change in the slope factors to which reference was made in the preceding section. Thus, for the complete oxidation process, we may picture as many as six parallel reaction paths. Under certain conditions one or another of these may predominate—in very acid solutions, for example, molecular hydroquinone is the only component present in kinetically significant concentration. That this is the only reactant is shown by the fact that hydrogen ion under these conditions exerts practically no retardation on the oxidation process. At the high positive potentials encountered in such a solution, it is probable that two electrons will be lost directly.

In a similar manner the reduction process may be viewed as being a composite of several parallel reactions. The molecule of quinone may react with either two, one or no hydrogen ions, taking up in each case either one or two electrons from the cathode. Examination of Fig. 9 indicates that the reduction becomes zero order with respect to hydrogen ion in slightly alkaline solutions, is close to first order in the range pH 6 to 0, and shows a trend to higher order at greater acidities.

Summary

1. An apparatus is described for measuring polarizations under conditions of rapid agitation and the exclusion of oxygen.

2. The catalytic properties of blank platinum for the oxidation and reduction of quinhydrone were investigated, and the optimum conditions for reproducibility determined.

3. The kinetics of the anodic and cathodic processes were ascertained by determining the current at fixed potential as a function of the concentrations of quinone, hydroquinone and hydrogen ion; and a general approximate equation was set up.

4. Several possible mechanisms were examined with the conclusion that the reaction mechanism is a complicated one involving several parallel reaction paths.

The Structure of the Hydrides of Boron. III.[1] Borine Carbonyl and Borine Trimethylammine

BY S. H. BAUER

Introduction

For many years the chemistry of the boron hydrides and their derivatives has provided a very interesting puzzle which has strongly resisted attempts at solution. A new method of attack on the problem is that of determining the structure of the molecules of these substances by electron diffraction or similar methods. The direct result of such an investigation is the determination of the nuclear configuration of the molecule. From the proximity of certain nuclei straightforward conclusions can be drawn regarding the distribution of valence bonds; it is possible also to make some statements regarding the nature of these bonds by the study of the experimentally determined values of the interatomic distances. However, the general interpretation of chemical properties in terms of molecular structures cannot

be made without the aid of some relationship connecting them, and very few correlations of this nature have been discovered.[2] As a working hypothesis to be used in the interpretation of the results communicated in the present paper, the author has adopted the program of assuming the relationship to be a simple one and interpreting the facts as far as possible from this viewpoint. It is very likely that as more data become available it may be necessary to refine or even alter the hypothesis.

In this paper an electron diffraction investigation of two derivatives of diborane,[3] borine carbonyl and borine trimethylammine, is described leading to unique assignments of structures to

(1) Papers which have appeared previously will be designated as follows: I, "The Pentaborane B₅H₉," S. H. Bauer and L. Pauling, THIS JOURNAL, **58**, 2403 (1936). II, "Diborane," S. H. Bauer, ibid., **59**, 1096 (1937).

(2) For an application to the case of the fluoromethanes see L. O. Brockway, J. Phys. Chem., **41**, 185 (1937), and discussion on page 317 of the same issue.

(3) Drs. Schlesinger and Burg suggested that these substances may be suitable for an electron diffraction investigation. A description of the methods of preparation and of some interesting chemical properties has recently been published [A. B. Burg and H. I Schlesinger, THIS JOURNAL, **59**, 780 (1937)].
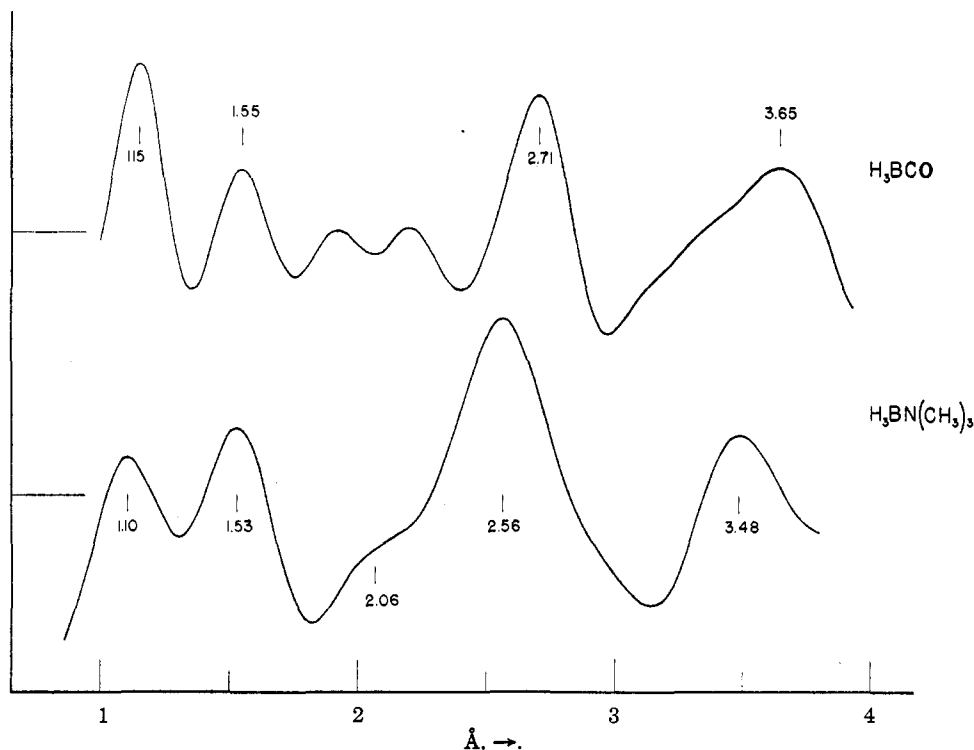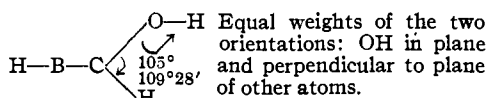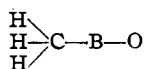
Fig. 1.—Visual appearance of electron diffraction photographs.

the compounds. An explanation is advanced for the very large difference in their thermal stability.

The Photographs.—The samples of borine carbonyl and borine trimethylammine were prepared by Dr. A. B. Burg at the University of Chicago. The carbonyl was shipped in dry ice to this Laboratory, purified by means of a fractional condensation at $-155°$ (to remove the diborane and carbon monoxide which resulted from a slight amount of decomposition) and immediately used in the diffraction experiments. These were performed with the gas at $-70°$ to prevent further decomposition. Using electrons of λ 0.0614, ten photographs of varying density showing up to seven rings were obtained for the borine carbonyl and five photographs showing up to five rings for the borine trimethylammine.[4] The characteristic features of the patterns are sketched in Fig. 1. In comparing these with the theoretically calculated intensity curves one should bear in mind that the latter are to be superposed on a continuously decreasing background introduced through the $(1/\sin^4(\theta/2))$ and incoherent scattering terms which have been neglected.[5]

Analysis of the Data

Radial distribution curves which have been calculated using corrected intensity factors (column

(4) This substance had to be heated to approximately 135° to obtain a sufficiently high vapor pressure for the diffraction experiment. Due to the design of the present high-temperature nozzle the borine trimethylammine had to be exposed to an atmosphere of dry nitrogen for about twenty minutes. Because of its extraordinary stability) this step did in no way affect the compound.

(5) For justification, see L. Pauling and L. O. Brockway, *J. Chem. Phys.*, **2**, 867 (1934).

5, Tables I and II) are plotted in Fig. 2. These factors were determined by means of a procedure developed by V. F. H. Schomaker.[6] Although all the prominent distances appear as well resolved peaks and are given to within a few per cent. of the values finally chosen, these curves are of no aid when a choice between several closely similar structures has to be made.

Borine Carbonyl.—The following types of models have been investigated in detail.

Type 1.　Linear B–C–O. H atoms tetrahedrally arranged around the B.

Model	a	b	c
A	1.17	1.51	1.15
B	1.17	1.56	1.15
C	1.10	1.56	1.15
D	1.22	1.59	1.15
E	1.17	1.61	1.15
F	1.22	1.61	1.15
G	1.17	1.66	1.15

Type 2.

B–H	1.17
B–C	1.56
C–H	1.08
C–N	1.25

Equal weights of the two orientations: H_2B in plane and perpendicular to plane of CHO group.

Type 3. A.

B–H	1.17
B–O	1.44
O–C	1.15

Linear—as in type 1

B. Equal weights taken of BH_3 group in two positions, through a rotation of 60°.

H–B	1.17
B–O	1.44
O–C	1.25

(6) A description of the method is soon to appear in THIS JOURNAL.

Fig. 2.—Modified radial distribution curves showing principal distances.

Type 4.

$$\text{H—B—C} \overset{\diagup \text{O—H}}{\underset{\diagdown \text{H}}{\overset{105°}{\underset{109°28'}{<}}}}$$

Equal weights of the two orientations: OH in plane and perpendicular to plane of other atoms.

H–B	1.17	C–H	1.08
B–C	1.40	O–H	0.96
C–O	1.44		

Type 5.

$$\overset{\text{H}}{\underset{\text{H}}{\overset{\text{H}}{>}}}\text{C—B—O}$$

Arrangement as in Type 1.

H–C	1.08
C–B	1.56
B–O	1.20

In complete accord with the available chemical data, types 2, 3, and 4 are eliminated immediately, on the basis of striking lack of agreement in the qualitative form of the pattern (Fig. 3); type 5 may be discarded on the basis of chemical evidence such as the following.[3] The decomposition reaction

$$2H_3BCO \rightleftarrows B_2H_6 + 2CO$$
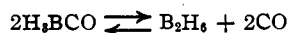
takes place readily at room temperature (although equilibrium is not reached in a short time unless the mixture is heated to 90°) while the replacement reaction

$$H_3BCO + N(CH_3)_3 \longrightarrow H_3BN(CH_3)_3 + CO$$
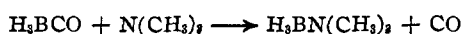
rapidly approaches completion at ordinary temperatures. These indicate that the initial fragments in the decomposition are probably borine

and carbon monoxide and that, accordingly, the molecule contains the groups BH_3 and CO.[3] Of the models of type 1 (Fig. 4), A, B, C, E, and G are seen to be unsatisfactory, leading to improper intensity relationships among the various peaks and in general to rather poor quantitative agreement with the measured ring diameters; both D

TABLE I

Max.	Min.	$s_{obsd.}$	I	$I_{corr.}$	Model 1 D	Ratio $s_{calcd.}/s_{obsd.}$ 1 E	1 F
1		5.64	10	28	(1.059)	(1.089)	(1.059)
	2	6.44			(1.084)	1.040	(1.065)
2		7.51	9	43	0.973	0.973	0.968
	3	8.68			1.029	1.037	1.034
3		9.76	4	27	0.990	0.976	0.984
	4	11.07			.950	.943	.964
4		12.37	6	56	.973	.970	.964
4a		14.07	3	32			
	5	15.47			.972	.974	.967
5		17.02	4	46	1.000	1.005	.994
5a		18.27	2	23			
6		21.1	1	11			
7		23.3	1	11			
		Mean ratio			0.984	0.990	0.982
		Mean deviation			.019	.028	.014
Final distances		B–C			1.56	1.59	1.58
		C–O			1.13	1.14	1.13
		B–H			1.20	1.16	1.20

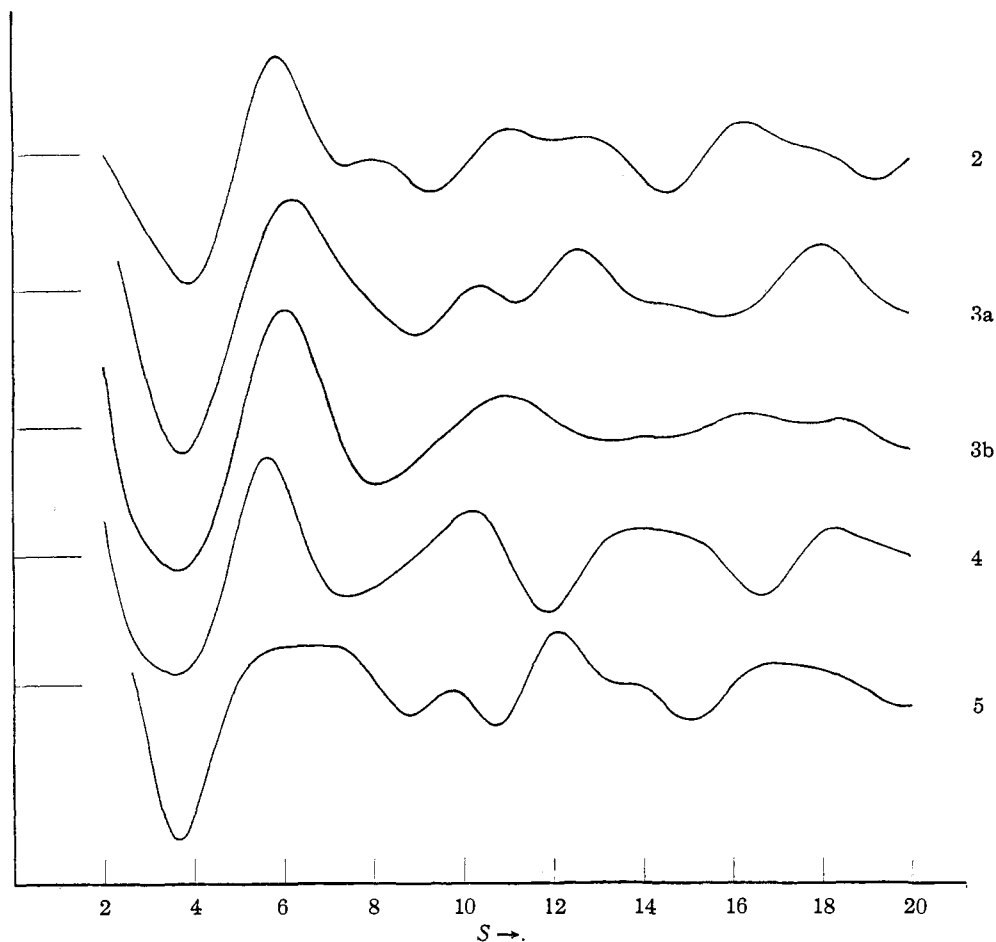The probable error was taken equal to or somewhat greater than the mean deviation.

Fig. 3.—Calculated intensity curves for H_3BCO.   Model numbers indicated.

and F reproduce very well all the features of the pattern and are in good quantitative agreement with the data (Table I). It is difficult to decide between them although D fits somewhat better the intensity distribution observed in the region of the first two peaks. The final values of the interatomic distances given by the two models are equal to within the experimental error.

On comparing $s_{obsd.}$ with $s_{calcd.}$ for models D and F, we reach the following conclusions regarding the structure of borine carbonyl: (a) the B–C–O atoms are linearly arranged and the H atoms complete the tetrahedron around the boron; (b) the best values for the interatomic distances are H–B = 1.20 ± 0.03 Å.; B–C = 1.57 ± 0.03 Å.; C–O = 1.13 ± 0.03 Å.

Borine Trimethylammine.—The generally accepted notions of valency lead one to expect a neopentane-like configuration for borine trimethylammine, and indeed not only are the diffraction patterns produced by these substances almost identical in form but also the corresponding ring diameters have nearly the same dimensions. The last column of Table II in which are given the ratios of $s_{obsd.}(H_3BN(CH_3)_3)/$ $s_{obsd.}(C(CH_3)_4)$ demonstrates this.[7] The fact that values of the ratio are observed on both sides of unity indicates that the mean molecular distances in borine trimethylammine are very near those of neopentane but that the former molecule has not the high symmetry of the latter. In calculating the theoretical intensity distributions it was found that the curve for the model in which free rotation of the methyl groups, etc., is assumed (2c, Fig. 5) differs imperceptibly in form and only slightly (±0.3) in the positions of the maxima and minima from the curve in which all the variable distances produced by the rotations are neglected (2a).[8]

(7) Data on neopentane were obtained from the publication of L. Pauling and L. O. Brockway, THIS JOURNAL, **59**, 1223 (1937).

(8) Pauling and Brockway discovered that this was true for neopentane, and suggested that it would also be applicable to borine trimethylammine.
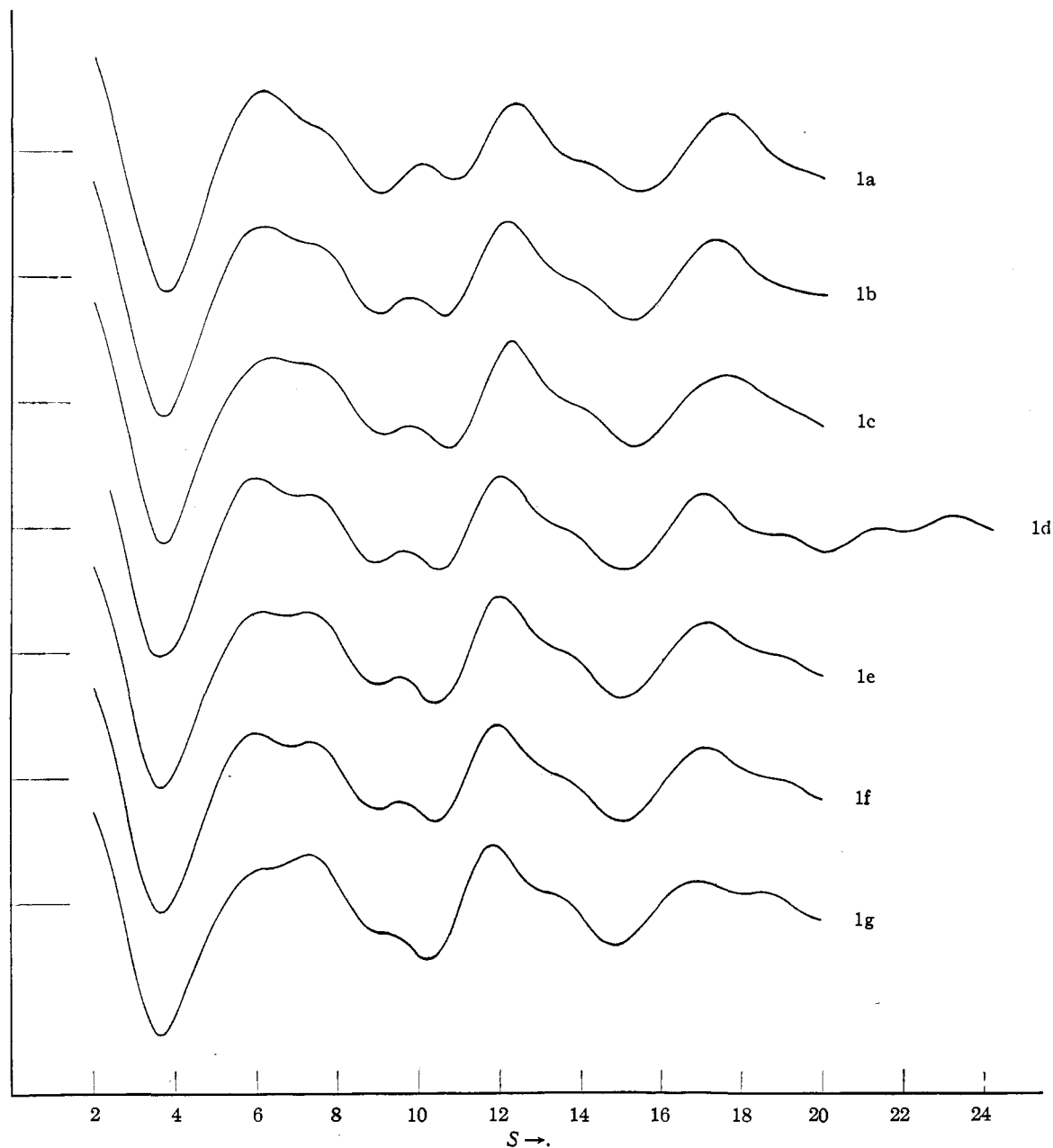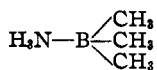
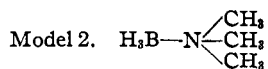Fig. 4.—Calculated intensity curves for various dimensions of model 1 of H_3BCO.

This simplification was consequently made use of in the detailed study of the various models. They were

Model 1.
$$H_3N—B \overset{/CH_3}{\underset{\backslash CH_3}{-CH_3}}$$

Tetrahedral valence angles on the nitrogen, boron, and carbon. Variable distances due to rotations neglected.

H–N = 1.02; H–C = 1.09; N–B = 1.56; B–C = 1.56.

Model 2.
$$H_3B—N \overset{/CH_3}{\underset{\backslash CH_3}{-CH_3}}$$

H–B = 1.20; H–C = 1.09; B–N = 1.61; N–C = 1.47.

(a) Tetrahedral angles on the boron, nitrogen, and carbon. Variable distances due to rotations neglected.

(b) Valence angles on the nitrogen distorted so that the boron and carbon atoms were at the corners of a regular tetrahedron (∠B–N–C = 105° 34′).

(c) Tetrahedral valence angles. All distances taken into account and free rotation for methyl and borine groups assumed.

Subsequent models have the atoms in the same configuration as 2a.

Model	B–N	N–C	H–B	H–C
3	1.40	1.47	1.20	1.09
4	1.35	1.47	1.20	1.09
5	1.70	1.47	1.20	1.09
6	1.75	1.47	1.20	1.09

Comparison of curve 1, Fig. 5, with the sketch (Fig. 1) indicates clearly that this particular model cannot be correct since its diffraction pattern would have an intense third maximum contrary to what is observed. Furthermore, in the study of the configuration $H_3BN(CH_3)_3$ it was soon discovered that large changes in the ratio of the B–N/N–C distances, besides shifting the entire pattern, alter only the relative intensities of the third maximum and its shoulder but keep the total area under them as well as the rest of the curve quite constant. We may therefore conclude that similar large variations in the N–B and B–C distances would not eliminate the observed discrepancy and hence the configuration $H_3NB(CH_3)_3$ is not compatible with the available electron diffraction data. The two methods of synthesis of borine trimethylammine,[3] viz.

$$H_3BCO + N(CH_3)_3 \longrightarrow$$
$$H_2BN(CH_2)_3 + CO \text{ (room temperature)}$$

$$B_2H_6 + 2N(CH_3)_3 \longrightarrow$$
$$2H_3BN(CH_3)_3 \text{ (even at } -110°)$$
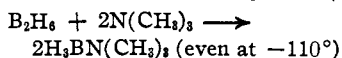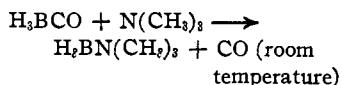
furnish the chemical evidence against configurations of type 1. This leaves the arrangement $H_3BN(CH_3)_3$ to be discussed.

Due to the large number of atoms and the high symmetry present in the molecule, relatively large changes in the ratio of the B–N/N–C distances produced little effect on the intensity distribution.

A lower limit for the above ratio which may be accepted is in the region of (1.40/1.47); model 4, with (1.35/1.47), is definitely excluded since the shoulder to the right of the third peak has practically vanished, contrary to what is observed. For an upper limit we may take a value in the vicinity of (1.70/1.47); model 6,
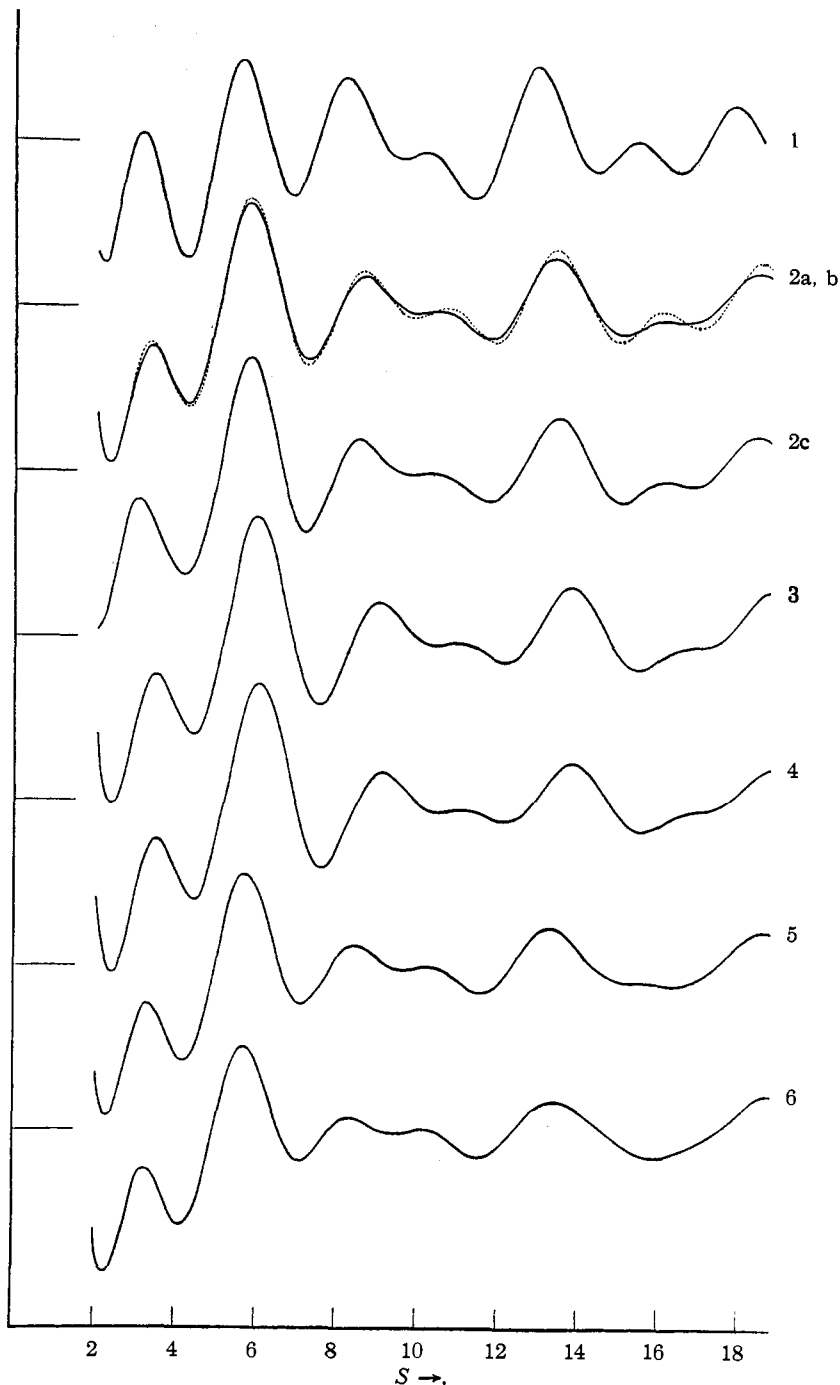

Fig. 5.—Theoretical intensity curves for various models of $H_3BN(CH_3)_3$. Curve 2a is solid; 2b is dashed.

with (1.75/1.47), may be eliminated because of the undue prominence of the shoulder on the third maximum. Models 3 and 5 (and all those included within these limits) reproduce very well all the features found and, except for the position of the third maximum and its shoulder, give good quantitative agreement with the data. The same difficulty with regard to the third peak was also encountered in the case of neopentane. The slight minimum observed between this troublesome maximum and its shoulder indicates that there is a small amount of distortion of the valence angles of the nitrogen tending to force the methyl and borine groups to the corners of a regular tetrahedron. The effect of such a distortion is illustrated by curve 2b, Fig. 5. On comparing $s_{obsd.}$ with $s_{calcd.}$ (Table II) we arrive at the following most acceptable values for the interatomic distances in borine trimethylammine: B–N = 1.62 ± 0.15, N–C = 1.53 ± 0.06.

TABLE II

Ratio $s_{calcd.}/s_{obsd.}$

Max.	Min.	$s_{obsd.}$	I	$I_{corr.}$	Model 3	Model 5	$\dfrac{s_{H_3BN(CH_3)_3}}{s_{C(CH_3)_4}}$
1		3.12	10	8	1.109	1.054	1.000
	2	4.41			0.995	0.948	1.045
2		5.61	10	27	1.061	1.016	1.002
	3	6.96			1.082	1.024	1.018
3		7.82	4	18	(1.151)	(1.078)	0.978
3a		9.61	2	11	(1.139)	(1.072)	1.018
	4	11.48			1.054	1.010	0.998
4		13.02	3	20	1.058	1.019	.994
5		17.3	1	5	1.083	1.076	.960
		Mean ratio			1.063	1.021	1.001
		Mean deviation			0.024	0.026	
Final distances[a]	B–N				1.49	1.74	
	N–C				1.56	1.50	

The probable error was taken equal to half the largest interval between models 3 and 5 introduced by the above mean deviations.

[a] The contribution of the H–B and H–C distances to the diffraction pattern is relatively unimportant. For this molecule the experimental error is much too large to warrant the placing of any significance in the values deduced from the measurements.

Discussion

Before one attempts to draw conclusions from the data presented above, he will find it interesting to note what would be expected on the basis of evidence already available.

(a) The carbon–oxygen distance in carbon monoxide is 1.15 Å. This value is close to the $C≡O$ value (1.11 Å.)[9] as would be expected from

(9) Obtained from the sum of the radii and the new triple bond factor.[7]

the resonance of the molecule among the structures[10]

$$:\overset{-}{C}:::\overset{+}{O}: \qquad :C::\overset{..}{O}: \qquad :\overset{+}{C}:\overset{..}{O}\overset{-}{:}$$
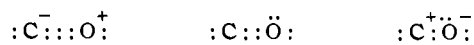
In borine carbonyl the corresponding distance should not differ appreciably from that found in carbon monoxide.

(b) The only boron–carbon distance which has been determined is that in boron trimethyl which is found to be 1.56 Å.[11]

However, these boron–carbon bonds are of the planar sp^2 type so that the interatomic distances may well be somewhat smaller than in borine carbonyl where the bonds are of the tetrahedral sp^3 type. The sum of the covalent radii is 1.66 Å.[12]

(c) To date the following boron–hydrogen distances are known: in B_5H_9, 1.17 (see I); in BH[13], 1.23; in B_2H_6, 1.27 (see II). The corresponding value for the two compounds under consideration should be in the vicinity of the first two figures quoted rather than in the neighborhood of the last one wherein the one-electron-bond contributions to the B–H binding are appreciable.

(d) No boron–nitrogen distance involving a single covalent bond has as yet been determined. Were we to assume the resonance in $B_3N_3H_6$ to be the same as in benzene, so that the shortenings of the interatomic distances in the two molecules below the covalent values are proportional, we could deduce a boron–nitrogen single bond separation from the work of Stock and Wierl.[14] In the above compound the planar hexagonal model was found to be correct and the boron–nitrogen distance given as 1.47 ± 0.07 Å., leading to the value 1.63 ± 0.08 Å. for the normal covalent separation. The sum of the radii is 1.59 Å.[12]

(e) An electron diffraction investigation of trimethylamine has already been made.[15] The molecule was found to be pyramidal with a nitrogen–carbon distance equal to 1.47 ± 0.02 Å. One would expect the corresponding interatomic separation in a compound with tetravalent nitrogen to be somewhat smaller ($≈0.03$ Å.) due

(10) L. Pauling, *Proc. Nat. Acad. Sci.*, **18**, 293 (1932); R. S. Mulliken, *J. Chem. Phys.*, **2**, 400 (1934).

(11) Data of H. Lévy, to be published subsequently in THIS JOURNAL.

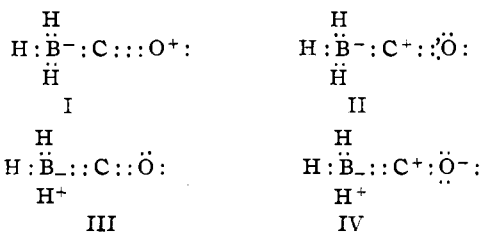(12) For indirect evidence regarding the extrapolated radius of boron see 11.

(13) W. Jevons, "Band Spectra of Diatomic Molecules," Cambridge University Press, 1932, p. 274.

(14) A. Stock and R. Wierl, *Z. anorg. allgem. Chem.*, **203**, 228 (1931).

(15) L. O. Brockway and H. O. Jenkins, THIS JOURNAL, **58**, 2036 (1936).

to the decreased shielding of the nuclear charge introduced by the sharing of all the nitrogen electron-pairs. Presumably the shortening of the nitrogen radius would be balanced out for the boron–nitrogen distance (d) since a similar but opposite effect would tend to increase the boron radius.
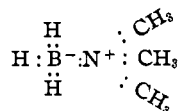
Borine Carbonyl.—Comparison of the experimental results with the tentatively predicted values in (a), (b), and (c) shows satisfactory agreement for the carbon–oxygen and boron–hydrogen distances. The boron–carbon separation is about 0.09 Å. shorter than the sum of the radii. An explanation may be found by considering the contributions of the various electron configurations which participate in the ground state of the molecule. Resonance may take place among the following Lewis structures

$$
\begin{array}{cc}
\text{H} & \text{H} \\
\text{H}\!:\!\ddot{\text{B}}^-\!:\!\text{C}\!:\!:\!:\!\text{O}^+\!: & \text{H}\!:\!\ddot{\text{B}}^-\!:\!\text{C}^+\!:\!\ddot{\text{O}}\!: \\
\ddot{\text{H}} & \ddot{\text{H}} \\
\text{I} & \text{II} \\
\text{H} & \text{H} \\
\text{H}\!:\!\ddot{\text{B}}_-\!:\!:\!\text{C}\!:\!:\!\ddot{\text{O}}\!: & \text{H}\!:\!\ddot{\text{B}}_-\!:\!:\!\text{C}^+\!:\!\ddot{\text{O}}^-\!: \\
\text{H}^+ & \text{H}^+ \\
\text{III} & \text{IV}
\end{array}
$$

The shielding effect discussed in (e) would not alter much the boron–carbon separation in II; structures III and IV, however, would definitely introduce a certain amount of double-bond character to this linkage and would thus tend to shorten the interatomic distance. It is not possible at present to estimate the relative contributions of the above configurations. Dipole moment data would be of great value in this regard. The fact that borine carbonyl is gaseous at relatively low temperatures (v. p. 314 mm. at −78.8°) indicates that the molecule cannot have a large moment so that the resonance of the carbon monoxide residue (I, II, and IV) apparently is not impeded in the formation of the molecule. (One must assume that all the structures listed in (a) contribute to the ground state of carbon monoxide to account for its very small dipole moment.)

Borine Trimethylammine.—Comparison of (d) and (e) with deductions based on the last column of Table II indicates that the boron–nitrogen and nitrogen–carbon distances in borine trimethylammine appear to be somewhat larger than is expected. The mean distance between the central and outer heavy atoms is evidently the same in

this compound as in neopentane, 1.54 Å. Only one Lewis structure may be written for the ground state of borine trimethylammine

$$
\begin{array}{cc}
\text{H} & \cdot\text{C}\text{H}_3 \\
\text{H}\!:\!\ddot{\text{B}}^-\!:\!\text{N}^+\!:\!\text{CH}_3 \\
\ddot{\text{H}} & \cdot\text{C}\text{H}_3
\end{array}
$$

This configuration has a fairly large dipole moment, in harmony with the observed high boiling point of the substance (171°).[3]

Thermal Stability of the Compounds

Characteristic of the difficulties encountered in attempting a rational systematization of the properties of the hydrides of boron is the extraordinary difference in the stabilities of borine carbonyl and borine trimethylammine.[16] From a valence-bond point of view the two bonds formed (B–N and B–C) are quite analogous, yet evidently the situation is a complicated one since it is not certain that strictly similar roles are played by the unshared electron-pairs in the carbon monoxide and nitrogen trimethyl. Were this possibility excluded one might undertake to explain the observed difference in the association products as being due to the fact that nitrogen is twice as far removed from boron on the electronegativity map as is carbon; consequently the B–N bond may be as much as 17 kcal. stronger than the B–C bond. (Some deduction, perhaps 3 kcal., should be made from this value for the possible double bond character of the latter linkage.) Since in the association of H_3B with CO or $N(CH_3)_3$ no bonds are broken and one covalent bond of the "donor" type is formed per compound, the activation energy is probably the same for these two reactions. But we have seen above that of the resulting bonds the one in borine carbonyl is weaker to the extent of ≈14 kcal. than the other; hence the activation energy for the dissociation is expected to be smaller for the carbonyl by the same amount, leading to the possibility that the rate constant for $H_3BCO = H_3B + CO$ is greater by a factor of 10^{10} than that for the analogous reaction for borine trimethylammine.

A molecular orbital treatment of the products resulting from the association of borine with carbon monoxide or trimethylamine seems to indicate that the bonds formed in the two cases are

(16) Prolonged heating at 125° has no effect on $H_3BN(CH_3)_3$ whereas H_3BCO decomposes rapidly at room temperature to give CO and B_2H_6 (Note 3).

not formally analogous. Whether this is real is largely a matter of opinion since in the interpretation of the available ionization potentials different investigators ascribe varying characteristics to the unshared electron-pairs; nevertheless, I consider the point sufficiently interesting to warrant its mention. In the discussion of the structure of carbon monoxide[17] from the molecular orbital point of view, Mulliken describes the slightly antibonding (unshared) pair of electrons attached principally to the carbon atom as occupying an orbital which is essentially an *s*-orbital of carbon. On the other hand, in his discussion of ammonia and its methyl derivatives[18] it is primarily the $2p_z$-orbital of nitrogen which is nonbonding in character. We would accordingly expect that the bonds with borine formed by carbon monoxide and by trimethylamine would be somewhat different, and indeed that the latter would form a stronger bond with borine than the former inasmuch as the bonding power of a *p*-orbital (with greater concentration in the bond direction) is known to be greater than that of an *s*-orbital. Were it convenient to describe the character of the various electrons more quantitatively than is

possible at present so that the effects of polarity and hybridization could be estimated, the 14 kcal. difference between the B–N and B–C bonds predicted above would no doubt become evident.

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Summary

Two derivatives of diborane, borine carbonyl and borine trimethylammine, were investigated by means of an electron diffraction experiment on the vapors. The former compound was found to have its B–C–O atoms linearly arranged with the hydrogen atoms completing the tetrahedron around the boron. The best values for the inter-atomic distances are H–B = 1.20 ± 0.03 Å.; B–C = 1.57 ± 0.03 Å.; C–O = 1.13 ± 0.03 Å. The latter compound has the configuration $H_3BN(CH_3)_3$ with the distances B–N = 1.62 ± 0.15 Å.; N–C = 1.53 ± 0.06 Å. A discussion of the electronic structures of the molecules is then given and an explanation is suggested for the extraordinary difference in the stability of these compounds.

(17) R. S. Mulliken, *Phys. Rev.*, **46**, 549 (1934); *Rev. Modern Phys.*, **4**, 1 (1932).

(18) R. S. Mulliken, *J. Chem. Phys.*, **3**, 506 (1935).

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The Standardization of Hydrogen Ion Determinations. I. Hydrogen Electrode Measurements with a Liquid Junction

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Introduction

Since it is not possible to determine the activity coefficient of a single type of ion in solution, or the value of a single liquid junction potential, it has been recognized (*cf.* Clark[1]) that *p*H values of aqueous solutions are expressed on an arbitrary scale. These values are obtained from the e. m. f. of cells such as

H₂, H⁺ in aqueous solution, KCl(satd.), HgCl, Hg(+) (A)

by an equation of the form

$$pH = -\log C_H f_H = (E - E_0)/k \qquad (1)$$

in which C_H and f_H are the concentration and the arbitrary activity coefficient of the hydrogen ion, E is the e. m. f. of the cell in volts, E_0 is the po-

tential of the reference electrode with respect to the normal hydrogen electrode, and k is 0.05915 for 25°. Some workers[2] have used in place of E in equation (1) a value corrected for the liquid junction potential, which they have tried to estimate either by the Bjerrum extrapolation or by Henderson's formula. In most cases, however, it has become customary, following Clark,[1] to define *p*H by equation (1) in terms of the observed e. m. f., neglecting liquid junction potentials. These differences in procedure have led to the use of scales of *p*H (or *p*aH) differing by 0.04 or 0.05 (10 to 12% in $C_H f_H$), and to E_0 values dif-

(1) Clark, "The Determination of Hydrogen Ions," Williams and Wilkins Co., Baltimore, 3rd ed., 1928.

(2) Sørensen and Linderstrøm-Lang, *Compt. rend. trav. lab. Carlsberg*, **15**, No. 6 (1924); Bjerrum and Unmack, *Kgl. Danske Videnskab. Selskab.*, *Math.-fys. Medd.*, **9**, 1 (1929); Guggenheim and Schindler, *J. Phys. Chem.*, **38**, 533 (1933).