distillations through the semi-micro fractionating tube were necessary to obtain a pure product: b.p. 93.7° (173 mm.); n^{25}_{D} 1.4072; d^{25}_{4} 0.8773; α^{25}_{D} −32.77°; $[\alpha]^{25}_{D}$ −37.35°.

Excess glycol was recovered by distillation at 7 mm.; weight 47.3 g.; b.p. 69.0–69.7°; α^{25}_{D} −12.82°; $[\alpha]^{25}_{D}$ −12.99°. Thus about 93% of the original glycol was accounted for. More important, the rotation was within 0.05° of the original glycol, thus showing that the sodium salt of the glycol does not tend to undergo racemization, even when heated.

meso-**2,3-Dimethoxybutane.**—To 30 ml. of anhydrous ethyl ether were added 2.3 g. of sodium shavings and 5.20 g. (0.05 mole) of L(+)-*erythro*-3-methoxy-2-butanol. After 24 hours hydrogen evolution had virtually ceased, leaving a clear reddish solution along with the excess sodium. The sodium was removed and an excess of methyl iodide, 10.6 g. (0.075 mole) was added. Fairly rapid formation of sodium iodide started after a few minutes. The mixture was heated under a reflux for 2 hours and allowed to stand 3 hours. The ether was removed by distillation, water was added to dissolve sodium iodide, the aqueous phase was shaken twice with portions of the ether previously removed and these were combined with the product. After the solution had been dried with potassium carbonate, distillation was carried out at 750 mm.; b.p. 107.3–108.0°; α^{25}_{D} +0.03°; crude yield, 3.79 g. (64%). The product was redistilled slowly through a semimicro fractionating tube and from metallic sodium which in the molten state reacted with unchanged starting material: b.p. 108.0° (750 mm.); n^{25}_{D} 1.3890; d^{25}_{4} 0.8435; α^{25}_{D} 0.00°.

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[CONTRIBUTION NO. 1611 FROM THE GATES AND CRELLIN LABORATORIES OF CHEMISTRY, CALIFORNIA INSTITUTE OF TECHNOLOGY, AND FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF SOUTHERN CALIFORNIA]

An Electron Diffraction Investigation of the Structures of the Aminodiboranes $(CH_3)_2NB_2H_5$ and $H_2NB_2H_5$[1,2]

BY KENNETH HEDBERG AND A. J. STOSICK

The structures of N-dimethylaminodiborane, $(CH_3)_2NB_2H_5$, and aminodiborane, $H_2NB_2H_5$, have been investigated by electron diffraction in the gases. The results are in accord with symmetrical structures having fourfold coördination about the nitrogen atom, and may be considered as derived from the diborane (B_2H_6) structure by the simple replacement of a bridge hydrogen atom with the NR_2 group. For $(CH_3)_2NB_2H_5$, assuming the group H_2B–BH_2 coplanar, the important bond distance and bond angle values with limits of uncertainty are: B–N = $1.55_4 \pm 0.02_6$ Å., C–N = $1.48_3 \pm 0.02_9$ A., B–B = 1.92 ± 0.11 Å. ∠C–N–B = 116.2 ± 1.0°, ∠C–N–C = 111.5 ± 2.5°, ∠B–N–B = 76.4 ± 5.5°, symmetry C_2v (assumed), B–H = 1.25 Å. (assumed), C–H = 1.09 Å. (assumed), ∠H–C–H = 109.5° (assumed), ∠H–B–H = 120° (assumed); the bridge hydrogen atom was neglected. The $H_2NB_2H_5$ investigation indicates that the coplanarity assumed for the group H_2B–BH_2 and the value 1.25 Å. assumed for B–H_{bond} are probably incorrect by substantial amounts; however, these assumptions are unimportant for $(CH_3)_2NB_2H_5$ and do not introduce error into the values of the determined parameters. For $H_2NB_2H_5$ the important distance and angle values are: B–N = $1.50_4 \pm 0.02_6$ Å., B–B = 1.93 ± 0.09 Å., B–H_{bond} = 1.15 ± 0.09 Å., ∠B–N–B = 76.2 ± 2.8°, ϵ (the angle between the extension of B–B and the plane of the –BH_2 group, the angle increasing as BH_2 rotates away from N) = 15 ± 20°, symmetry C_{2v} (assumed), N–H = 1.02 Å. (assumed), B–H_{bridge} = 1.35 Å. (assumed), ∠H–N–H = 109.5° (assumed), and ∠H–B–H = 120° (assumed). The expected B–N–B angle stress and the lesser "electron deficiency" in $R_2NB_2H_5$ as compared to B_2H_6 accounts satisfactorily for the observed distances.

The boron hydrides and their derivatives have held interest for chemists for a long time, an interest arising largely from the fact that many of these substances do not have enough valence electrons to form all of the electron pair bonds which their compositions suggest to be necessary. These substances are especially interesting from a structural standpoint because the spatial arrangements of the atoms in the molecules (which are certainly most important for understanding them) are not at all obvious.

Recently, investigations of the structures of diborane[3] (B_2H_6) and decaborane[4] ($B_{10}H_{14}$) have provided conclusive evidence in support of structures having hydrogen bridges[5] (*i.e.*, protonated double bonds), and in the light of these discoveries it is reasonable to suppose that the hydrogen bridge plays an important role in the "electron deficient" bonding encountered in all the boron hydrides and in many of their derivatives. In 1947 one of us (A. J. S.) proposed that the amino derivative of B_2H_6 might have a structure derived by replacement of one bridge hydrogen atom with a –NR_2 group to form in its place a nitrogen bridge, the nitrogen atom forming essentially normal covalent single bonds to each boron atom.[6] Such a structure accounts very satisfactorily for the chemical behavior of these compounds, whereas other structures do not.[7] It was supposed that certain other derivatives of B_2H_6 might have analogous structures. The current investigation arose directly from our desire to test this hypothesis, and for this purpose we selected for study the compounds $(CH_3)_2NB_2H_5$, $H_2NB_2H_5$ and Br-B_2H_5. Dimethylaminodiborane had been newly discovered by Burg and Randolph[6a] and, like Br-B_2H_5, had not previously been studied by structural

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(1) Preliminary results presented at the San Francisco Meeting of the American Chemical Society, April, 1949: A. J. Stosick, Abstracts, Division of Physical and Inorganic Chemistry, p. 26-O.

(2) This work was supported by the Office of Naval Research under contracts N6onr-238-TO-I and N6onr-24423.

(3) (a) W. C. Price, *J. Chem. Phys.*, **16**, 894 (1948); **15**, 614 (1947); (b) K. Hedberg and V. Schomaker, THIS JOURNAL, **73**, 1482 (1951).

(4) J. S. Kasper, C. M. Lucht and D. Harker, *Acta Cryst.*, **3**, 436 (1950).

(5) Discussion of this or apparently related types of structure have been given by many authors. See, for example, W. Dilthey, *Z. angew. Chem.*, **34**, 596 (1921); E. Wiberg, *Ber.*, **69**, 2816 (1936); H. C. Longuet-Higgins and R. P. Bell, *J. Chem. Soc.*, 250 (1943); K. S. Pitzer, THIS JOURNAL, **67**, 1126 (1945); R. E. Rundle, *ibid.*, **69**, 1327 (1947).

(6) See (a) A. B. Burg and C. L. Randolph, *ibid.*, **71**, 3451 (1949), and (b) A. B. Burg, First Annual Summary Report of Investigations on Water-Reactive Chemical Compounds, N6onr-238-TO-I, p. 10 (1947). Essentially the same suggestion has been made independently by E. Wiberg, A. Balz and P. Buchheit, *Z. anorg. Chem.*, **256**, 286 (1948), and Ya. K. Syrkin and M. E. Dyatkina, "The Structure of Molecules," Interscience Publishers, Inc., New York, N. Y., 1950, p. 404; Russian edition published in 1946 describe B_2NH_7 as probably having this structure.

(7) H. I. Schlesinger, D. M. Ritter and A. B. Burg, *ibid.*, **60**, 2297 (1938).

techniques; $H_2NB_2H_5$ had been investigated by electron diffraction[8] several years earlier but reinvestigation seemed worthwhile. We were able to evaluate the important structural parameters of $(CH_3)_2NB_2H_5$ and $H_2NB_2H_5$ but no suitable photographs of B_2H_5Br were obtained.[9]

Experimental

Electron diffraction photographs of both amino compounds were prepared in the apparatus described by Brockway[10] with a camera distance of about 11 cm. The electron wave length was determined to be about 0.06 A. in a separate experiment by calibration against zinc oxide.[11] Corrections were made for film expansion. The photographs were interpreted visually in the usual way, and radial distribution curves calculated[12,13] from the resulting visual intensity curves (Figs. 2 and 3) according to the equation[12,14]

$$rD(r) = \sum_{q=1,2\cdots}^{q_{\max}} I(q)_{\text{vis}} \exp(-aq^2) \sin (\pi qr/10$$

with $q = (40/\lambda) \sin \varphi/2$ and $\exp(-aq^2_{\max}) = 0.1$. Theoretical intensity curves were calculated from the equation[12,14]

$$I(q) = \sum_{i,j}{}' Z_iZ_jr_{ij}^{-1} \exp(-a_{ij}q^2) \sin (\pi qr_{ij}/10)$$

Terms were included for X–X, X···X, X–H, and X···H interactions through one bond angle except for terms involving the bridge hydrogen atom. However, $B-H_{\text{bridge}}$ was included for $H_2NB_2H_5$. For hydrogen an effective Z value of 1.25 was used in order to approximate better its low-angle scattering relative to boron and nitrogen. The a_{ij} values used were 0.00016 for C–H, $B-H_{\text{bond}}$ and N–H, 0.00030 for $N\cdots H_C$, and 0.00060 for $N\cdots H_B$ and $B\cdots H_B$.

$(CH_3)_2NB_2H_5$, N-Dimethylaminodiborane.—The radial distribution curve (Fig. 2) has strong peaks at 1.51_5 Å. and 2.57 Å., a broader peak with centroid at about 1.15 Å., and a weak peak at 1.94 Å. The peak at 1.51_5 Å. is interpreted as due to unresolved B–N and C–N distances, that at 2.57 Å. principally to the non-bonded C.···B distances, and that at 1.15 Å. to C–H and B–H distances. For C–N 1.48 Å., B–N 1.55 Å.,[15] B···C 2.58 Å., ∠ C–N–C 111° (as in dimethylamine[16]), and heavy-atom symmetry C_{2v}, B···B and C···C are calculated to be 1.91 and 2.44 Å., respectively, in good agreement with the weak peak at 1.94 Å. and the gradual inner slope of the peak at 2.57 Å.

Theoretical intensity curves (representative ones are shown in Fig. 2) were calculated for models of symmetry C_{2v} with the group H_2BBH_2 coplanar (see Fig. 1) over the following parameter ranges: B–N/C–N = 1.57/1.46 to 1.54/1.49, ∠ C–N–B = 115 to 118°, and ∠ C–N–C = 108 to 115°. The remaining relatively unimportant structural parameters were given the following values: C–H = 1.09 A., $B-H_{\text{bond}}$ = 1.25 A., ∠ H–C–H = 109.5° and ∠ H_{bond}–B–H_{bond} = 120° (as previously mentioned, the bridge hydrogen atom was ignored) in all models except in one or two (not shown) where it was ascertained that reasonable variations in them did not affect the conclusions reached regarding the parameters determined. Considerations[17] based upon

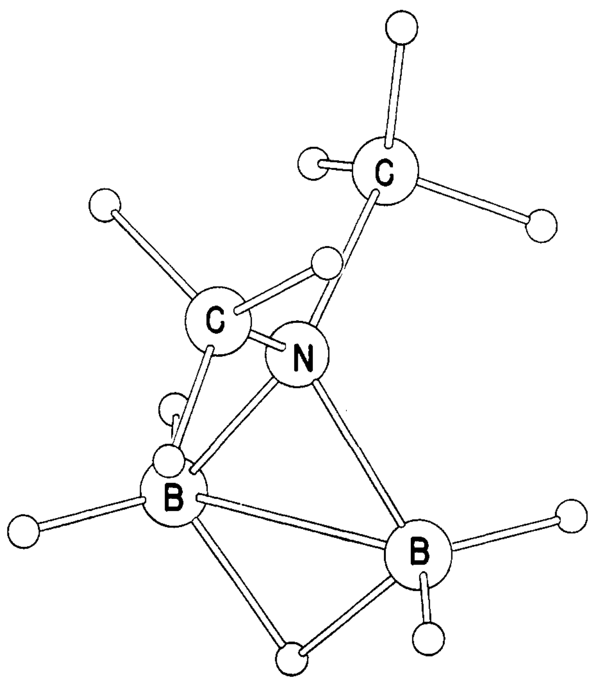

Fig. 1.—N-Dimethylaminodiborane.

comparisons between the various theoretical intensity curves and the visual intensity, and upon the relative positions of the observed and calculated maxima and minima, suggest that the best agreement would be obtained from a model located about half-way between H and I.[18] The final parameters and limits of uncertainty[19] (see Table I for quantitative comparisons) are: symmetry C_{2v}, with coplanar group H_2B-BH_2 (assumed), B–N/C–H = 1.431 (assumed) B–N/$B-H_{\text{bond}}$ = 1.247 (assumed), ∠ H–C–H = 109.5° (assumed), ∠ H–B–H = 120° (assumed), B–N/C–N = $1.047 + 0.019 - 0.012$, ∠ C–N–B = 116.2 ± 1°, ∠ C–N–C = 111.5 ± 2.5°; ∠ B–N–B = 76.4 ± 5.5°, B–N = $1.55_4 \pm 0.02_6$ Å., C–N = $1.48_3 \pm 0.02_9$ Å., B–B = 1.92 ± 0.11 Å. Although the assumptions of coplanarity for the group H_2B-BH_2 and of the value 1.25 Å. for $B-H_{\text{bond}}$ are certainly incorrect (for $H_2NB_2H_5$ a determination of

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

(9) During 1950 additional attempts to prepare photographs of B_2H_5Br were successful, and their interpretation is in progress.

(10) L. O. Brockway, *Rev. Modern Phys.*, **8**, 231 (1938).

(11) C. S. Lu and E. W. Malmberg, *Rev. Sci. Instruments*, **14**, 271 (1943); a = 3.2492 Å., c = 5.2053 Å.

(12) P. A. Shaffer, Jr., V. Schomaker and L. Pauling, *J. Chem. Phys.*, **14**, 659 (1946).

(13) *Ibid.*, **14**, 648 (1946).

(14) R. Spurr and V. Schomaker, THIS JOURNAL, **64**, 2693 (1942).

(15) The value for C–N is reasonable in terms of the single bond radii and the two values correspond well with the split indicated by the width of the radial distribution peak.

(16) See P. W. Allen and L. E. Sutton, *Acta Cryst.*, **3**, 46 (1950).

(17) Curves D, H, I and K are acceptable, A, J, M, N, and O are inacceptable, while B, C, G, F, E and L are near the edge of the region of acceptability. The following items are particularly important for this classification: (1) The appearance of the doubled maxima 3–4; (2) the strength and position of maximum 6; (3) the strength and position of maximum 8; (4) the appearance of the doubled maxima 10–11.

It is interesting that Curve O, which is derived from the model mentioned in the preliminary report of this work (reference 1) corresponds with all the coarser details of the pattern (but does not correspond at all well with the finer details and may therefore be rejected) while curves for models having bond angles midway between the preliminary and final values are in complete disagreement in regard to both the coarse and fine details.

(18) Such a model would be in excellent agreement with the visual curve in all the more important details of the pattern. The following points of disagreement, however, shown by both curves H and I, would be present and deserve mention: (1) the position of maximum 1, which occurs too far out in the calculated curves; (2) the depth of minimum 4 (and the associated degree of splitting of maxima 3–4); and (3) the region of q = 97. The first of these arises entirely from the omission of the very long heavy atom-hydrogen terms; inclusion of these terms shifts the position of this maximum nearly a q unit into much better agreement and at the same time improves the relative depths of minima 1 and 2. The second is due partly to the use of the certainly too large value 1.25 Å. for $B-H_{\text{bond}}$ (as shown by the $H_2NB_2H_5$ investigation) and partly to errors in the visual curve, arising from St. John effects and from a simple misinterpretation. Careful re-examination of the photographs by us and an examination by another observer (Professor V. Schomaker) confirmed this conclusion. The last item is of no consequence, inasmuch as this part of the pattern is very faint.

(19) V. Schomaker and J. M. O'Gorman, THIS JOURNAL, **69**, 2642 (1947). Although the limits for the ratio parameter are unsymmetrical, the limits for the derived distances have been made symmetrical in accordance with usual practice.

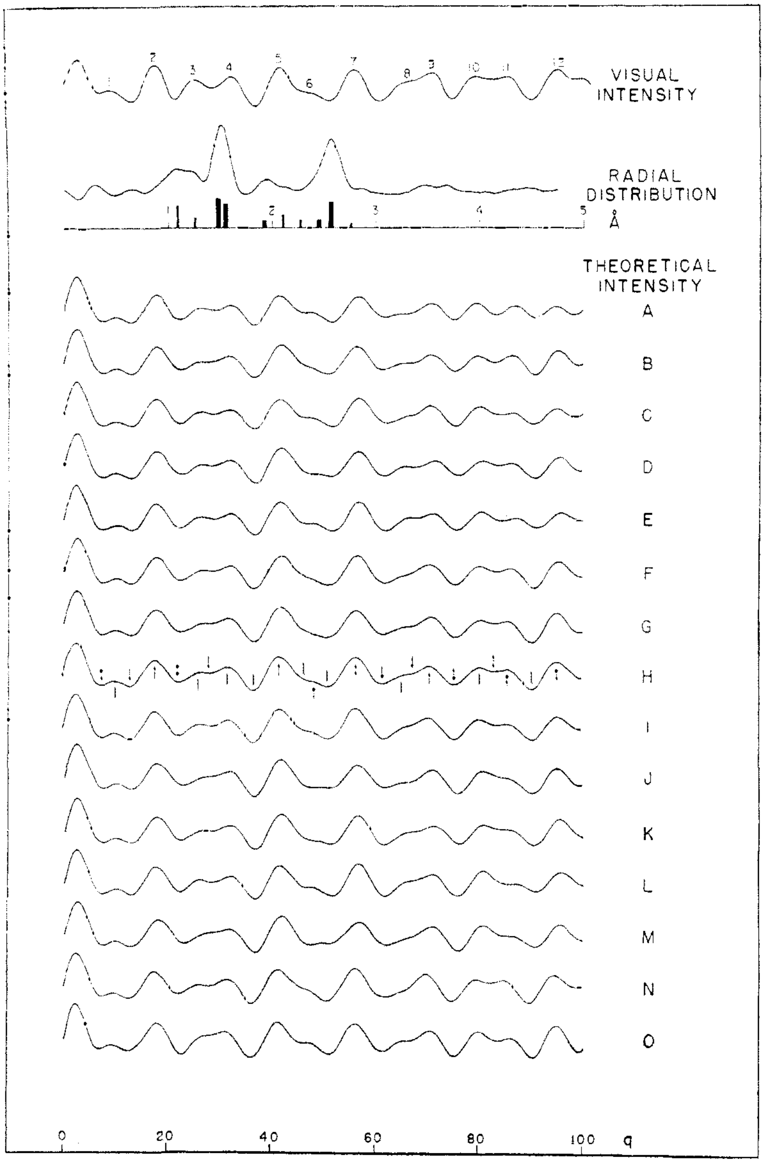

Fig. 2.—N-Dimethylaminodiborane: the theoretical intensity curves are for the following.

Curves	B-N/C-N	<C-N-B	<C-N-C	<B-N-B
A	1.57/1.46	117°	112°	71.4°
B	1.56/1.47	117	110	75.3
C	1.56/1.47	117	112	71.4
D	1.56/1.47	116	112	76.8
E	1.56/1.47	116	114	72.8
F	1.55/1.48	117	110	75.4
G	1.55/1.48	116.5	110	77.9
H	1.55/1.48	116.5	111	76.0
I	1.55/1.48	116.5	112	74.1
J	1.55/1.48	116	110	80.3
K	1.55/1.48	116	112	76.8
L	1.55/1.48	116	114	72.8
M	1.55/1.48	115	112	81.8
N	1.54/1.49	117	110	75.3
O	1.56/1.49	115.4	106	89.0

parameters involving these assumptions was made, and there is no reason to expect much difference between the two compounds in these regards), these assumptions have no effect on the determination of the heavy atom configuration largely because of the small relative weight of the related terms and, further, the temperature effect associated with them.

$H_2NB_2H_5$, Aminoborane.—Aminodiborane is in some ways a more difficult structural problem than N-dimethylaminodiborane, largely because of circumstances involving the non-bonded X···H distances. In $H_2NB_2H_5$, for example, the X···H interactions have a considerably greater total weight than the interesting B···B interaction, and at the same time may compose several groups of distances in the same region as B···B but of unknown exact positions. In $(CH_3)_2NB_2H_5$, on the other hand, the weight relationships are much more favorable, especially so when account is taken of the N···H_{carbon} term whose value is well known and need not be treated as a variable parameter.[20] Consequently, a complete parameter determination (or even one excluding H_{bridge}) would no doubt have proved impossible for $H_2NB_2H_5$; instead we have only determined B–N/B–H_{bond}, B–N/B–B and B–N/N···H_{boron}, subject to assumptions regarding the remaining hydrogen parameter values which appear to be reliable in view of their values in other compounds and the nature of the molecules as inferred from the results for $(CH_3)_2NB_2H_5$.

The radial distribution curve (Fig. 3) has strong peaks at 1.56 Å. and at 2.25 Å., which may be interpreted as corresponding to the B–N distance and to the non-bonded N···H_{boron} and B···H_{nitrogen} distances, respectively; the broad feature with centroid at about 1.20 Å. corresponds to the bonded B–H and N–H distances. The small shelf-like feature at about 2.00 Å. may be interpreted as due to the B–B distance, and the weak peak at 2.68 Å. to the B···H_B distances.[21]

Theoretical intensity curves (representative ones are shown in Fig. 3) were calculated for models of symmetry C_{2v} over the parameter ranges B–N/B–H_{bond} = 1.56/1.10 to 1.56/1.25, B–N/B–B = 1.56/1.68 to 1.56/2.39, and ϵ (the angle between the extension of B–B and the plane of the BH_2 groups, the angle increasing as BH_2 rotates away from N) = 0 to 30°, the parameters B–N/N–H, ∠ H–N–H and ∠ H–B–H being assumed as 1.02/1.56, 109.5° and 120°, respectively.[22]

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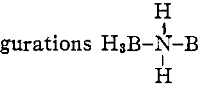
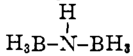
[20] Assuming $H_2NB_2H_5$ to be configurationally similar to $(CH_3)_2NB_2H_5$, the weight ratios X···H/B···B and X···H/B···B + C···C, which may be taken as a rough index of the difficulty of determining the B···B distance in $H_2NB_2H_5$ and $(CH_3)_2NB_2H_5$ (in the latter this determination is aided through the C···B interactions by the C···C), have the values 2.70 and 1.78; when the N···H_{carbon} interactions are eliminated, the value for $(CH_3)_2NB_2H_5$ is only 0.89.

[21] These assignments are uncertain since the error peaks (due to errors in the visual curve) which are encountered in our radial distribution curves are sometimes as strong as the features at 2.00 and 2.68 Å. The areas of these peaks, however, are of the right order of magnitude: the area ratios for the peaks at 1.56, 2.00, 2.25 and 2.70 Å. are approximately 1:0.20:0.78:0.10, as compared with the ratios 1:0.28:0.60:0.21 to be expected from the assignments given.

[22] Variation of N–H, ∠H–N–H and ∠H–B–H in the ranges 1.00–1.04 Å., 106.5–112.5°, and 115–125°, respectively, change the B···H_{nitrogen}, N···H_{boron}, and B···H_{boron} distances by a maximum amount of 0.04 Å., which, when the terms are reasonably temperature factored, cause only very minor changes in the calculated intensity curves even though the weight of each of these terms is about the same as the weight of B–B. We feel that the assumed values are surely correct to within the variations just mentioned (perhaps a somewhat better value for ∠H–B–H would have been 121.5°, as in dibor-

The best agreement with the observed pattern would be given by a model located about half-way between G and H.[23] The final parameters and limits of uncertainty are: symmetry C_{2v} (assumed), B–N/B–H_{bridge} = 1.155 (assumed), B–N/N–H = 1.530 (assumed), ∠ H–N–H = 109.5° (assumed), B–N/B–B = 0.810 + 0.026 − 0.024, B–N/B–H_{bond} = 1.355 + 0.078 − 0.077, ϵ (defined above) = 15° ± 20°, B–N = $1.56_4 \pm 0.02_6$ Å., B–B = 1.93 ± 0.10 Å., B–H_{bond} = $1.15_4 \pm 0.09_0$ Å., ∠ B–N–B = 76.2 ± 2.8°.

There seemed to us no reason to expect a configuration for $H_2NB_2H_5$ different from the one assumed (and supported in a convincing manner by the diffraction data for the doubtless similar $(CH_3)_2NB_2H_5$). It did seem worthwhile, however, to examine briefly the configurations 
$H_3B{-}\overset{H}{\overset{\downarrow}{\underset{\underset{H}{|}}{N}}}{-}BH_2$
and 
$H_3B{-}\overset{H}{\overset{|}{N}}{-}BH_3$
previously suggested,[8] and we have accordingly ascertained that such configurations are incompatible with our data over the parameter ranges B–N/B–H = 1.56/1.15 to 1.56/1.20, ∠ B–N–B = 104.5 to 114.5°, ∠ H–B–H = 104.5 to 114.5°, which includes the model favored by Bauer (B–N = 1.56 ± 0.03 Å., ∠ B–N–B = 109.5 ± 4°, B–H = 1.20 Å., ∠ H–B–H = 109.5° (assumed)). It is to be noted, however, that our value for B–N is in good agreement with Bauer's.

Discussion

It is now clear that the aminodiboranes may be regarded as derived from diborane itself by a simple replacement of a bridge hydrogen atom with a $-NH_2$ group to form in its place a nitrogen bridge; these compounds are, so far as we are aware, the only known examples of diborane derivatives in which the substituent has entered the bridge position. The C–N distance (1.48 Å.) in $(CH_3)_2NB_2H_5$ and the C–N–C angle (111.5°, about the same as in dimethylamine) must be regarded as normal. On the other hand, the B–N and B–B separations of 1.55 and 1.92 Å. in $(CH_3)_2NB_2H_5$ and 1.56 and 1.93 Å. in $H_2NB_2H_4$ correspond to bonds considerably weaker than normal covalent single bonds, as may be seen either by comparison with the sums of the covalent single bond radii 1.45 and 1.60 Å. obtained by adaption of the value 0.80 Å. for boron[24] and the Schomaker–Stevenson radius for nitrogen[25] corrected for differ-

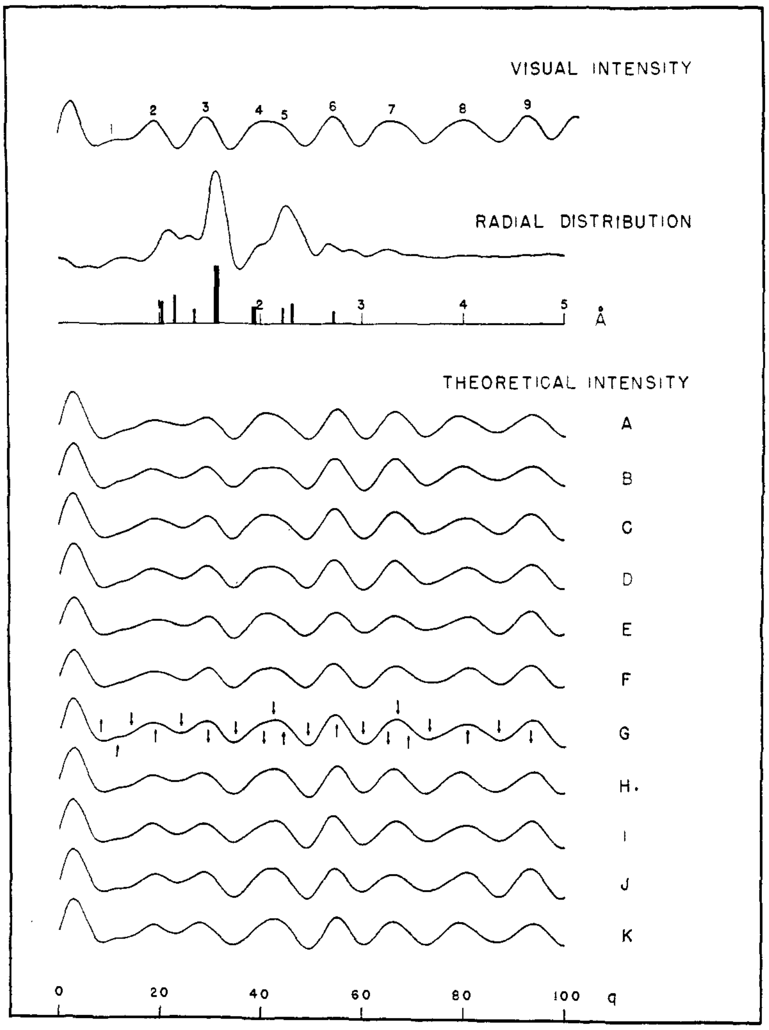


Fig. 3.—Aminodiborane: theoretical intensity curves are for the following

Curves	B–N/B–B	B–N/B–H	<B–N–B	ϵ
A	1.56/1.91	1.56/1.15	75°29′	0°
B	1.56/1.91	1.56/1.20	75 29	0
C	1.56/1.94	1.56/1.18	76 54	0
D	1.56/1.94	1.56/1.20	76 54	0
E	1.56/1.97	1.56/1.15	78 18	0
F	1.56/1.97	1.56/1.20	78 18	0
G	1.56/1.94	1.56/1.18	76 54	10
H	1.56/1.91	1.56/1.12	75 29	20
I	1.56/1.94	1.56/1.18	76 54	20
J	1.56/1.97	1.56/1.12	78 18	20
K	1.56/1.91	1.56/1.12	78 18	30

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ane), so that they cannot give rise to any uncertainty in the parameters to be determined.

[23] The visual curve does not represent well the appearance of the pattern in respect to the shape of the second maximum, the depth of the third minimum, the depth of the sixth minimum, and the shape of the seventh maximum. After careful re-examination of the photographs it is our conclusion (which has been verified by another observer, Professor V. Schomaker) that these items represent errors in the visual curve, and that the best theoretical curves are actually in good agreement with the observed pattern in all regards. Of the errors in the visual curve, the incorrectly represented depth of the third minimum is the hardest to understand. This minimum appears on the photographs as deeper relative to the first and fourth minima than is shown by the better theoretical curves, but appears to be in agreement with the relative depths of the succeeding fourth and sixth minima. This effect doubtless arises from the difficulty of judging the depth of the first minimum due to the heavy background in this region. Of the curves shown in Fig. 3, C, D, F, G, H and K are acceptable and the remaining are close to the limits of uncertainty.

The preliminary, incorrect value of the B–N–B angle in $H_2B_2H_5$ (reference 1) arose partly from erroneous assignment of the peak at 2.25 Å. to the B···B interaction (an assignment related to the assumption that the value 2.53 Å. for B···B representing ∠B–N–B = 109.5° as obtained in the original investigation, reference 8, would not prove to be entirely incorrect) and partly from the errors in the visual curve outlined above, which were misleading. However, the radial distribution curve does suggest the possibility of a still smaller B–N–B bond angle, and even the original visual curve is in better agreement with the final model than with the preliminary model.

[24] L. Pauling, THIS JOURNAL, 69, 542 (1947).

[25] V. Schomaker and D. P. Stevenson, *ibid.*, 63, 37 (1941).

TABLE I

COMPARISONS OF OBSERVED AND CALCULATED POSITIONS OF MAXIMA AND MINIMA

	$(CH_3)_2NB_2H_5$ (Curve H)				$H_2NB_2H_5$ (Curve G)			
	Min.		Max.		Min.		Max.	
No.	$q_{obsd.}$	$q/q_{obsd.}$	$q_{obsd.}$	$q/q_{obsd.}$	$q_{obsd.}$	$q/q_{obsd.}$	q	$q/q_{obsd.}$
1	7.05	(1.050)	9.15	(1.093)	7.80	(1.142)	10.95	(1.005)
2	13.49	(0.956)	17.66	1.002*	14.02	(0.956)	18.64	(0.987)
3	21.56	1.030	25.14	1.038	23.75	1.011*	29.10	0.997*
4	28.56	0.977*	32.28	0.979	34.35	0.996*	40.14	.967
5	36.88	.998*	41.90	.995*	41.85	.980	44.02	.988
6	44.69	1.041	47.62	1.014	48.79	1.004*	54.46	1.001*
7	51.57	0.989	56.07	1.006*	59.73	1.006*	66.64	0.998
8	61.00	1.007	65.60	0.994	72.94	1.002*	80.27	1.003*
9	68.31	0.987	71.03	.995	86.46	1.006*	92.82	1.006*
10	75.13	1.005*	79.23	1.015				
11	82.24	1.012*	85.79	0.993				
12	90.21	1.003*	95.28	0.999*				
Av.	21 features		1.003_8		14 features		0.997_5	
Av. dev.			0.013				0.008	
Av.	9 starred features		0.999_7		10 starred features		1.003_2	
Av. dev.			0.007				0.003	

Best model: B–N = 1.003_1 × 1.55 = 1.55_4
B–N/C–N = 1.047

1.002_8 × 1.56 = 1.56_4
B–N/B–B = 0.810
B–N/B–N = 1.355

ence in electronegativity, or with the values 1.50 and 1.60 Å. obtained from the same boron radius and from the Pauling–Huggins[26] radius for nitrogen. This conclusion is probably correct even though the boron radius is somewhat uncertain (the older radii 0.88,[26] 0.86[8] and 0.85[27] are certainly too large, at least for compounds in which boron displays a coördination number of 5 or 6) and even though the best choice of recipe for combining the radii (Schomaker–Stevenson, Pauling–Huggins, or still others) is not evident.

It is interesting to compare the important distances in $R_2NB_2H_5$ with those in B_2H_6. A plausible interpretation of these distances may be made by consideration of two obviously important factors: (1) the relative "electron deficiency" of $R_2NB_2H_5$ and B_2H_6, a quantity which is certainly less for the former because of the two additional electrons from nitrogen available for bonding the same number of boron ligands and (2) the B–N–B angle stress. The first item might be expected to increase the apparent bond order of the B–N bonds relative to the corresponding B–H_{bridge} bonds in B_2H_6 and to decrease the B–H_{bond} distance, but, since in general as electron deficiency in compounds of boron is reduced the number of boron ligands tends to be reduced,[28] this item might be expected to increase the B–B distance. The second item would be expected to have little effect on the B–H_{bond} bonds, to increase the B–B distance, and to increase the apparent bond order of the B–N bonds relative to B–H_{bridge} in B_2H_c.[29] The observed distances correspond perfectly with expectation based on these ideas, the apparent bond order of the B–N bonds calculated from Pauling's equation[24] $R(l) - R(n) = 0.6 \log n$ being 0.66 and 0.79 by use of the Schomaker–Stevenson and Pauling–Huggins recipes, respectively, as compared with the corresponding values 0.52 and 0.41 for the B–H_{bridge} bond in diborane; the B–H_{bond} distance being about 0.04 Å. shorter; and the B–B distance being about 0.15 Å. longer.

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(26) L. Pauling and M. L. Huggins, *Z. Krist.*, [A] **87**, 205 (1934); see also L. Pauling, "The Nature of the Chemical Bond," Cornell University Press, Ithaca, N. Y., 1940, chap. 5.

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

(28) V. Schomaker, *J. chim. phys.*, **46**, 262 (1949).

(29) The actual situation is certainly more complicated than it appears at first sight. The elongation of the B–B bond depends upon the amount of stress of each of the angles B–N–B, N–B–B and B–B–N; if these stresses are equal, of course no elongation may occur. It seems reasonable, however, to expect the B–N–B angle stress to exceed that at each of the other angles, its value being approximately 33° less than the normal tetrahedral value.

A crude calculation of the balance among the B–N–B angle strain, the B–B stretch, and the B–N compression ignoring the B–B–N and N–B–B angle strains altogether and based upon reasonable force constants, predicts an elongation of B–B and 0.08 Å. over that in diborane, and an increase of 0.11 in the apparent bond order of B–N over B–H_{bridge} in diborane. These values represent the maximum changes which can be expected from the B–N–B angle stress effect.