powder photograph showing seven diffuse lines,[9] in positions corresponding to lines on the PdO photographs. The data are not sufficient to permit a rigorous structure determination to be made for PtO, but the similarity to the PdO photographs makes it highly probable that platinous oxide has the PdO structure; measurement of the three best lines ({101}, {103}–{200}, {211}) led to the unit dimensions $a_0 = 3.04 \pm 0.03$ Å., $c_0 = 5.34 \pm 0.05$ Å.

Discussion of the Structures.—In PbO and SnO each oxygen atom is surrounded tetrahedrally by four metal atoms (M–O–M bond angles 118° (4) and 105° (2)) and each metal atom is bonded to four oxygen atoms which form a square to one side of it (O–M–O bond angles 75° (4), 118° (2)). We suggest that the orbital arrangement for Pb^{II} and Sn^{II} in these crystals is that of a square pyramid, four bond orbitals being directed from the metal atom within the pyramid toward the four corners of the base and a fifth orbital, occupied by a stereochemically-active unshared electron pair, being directed toward the apex. The bond distance Pb–O is 2.30 ± 0.01 Å., and Sn–O is 2.21 ± 0.01 Å., corresponding to the radii 1.64 Å. for Pb^{II} and 1.55 Å. for Sn^{II}. These compare reasonably with known radii: Pb^{IV}, octahedral 1.50, tetrahedral 1.46; Sn^{IV}, octahedral 1.45, tetrahedral 1.40 Å. The Pb–Pb distances are 3.67 Å. (separate layers with oxygen layer between), 3.82 Å. (van der Waals contact), and 3.95 Å. (between atoms in the same layer); the corresponding Sn–Sn distances are 3.51, 3.70, and 3.80 Å.

In PdO and PtO each oxygen atom is surrounded tetrahedrally by metal atoms (M–O–M bond angles 98° (2) and 116° (4)), and each metal atom is at the center of a rectangle of oxygen atoms (O–M–O bond angles 82°, 98°). The distortion from the regular tetrahedron and square expected for oxygen and quadricovalent Pd^{II} and Pt^{II} represents a compromise required by the nature of the structure. The bond distances are Pd–O = 2.01 ± 0.01 Å. and Pt–O = 2.02 ± 0.02 Å., corresponding to square radii 1.35 Å. for Pd^{II} and 1.36 Å. for Pt^{II}.

Summary

Powder photographic X-ray data are used to show that the tetragonal crystal PbO has the structure assigned it by Dickinson and Friauf, and not that suggested by Levi and Natta. SnO has a similar structure.

$D_{4h}^7 - P4/nmm$: 2O at 000, $\frac{1}{2}\frac{1}{2}0$; 2Pb(Sn) at $\frac{1}{2}0z\ 0\frac{1}{2}\bar{z}$.
PbO: $a_0 = 3.947 \pm 0.006$, $c_0 = 4.988 \pm 0.008$ Å., $z = 0.2385 \pm 0.0011$.
SnO: $a_0 = 3.796 \pm 0.006$, $c_0 = 4.816 \pm 0.008$ Å., $z = 0.2356 \pm 0.0019$.

The tetragonal crystals PdO and PtO have a different structure (suggested by Huggins), in which the metal atom forms a coplanar rectangular coördination group.

$D_{4h}^9 - P4/mmc$: 2Pd(Pt) at 000, $\frac{1}{2}\frac{1}{2}\frac{1}{2}$; 2O at $\frac{1}{2}0\frac{1}{4}$, $\frac{1}{2}0\frac{3}{4}$.
PdO: $a_0 = 3.02 \pm 0.01$, $c_0 = 5.31 \pm 0.01$ Å.
PtO: $a_0 = 3.04 \pm 0.03$, $c_0 = 5.34 \pm 0.05$ Å.

Pasadena, California Received February 17, 1941

---

[9] Some of the lines were much more diffuse than others; {110} and {112} gave very broad and apparently weak lines, much broader than the lines {101}, {103}–{200}, and {211}.

[Contribution from the Departments of Chemistry of Cornell and Princeton Universities]

The Structures of Methyl Borate and Trimethyl Triborine Trioxane. Interatomic Distances in Boron Compounds

By S. H. Bauer and J. Y. Beach

The correlation of interatomic distances in compounds containing boron with the table of covalent radii[1] faces several difficulties. For many of the compounds investigated the use of the extrapolated radius (0.88 Å.) leads to the observed interatomic distances provided that resonance with several Lewis structures is considered; notable exceptions are the interatomic distances B–C, B–O, and B–F which would best be accounted for by assuming a radius in the neighborhood of 0.80 Å. Several proposals have been advanced to explain this divergence from additivity—in particular, Levy and Brockway[2] postulated that the short B–C distance in boron trimethyl is due to the incompleted valence shell (sp^2 type bonding) around the boron atom, and that the similar shortening in borine carbonyl is

---

[1] L. Pauling and M. L. Huggins, *Z. Krist.*, **A87**, 205 (1934).

[2] H. A. Levy and L. O. Brockway, This Journal, **59**, 2084 (1937).

due to a sextet about the carbon atom. On the other hand, the short B–O and B–F distances are supposed to be due to the extensive ionic character of these bonds.[3] We have undertaken an electron diffraction study of several volatile compounds of boron in an attempt to test these hypotheses. In this paper we are presenting the structural data obtained on $B(CH_3O)_3$ and $(BCH_3O)_3$. Pure samples of both substances were furnished by Dr. A. B. Burg.[4] We wish to acknowledge our indebtedness to him, and to thank him sincerely for his coöperation.

Analysis of the Data

The electron diffraction photographs were interpreted by the visual correlation and radial distribution methods.[5] For the radial distribution curve the positive intensities of the maxima and the negative intensities of the minima were estimated so that their absolute magnitudes fell off on the average as $1/s$.[6] The density function was

$$M(r) = \frac{r^2 \cos ar}{\pi^2 - 4a^2r^2} \sum_k s_k^2 I_k \frac{\sin s_k r}{s_k r}$$

wherein a is the average half width of the maxima and minima, and the sum was taken over all of them.

In calculating the theoretical intensity curves, atomic numbers were used in place of the $(Z - f)_i$ factors except in one model for $B(OCH_3)_3$, and in the case of the hydrogen atoms. The effective atomic number of hydrogen was set equal to 1.2. When this is done, the ratios of the atomic numbers of the atoms in these molecules is nearly equal to the ratios of the $(Z - f)_i$ factors.[5] A temperature damping term $e^{-A_{ij}s^2}$, with $A_{ij} = 0.003$,[7] was included for the C–H bond distances, for the shortest O—H distances in methyl borate and for the shortest B—H distances in trimethyl triborine trioxane. Other terms involving hydrogen atoms were omitted because of their relative unimportance and severe temperature factors. Except for terms affected by internal rotations in methyl borate, and for the long distance terms in trimethyl triborine trioxane, A_{ij} was set equal to zero. This will be discussed in the following sections.

Methyl Borate

Ten photographs of various densities were taken with the sample at 50°. Seven maxima and six minima were measured; their positions and intensities are given in Table I. The fourth maximum is very close to the third and is separated from it by a shallow but definite minimum. The fifth minimum is wide and deep while the sixth maximum is weaker than the seventh and is somewhat closer to the fifth than to the seventh. The appearance of the photographs is closely represented by curve E, Fig. 1, superposed on a continually decreasing background.

Chemical data clearly suggest that the general form of the molecule is three methoxy groups bonded to a central boron atom. By analogy with the configurations of $B(CH_3)_2$, BF_3, BCl_3, BBr_3,[2] and H_3BO_3[8] it appears evident that in methyl borate the three B–O bonds lie in a plane at angles of 120°. This type of model is supported by the radial distribution function shown in Fig. 2. The peak at 1.41 Å. represents an average of the B–O and O–C bond distances. From the table of normal covalent radii C–O = 1.43, while the B–O distance is probably close to that found in boric acid (1.36[8]), and is thus much shorter than the sum of the single covalent radii, 1.54 Å. The peak at 2.38 Å. represents the O—O and the B—C distances. If the B–O distance were 1.38 A., and the BO_3 group planar, the O—O separation would be 2.39 Å. The radial distribution function shows, therefore, that the BO_3 group is at least approximately planar. The peaks at 2.85, 3.71 and 4.34 Å. will be shown to represent the average values of interatomic distances affected by the rotations of the methoxy groups.

Twenty-five theoretical intensity patterns were calculated for various configurations of the molecule. A series of curves were first computed in which it was assumed that the molecule was planar (except for the H atoms) with a three-fold rotational axis, and static. The B–O–C angle, α, was taken as 112°; this value for the oxygen valence angle has been found in dimethyl ether[9] and α-methylhydroxylamine.[10] Curves were calculated for such models in which ρ (= B–O/O–C) had the values 1.54/1.43, 1.50/1.43, 1.46/1.43, 1.42/1.43, 1.38/1.43 and 1.34/1.43. All of these

---

[3] L. Pauling, "The Nature of the Chemical Bond," Cornell University Press, Ithaca, N. Y., 1939, pp. 197, 221.

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

[5] L. O. Brockway, *Rev. Mod. Phys.*, **8**, 231 (1936).

[6] John Walter and J. Y. Beach, *J. Chem. Phys.*, **8**, 601 (1940).

[7] A_{ij} is half of the mean square of the displacement from equilibrium interatomic separation.

[8] W. H. Zachariasen, *Z. Krist.*, **88**, 150 (1934).

[9] L. E. Sutton and L. O. Brockway, THIS JOURNAL, **57**, 473 (1935).

[10] L. O. Brockway, J. Y. Beach and L. Pauling, *ibid.*, **57**, 2693 (1935).

show the fourth and fifth maxima incorrectly and an unobserved hump in the broad fifth minimum. The trend is illustrated by Curve A, Fig. 1, which is the intensity pattern to be expected for $\rho = 1.54/1.43$ (all distances single bond) and curve B, for which $\rho = 1.38/1.43$. The latter approaches the appearance of the observed pattern, but is still unsatisfactory. To obtain agreement with the data, large temperature factors were assumed in the planar model for the terms involving interatomic distances affected by internal rotations; *i. e.*, $A_{ij} = 0.003$ for the C–H and O—H distances as previously, and $A_{ij} = 0.007$ for the C—O and C—C distances, those which could vary over wide ranges if rotation about the B–O bonds were permitted. Curve C, Fig. 1, was computed in this manner for $\alpha = 112°$ and $\rho = 1.38/1.43$. It reproduces the observed pattern except for the fourth maximum which is somewhat too high and is not preceded by a sufficiently pronounced minimum. Neither variation of the oxygen bonding angle nor the introduction of larger temperature factors improved the agreement.

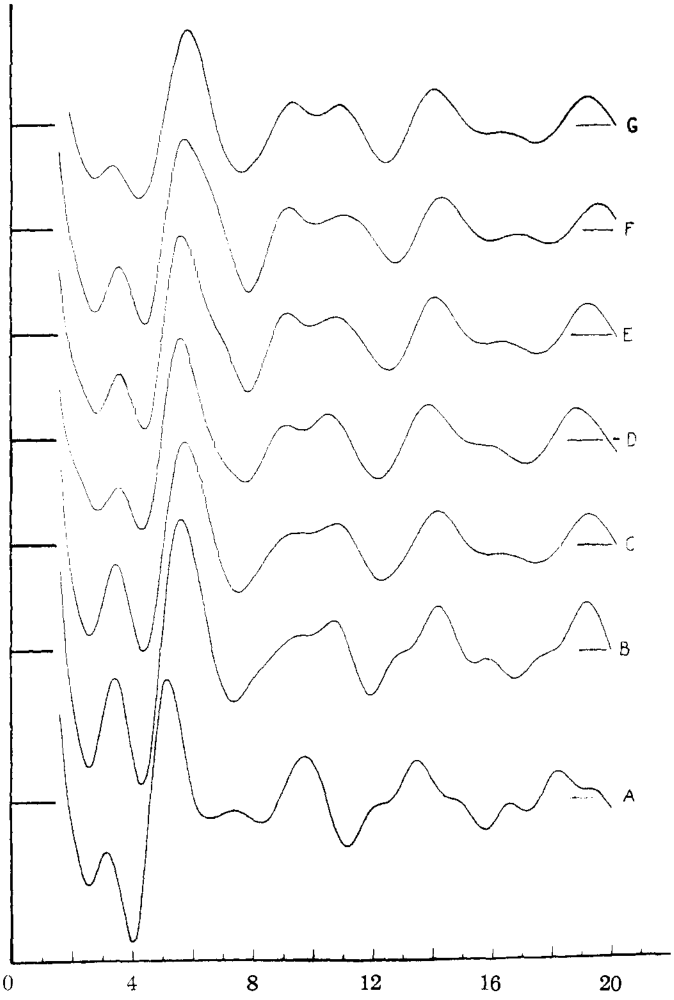


Fig. 1.—Intensity curves for methyl borate: Curves A and B, planar with no temperature factors, $\rho = 1.54/1.43$ and $\rho = 1.38/1.43$ with $\alpha = 112°$, respectively; Curve C, planar with temperature factor, $\rho = 1.38/1.43$, $\alpha = 112°$; Curves D, E, and F, non-planar with temperature factors, using radial distribution distances directly, $\rho = 1.42/1.43$ $1.38/1.43$ and $1.34/1.43$, respectively, and $\alpha = 112°$, 112°, and 116°, respectively; Curve G, $\rho = 1.38/1.43$, $\alpha = 112°$, $\theta_1 = 54°$, $\theta_2 = -54°$, $\theta_3 = 0$.

In the search for molecular models on the basis of which one could predict the observed relative intensities of the third and fourth rings, we considered the following items: (a) Planar symmetric models appear to be unsatisfactory, even when considerable displacements from the equilibrium positions are permitted. Furthermore, the peaks at 2.85, 3.71, and 4.34 Å. in the radial distribution curve do not correspond to the equilibrium separations in such models (2.61, 3.62 and 4.04 Å., respectively). This leads to the conclusion that in the most probable configurations of methyl borate, the CH_3 groups are displaced from the plane of the BO_3 group (Fig. 3). (b) During the motion of the methyl groups, the C—C distance must always remain greater than 3.5 Å. Hence the rotations about the B–O bonds must be synchronized. (c) Added evidence that these rotations are appreciably synchronized may be derived from the fact that the dipole moment of methyl borate was found to be 0.8 *D.*[11] whereas the moment *per methoxy group* is approximately 1.1 *D.*[12] Clearly, as one CH_3 group moves above the plane, another must move below it, so that the major components of their moments cancel.[13]

To obtain the final and satisfactory fit for the intensity pattern we calculated intensity curves for two types of models. The two peaks at 2.85 and 3.71 Å. on the radial distribution curve

---

[11] G. L. Lewis and C. P. Smyth, This Journal, **62**, 1529 (1940).

[12] C. P. Smyth, "Dielectric Constant and Molecular Structure," Chemical Catalog Co., New York, N. Y., 1931.

[13] The fact that the observed moment for methyl borate is even less than that expected for one methoxy group will be discussed below.

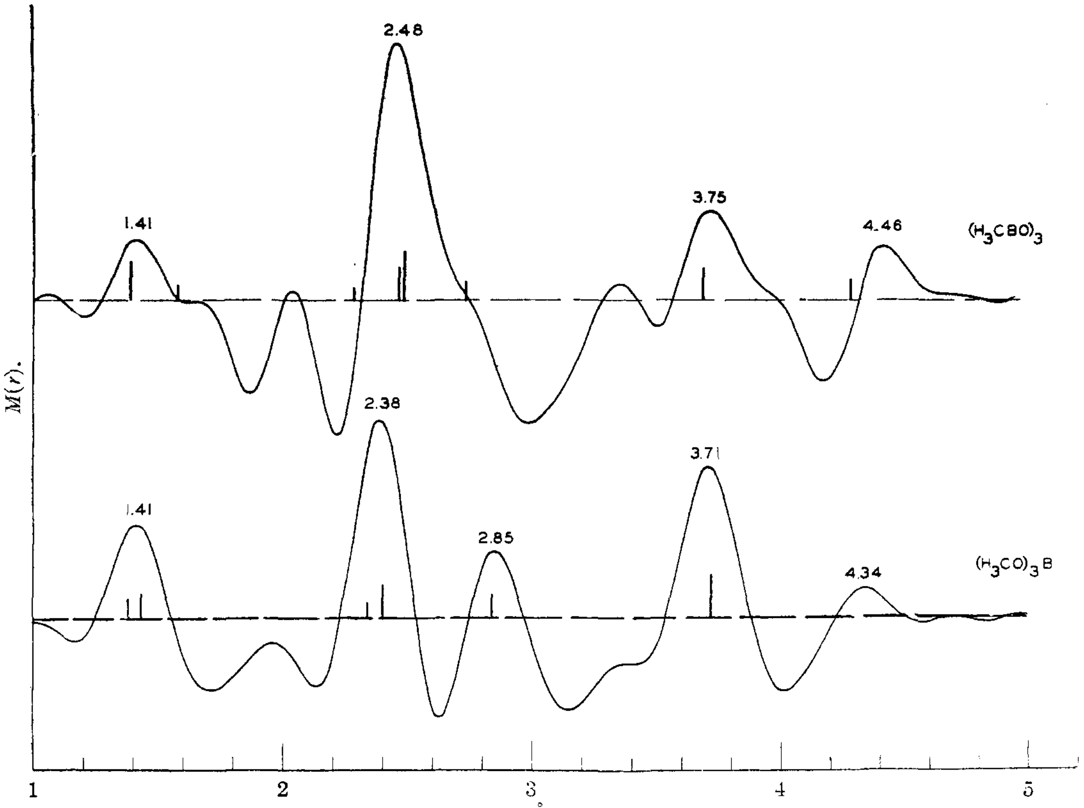


Fig. 2.—Radial distribution curves for methyl borate and trimethyl triborine trioxane.

were assumed to represent the most probable values for the variable C—O and C—C distances. In the first set, curves were computed for a planar BO_3 group, with only the above interatomic separations directly inserted as the C—O and C—C contribution, these being subjected to large temperature damping ($A_{ij} = 0.007$ and 0.012). Again ρ was assigned successively the ratios 1.54/1.43, 1.42/1.43, 1.38/1.43, and 1.34/1.43; also α was varied from 112 to 120°; curves D, E, and F of Fig. 1 are examples. The combination $\rho = 1.38/1.43$; $\alpha = 112°$ and $A_{ij} = 0.007$ leads to a curve E which is in excellent qualitative and quantitative agreement with the data (Table I). While no fit could be obtained for larger values of ρ (curve D), smaller values (1.34/1.43) led to an acceptable pattern provided α was increased to 116° (curve F). However, since the radial distribution curve is best accounted for when $\rho = 1.38/1.43$, we selected this as the most probable value. The two sets of interatomic distances deduced from E and F are well within the experimental error of each other. Variation of A_{ij} from 0.007 to 0.012 had a negligible effect on the predicted pattern. The former value corresponds to a root mean square displacement of 0.12 Å. and the latter to a little over 0.15 Å.

Since no specific molecular model of $(CH_3O)_3B$ corresponds to the particular distances used one might object to the above procedure for obtaining theoretical intensity curves. We therefore computed a second set of curves using specific models of the type illustrated in Fig. 3. Thus curve G, Fig. 1, is for $\rho = 1.38/1.43$, $\alpha = 112°$, $\theta_1 = 54°$, $\theta_2 = -54°$, and $\theta_3 = 0$; $A_{ij} = 0.007$ for the C—O distances, and 0.011 for the C—C distances; $(Z—f)$ values were used throughout. The longer interatomic separations of this configuration are

2C–O	at 2.85 Å.	1C–O	at 2.61 Å.
2C–O	3.44	1C–O	3.63
2C–C	4.18	1C–C	3.71

In this manner the radial distribution curve is fairly well accounted for; the dipole moment of such a model would be approximately that of one methoxy group; and the predicted pattern is in good qualitative and quantitative agreement with the photographs (Table I). Other models having different θ's are probably also satisfactory.

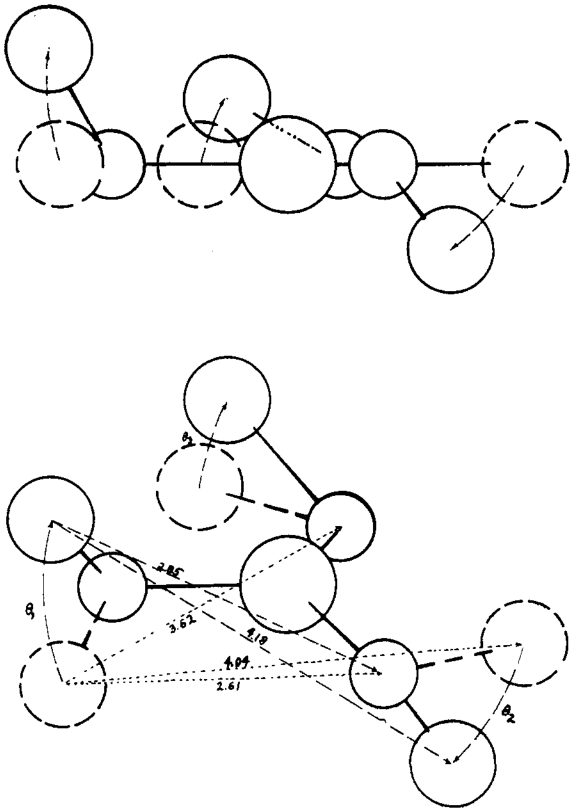


Fig. 3.—A model for methyl borate. Positions indicated by the broken circles are for a planar symmetric model. An end view is also shown.

We may therefore conclude that methyl borate probably has a flat BO_3 group with the boron valence angles equal to 120°, but that there is considerable motion of the methyl groups from the flat configuration. The internal rotations about the B–O bonds appear to be synchronized so that the most probable or perhaps average configuration is somewhat like that illustrated in Fig. 3. The B–O distance is 1.38 ± 0.02 Å.; the C–O distance 1.43 ± 0.03 Å.; and the B–O–C angle 113 ± 3°.

Trimethyl Triborine Trioxane

Electron diffraction photographs showing seven maxima were obtained with the sample at 55°. The positions of the maxima and minima and their visually estimated intensities are given in Table II. The appearance of the photographs is well reproduced by curve E of Fig. 4, superposed on a continually decreasing background. Note that the third maximum is broad and probably double although the minimum between the two components is barely visible; this was assumed to be the case. The radial distribution curve is shown in Fig. 2; principal peaks appear at 1.41, 2.48, and 3.75 Å. In interpreting this curve and in calculating the intensity patterns to be expected, only mesitylene-like models, were considered. Whereas other possible configurations look very unreasonable, this one may be justified by the fact that definite (RBO) trimers of high thermal stability are formed during the dehydration and subsequent polymerization of

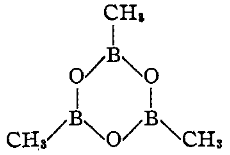


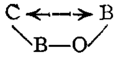
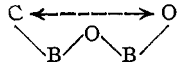
Table I

Methyl Borate

Max.	Min.	I_0	s_0	Curve E s_c	s_c/s_0	Curve G s_c	s_c/s_0
1		10	3.47	3.57	(1.029)	3.41	(0.983)
	2	−15	4.38	4.39	1.002	4.24	.968
2		25	5.70	5.65	0.991	5.86	1.028
	3	−10	7.99	7.83	.980	7.64	0.956
3		10	9.01	9.12	1.012	9.31	1.033
	4	− 4	9.80	9.90	1.010	10.13	1.034
4		6	10.78	10.72	0.994	10.88	1.009
	5	− 8	12.58	12.48	.992	12.41	0.986
5		8	13.88	14.00	1.009	14.03	1.011
	6	− 2	15.02	15.57	1.037	15.65	1.042
6		1	15.96	16.17	1.013	16.27	1.019
	7	− 1	17.48	17.39	0.995	17.42	0.997
7		2	19.02	19.04	1.001	19.10	1.004
				Average	1.003		1.007
				Average deviation	0.011		0.020

s_c computed for B–O = 1.38; O–C = 1.43; C–H = 1.09; ∠OBO = 120°, ∠COB = 112°; ∠HCH, ∠HCO = $109^1/_2$°.

boronic acids,[14] and *a posteriori* by the fact that the general features of the observed pattern are reproduced in the computed curves for any reasonable assumptions of the interatomic distances of the model.

Assuming this type of structure, the radial distribution peaks are accounted for as follows. The peak at 1.41 Å. represents the average of the B–O and B–C separations. As the B–O distance is about three times as important in scattering power as the B–C distance, this peak is principally due to the former. Now in boron trimethyl B–C = 1.56 Å.; if it is the same in this compound, the B–O distance is probably somewhat under 1.41 Å. The maximum at 2.48 Å. represents the scattering due to O—O, B—B, C—O and long B—O distances, which are not resolved. The peak at 3.75 Å. is due to the  distance, while the final maximum at 4.46 Å. is probably produced by the long  scattering.

Theoretical intensity curves were calculated for eighteen models; temperature factors were included in the last seven. In these A_{ij} was set equal to 0.003 for the C–H and B—H distances, and to 0.007 for the long C—B, C—O, and C—C distances. The B–O–B angle, α, was varied from 120° to 105°; the O–B–O angle, β, from 130° to 110°; and the ratio of the B–O to B–C distance, ρ, was assigned values from 1.38/1.48 to 1.38/1.64. In some of the models the B_3O_3 ring was a plane regular hexagon, in some it was a plane trigonal hexagon, and in others the ring was puckered. None of the intensity patterns predicted on the basis of the non-planar models (boron valence angles 120°, oxygen valence angles 105° and 110°) or of the staggered ring models (boron and oxygen valence angles $109^{1}/_{2}$°), as in paraldehyde,[15] was in agreement with the photographs. In the former case the appearance of the third and fourth peaks was particularly unsatisfactory; Curve A_1 of Fig. 4 is for the tub form of the configuration, ρ = 1.39/1.56, α = 105° and

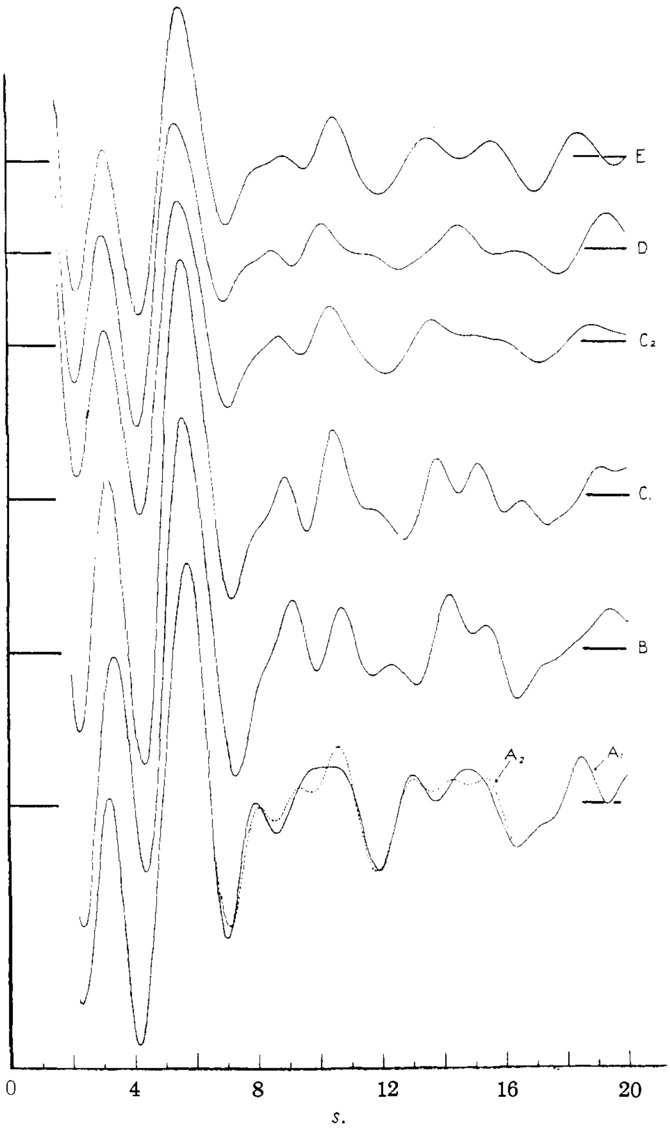


Fig. 4.—Intensity curves for trimethyl triborine trioxane; C_2, D, and E are plotted on a smaller scale than are $A_{1,2}$, B, and C.

β = 120°, while curve A_2 is for the Z form of the same model. Variation of ρ and of α introduced unobserved features in other parts of the curve but did not alter properly the region of the third ring. Of all the paraldehyde-type models studied curve B of Fig. 4, corresponding to ρ = 1.39/1.56 and α = β = $109^{1}/_{2}$° appears to be most like the pattern observed. It is nevertheless unsatisfactory because of the poor quantitative fit at the third and fourth maxima. Further, an unobserved subsidiary peak is present in the broad fifth minimum, and the shape of the fifth and six maxima differ from that which is present on the photographs. Again, variation of ρ introduced

[14] C. R. Kinney and D. F. Pontz, THIS JOURNAL, 58, 197 (1936); H. R. Snyder, J. A. Kuck and J. R. Johnson, *ibid.*, 60, 105 (1938).

[15] D. C. Carpenter and L. O. Brockway, *ibid.*, 58, 1270 (1936).

undesirable features into the right-hand half of the curve.

The intensity pattern predicted for a plane regular hexagonal model, $\alpha = \beta = 120°$ and $\rho = 1.38/1.54$ (no temperature factor) is shown in Fig. 4, curve C_1. It is unsatisfactory because of the shape of the third maximum, the shoulder on the right of the fourth ring, and the appearance of the seventh peak. The curve for the same model, temperature factors included, is marked C_2; it predicts an incorrect intensity relation between the fifth and sixth peaks. Changing ρ to 1.38/1.64, still using temperature factors, makes the disagreement more prominent (curve D); note the shelf on the fourth maximum. However, when the B_3O_3 ring is distorted to make $\alpha = 110°$ and $\beta = 130°$, with $\rho = 1.38/1.56$, curve E results which is in satisfactory qualitative and quantitative agreement with the photographs. For smaller values of ρ the sixth ring becomes more intense than the fifth, which is not observed. On the other hand, if ρ is increased, the third maximum becomes too unsymmetrical.

TABLE II

TRIMETHYL TRIBORINE TRIOXANE

Max.	Min.	I_0	s_0	s_c/s_0
1		12	3.30	(0.945)
	2	−15	4.35	(.972)
2		20	5.62	.997
	3	− 8	6.83	1.035
3		4 and 5	8.02 (mean)	
	4	− 6	9.33	1.027
4		6	10.25	1.027
	5	− 3.5	11.97	1.003
5		3.5	13.35	1.016
	6	− 2	14.92	0.984
6		2	15.76	.991
	7	− 1.8	17.30	.986
7		1.8	18.90	.976
			Mean	1.004
			Average deviation	±0.017
			B–O	1.39 Å.
			B–C	1.57 Å.

s_c calculated for plane model, C = 1.38/1.56, $\alpha = 110°$, C–H = 1.09 and HCH = 109.5°.

Quantitative comparison of curve E and the photographs is made in Table II. Hence this study leads to the conclusion that trimethyl triborine trioxane is probably a mesitylene-like molecule, with all the atoms except hydrogen in a plane. In the B_3O_3 ring the B–O–B angle is 112 ± 3°; the B–O distance is 1.38 ± 0.02 Å.; and the B–C distance is 1.57 ± 0.03 Å.

Discussion

The C–O distance observed in methyl borate, 1.43 Å., is equal to the sum of the covalent radii[1]; however, the B–O distance in that molecule, 1.38 Å., is quite different from the sum of the radii of B and O, 1.54 Å. This low value for B–O has been found previously in boric acid,[8] potassium metaborate,[16] and calcium metaborate.[17] In the BO_3 groups of boric acid and calcium metaborate the boron–oxygen separations are 1.35 and 1.36 Å., respectively. The B–O distance in the B_3O_3 ring in potassium metaborate is 1.38 Å., and the corresponding distance observed in the B_3O_3 ring in $(CH_3BO)_3$ is also 1.38 Å. However, in the metaborate group ($B_3O_6^{\equiv}$), the oxygen atoms outside the ring are only 1.33 Å. from the boron atoms. Pauling[3] has discussed these shortenings in terms of graphite-like resonance of a double bond around the boron atom and electronegativity effects, as mentioned in the introduction. The existence of B–O distances less than 1.38 Å. is particularly difficult to explain on this basis. Further, it seems unsatisfactory to have the electronic structures consist completely of double bonded structures which have a B^- and O^+.

Parallel to the above case, there is also difficulty with respect to the B–F distance in BF_3. The observed value is 1.30 Å. while the sum of the single bond radii is 1.52 Å. Similar apparent shortenings are observed in BCl_3 and BBr_3, but in the latter two compounds the data can be accounted for by assuming a graphite-like resonance of a double bond[2]; in the fluoride the decrease below the expected value is so great that this explanation is no longer adequate.

The B–C separation we find in $(CH_3BO)_3$ 1.57 Å., is less than the sum of the covalent radii,[1] 1.65 Å., but our value agrees with those which have been obtained previously for $(CH_3)_3B$[2] and H_3BCO.[18] In these two compounds the shortening has been attributed[2] to an incomplete shell of electrons around the boron atom. While this is a possible explanation it does not seem conclusive if the strengths of sp^2 bonds and sp^3 bonds as calculated by Pauling[19] are significant. The strengths of the two types are nearly equal, being 1.991 and 2.000, respectively. Furthermore, a little consideration will show that the dimensions of the $(CH_3BO)_3$ molecule exclude *either* the

---

[16] Zachariasen, *J. Chem. Phys.*, **5**, 919 (1937).

[17] Zachariasen and Ziegler, *Z. Krist.*, **83**, 354 (1932).

[18] S. H. Bauer, THIS JOURNAL, **59**, 1804 (1937).

[19] Pauling, "Nature of the Chemical Bond," pp. 86 and 88.

explanation offered for the short B–O or that for the short B–C distances. A short B–C means that the normal single bond structure is important, therefore the B–O should be longer than is observed.

We believe that many of these questions regarding boron can be answered in the light of the suggestions made by Schomaker and Stevenson.[20] Since they have not applied their method for estimating interatomic distances to compounds of boron we have undertaken to do so. We plotted the new single covalent radii for F, O, N, C and Li and interpolated a radius for boron. From several interpolations the value seems to be 0.83 or 0.84 Å. Dr. Stevenson pointed out to us that the spectroscopically determined interatomic distance in B–H could be used to calculate a B radius. This value is 0.86 Å. We have adopted the value 0.85 Å. With this value we have computed the expected single bond distances for various elements attached to boron; the results are summarized in Table III. The interatomic separations deduced by adding the covalent radii[1] are also shown. Both sets are compared with the observed distances obtained from X-ray and electron diffraction studies.

From Table III it appears that: (a) the discrepancy between the distances expected and those observed has been increased for the hydrides of boron. The explanation given previously[23] that the large B–H and B–B separations in diborane are due to its electron deficiency, and that these distances become shorter in compounds having a smaller proportional deficiency, is still applicable. However, the effect of resonance with one-electron-bond and no-bond structures seems to be greater than was previously thought; in fact, it now appears in the average B–B separation of B_5H_5. Thus another question is partially answered, for on the basis of the Pauling and Huggins table, the boron–boron distance in that compound was equal to the sum of the radii, in spite of its having a deficiency of four electrons. (b) In the crystals CaB_6, AlB_2, and FeB the B–B distances are greater than those predicted from our value for R_B. Again, this is a more reasonable situation than has previously existed when the values expected were larger than the observed ones, since in all these configurations the boron atoms do not have a sufficient number of electrons to make all the equivalent bonds electron pair bonds. Thus in CaB_6, the boron atoms are at the corners of octahedra so situated that each B is equidistant from five other boron atoms; in AlB_2, the borons are found in graphite-like layers between which aluminum atoms build a simple hexagonal lattice, so that each boron atom contacts three other B's and six Al's; in FeB, the boron atoms form zigzag chains, but the borons also lie at the center of trigonal prisms formed by six iron atoms, so that each boron atom has two B's and six Fe's for its nearest neighbors. However, we have no unique way of estimating the extent of the electron deficiency per bond in these crystals. (c) The new value for the B–C distance agrees perfectly with the one observed, and thus the necessity of making an assumption which was not very convincing has been removed. (d) The discrepancy between the observed and predicted B–N distances has been lessened for the case of boron nitride and of triborine triamine, through the use of the new table of radii. The previous large distance was accounted for by assuming graphite-like resonance in the former compound ($^1/_3$ double bond character), and benzene-like resonance in the latter ($^1/_2$ double bond character). The explanation for the small remaining discrepancy is presumably the same as before except that the structures involving double bonds are much less important. (e) Since the average B–N distance in B_2NH_7 checked so well the value predicted on the basis of the P and H table of radii, there is a considerable discrepancy with the prediction made at present. Although the electron diffraction data do not eliminate completely the configuration ($H_3B:NH_2:BH_2$) they support more strongly an arrangement analogous to dimethylamine ($H_3B:NH:BH_3$); it is not surprising therefore that the B–N separation is larger than the value calculated, for $(H_3B)_2NH$ has two electrons less than does $(H_3C)_2NH$. Since there is a tendency for N to maintain its unshared electron pair[20a] (otherwise it must assume a formal charge of +2), an "electron deficiency" in the molecule as a whole results. In $H_3BN(CH_3)_3$ the B–N dis-

---

(20) V. Schomaker and D. P. Stevenson, THIS JOURNAL, **63**, 37 (1941). Their method for calculating interatomic distances is the following:

$$r_{AB} = r_A + r_B - 0.09 \,|\, x_A - x_B$$

where r_{AB} is the interatomic distance, r_A and r_B are radii for atoms A and B, x_A, x_B are the electronegativities of the elements as given by Pauling, "Nature of the Chemical Bond," p. 64. Schomaker and Stevenson proposed new values for some atomic radii.

(20a) Pauling, reference 3, p. 86. Compare with R. S. Mulliken, *J. Chem. Phys.*, **3**, 506 (1935).

TABLE III

Bond	Compound	Distance observed	S. B. dist. S and S	Sum S. B. R. P and H	References and notes; see below
B—H	BH	1.225 Å.	1.21 Å.	1.18 Å.	21
	B_2H_6, B_4H_{10} B_5H_{11}, $Al(BH_4)_3$	1.27 ± 0.03			22,[a]
	B_5H_9	1.17 ± 0.04			23
	H_3BCO	1.20 ± 0.03			18
B—B	B_2	1.595 1.628	1.70	1.76	24
	CaB_6	1.716			25, *b*
	AlB_2	1.73			26, *b*
	FeB	1.77			27, *b*
	B_2H_6	1.86 ± 0.04			22, *a*
	B_4H_{10}	1.84 ± 0.04			22, *a*
	B_5H_{11}	1.81 ± 0.03			22, *a*
	B_5H_9	1.76 ± 0.02			23, *a*
B—C	$B(CH_3)_3$	1.56 ± 0.02	1.57	1.65	2, *c*
	H_3BCO	1.57 ± 0.03			18, *c*
	$(OBCH_3)_3$	1.57 ± 0.03			B and B, *c*
B—N	BN(s)	1.45 ± 0.01	1.50	1.58	28, *d*
	$B_3N_3H_6$	1.44 ± 0.02			29, *d*
	B_2NH_7	1.56 ± 0.03			29, *e*
	$H_3BN(CH_3)_3$	1.62 ± 0.15			18, *e*
B—O	BO	1.20	1.45	1.54	30
	$BAsO_4$	1.49			31
	BPO_4	1.44			31
	$(CH_3O)_3B$	1.38 ± 0.02			B and B, *f*
	$(OBCH_3)_3$	1.39 ± 0.02			B and B, *f*
	CaB_2O_4, H_3BO_3	1.35, 1.36			8, 17, *f*
	$K_3B_3O_6$	1.38, 1.33			16, *f*
B—F	BF	1.312	1.39	1.52	32
	BF_3	1.30 ± 0.02 1.29			2, *g* 33
	KBF_4	1.45			34
B—Cl	BCl	(1.71)	1.75	1.87	35
	BCl_3	1.74 ± 0.02			2, *h*
B—Br	BBr	(1.84)	1.92	2.02	35
	BBr_3	1.87 ± 0.02			2, *h*
B—Al	AlB_2	2.37			26
	$Al(BH_4)_3$	2.14 ± 0.02	<2.14	2.14	36
B—Fe	FeB	2.12–2.18	<2.11	2.11	27

[a] Letters, a–h refer to sections of text following this table.

---

(21) G. W. King, *J. Chem. Phys.*, **6**, 378 (1938). The value quoted is that for r_e of the ground state, $^1\Sigma^+$; however, the equilibrium interatomic distance changes little in going from the lowest to any of the three known excited states.

(22) S. H. Bauer, THIS JOURNAL, **59**, 1096 (1937); **60**, 805 (1938).

(23) S. H. Bauer and L. Pauling, *ibid.*, **58**, 2403 (1936).

(24) A. E. Douglas and G. Herzberg, *Phys. Rev.*, **57**, 752 (1940). The configuration of the lower (not ground) state is given as $^3\Sigma^-_g$, with four bonding and two antibonding electrons. One must therefore assume that the four are somewhat more strongly bonding than the two are antibonding, resulting in a bond of order greater than unity.

(25) L. Pauling and S. Weinbaum, *Z. Krist.*, **87**, 181 (1934).

(26) W. Hofmann and W. Janiche, *Z. physik. Chem.*, **B31**, 214 (1936).

(27) "Strukturberichte." Vol. 111, 1937, p. 12.

(28) O. Hassel, *Norsk. geol. Tidskrift*, **9**, 266 (1926).

(29) S. H. Bauer, THIS JOURNAL, **60**, 524 (1938).

(30) R. S. Mulliken, *Rev. Modern Phys.*, **4**, 1 (1932). The ground state, $^2\Sigma^+$, was assigned five more bonding than antibonding electrons, and hence has a bond order of approximately $2^1/_2$. The short interatomic distance is therefore entirely reasonable.

(31) G. E. R. Schultze, *Z. physik. Chem.*, **B24**, 215 (1934). Average values given.

(32) F. W. Paul and H. P. Knauss, *Phys. Rev.*, **54**, 1072 (1938). R_e quoted is for the lowest state observed, $^3\pi$, which probably is not the ground state. However, since the molecule is isoelectronic with N_2 and CO, it is entirely reasonable to suppose that its interatomic distance corresponds to partial double bond character, as indicated by its low value.

(33) D. M. Gage and E. F. Barker, *J. Chem. Phys.*, **7**, 455 (1939); from moment of inertia deduced from parallel fundamental band (ν_3).

(34) C. Finbak and O. Hassel, *Z. physik. Chem.*, **B32**, 433 (1936); J. L. Hoard and V. Blair, THIS JOURNAL, **57**, 1985 (1935)—average value selected. An accurate parameter determination was not made in either case.

(35) E. Miescher, *Helv. Phys. Acta*, **8**, 279, 486 (1935). The interatomic distances for BCl and BBr were deduced from spectral data through the use of Badger's rule.

(36) J. Y. Beach and S. H. Bauer, THIS JOURNAL, **62**, 3440 (1940).

tance is not known with a sufficient accuracy because of the complexity of the molecule. (f) The B–O distances observed in BO_3 groups and in B_3O_3 rings are only 0.07 Å. lower than the separations predicted for the single covalent bonds, whereas in comparison with the former radius sum the divergence was of the order of 0.16 Å. The difficulty stressed in the introduction is thus removed. The remaining shortening is probably due to double bond structures (graphite-type resonance in BO_3 and $B_3O_6^{\equiv}$ groups, benzene-type resonance in the B_3O_3 ring of trimethyl triborine trioxane) but these can now be said to contribute to a smaller and hence to a more reasonable extent. Nevertheless, the fact that $>B^{-}{=}\ddot{O}^{+}{-}$ groups do participate in the representation of the ground state may help to reduce the moment of methyl borate[11] by reducing the O–C moment. (g) The case of BF_3 is analogous to that presented above for the BO_3 group; the percentage shortening below single bond values is approximately the same in both. (h) The B–Cl distance in BCl_3 is seen in Table III to agree with the newly predicted separation. This eliminates the previous necessity of ascribing to the ground state large contributions of configurations such as $>B^{-}{=}\ddot{\underset{..}{Cl}}{:}^{+}$. In BBr_3, a slight participation of such structures would account for the small remaining shortening.

It seems evident that in attempting to account for the observed distances in boron compounds the new method of calculating interatomic distances is a definite step forward.

Summary

An electron diffraction investigation of the vapors of methyl borate and of trimethyl triborine trioxane led to the following structures for these compounds.

Methyl borate: Planar BO_3 group, with B—O = 1.38 ± 0.02 Å.; O–C = 1.43 ± 0.03 Å.; and the B–O–C angle equal to 113 ± 3°. Rotation of the methoxy groups about the B–O bonds is indicated.

Trimethyl triborine trioxane: Planar six membered ring, with alternating boron and oxygen atoms. The methyl groups are bonded to the boron atoms, and are in the plane of the ring. B–O = 1.39 ± 0.02 Å.; B–C = 1.57 ± 0.03 Å.; and the B–O–B angle is 112 ± 4°.

The electron configurations of these substances are discussed. The available data on boron compounds are reviewed and it is decided that the method recently suggested by Schomaker and Stevenson for calculating interatomic distances is the most successful method available at present for accounting for the interatomic distances observed in boron compounds.

PRINCETON, N. J.
ITHACA, N. Y.

RECEIVED JANUARY 24, 1941

[JOINT CONTRIBUTION FROM THE DEPARTMENTS OF CHEMISTRY OF POMONA COLLEGE, AND THE UNIVERSITY OF SOUTHERN CALIFORNIA]

The Configuration of Hydrogenated Cupric Disalicylaldehyde by Means of Magnetic Measurements

BY GEORGE N. TYSON, JR., AND ROBERT E. VIVIAN

The catalytic properties of coördinated compounds of the transition elements have been well known for some time.[1] In particular, Calvin[2] has lately studied kinetics of hydrogenations using copper disalicylaldehydes and other copper compounds. In the work reported by Calvin,[2] it has been stated that the hydrogenation of cupric disalicylaldehyde results in a reduction of the compound to cuprous disalicylaldehyde. The experimental work reported in this paper requires another interpretation of the mechanism that occurs from hydrogenation of the cupric disalicylaldehyde, which satisfactorily accounts for the catalytic activity of the hydrogenated compound.

When green cupric disalicylaldehyde is dissolved in pyridine, a solution of the same color results. After hydrogenation has been effected, the solution becomes deep ruby-red. No precipitate was present, nor was the Tyndall effect evidenced with either of the solutions, and it was therefore assumed that the compounds were present in true solution. By means of magnetic susceptibility measurements, it is found that the copper is present as cupric ion in both the green and red solutions. Thus, the change in color of the solu-

---

[1] Baudisch and Welo, *Chem. Rev.*, **15**, 1 (1934).

[2] M. Calvin, *Trans. Faraday Soc.*, **34**, 1181 (1938).