

[CONTRIBUTION FROM THE RESEARCH LABORATORY, OLIN MATHIESON CHEMICAL CORPORATION]

Identification of an Intermediate Compound in the Partial Oxidation of Pentaborane-9¹

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In the partial oxidation of pentaborane-9 an intermediate compound which is not a pure boron hydride has been isolated and identified by using isotopic substitution techniques in conjunction with mass, infrared and nuclear magnetic resonance spectrometry. The intermediate has the formula $B_2H_2O_3$, in which each hydrogen atom is attached directly to a boron atom and in which the two boron atoms exist in identical configurational environments. The possible structural configurations of the compound are discussed, with the evidence pointing toward a trigonal bipyramid (D_{3h}) model.

The partial oxidation of pentaborane-9 results in several products, including diborane,² tetraborane and an unknown compound that was tentatively assigned the formula $B_4H_{12}O$.³ Mass spectra presented in support of this formula, however, did not bear out such an assignment. Our interest in this problem was prompted by the expected analogy of oxidation to the hydrolysis of boron hydrides,^{4,5} since similar mechanisms may serve in both cases. A knowledge of the compositions of the various intermediate compounds should assist in understanding the oxidation and hydrolysis mechanisms.

The chemical composition of the intermediate compound was determined by utilizing isotopic substitution techniques (both boron and hydrogen) in conjunction with mass, infrared and nuclear magnetic resonance spectrometry. The data presented here indicate that this compound has the formula $B_2H_2O_3$, in which there are two B-H groups existing in identical configurational environments. Three possible configurations are discussed.

This work was limited to determination of the structure of the intermediate, with a few added observations concerning the stability of the compound.

Experimental

Isotopically Normal Compound.—The usual high vacuum techniques were employed throughout this work. As a word of caution, however, the compound is unpredictably explosive when in a condensed state and requires rather careful handling.

The isotopically normal compound was prepared by adding oxygen through a very small diameter capillary to pentaborane-9 (50 mm. pressure, room temperature) in a 100-ml. Pyrex bulb. The oxygen flow rate, controlled by the pressure head of oxygen, was maintained at about $1.0\text{--}1.3 \times 10^{-3}$ mole/hour. Reactions were allowed to run about 45 minutes, after which time the volatile gases were pumped out through liquid nitrogen traps. The intermediate has a volatility only slightly less than that of another product, tetraborane, which has a vapor pressure of *ca.* 0.1 mm. at -113° . This similarity in volatility makes separation of tetraborane from the intermediate somewhat difficult and results in some loss of the intermediate compound. On the other hand, diborane and unused pentaborane-9 are readily removed by normal vacuum fractionation.

B^{10} -Enriched Compound.—This compound was prepared by the reaction of B^{10} -enriched pentaborane-9 and oxygen, using the above procedure. To minimize loss of the compound, which was prepared in a smaller quantity than the isotopically normal compound, no attempt was made to separate it from the resulting B^{10} -enriched tetraborane.

(1) Presented at the 134th Meeting of the American Chemical Society, Chicago, Illinois, September, 1958.

(2) H. C. Baden, S. E. Wiberly and W. H. Bauer, *J. Phys. Chem.*, **59**, 287 (1955).

(3) W. H. Bauer and S. E. Wiberly, Abstracts of Papers of 133rd Meeting, American Chemical Society, San Francisco, April, 1958, 13L.

(4) I. Shapiro and H. G. Weiss, *THIS JOURNAL*, **76**, 1203 (1954).

(5) I. Shapiro and H. G. Weiss, *ibid.*, **76**, 6020 (1954).

Consequently, its infrared spectrum (Fig. 2c) shows additional absorption in the 2500 cm.^{-1} region due to the $B_4^{10}H_{10}$ impurity.

Deuterated Compound.—Several attempts to prepare this compound from deuterio-pentaborane-9⁶ and oxygen resulted unexpectedly in flashing of the mixture rather than slow oxidation. Such difference in behavior is not necessarily unique, however, for the energetics of deuterio compounds can be appreciably different from the corresponding protonated compounds. The pyrolysis of deuteriododecaborane, for example, is reported to be considerably slower than that of decaborane.⁷ The intermediate compound ultimately was prepared, however, by allowing the normal (protium) compound to exchange with successive amounts of B_2D_6 at room temperature. The fact that the intermediate readily exchanges in this manner is evidence that it contains hydridic hydrogens as exist in boron hydrides.

Instrumental Analysis.—Mass spectra were determined with a Consolidated Model 21-103 Spectrometer operating at an ionizing potential of 70 volts. Infrared spectra were recorded on a Perkin-Elmer Model 21 Infrared Spectrophotometer equipped with NaCl optics. Nuclear magnetic resonance spectra were obtained with a Varian High Resolution NMR Spectrometer operating at 12.8 megacycles.

Gas Density Measurements.—Gas density measurements were made with a 50-ml. light-weight (6 grams) Pyrex bulb equipped with a silicone plug instead of a stopcock, thus eliminating grease from the weighing bulb. Material was transferred into the bulb through a hypodermic needle, one end of which was inserted through this plug and the other end through a second plug attached to the vacuum rack. All weighings were made against a tare bulb of the same volume and weight. The bulb was calibrated with oxygen, and several checks with nitrogen gave a molecular weight of 28.1 ± 0.2 .

For measurements involving the intermediate compound it was necessary to analyze borane impurities by letting the sample expand into a small infrared cell simultaneously with expansion into the weighing bulb, then applying appropriate corrections for impurities. Non-condensable gases were negligible in all samples.

Stability of the Intermediate Compound.—Preservation of the isolated intermediate constituted somewhat of a problem until it was observed that this compound is more stable in the gas phase at room temperature than when stored in a condensed phase at low temperatures. When the compound was stored in an infrared cell at room temperature, a slow buildup of a characteristic B-H bridge band at 1600 cm.^{-1} indicated that diborane was forming (more than could have been formed from the small amount of tetraborane impurity that was present). Also, B_2O_3 (and probably H_2) was formed under these conditions. The bulk of the material can be preserved for a few days in this state.

Addition of diborane to the intermediate was found to enhance its stability rather substantially, enough to preserve it several days longer than normally. This observation suggests the possibility of equilibrium between diborane and the intermediate, although the effect may be one of dilution or of weak complexing rather than equilibrium.

As will be shown later, the intermediate compound contains two B-H groups. Consequently, its decomposition into diborane is not particularly unusual, for similar activity has been displayed by other compounds containing B-H groups. Dimethoxyborane, for example, forms diborane under similar conditions.⁸

(6) I. Shapiro and J. F. Ditter, *J. Chem. Phys.*, **26**, 798 (1957).

(7) H. C. Beachell and J. F. Haugh, *THIS JOURNAL*, **80**, 2939 (1958).

(8) A. B. Burg and H. I. Schlesinger, *ibid.*, **55**, 4020 (1933).

Spectral Results

Mass Spectra.—The polyisotopic mass spectrum of the isotopically normal oxidation intermediate (corrected for trace amounts of boron hydride impurities) is given in Table I. The top mass cut-off

TABLE I

POLYISOTOPIC MASS SPECTRUM OF $B_2H_2O_3$

(Sensitivity for m/e 71 = 9.89 divisions per micron, based on butane sensitivity for m/e 43 of 50.00 divisions per micron.)

m/e	Intensity	m/e	Intensity	m/e	Intensity
74	0.32	47	0.38	29	22.6
73	0.82	46	0.26	28	54.1
72	34.4	45	13.2	27.5	1.41
71	100.0	44	54.8	27	24.2
70	52.7	43	18.5	26.5	0.15
69	9.95	42	2.30	26	3.11
68	0.73	41	0.66		
67	0.13	40	0.65	20	4.49
		39	1.35	19.5	2.33
57	0.42	38	1.33	19	0.43
56	0.90	37	0.46		
55	8.69	36	.49	16	2.13
54	8.57	35	.17	15	0.74
53	2.77	34.5	tr	14	.41
52	0.20	34	0.83	13	.74
51	.05	33	0.41	12	5.71
50	.85	32	1.30	11	34.2
49	.78	31	0.30	10	7.9
48	.00	30	0.29	2	44.2

compounds from further consideration. For $B_3H_7O_2$ the cut-off at m/e 68 would represent the $B_3^{10}H_6O_2^+$ species, while the cut-off at m/e 72 would be the $B_3^{11}H_7O_2^+$ species. This would necessitate the loss of only one hydrogen atom during fragmentation of the parent group, a conclusion which is untenable in view of the lower mass (below m/e 68) fragments observed (Table I). A similar situation would prevail for the formula $B_4H_{12}O$, except that in this case *no* hydrogen atoms would be lost on electron impact; *i.e.*, m/e 68 would be $B_4^{10}H_{12}O$, while m/e 72 would be $B_4^{11}H_{12}O$. The $B_2H_2O_3$ fragmentation, of course, fits the data.

Confirmatory evidence for the formula $B_2H_2O_3$ has been obtained from the mass spectra of the B^{10} -enriched compound ($B^{11}/B^{10} = 6/94$) and of the deuterated compound (95% deuterium). The mass cut-off of the B^{10} -enriched material, after correcting for the 6% B^{11} , is m/e 70, two units lower than that for the normal compound, while the cut-off for the deuterated species is m/e 74, two units higher than that for the normal compound. These spectral shifts definitely indicate that the compound contains two boron and two hydrogen atoms. A comparison of the parent groups for the three isotopic compounds is shown in Fig. 1.

The remainder of the polyisotopic spectrum in Table I was stripped down on the basis of the $B_2H_2O_3$ formula, assuming all possible combinations of

TABLE II

STRIPPING OF PARENT FRAGMENTS ($B^{11}/B^{10} = 4.0$)

m/e	Peak height	O^{18} Contribution	Δ	$B_2^{11}O_3H_2^+$	Δ	$B_2^{11}O_3H_1^+$	Δ	$B_2^{11}O_3^+$	Δ
74	0.32	0.21	0.11						+0.11
73	0.82	.61	0.21						+0.21
72	34.4	.32	34.1	34.1					
71	100.0	.06	99.9	17.1	82.8	82.8			
70	52.7	tr	52.7	2.1	50.6	41.4	9.2	9.2	
69	9.95	0.00	9.95		9.95	5.18	4.77	4.6	+0.17
68	0.73	0.00	0.73		0.73		0.73	0.58	+0.15

(excluding the small O^{18} contributions) occurs at m/e 72. Infrared and n.m.r. evidence (discussed later) indicate that this cut-off corresponds to the parent ion. Since only boron, oxygen and hydrogen are present and since the various combinations of these atoms must add up to a molecular weight of 72 mass units, the empirical formula of the corresponding molecule would be one of the following (assuming a reasonable number of hydrogen atoms in the molecule): $B_2H_2O_3$, $B_3H_7O_2$ or $B_4H_{12}O$. The latter formula has already been postulated.³ When the parent group (m/e 72–68) is stripped down monoisotopically for each of these formulas on the basis of a B^{11}/B^{10} ratio of 80/20,⁹ the B_3 and B_4 species gave absurdly large positive and negative residues, whereas the B_2 compound strips down with acceptable minimum residues, as indicated in the last column of Table II.

An analysis of the bottom cut-off (m/e 68) of the parent group also eliminates the B_3 and B_4

(9) The best B^{11}/B^{10} ratio for stripping mass spectra varies somewhat for different compounds, probably due to differences in fragmentation for B^{11} and B^{10} species on electron bombardment. For boron hydrides the ratio 80/20 seems to give the best over all results. (For discussion and further references see Footnote 10 of reference 6.)

boron, oxygen and hydrogen. The residues were generally of the order of a half per cent. or less, with no residues greater than 1%. The resultant monoisotopic spectrum is given in Table III. Doubly-charged ion species, determined from half-peaks with the assistance of spectra of the B^{10} enriched and deuterated compounds, also are listed. Several monoisotopic fragments of very small intensity have been included in the table, but in view of their negligibly small values they may actually be non-existent.

Small peaks also were observed in the vicinity of m/e 80–84. The intensity of m/e 83 varied from 2 to 7% of the intensity of m/e 71, the percentage being a function of the history of the particular sample. Such variation indicates an impurity, and it was observed that greater care in removing less volatile species resulted in smaller amounts of the impurity in the mass spectral trace. These impurity peaks, as confirmed by the B^{10} and the deuterated spectra, corresponded satisfactorily to a three-boron compound, while the top mass cut-offs suggested that it might be the cyclic compound boroxin, $B_3H_3O_3$. The preparation of boroxin

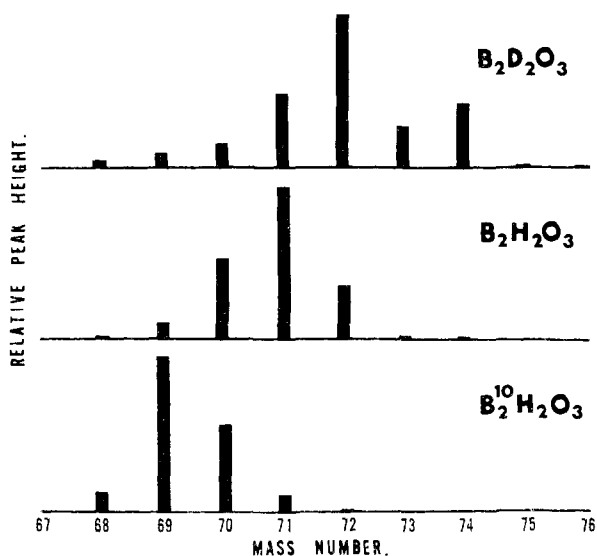


Fig. 1.—Comparison of mass spectral parent groups of isotopic derivatives of the intermediate compound.

has not been reported heretofore. If boroxin is the impurity, it would make the spectrum of $B_2H_2O_3$ susceptible to an unknown error, since the two compounds would have mutual fragments which would strip down in identical fashion.

TABLE III
MONOISOTOPIC SPECTRUM OF $B_2H_2O_3$

Ion species	Intensity	Ion species	Intensity
$B_2H_2O_3$	41.2	B_2H_2O	0.8
B_2HO_3	100.0	B_2HO	1.2
B_2O_3	11.1	B_2O	0.9
$B_3H_2O_2$	1.1	H_2O_2	0.6
B_2HO_2	10.0	HO_2	0.3
B_2O_2	5.3	O_2	1.0
H_2O	0.7	BH_2O^a	21.7
HO_3	0.6	BHO	46.8
O_3	0	BO	10.5
BH_2O_2	12.8	O	1.7
BHO_2	49.8	BH_2	0.6
BO_2	5.4	BH	5.4
		B	31.7

Doubly-charged ion species

$B_2O_3^{++}$	$B_2HO_2^{++}$	$B_2H_2O^{++}$
$B_2H_2O_2^{++}$	$B_2O_2^{++}$	B_2HO^{++}

^a Principal rearrangement fragment.

To remove the possibility that boroxin might be the major constituent of the sample (with principal peaks at m/e 68–73 and only minor peaks corresponding to the parent ion) the molecular weight of the intermediate was checked by gas density measurements. The result of three determinations, making maximum possible allowance for borane impurities, was 74 ± 2 , a value which would eliminate the above-mentioned possibility.

Infrared Spectra.—In the infrared spectrum (Fig. 2-b) of the isotopically normal intermediate compound the single sharp peak at 2667 cm.^{-1} indicates a B–H terminal stretching mode. It further shows that there is only one hydrogen per

boron atom, for a BH_2 group would have given a doublet¹⁰ (symmetric and asymmetric stretching) rather than a singlet. Moreover, the fact that there is no absorption above 3000 cm.^{-1} indicates there are no O–H groups, while the absence of bands around 1600 cm.^{-1} indicates there are no B–H bridge groups. Hence, since mass spectral evidence shows there are two borons in the molecule, there must also be only two hydrogen atoms present, and each hydrogen must be attached to separate boron atoms. This evidence eliminates the possibility of a formula such as $B_2H_3O_3$ (three hydrogens), in which the observed ion species $B_2H_2O_3^+$ represents fewer hydrogen atoms than really exist in the compound.¹¹

The B–H stretching band in $B_2H_2O_3$ occurs in the same general region as B–H terminal stretching bands in the boron hydrides, indicating similar type bonding. Replacement of hydrogen with deuterium (Fig. 2a) shifts this band from 2667 to 1990 cm.^{-1} , which is the B–D stretching region for boranes.¹² Another major change that is observed involves a shift of the band in the 885 cm.^{-1} region to the 770 cm.^{-1} region, corresponding to B–H bend and B–D bend, respectively.¹²

The infrared spectrum of the B^{10} -enriched compound, $B_2^{10}H_2O_3$ (Fig. 2c), shows a boron isotope effect in every major band. In particular the B–H bending vibration in the 885 cm.^{-1} region underwent remarkable simplification, for it clearly shows an A-type band in the B^{10} spectrum (which is essentially monoisotopic). The B_2^{11} , $B^{10}B^{11}$ and B_2^{10} effects are very evident here. An extra peak at 875 cm.^{-1} in the normal compound is essentially absent in the B^{10} -enriched compound and is very weak in the deuterio compound (755 cm.^{-1}), and it probably is due to weak B–B coupling in the isotopically normal compound. The bands at 2600 , 2500 and 2150 cm.^{-1} in the B^{10} spectrum (Fig. 2c) are due to $B_4^{10}H_{10}$ impurity.

Inspection of Fig. 2b reveals also that there are no B=O groups, as indicated by the absence of absorption in the vicinity of 2000 cm.^{-1} . With regard to the B=O group frequency, emission spectra of gaseous B_2O_3 ^{13,14} show a strong band in the 2013 – 2040 cm.^{-1} region, which presumably is due to a B=O stretching vibration. The interpretation is based on the V-bent model¹⁴ (which would have two B=O groups) as the correct structure for gaseous B_2O_3 . Taylor¹⁵ has applied the Teller–Redlich product rule to the various possible structures, and his results combined with those of White, *et al.*,¹⁴ point to the V-bent model as the correct one. The characteristic single-bond B–O frequency, on the other hand, as in trimethoxyborane¹⁶ and in a number of other

(10) I. Shapiro, C. O. Wilson and W. J. Lehmann, *J. Chem. Phys.*, **29**, 237 (1958).

(11) In the mass spectra of several boranes, *e.g.*, tetraborane and pentaborane-11, the mass cut-off peak corresponds to a species containing fewer hydrogen atoms than the parent compound.

(12) For example, see R. C. Lord and E. Nielsen, *J. Chem. Phys.*, **19**, 1 (1951), for characteristic frequencies in B_2H_4 and B_2D_4 .

(13) D. A. Dows and R. F. Porter, *This Journal*, **78**, 5165 (1956).

(14) D. White, P. N. Walsh and D. E. Mann, *J. Chem. Phys.*, **28**, 508 (1958).

(15) W. J. Taylor, *ibid.*, **28**, 625 (1958).

(16) R. R. Servoss and H. M. Clark, *ibid.*, **26**, 1179 (1957).

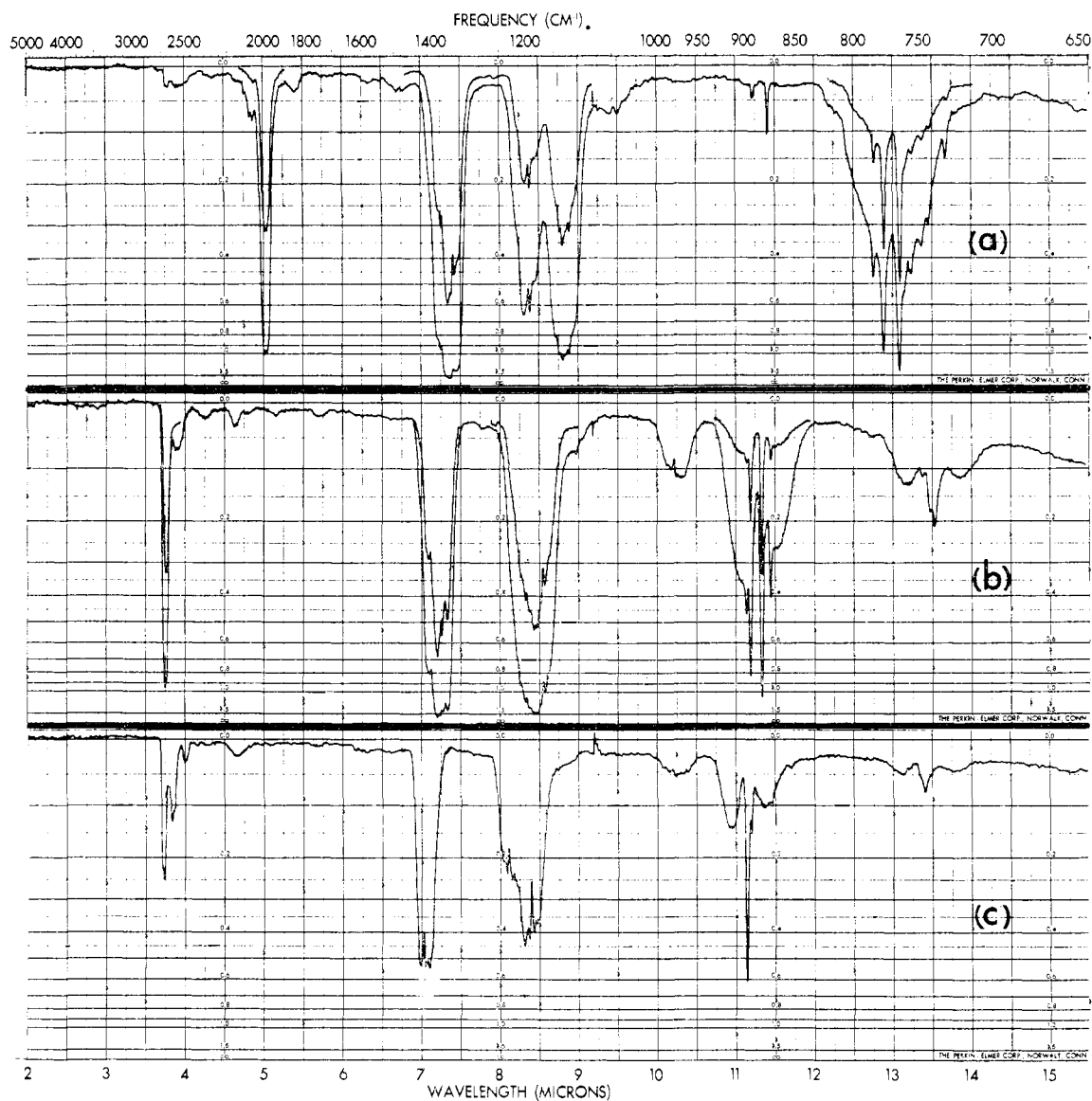


Fig. 2.—Infrared spectra of: (a) $B_2D_2O_3$ —35 and 12 mm. pressure; (b) $B_2H_2O_3$ —35 and 12 mm. pressure (35 and 6 mm. for 880 cm.^{-1} band); (c) $B_2^{10}H_2O_3$ —10 mm. pressure. Spectra were obtained at room temperature with gas cells (5 cm. path length) equipped with NaCl windows.

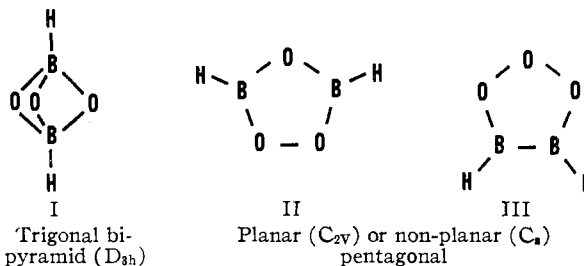
borates,¹⁷ occurs in the vicinity of 1400 cm.^{-1} , which suggests that the 1390 cm.^{-1} band in Fig. 2b is due to a B—O stretching vibration.

Nuclear Magnetic Resonance Spectrum.—The B^{11} n.m.r. spectrum of isotopically normal $B_2H_2O_3$ consisted of a sharp doublet occurring at lower field than the B^{11} resonance in any of the common boron hydrides. This doublet (two peaks of recognizable separation) represents the spectrum characteristic of a single terminal proton on a boron atom; a BH_2 group would yield a triplet instead of a doublet. This uncomplicated spectrum also indicates that the two boron atoms exist in identical electronic environments and almost certainly in identical spatial configuration.

Possible Structural Configurations.—In brief, the foregoing evidence has indicated the following:

(17) R. L. Werner and K. G. O'Brien, *Australian J. Chem.*, **8**, 355 (1955).

(1) the empirical formula is $B_2H_2O_3$; (2) there are two B—H (terminal) groups in identical configurational environments; (3) there are no BH_2 groups, no B—H bridge bonds, no O—H bonds and no B=O bonds. In view of this the structure should be one of the three shown, I-II-III



Structure I is a trigonal bipyramid with the three oxygen atoms in a plane that is perpendicular to

the vertical axis and with the two B-H groups in apical positions along the axis. Except for the tetravalent borons this structure is analogous to the configuration proposed for gaseous B_2O_3 by Dows and Porter¹³ but which was found^{14,15} to be incompatible with the observed isotopic shifts of infrared bands. If we assume a normal B-O bond length¹⁸ of 1.38 Å. and an average B-B distance¹⁹ of 1.70 Å., then the bond angles would be 76° for B-O-B and 86° for O-B-O, which would signify a fair amount of strain in the molecule. There is no assurance, however, that these distances would prevail in the molecule.

Aside from any structural or chemical reasons, structure III seems highly improbable in view of the absence of mass spectral species $B_2H_2^+$, B_2H^+ and B_2^+ (see Table III). The $B_2H_2^+$ fragment, in particular, is a fairly intense one in the boron hydrides, and, if $B_2H_2O_3$ had adjoining boron atoms, one would certainly expect to find at least a trace of this ion fragment.

The high volatility of the intermediate compound, considering its molecular size, would suggest structure I, since it has the highest symmetry of the three and has zero dipole moment. In support of this are the results predicted by a normal coordinate treatment of the three symmetry types, D_{3h} , C_{2v} and C_s . The representations for the various symmetry species for the three point groups are

$$\begin{aligned} \Gamma_{D_{3h}} &= 3(A'_1)_R + 3(E')_{IR,R} + 2(A_2'')_{1R} + 2(E'')_R \\ \Gamma_{C_{2v}} &= 6(A_1)_{1R,R} + 2(A_2)_R + 2(B_1)_{1R,R} + 5(B_2)_{1R,R} \\ \Gamma_{C_s} &= 8(A')_{1R,R} + 7(A'')_{1R,R} \end{aligned}$$

The calculations and symbolism are standard.²⁰ Raman and infrared activities of the various species are given in the subscripts, and from this it can be seen that the D_{3h} , C_{2v} and C_s models would have, respectively, 5, 13 and 15 infrared active vibrations. The observed spectra (Fig. 2) support the D_{3h} model (five fundamentals), although it is possible that additional fundamental bands may lie beyond the range of NaCl optics. If we assume that the D_{3h} model is the correct one, then its five fundamentals would seem to be the following (based on $B_2^{11}H_2O_3$): 2667, 1370, 885 and two overlapping ones in the 1175 cm^{-1} region (split when isotopically substituted), since these are the bands of greatest intensities in the recorded spectrum. An attempt was made to apply the Teller-Redlich Product Rule by comparing predicted product ratios (readily calculated from normal coordinate data) with all possible combinations of observed isotopic product ratios, but the two overlapping bands in the 1175 cm^{-1} region prevented determi-

(18) S. H. Bauer and J. Y. Beach, *THIS JOURNAL*, **63**, 1394 (1941).

(19) M. Atoji and W. N. Lipscomb, *J. Chem. Phys.*, **21**, 172 (1953);

W. J. Dulmage and W. N. Lipscomb, *THIS JOURNAL*, **73**, 3539 (1951).

(20) For example, see Wilson, Decius and Cross, "Molecular Vibrations," McGraw-Hill Book Co., New York, N. Y., 1955.

nation of reliable data. Application of this rule must await a more complete configurational analysis based on internal coordinates.

The B-H terminal stretching band of $B_2H_2O_3$ (Fig. 2b) occurs at a higher frequency (2667 cm^{-1}) than in any other known borane or derivative. This band in pentaborane-9 (2600 cm^{-1})²¹ is the highest of previously published compounds. Moreover, diethoxyborane,²² which is similar to $B_2H_2O_3$ in that it has two oxygens adjacent to a B-H group, has a B-H stretching band at 2500 cm^{-1} , substantially lower than in $B_2H_2O_3$. If structure II were correct, one might expect the observed frequency to be in the vicinity of that for diethoxyborane, since the environments of the B-H groups in the two structures are similar. Both structures, for example, have trivalent boron attached to one hydrogen atom and to two oxygen atoms. However, the effect of any ring resonance in structure II probably would increase the frequency. The cyclic compound borazene, $B_3N_3H_6$, which exhibits resonance comparable to that in benzene, has a B-H frequency of 2530 cm^{-1} , a value which is roughly 130 cm^{-1} higher than that of the "aliphatic" compound aminodimethylborane, $(CH_3)_2NBH_2$.²³ A similar effect might exist here, with extra electrons from the oxygens contributing to the ring and at the same time increasing the effective negative charge on the borons. On the other hand, resonance in the bipyramidal cage structure could create comparable behavior. This is substantiated by the observation that other cage-type compounds prepared in this Laboratory²⁴ have B-H stretching frequencies in the vicinity of 2600 cm^{-1} , about 100 cm^{-1} higher than for corresponding "aliphatic" compounds. Hence, the spectral evidence still supports structure I.

In summarizing evidence concerning the possible configurations, the bipyramidal model (D_{3h}) is favored by the high volatility, by the number of observed infrared bands and by the high frequency of the B-H stretching mode, although on this last point the cyclic structure II is also a possibility. Structure III (adjacent borons) is essentially eliminated by the observation that the $B_2H_2^+$ ion species is missing in the mass spectrum of $B_2H_2O_3$.

Acknowledgment.—We are grateful to Dr. R. E. Williams of this Laboratory for assistance in obtaining and interpreting the n.m.r. spectrum of $B_2H_2O_3$.

PASADENA, CALIF.

(21) H. J. Hrostowski and G. C. Pimentel, *THIS JOURNAL*, **76**, 998 (1954).

(22) I. Shapiro and H. G. Weiss, Abstracts of Papers of 134th Meeting, American Chemical Society, Chicago, Illinois, September, 1958, 22N.

(23) W. C. Price, R. D. B. Fraser, T. S. Robinson and H. C. Longuet-Higgins, *Disc. Faraday Soc.*, **9**, 131 (1950).

(24) To be published.