5. The Action of Dry Hydrogen Chloride on the Precipitate Produced by the Action of Dilute Ammonium Hydroxide on Mercurous Chloride.—Ullgren[21] observed that the black precipitate readily adsorbed hydrogen chloride to form mercurous chloride and ammonium chloride. His experiment was repeated on a precipitate for which the time of reaction did not exceed fifteen minutes. The precipitate was dried in nitrogen according to the procedure described. The dry hydrogen chloride was passed over a sample of this dry precipitate for several hours and over two samples which had been moistened.

Result.—It was found that the dry precipitate did not react, but merely adsorbed hydrogen chloride which it again liberated on standing in a vacuum desiccator. The moist precipitate, however, reacted immediately and formed mercurous chloride.

Summary

1. When ammonium hydroxide reacts with mercurous chloride, the product formed is a mixture the composition of which depends upon the time of reaction and the concentration of the ammonium hydroxide. When dilute ammonium hydroxide is used, the mercurous oxide which is first formed can be identified, and the reaction ceases, under ordinary conditions, with the formation of $HgNH_2Cl$ and Hg. However, if concentrated ammonium hydroxide is used, the water-soluble amine $HgCl_2 \cdot 2NH_3$ is formed in addition.

In view of the fact that the product is a mixture the reaction occurring under ordinary conditions between mercurous chloride and ammonium hydroxide is best represented by means of the equation

$$2Hg_2Cl_2 + 4NH_4OH \longrightarrow [Hg + Hg_2O + NH_2HgCl] + 3NH_4Cl + 3H_2O$$

2. Dry hydrogen chloride does not react with the dry black precipitate, but yields mercurous chloride with the moist precipitate.

MINNEAPOLIS, MINN. RECEIVED OCTOBER 28, 1937

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[21] Ullgren, *Pogg. Ann.*, **42**, 381 (1837).

[CONTRIBUTION FROM THE GATES AND CRELLIN LABORATORIES OF CHEMISTRY, CALIFORNIA INSTITUTE OF TECHNOLOGY, No. 622]

The Structures of the Hydrides of Boron. IV. B_2NH_7 and $B_3N_3H_6$. The Structure of Dimethylamine

BY S. H. BAUER*

An interesting derivative of diborane, B_2NH_7, recently has been discovered by D. M. Ritter working under the direction of Professor Schlesinger. Details of the preparation have not yet appeared in the literature. The existence of the compound was called to my attention by Dr. Anton B. Burg, who very kindly furnished the samples of this substance and of triborine triamine used in the electron diffraction experiments. These investigators were particularly interested in the structure determination since their studies, soon to be published, on the diammonate of diborane, $B_2H_6 \cdot 2NH_3$, led to the conclusion that in the latter compound the boron atoms are not linked to each other but are both linked to a nitrogen atom, thus forming the boron–nitrogen chain B–N–B. The diammonate is not itself suitable for an electron diffraction experiment due to its involatility; the compound B_2NH_7, in which a similar link was suspected, is a volatile liquid at room temperature. In turn, the configuration of the diammonate is significant in that important conclusions regarding the structure of diborane and of similarly constituted boron hydrides may be deduced from it. The experimental results herein reported show that the order of arrangement in B_2NH_7 is B–N–B thus being in accord with the conclusions reached by Burg and Schlesinger concerning the diammonate of diborane.

As an aid in the structure determination, I considered it advisable to reinvestigate the interatomic distances in $B_3N_3H_6$[1] so that a value for the single covalent separation of boron and nitrogen could be deduced, and to obtain electron diffraction photographs of dimethyamine for comparison with those of B_2NH_7.

Triborine Triamine.—The purity of the material used in the electron diffraction experiment was

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* Present address: The Pennsylvania State College, School of Mineral Industries.

[1] A. Stock and R. Wierl, *Z. anorg. allgem. Chem.*, **203**, 228 (1931), found the B–N separation to be 1.47 ± 0.07 Å. The single-bond B–N distance in borine trimethylammine is also known with a relatively large uncertainty—1.62 ± 0.15 Å., S. H. Bauer, THIS JOURNAL, **59**, 1804 (1937).

checked by means of its vapor pressure (84 mm. at 0°). Ten photographs of varying density showing up to eight rings were prepared, using electrons of λ 0.0613 and a camera distance of 10.86 cm. The characteristic features of the pattern are sketched in Fig. 1a in which I have attempted to indicate the close similarity between the diffraction photographs given by triborine triamine and benzene. The patterns are superposable except for a change in scale (a shrinking by a factor of 1.029) due to the unlike sizes of the two molecules, and for the minor differences indicated by the dotted lines. The latter dissimilarities are introduced by the differences in the C–H, B–H, and N–H distances, since it may be shown[2] that the first and third peaks of the theoretical intensity curves are the most affected when varying C–H separations are assumed for benzene. We may conclude tentatively that triborine triamine has a benzene-like configuration. Comparison of the s_0 values for the two compounds[3] leads to the values in the last column of Table I from which one may deduce approximately the length of a side of the hexagon: *viz.*, 1.029 × 1.39 = 1.43 Å. This is strongly supported by the modified radial distribution plot (Fig. 2a)[4] of which the most prominent peaks, 1.47 and 2.49 Å., correspond to the ortho and meta separations in the ring, respectively.

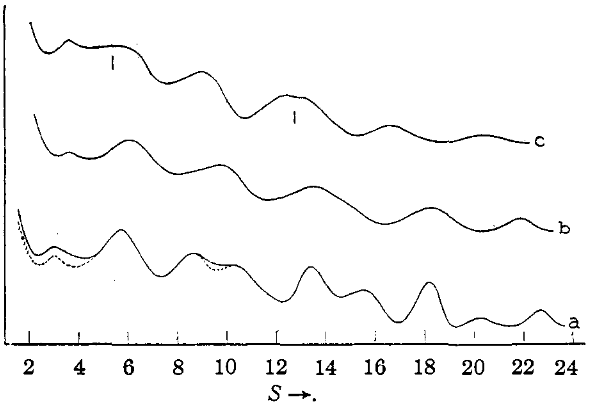

Fig. 1.—Visual appearance of electron diffraction photographs: (a) $B_3N_3H_6$ with dotted portion representing the appearance of the benzene pattern shrunk by the factor 1.029; (b) $(CH_3)_2NH$; (c) B_2NH_7—arrows indicate probable positions measurements were made.

TABLE I

Max.	Min.	I	$I_{corr.}$	s_0	$\frac{s_{calcd.}}{s_{obsd.}}$	$\frac{s_{C_6H_6}}{s_{B_3N_3H_6}}$
1		10	6	3.03	(0.941)	1.058
	2			4.30	(.940)	1.002
2		20	30	5.73	.972	1.000
	3			7.32	.993	1.041
3		5	29	8.63	(1.101)	(1.102)
3a		3	22	10.31	(1.038)	(1.089)
	4			12.30	0.984	1.016
4		4	41	13.39	1.011	1.021
	5			14.63	1.013	1.018
5		2	23	15.62	0.991	1.026
	6			16.92	.992	1.033
6		2	23	18.17	1.007	1.028
7		$^1/_2$	5	20.24	1.016	1.056
8		1	10	22.71	1.012	1.052
				Mean	0.999	1.029

Average deviation 0.013

Final B–N distance 1.44 ± 0.02 Å.

In their initial investigation of triborine triamine, Stock and Wierl found that for a model having the boron and nitrogen atoms placed alternately at the corners of a hexagonal ring but with the atoms staggered out of a plane the theoretically calculated curve and the visual appearance of the photographs have little in common, but that good agreement could be obtained for a planar model. How large a distortion may be per-

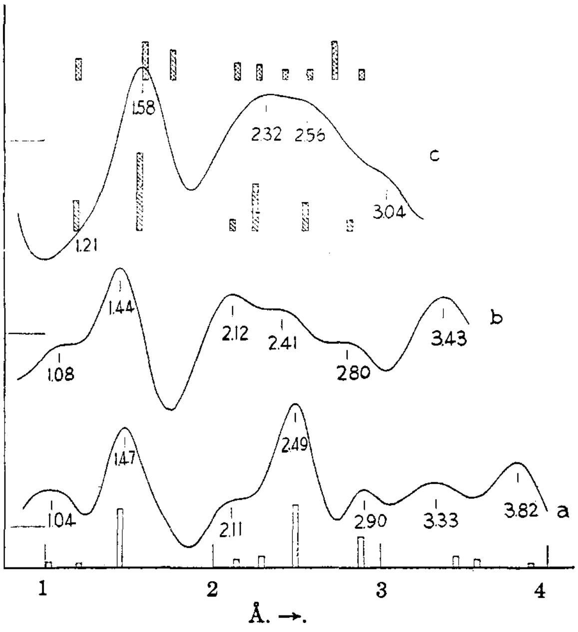

Fig. 2.—Modified radial distribution curves: (a) $B_3N_3H_6$; (b) $(CH_3)_2NH$; (c) B_2NH_7. Heights of rectangles indicate intensities of peaks to be expected: OPEN—for benzene-like model of $B_3N_3H_6$; SINGLE STROKE—for model 4b of B_2NH_7; CROSS STROKE—for model 5c of B_2NH_7.

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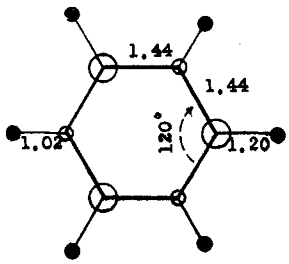
[2] Private communication from V. F. H. Schomaker of results to appear in THIS JOURNAL.

[3] Data for benzene obtained from the report of L. Pauling and L. O. Brockway, *J. Chem. Phys.*, **2**, 867 (1934).

[4] A description of the modifications suggested by V. F. H. Schomaker is soon to appear in THIS JOURNAL. The corrected intensity factors ($I_{corr.}$) are tabulated.

mitted before a serious discrepancy becomes evident has not been investigated, but by comparison with benzene[3] we would conclude that it could amount to 0.1 Å. to either side of the plane. Since theoretical considerations lead to a large resonance energy for the planar configuration (about 34 kcal. for benzene) which would be to a great extent inhibited in the distorted arrangements, and since triborine triamine is one of the most stable of the derivatives of the boron hydrides, it is reasonable to conclude that it is planar. Indeed, this is well supported by the close agreement between the s_0 values observed and those calculated for the model



H, black circles
N, small open circles
B, large circles

In summary, triborine triamine has a benzene-like configuration (symmetry D_{3h}) with alternate boron and nitrogen atoms at the corners of a regular hexagon, and with the boron–nitrogen separation equal to 1.44 ± 0.02 Å. This is presumably somewhat more reliable than Stock and Wierl's value, 1.47 ± 0.07 Å. Assuming the resonance in triborine triamine to be the same as in benzene, so that the shortening of the interatomic distances in the two molecules below the single-covalent value are proportional, we may deduce the boron–nitrogen single-bond separation to be 1.59 Å.

Dimethylamine

The sample of dimethylamine (an Eastman product) was purified by repeated fractional condensations *in vacuo*. Under the conditions specified above, five photographs were obtained possessing the features diagrammatically shown in Fig. 1b. A modified radial distribution plot (Fig. 2b) suggests a number of interatomic distances all within several per cent. of the values which may be predicted from the electron diffraction investigation of trimethylamine.[5] Since we can assume that the diamine molecule consists of two methyl groups attached to NH, our problem involves only the determination of the values of the parameters which give the curve best reproducing the observed pattern. Theoretical intensity distributions for the following models were calculated: N–C 1.47 Å., C–H 1.08 Å.; tetrahedral angles on the methyl groups; *cis-* and *trans-*positions given equal weight; with

1.	C–N–C angle	109.5°	$Z_{\text{eff.}}$ on H	1.00[6]	Curve 3b
2.		109.5°		1.23	Curve 3c
3.		112.5°		1.00	
4.		106.5°		1.00	
5.		109.5°		1.23	

The results presented in Table II show that changes as large as 0.03 Å. in the C–H distance have very little effect on the intensity of scattering; however, the radial distribution curve shows a distinct shoulder at about 1.09 Å. and this value of the C–H distance is also found in many other molecules.

Careful comparison of the calculated curves with the pattern observed leads to the conclusion that the best agreement can be obtained if the C–N–C angle is assumed to be between 109.5 and 106.5°. It will be noticed (Fig. 1b and 3b, c) that neither the first observed peak nor the slight shoulder on the fourth maximum appears distinctly on the calculated curve. The shoulder to the left of the first calculated maximum ($s \approx 6.1$) accounts for the observed narrow ring at $s = 3.55$, since a small variation from a smooth decrement in this region where the background is changing rapidly introduces an exaggerated visual effect.

The data regarding dimethylamine are assembled in Table II. Ratios of $s_{\text{calcd.}}/s_{\text{obsd.}}$ for models 2, 4, and 5 are given. We may conclude that in dimethylamine the N–C distance is equal to 1.46 ± 0.03 Å.; the C–N–C angle is 108 ± 4°; and the C–H separation is 1.08 ± 0.03 Å. These values are in excellent agreement with the ones determined by Brockway and Jenkins[5] who found the N–C distance in trimethylamine to be 1.47 ± 0.02 Å. and the C–N–C angle to be 108°.

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(5) L. O. Brockway and H. O. Jenkins, This Journal, **58**, 2036 (1936).

(6) It has been suggested by V. F. H. Schomaker that one way of taking into consideration the proportionately larger scattering power of hydrogen in compounds where such scattering predominated is to use an effective nuclear charge (Z) rather than unity in the theoretical intensity calculations. This may be determined by plotting $(Z - f)/Z$ (where f is the atomic structure factor for X-rays) against $(\sin \theta/2)/\lambda$ for the elements, and sliding the vertical scale until the best superposition of the curves is obtained. Relative to carbon, hydrogen has an effective scattering power of 1.23, relative to boron, 1.25. Comparison of curves 3b and 3c demonstrates the slight effect this difference has on the form of the pattern except in the region of very small s values where it serves to bring the calculated curve into closer agreement with the observed intensity distribution.

TABLE II

Max.	Min.	I	$I_{corr.}$	s_0	s_c/s_0 (Mod. 2)	s_c/s_0 (Mod. 4)	s_c/s_0 (Mod. 5)
1		6	6	3.55			
	2			4.56			
2		10	30	6.05	1.016	1.013	1,013
	3			7.95	0.960	0.952	0.953
3		6	34	9.76	.956	.962	.972
	4			11.70	.975	.979	.982
4		4	26	13.58	.988	.989	.987
	5			16.36	.987	.979	1.000
5		2	10	18.26	(1.027)	1,028	(1.037)
	6			20.14	1.016	1.021	1.006
6		1	3	21.89	0.999	1.019	1.008
				Mean	.992	0.994	0.990
				Average deviation	.020	.024	.017
				Calculated C–N distance	1.458	1.462	1.456

Final C–N distance 1.46 ± 0.03 Å.
(from radial distribution curve) C–H distance 1.08 ± 0.03 Å.
C–N–C 108 ± 4°

B_2NH_7.—The material used in this investigation was purified by a fractional condensation at −90°; as a check its vapor pressure was determined and found to have the value 31.5 mm. at 0° in agreement with the accepted value 32 mm.[10] The diffraction experiment was performed with the sample at 35° at which temperature it is quite stable.[7] Significant features of the pattern are sketched in Fig. 1c, which makes evident the similarity of the resulting photographs to those given by dimethylamine. Points of interest which should be stressed are: first, the inner small peak and the intense second maximum are not so well resolved in B_2NH_7 (no minimum between them could be measured) as are the corresponding ones in dimethylamine; second, the fifth peak at s = 16.7 is evidently narrower than the fourth; third, the sixth maximum seems to be broad, although, due to its faintness, its exact structure is in some doubt. The modified radial distribution plot[4] (Fig. 2c) indicates important interactions at 1.58, 2.32, and 2.56 Å. with suggestions of shoulders at about 1.20 and 3.00 Å. From these values definite conclusions regarding the structure of the compound can be drawn. The peak at 1.58 Å. clearly corresponds to a B–N separation. The fact that it is sharp and pronounced indicates that the configuration is B–N–B rather than B–B–N since the latter arrangement would give two peaks of almost equal height at about 1.76 and 1.58 Å. The humps at 2.32 and 2.56 which are not well resolved correspond to non-bounded B, H and B, B interactions respectively.

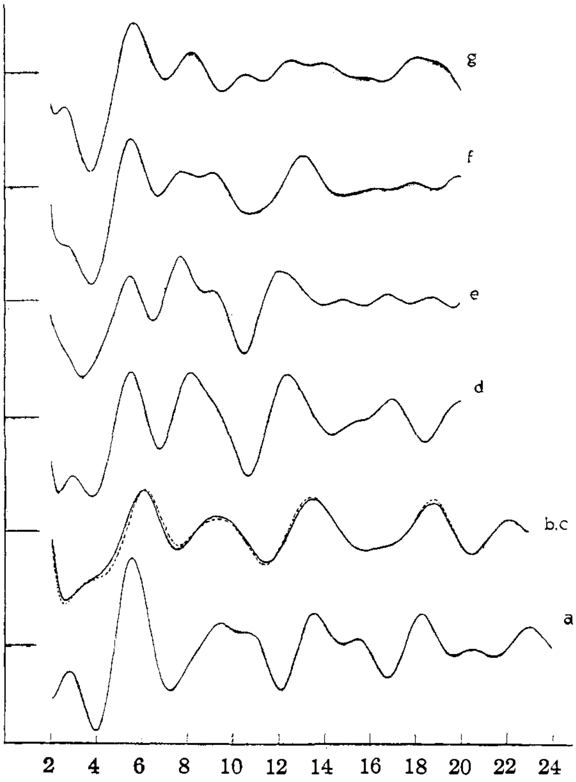
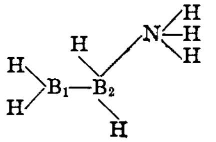


Fig. 3.—Theoretical intensity curves for triborine triamine, dimethylamine, and B_2NH_7: (a) $B_3N_3H_6$; (b) $(CH_3)_2NH$, continuous curve; (c) $(CH_3)_2NH$, dashed curve; (d) to (g) various models of B_2NH_7.

This conclusion regarding the B–B–N arrangement is well supported by the entire lack of qualitative agreement between the pattern and the theoretical intensity of scattering calculated for the models

(1)

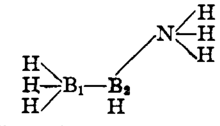


B-H = 1.20
N-H = 1.02

Valence angles on the N and B_2 atoms tetrahedral; on the B_1 atom planar at 120°.
No rotation of the NH_3 group was assumed.[8]

d. B_1–B_2 = 1.66; B_2–N = 1.58; ratio 1.050 Curve 3d
e. B_1–B_2 = 1.76; B_2–N = 1.58; ratio 1.113 Curve 3e

(2)



all angles tetrahedral

f. B_1–B_2 = 1.66; B_2–N = 1.48; ratio 1.122 Curve 3f

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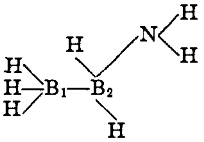
[7] Dr. Burg in a private communication states that heating for an hour at 50° produces only a 2% decomposition.

[8] I have already shown that rotation of the methyl groups in propane produces little effect on the pattern [S. H. Bauer, *J. Chem. Phys.*, **4**, 407 (1935)]. The same conclusion was reached regarding the rotation of the borine groups in diborane, S. H. Bauer, THIS JOURNAL, **59**, 1096 (1937).

(3)

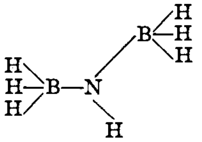


all angles tetrahedral

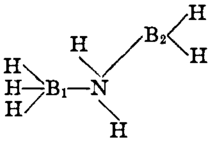
g. B_1–B_2 = 1.76; B_2–N = 1.48; ratio 1.189 Curve 3g

As will be shown below, the shifting about of one hydrogen atom affects the intensity only slightly; the testing of the above models was performed merely to demonstrate that even large changes in the (B–B)/(B–N) ratio cannot alter sufficiently the general appearance of the curves characteristic of this arrangement to bring it in harmony with observation. On the other hand, for both the models

(4)



and (5)



corresponding to the B–N–B arrangement, the predicted intensity distributions have the essential contours of the diffraction pattern. The following configurations were investigated in detail.

(4a) B–H = 1.20 N–H = 1.02 B–N = 1.58 All valence angles were assumed to be tetrahedral; the *cis*- and *trans*-positions of the borine groups were given equal weight.

$Z_{\text{eff.}}$ for hydrogen assumed to be 1.00.

(b) As in 4a; $Z_{\text{eff.}}$ for H = 1.25.

(c) As in 4a; B–N–B angle assumed to be 112.5°.

(d) As in 4c; B–H distance assumed to be 1.23.

(5a) B–H = 1.20 N–H = 1.02 B_1–N = B_2–N = 1.58 All valence angles tetrahedral except those on B_2 which were assumed to be planar (120°).

$Z_{\text{eff.}}$ for hydrogen = 1.00.

(b) As in 5a; $Z_{\text{eff.}}$ for H = 1.25.

(c) As in 5a; B_1–N = 1.58 Å.; B_2–N = 1.48.

Although a relatively small change is introduced by shifting one hydrogen atom from the boron to the nitrogen, comparison of the two sets of curves with the observed pattern apparently favors those in Fig. 4 as best reproducing the various features. The arguments may be summarized as follows. (α) Whereas the curves of group 4 have shoulders to the left of the first intense maximum which would give the visual effect of a small sharp inner ring as in the case of dimethylamine (but not so well resolved from the main peaks due to its lesser prominence), those of group 5 lack this characteristic. (β) The theoretical intensity distributions plotted for model 5 (Fig. 4) indicate a broad peak at $s \approx 17$ but a relatively sharp one at $s \approx 12.5$, the converse relationship to what is observed. In this region, the intensity relations predicted from models 4 are as well reproduced as those predicted for the corresponding region in the dimethylamine photographs. (γ) On the opposite side, all the curves of model 4 have a shoulder of lesser or greater height to the right of the last maximum. It seems probable, however, that this shoulder for curves 4a, b would not be visible on the films because of the over-all weakness of the last ring.

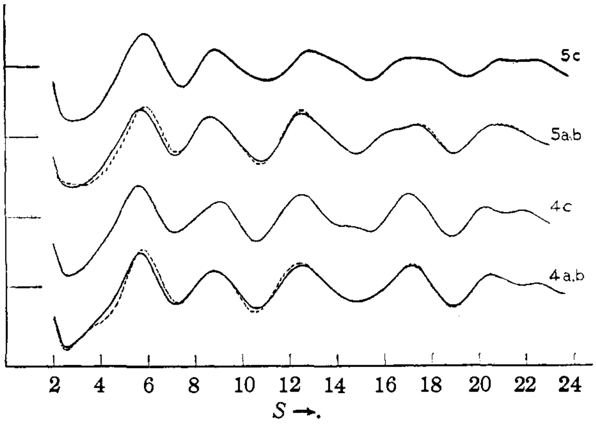
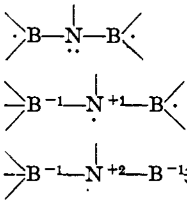


Fig. 4.—Theoretical intensity curves for models 4 and 5 of B_2NH_7: continuous curve—a; broken curve—b.

Of the two groups, models 4b and 5b are the most acceptable.[9] It is, however, difficult to decide which represents the correct configuration, for although the electron diffraction data seem to point toward the former, preliminary chemical experiments somewhat favor the latter.[10] Model 4b would resonate among Lewis structures of the types



Dashes represent electron-pair bonds; dots, one-electron or unshared electrons.

The importance of the contribution made by the first structure to the ground state would determine the extent to which B_2NH_7 possesses the characteristics usually associated with a free-electron-pair on a nitrogen atom such as salt formation with hydrogen chloride at low temperatures. Actually, it reacts vigorously under these conditions to give hydrogen and a B-Cl link which might be accepted as evidence against Model 4. In answer one may cite the fact that

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[9] Although the variations from 4a produced by the changes in the B–H distance and the B–N–B angle are relatively small, they tend to introduce divergences from the data. Model 5c is definitely eliminated by the radial distribution curve.

[10] Private communication from Dr. Burg.

other derivatives of the hydrides of boron show a puzzling behavior with hydrogen chloride[11];

$$B_5H_9{\cdot}4NH_3 + 4HCl = B_5H_9Cl_4{\cdot}4NH_3 + 4H_2 \text{ (vigorous)}$$
$$B_3N_3H_6{\cdot}3H_2O + 3HCl = B_3N_3H_3Cl_3{\cdot}3H_2O + 3H_2 \text{ (at } 50^\circ\text{)}$$

Moreover, resonance with the second and third structures, if extensive, will serve to quench the base-like characteristics of the nitrogen atom as the somewhat similar type of resonance has done in pyrrole. Finally, as far as I am aware, in none of the boron hydrides nor in their derivatives (except in the very doubtful phenyl borine, $H_2BC_6H_5$) does a boron atom occur as tri-coördinated with two of its bonds to hydrogen. If model 5 were correct, B_2NH_7 would be the first case of this type.

TABLE III

Max.	Min.	I	$I_{\text{corr.}}$	s_0	s_c/s_0 (Mod. 4b)	s_c/s_0 (Mod. 5b)	$\frac{s_{(CH_3)_2NH}}{s_{0B_2NH_7}}$
1		12	14	3.61			(0.983)
2		9	22	5.38	(1.074)	(1.098)	(1.125)
	3			7.53	0.965	0.959	1.056
3		3	16	9.04	.977	.954	1.079
	4			10.69	.988	1.007	1.094
4		2	13	12.74	.973	0.981	1.066
	5			15.19	.981	.978	1.077
5		1	6	16.65	1.032	1.021	1.097
6		$^1/_2$	2	20.26	1.014	1.030	1.080
				Mean	0.990	0.990	1.078
				Average deviation	.019	.025	
				Final B–N distance	1.56 ± 0.03 Å.		
				B–H	1.20		
				B–N–B angle	109 ± 4°		

The observed s_0 values are somewhat more consistent with those calculated from the models 4b than with the ones from 5b. In Table III the two sets of ratios are compared; in the last column ratios of $s_{0NH(CH_3)_2}/s_{0B_2NH_7}$ are given, thus furnishing a check on the magnitude of the B–N distance, *viz.*, 1.078 × 1.46 = 1.57 Å. We may therefore conclude (a) that the arrangement of the heavy atoms in B_2NH_7 is B–N–B rather than B–B–N; (b) that the electron diffraction data strongly favor the configuration H_3B–NH–BH_3, a structure analogous to dimethylamine (I do not consider the evidence sufficiently weighty, however, to eliminate unambiguously the configuration H_3B–NH_2–BH_2[12]); and (c) that the boron atoms are closely equidistant from the nitrogen atom, the mean B–N separation being 1.56 ± 0.03 Å. The B–N–B angle is tetrahedral to within four degrees, while the B–H distance is close to 1.20 Å. but no definite limit to the probable error can be assigned on the basis of this experiment.[13]

Remarks on the Radius of Boron

In their discussion of the interatomic distances observed in the boron trihalides and boron trimethyl, Levy and Brockway[14] postulated that when boron and carbon form sp^2 (three univalent planar) bonds their radii are 0.1 Å. shorter than when these atoms are engaged in tetrahedral sp^3 bonds. If this is accepted, configuration 5 of B_2NH_7 would require unequal B–N separations (curve 5c), a situation which is excluded by the radial distribution curve.

These investigators have conveniently collected the available data on the radius of boron. Except in the case of boron linked to fluorine, oxygen,[15] and carbon, the deduced radius is either close to 0.89 Å. or an explanation usually involving multiple bond resonance is available to account for the discrepancy. The mean B–N separation in B_2NH_7 leading to 0.86 as the radius of boron lends further support to this statement. Under any circumstances, the radius generally deduced for boron is equal to or less than 0.89 Å.,[16] so that the unusually large boron–boron distance observed in diborane must find its explanation in a weaker boron–boron bond, as postulated by the author.[17]

Acknowledgments.—I am greatly indebted to Dr. Burg for providing the samples and for making available the unpublished data on B_2NH_7, to Professor Pauling for helpful advice, and to Dr. L. O. Brockway for the use of his apparatus.

Summary

Triborine triamine, dimethylamine, and the newly discovered compound B_2NH_7 were studied by means of an electron diffraction experiment. The benzene-like structure of the first of these

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[11] A. Stock, "Hydrides of Boron and Silicon," Cornell University Press, Ithaca, N. Y., 1933, p. 96, and Chapter XXII.

[12] Due to the fact that the available evidence is not sufficient to permit a definite choice, this substance cannot yet be properly named.

[13] Accurate estimates of the B–H separation have been made in the case of pentaborane and borine carbonyl (papers I and III of this series); they are 1.17 and 1.20 ± 0.03 Å., respectively.

[14] H. A. Levy and L. O. Brockway, THIS JOURNAL, **59**, 2085 (1937).

[15] The mean B–O separation for tri-coördinated boron is 1.36 ± 0.03 Å. W. H. Zachariasen, *Z. Krist.*, **76**, 289 (1931) on Be_2BO_3OH; *Z. Krist.*, **83**, 354 (1932), on CaB_2O_4; *J. Chem. Phys.*, **5**, 919 (1937), on potassium metaborate. The sum of the radii (assuming boron 0.88) is 1.54 Å., which would lead to an expected B–O distance of 1.42 Å. for graphite-like resonance.

[16] The B–N separation in $H_3BN(CH_3)_3$ is known only to within a large experimental error, hence the large boron radius deduced therefrom is without significance.

[17] Publication II of this series.

(*sym.* D_{3h})[18] was confirmed and the B–N distance found to be 1.44 ± 0.02 Å. The best values for the parameters of dimethylamine are: C–N = 1.46 ± 0.03 Å., C–H = 1.08 ± 0.03 Å.; and the C–N–C angle = 108 ± 4°. The arrangement of the heavy atoms in B_2NH_7 was determined to be B–N–B, but the electron diffraction investigation could not eliminate definitely the configuration $H_3B–NH_2–BH_2$ in preference to $H_3B–NH–BH_3$. The mean B–N separation is 1.56 ± 0.03 Å. and the B–N–B angle is tetrahedral to within four degrees.

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[18] Professor Zachariasen called my attention to the structure determination of boron nitride made by V. M. Goldschmidt [*Norsk. geol. Tidskrift*, **9**, 258 (1926)] and O. Hassel (*ibid.*, p. 266). The compound was found to have a graphite-like structure with a B–N separation equal to 1.45 Å., somewhat lower than would be expected, but still within the experimental error, in agreement with the electron diffraction investigation of triborine triamine.

[CONTRIBUTION FROM THE LABORATORY OF PHYSICAL CHEMISTRY OF THE UNIVERSITY OF WISCONSIN]

Polar Group Orientation in Linear Polymeric Molecules. The Omega-Hydroxydecanoic Acids[1]

BY W. B. BRIDGMAN

Recent investigations of dielectric constant–frequency relationships in dilute solutions have shown that the observed times of relaxation of such substances as zein, gliadin, lignin, hemoglobin, etc., are in agreement with the values calculated from the molecular weights of these substances as obtained by classical diffusion, sedimentation, and osmotic pressure methods. In these cases the identity of the electrical and molecular kinetic units is established.

However, equality of the electrical and molecular kinetic units is not to be expected in all cases. It has been shown by workers in this Laboratory that there is a class of molecules, to which certain linear polymers belong, which shows a different but characteristic behavior in dilute solution. As typical of the polymeric substances of this class we have chosen the molecules produced by interesterification of ω-hydroxydecanoic acid. These polymers may be represented by the formula

$$HO[(CH_2)_9COO]_{n-1}(CH_2)_9COOH$$

The behavior of these molecules can best be explained by considering that the electrical unit orienting in the applied field is but a small portion of the molecular kinetic unit. This type of molecule shows a definite contribution to the polarization due to orientation of dipoles, but shows no variation of dielectric constant with frequency in the region where dispersion should occur if the entire molecule were being oriented by the field. Further, the specific polarization is found to be independent of the molecular weight and the dipole moment is proportional to the square root of the molecular weight.

Apparatus

The apparatus used for the greater part of the experimental work was a modified resonance type of dielectric constant apparatus. It was composed of three units; a crystal controlled oscillator, a variable oscillating detector, and a resonating circuit containing the cell. The crystal controlled oscillator used a '37 tube with a crystal having a fundamental of 954.7 kilocycles (314 meters). This oscillator was rich in harmonics, it being readily possible to detect harmonics as high as the twentieth. The variable oscillating detector utilized a 6-A-7 tube and by means of plug-in coils could be operated at frequencies varying from 20,000 to 850 kilocycles (15 to 360 meters). This detector was inductively coupled to the crystal oscillator. In use it was tuned to zero beat with the desired harmonic of the crystal oscillator. The resonator consisted of a special General Radio Company Precision Condenser, Type 222-L, with total capacity of about 100 μμ fd., connected in parallel with the cell and across an inductance coil. The resonator was capacitatively coupled to the oscillating detector and the point of resonance could be determined quite sharply by listening to the heterodyne beat note generated between the two oscillators. The cell used for this work consisted of a small variable condenser, the plates of which were immersed in the dielectric medium. In making a dielectric constant determination, the position of the rotor was varied between two reproducible positions. The difference in capacity between these positions when the plates of the condenser were covered with solution divided by the difference in capacity between the same positions when the cell was filled with solvent, gave the relative dielectric constant of the solution.[2] These relative dielectric constants

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[1] A preliminary account of the results of this research appeared in the Communications to the Editor section of THIS JOURNAL, **59**, 1579 (1937). More complete details are to be found in a thesis submitted to the faculty of the University of Wisconsin in partial fulfilment of the requirements for the Ph.D. degree in August, 1937.

[2] Daniels, Mathews and Williams, "Experimental Physical Chemistry," 2d ed., McGraw-Hill Book Co., New York, 1934, p. 247.