
116.1	22.7	28.8	30.2
125.0	23.2	30.3	30.9
132.5	23.6	31.2	31.5
142.0	24.2	32.0	32.2
149.8	24.6	32.7	32.7
161.8	25.3	33.6	33.7

Discussion

Dihydroxy-*n*-butylborane crystallizes in large thin plates which mat together and make it difficult to remove the residual solvent. At one time it was thought that hydrates were formed when water was used for recrystallization.[13] It is easy to show that this is not the case by comparing the measured density with the density calculated from the dimensions of the unit cell. The difference is about 3% when the calculation is based on the formula $C_4H_9(OH)_2$, but about 14% when the formula of a monohydrate is used.

In distinction from dihydroxyboranes, most other alkyl boron compounds are liquids. The difference is to be explained by noting that the former possess ample opportunity for hydrogen bond formation which can tie the molecules together in a three-dimensional structure. The stability of the crystals is indicated by the rather low solubility of $C_4H_9B(OH)_2$ in toluene and by the fact that the heat of solution is sufficiently high to make toluene a good solvent for use in recrystallization.

The magnitude of the heat of sublimation, 16.7 kcal. per mole, also is an indication of hydrogen bonding. A non-hydrogen-bonded molecule of the same molecular weight is $[(CH_3)_2B]_2O$. Its heat of vaporization is only 7.4 kcal.[14] representing chiefly energy needed to overcome dispersion forces The difference between 16.7 and 7.4 is the energy of hydrogen bonding if the vapor contains only $C_4H_9B(OH)_2$ molecules. The energy of hydrogen bonding may be estimated as 4.5 kcal. per mole of bonds.

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[12] N. V. Sidgwick and A. W. Laubengayer, THIS JOURNAL, **54**, 948 (1932).

[13] Ref. 4, p. 106.

[14] F. L. McKennon, "Reactions and Compounds of the $(CH_3)_2B$-Group," University of Chicago Libraries, Chicago, Illinois, 1939.

Aliphatic carboxylic acids have even stronger hydrogen bonding, averaging about 7.5 kcal. per mole of bonds, but the energy is released in the formation of dimers which persist in all states of matter except in many polar solvents.[15] Consequently these compounds differ from dihydroxyboranes of the same molecular weight in being liquids and in being miscible with non-polar solvents.

In solution any $C_4H_9B(OH)_2$ aggregates which may exist in the solid are largely broken up. This paper reports slightly high molecular weights in water at the freezing point but nearly normal values in benzene. Snyder, Kuck and Johnson[4] got the same results in acetone at the boiling point, and the evidence of dipole moments reported by Otto[16] likewise points to the absence of association in benzene. However, French and Fine[17] obtained data which show that dihydroxy-*n*-butyl-, dihydroxy-*n*-amyl and dihydroxyphenylboranes are associated in benzene, although the same compounds in nitrobenzene were found to be monomeric. These facts are inconsistent with each other and for the present we prefer to regard $C_4H_9B(OH)_2$ as largely unassociated in benzene.

The heat of the vapor phase dehydration of $C_4H_9B(OH)_2$ can be calculated from the data of Dworkin and Van Artsdalen[18] who report

$$(C_4H_9BO)_3(l) + 3H_2O(l) = 3C_4H_9B(OH)_2(c) \qquad \Delta H = -19.6 \pm 0.4 \text{ kcal.}$$

This may be combined with the heat of vaporization of $(C_4H_9BO)_3$ and the heat of sublimation of $C_4H_9(OH)_2$, both as reported in this paper, together with 10.5 kcal. per mole for the heat of vaporization of water at 25° to give

$$3C_4H_9B(OH)_2(g) = (C_4H_9BO)_3(g) + 3H_2O(g) \qquad \Delta H^\circ = +14.3 \pm 0.5 \text{ kcal.}$$

or about 4.9 kcal. per mole of $C_4H_9B(OH)_2$. The errors are such that this result probably can be applied over the whole temperature range considered here. Burg[3] obtained + 9.3 kcal. for the heat of vapor phase dehydration of three moles of $CH_3B(OH)_2$.

The composition of the vapor can be approximated in the temperature range over which vapor pressures were measured by using $\Delta H^\circ = 14.3$ kcal. and choosing an approximate value for ΔS°. This is estimated to be + 22 e.u. by analogy with the result of Burg.[3] At 60°, for example, it is found that less than 1% of $C_4H_9B(OH)_2$ has been dehydrated. This leads to a correction in the heat of sublimation of roughly 0.05 kcal. per mole which is small enough to be neglected.

Attempts to utilize the vapor density data in Table VIII on the assumption that only $C_4H_9B(OH)_2$, $(C_4H_9BO)_3$ and water were present led to anomalous results. A plot of log K *vs.* $1/T$ was distinctly curved and indicated a very high heat of reaction. We believe, therefore, that the vapor is a complex mixture.

The fact that the dehydration reaction is quite endothermic needs some comment since it appears to be at variance with the common assumption that the boroxine ring is stabilized by resonance. The boron–oxygen distance in 2,4,6-trimethylboroxine, as determined by Bauer and Beach,[19] is 1.39 Å., which is considerably shorter than 1.45 Å., calculated as the "single bond" distance. But essentially the same boron–oxygen distance was found in methyl borate, implying some double bond character in these bonds. One can expect that the same is true of dihydroxyboranes, since all of these compounds possess tercovalent boron atoms bonded to at least two oxygen atoms having unshared electrons. Thus the resonance which is ascribed to the boroxine ring can be matched with double bonding in dihydroxyboranes such that in the formation of the ring the energy gain from this source is small if not zero. Effects such as strain in the ring may contribute to the endothermicity of ring formation.

The absorption of heat in the dehydration process is one reason for the fact that difunctional boron oxides do not readily form chain polymers. Six-membered rings have been reported in all cases except for one in which a small amount of a higher polymer was found.[20] The unit of reaction used in this paper, three moles of $C_4H_9B(OH)_2$, is accomplished by breaking and reforming a total of six moles of bonds, so that the amount of heat absorbed per bond is rather small. However, the formation of an extended chain polymer through a condensation reaction which is even slightly endothermic can be made to occur only if a suitable method of forcing the removal of water can be found. When the process is actually carried out by heating $C_4H_9B(OH)_2$ the formation of the cyclic boroxine seems not only to be a facile process, but it is also accompanied by favorable entropy change. A chain polymer would be expected only under conditions such that the ring would not form. Even then, the general lability of boron compounds suggests that a high polymer might depolymerize under moderate conditions.

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