

From the entropy of solid  $\text{NH}_4\text{Cl}$ , 23.6, and the value for  $\text{Cl}^-$ , 9.7, the value for  $\text{NH}_4^+$  in solid salts is 13.9.

Table V includes all of the common negative ions, and the diversity of ion-types is such that estimates may be made on less common ions by comparison with the value for a similar ion given in the table.

TABLE V

SUMMARY OF ENTROPY CONTRIBUTION, IN CAL. PER DEGREE PER MOLE, OF NEGATIVE IONS IN SOLID COMPOUNDS AT 298°K.

Negative ion	Charge on positive ion			
	+1	+2	+3	+4
$\text{F}^-$	(5.5)	4.7	(4.0)	5.0
$\text{Cl}^-$	9.7	8.1	6.9	8.1
$\text{Br}^-$	13.0	10.9	(9)	(10)
$\text{I}^-$	14.6	13.6	12.5	13.0
$\text{CN}^-$	7.2	(6)		
$\text{OH}^-$	(5.0)	4.5	3.0	
$\text{ClO}^-$	(14)	(10)	(8)	
$\text{ClO}_2^-$	19.2	(17)	(14)	
$\text{ClO}_3^-$	24.9	(20)		

$\text{ClO}_4^-$	26.0	(22)		
$\text{BrO}_3^-$	26.5	22.9	(19)	
$\text{IO}_3^-$	25.5	(22)		
$\text{H}_4\text{IO}_6^-$	33.9	(30)		
$\text{NO}_2^-$	17.8	(15)		
$\text{NO}_3^-$	21.7	17.7	(15)	(14)
$\text{VO}_3^-$	20.0	(18)		
$\text{MnO}_4^-$	31.8	(28)		
$\text{O}^{--}$	2.4	0.5	0.5	1.0
$\text{S}^{--}$	8.2	5.0	1.3	2.5
$\text{Se}^{--}$	(16)	11.4	(8)	
$\text{Te}^{--}$	(16.5)	12.1	(9)	
$\text{CO}_3^{--}$	15.2	11.4	(8)	
$\text{SO}_3^{--}$	(19)	14.9	(11)	
$\text{C}_2\text{O}_4^{--}$	(22)	17.7	(14)	
$\text{SO}_4^{--}$	22	17.2	13.7	(12)
$\text{CrO}_4^{--}$	26.2	(21)		
$\text{SiO}_4^{--}$	(19)	13.8	(9)	7.9
$\text{SiO}_3^{--}$	16.8	10.5	(7)	
$\text{PO}_4^{--}$	(24)	17.0	(12)	
$\text{HCO}_2^-$	17.4	(13)	(10)	
$\text{H}_2\text{PO}_4^-$	22.8	(18)		
$\text{H}_2\text{AsO}_4^-$	25.1	(21)		

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## A Reinvestigation of the Structures of Diborane and Ethane by Electron Diffraction<sup>1,2</sup>

BY KENNETH HEDBERG AND VERNER SCHOMAKER

The ethane-like model for diborane has been eliminated and the bridge model confirmed in an electron-diffraction reinvestigation of diborane and ethane which has led to the bond angle and bond distance values  $\angle \text{H}_{\text{bond}}\text{-B-H}_{\text{bond}} = 121.5 \pm 7.5^\circ$ ,  $\text{B-B} = 1.770 \pm 0.013 \text{ \AA}$ ,  $\text{B-H}_{\text{bond}} = 1.187 \pm 0.030 \text{ \AA}$ , and  $\text{B-H}_{\text{bridge}} = 1.334 \pm 0.027 \text{ \AA}$  for diborane, and  $\angle \text{C-C-H} = 110.5 \pm 3.5^\circ$ ,  $\text{C-H} = 1.114 \pm 0.027 \text{ \AA}$ , and  $\text{C-C} = 1.536 \pm 0.016 \text{ \AA}$  for ethane. A reasonable combination of the values for ethane with the spectroscopic moments of inertia gives  $\angle \text{C-C-H} = 110.4^\circ$ ,  $\text{C-H} = 1.110 \text{ \AA}$ , and  $\text{C-C} = 1.535 \text{ \AA}$ , in excellent agreement with the purely electron-diffraction results and considerably more precise.

An early electron diffraction investigation of the structure of diborane by S. H. Bauer<sup>3</sup> led to the conclusion that the molecule had a configuration like that of the ethane molecule, in apparent agreement with certain other lines of physical evidence. More recently, the "bridge" or "protonated double bond" model of symmetry  $D_{2h}$ , illustrated in Fig. 1, has been strongly supported on the basis of reinterpretations of the older chemical and physical data<sup>4</sup> and by new evidence,<sup>4,5</sup> of which the spectroscopic results of Price<sup>5</sup> seem especially conclusive, and Bauer has evaluated its structural parameters (it had not been tested in his original investigation) by a partial reconsideration<sup>6b,c</sup> of the diffraction data. However, Bauer has maintained,<sup>6</sup> at least until the appearance of Price's results, that this model is in

fact incompatible with the existence of a certain visible inner ring of the diffraction photographs and should accordingly be regarded as very probably incorrect or even eliminated from consideration.

In view of this situation the present independent reinvestigation of diborane with full consideration of both bridge and ethane-like models still seems to be in order. It was anticipated when this work was begun<sup>7</sup> that a choice between the two types of models by electron diffraction might be difficult or impossible because there would not necessarily be any differences between them in the magnitudes of the interatomic distances  $\text{B-B}$ ,  $\text{B-H}$ , and  $\text{B} \cdots \text{H}$  which make the principal contributions to the molecular scattering, while the corresponding numbers of distances (1:4,4:4 and 1:6:6) are different only by such rather small amounts as would probably not lead to a definite conclusion, at least not from visual interpretations of the diffraction pattern. It was to be hoped, however, that photographs could

(7) Active reconsideration of the diborane problem was initiated in this laboratory in the summer of 1946 by Dr. Wm. Shand, Jr., just before his death. It was taken up again by the Authors in January, 1947, with the preparation of new photographs. Our conclusion as to type of model had already been reached on the basis of the photographs and some theoretical curves of Dr. Shand's before we learned of Price's results, but it had not been thoroughly checked.

(1) This work was supported in part by the Office of Naval Research under Contract N6onr-24423.

(2) Presented before the Physical and Inorganic Chemistry Division of the American Chemical Society, 116th Meeting, Atlantic City, N. J., September, 1949.

(3) S. H. Bauer, *THIS JOURNAL*, **59**, 1096 (1937).

(4) See K. S. Pitzer, *ibid.*, **67**, 1126 (1945).

(5) W. C. Price, *J. Chem. Phys.*, **16**, 894 (1948); **15**, 814 (1947).

(6) (a) Private communication quoted by F. Stitt, *ibid.*, **9**, 785 (1941); (b) S. H. Bauer, *Chem. Revs.*, **31**, 46, 54 (1942); (c) private communication quoted by H. C. Longuet-Higgins and R. P. Bell, *J. Chem. Soc.*, 253 (1943); (d) S. H. Bauer, *THIS JOURNAL*, **70**, 119 (1948).

be made with rings extending to high enough scattering angles to permit this choice (assuming that an ethane-like diborane molecule would be symmetrical) if the structure was of the bridge type and had unequal bridge and peripheral B-H distances, as suggested by Bauer's<sup>6</sup> reconsiderations; it was expected that the remaining discrepancies<sup>6</sup> between the diffraction data and the otherwise favored bridge model could be elucidated and that on the assumption of either type of structure values of the structural parameters more accurate than those from the earlier studies could be obtained.

Photographs of ethane were taken primarily for use in connection with the interpretation of the diborane photographs. It became evident as the work progressed, however, that a full reinvestigation would be worthwhile.

**Experimental.**—Diborane containing less than 0.5% of ethane was kindly provided by Professor A. B. Burg. It was freed from hydrogen, which was present as an intentional contaminant, by fractional condensation. The sample of ethane (Phillips Research Grade; propane, <1.5%; air <0.5%) was kindly supplied by the Consolidated Engineering Corporation.

The photographs were taken in the apparatus described by Brockway,<sup>8</sup> with a camera distance of about 11 cm. For some of the photographs a beam catcher was used. The electron wave length, about 0.06 Å., was determined by zinc oxide calibration.<sup>9</sup> Corrections were made for film expansion.

The photographs were interpreted visually in the usual way except for the addition of detailed inter-comparisons of the two sets in order that small differences would be both more obvious and more susceptible to reliable interpretation. The two patterns do show differences in detail throughout (as represented by the visual curves of Figs. 2 and 3 many of the differences are hardly obvious and some are obscured in reproduction) but on both patterns, in agreement with the earlier report, the inner rings are similar in general character and the outer rings alike in showing no very great deviations from the simple diatomic pattern.<sup>10</sup>

The radial distribution curves were calculated<sup>11,12</sup>

(8) I. O. Brockway, *Rev. Modern Phys.*, **8**, 231 (1936).

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

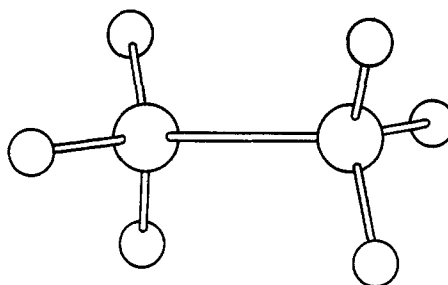
(10) It is difficult, however, to account for the earlier statement<sup>3</sup> that "except for a change in  $s$  scale (due to the larger dimensions of the borane molecule its entire pattern is compressed) the two are identical." Perhaps the differences were overlooked because they are small compared to the great differences between both patterns and the ethylene pattern, or just conceivably the new ethane photographs are different from the old, which have been lost; at any rate, the new diborane photographs show the same pattern as a good medium one of the old set, the only one that could be found for comparison.

The general similarity of the ethane and diborane patterns and the great contrasts of both with the ethylene pattern do not, of course, have the origin in type of structure which seems to be implied in the previous report<sup>3</sup> by the prominence given to direct comparisons of the appearance and measurements of the diborane and ethane patterns; instead, the similarities and contrasts probably depend mainly upon the ratios of interatomic distance values, C-H:C-C:C··H = 0.72:1:1.43 and B-H:B-B:B··H = 0.72:1:1.52 for ethane and diborane and C-H:C=C:C··H = 0.80:1:1.58 for ethylene, the X-H/X-X ratio being the more important both because of the smaller initial weights and more severe temperature factors of the X··H terms.

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

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

### ETHANE-LIKE



### BRIDGE

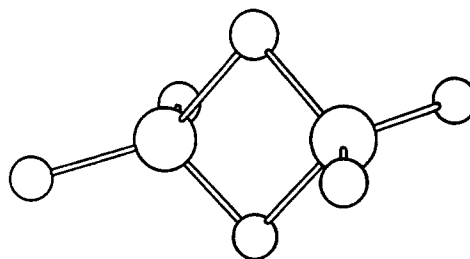


Fig. 1.—Models of diborane. The drawing is not intended to imply any concept of the nature of the bonding of the bridge hydrogen atoms.

from the visual intensity curves (Figs. 2 and 3) according to the equation<sup>13,11</sup>

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

with  $q = (40/\lambda) \sin \frac{\varphi}{2}$  and  $\exp(-aq_{max}^2) = 0.1$ . In the calculation of the theoretical intensity curves all terms of the function<sup>13,11</sup>

$$I(q) = \sum_{i,j} \frac{Z_i Z_j}{r_{i,j}} \exp(-a_{ij} q^2) \sin \frac{\pi}{10} r_{i,j} q$$

were included, and for hydrogen  $Z$  was replaced by an effective value 1.25 in order to approximate better its low-angle scattering power relative to carbon and boron. The  $a_{ij}$  values for the bridge model of diborane, 0.00016 for B-H<sub>bo</sub>, 0.00028 for B-H<sub>br</sub>, 0.00062 for B··H, and 0.00100 for H··H terms, were derived from the forms of the normal vibrations, as defined by symmetry or very roughly estimated, and Pitzer's assignments<sup>4</sup> of their frequencies. The remaining  $a_{ij}$  values are  $a_{B-H} = 0.00020$ ,  $a_{B\dots H} = 0.00035$ ,<sup>14</sup> and  $a_{H\dots H} = 0.00100$  for the ethane-like model of diborane, and  $a_{C-H} = 0.00016$ ,  $a_{C\dots H} = 0.00030$ , and  $a_{H\dots H} = 0.00100$  for ethane itself. For all the ethane type of models the staggered D<sub>3d</sub> orientation was assumed.<sup>15</sup>

**Diborane.**—The radial distribution curve has a peak at 1.275 Å., notably broad compared with the

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

(14) Use of the more likely value 0.00060 does not significantly change or improve the theoretical curves.

(15) It was found that omitting the internal-rotation dependent H··H terms altogether had no perceptible effect except for a small outward shift of the weak inner ring; accordingly, no further attention was given the internal rotation problem.

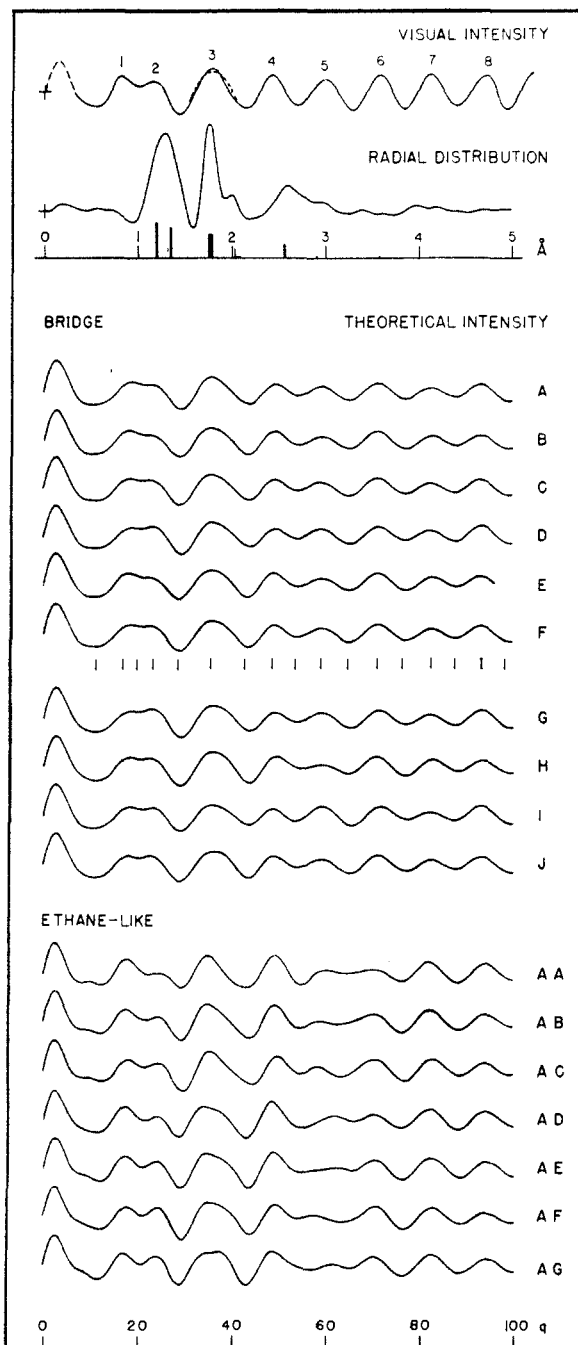


Fig. 2.—Visual and radial distribution curves for diborane. Theoretical intensity curves for the following models of diborane:

Model	Bridge		
	$\angle \text{H}_{\text{bo}}\text{-B-H}_{\text{bo}}$ , deg.	B-H <sub>br</sub> /B-H <sub>bo</sub>	B-B/B-H <sub>av</sub> .
A	130.0	1.33/1.18	1.76/1.255
B	125.0	1.35/1.20	1.76/1.275
C	125.0	1.33/1.18	1.76/1.275
D	125.0	1.31/1.16	1.76/1.235
E	120.0	1.35/1.20	1.76/1.275
F	120.0	1.33/1.18	1.76/1.255
G	120.0	1.31/1.16	1.76/1.235
H	120.0	1.31/1.20	1.76/1.255
I	120.0	1.35/1.16	1.76/1.255
J	115.0	1.33/1.18	1.76/1.255

Ethane-like		
AA	109.5	1.76/1.30
AB	106.5	1.76/1.27
AC	106.5	1.76/1.24
AD	102.8	1.76/1.30
AE	102.8	1.76/1.27
AF	102.8	1.76/1.24
AG	97.2	1.76/1.27

On this and the following figure the broad, intermediate and narrow bars beneath the radial distribution curves represent, respectively, the M...M, M...H, and H...H distances in the final models. The lengths of the bars indicate the relative weights of the distances.

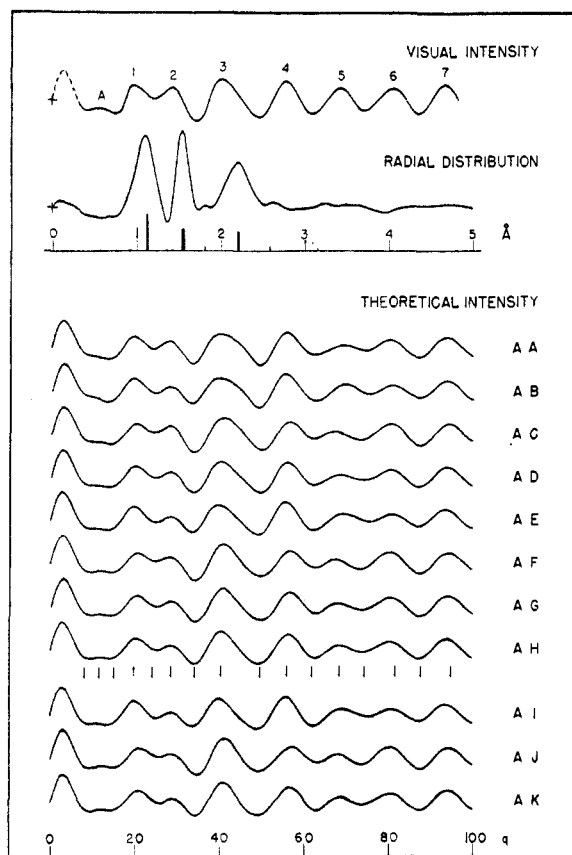


Fig. 3.—Visual and radial distribution curves for ethane. Theoretical intensity curves for the following models of ethane:

Model	$\angle \text{C-C-H}$ , deg.	C-H/C-C
AA	115.0	1.12/1.54
AB	115.0	1.15/1.54
AC	112.2	1.09/1.54
AD	112.2	1.12/1.54
AE	112.2	1.15/1.54
AF	109.5	1.09/1.54
AG	109.5	1.11/1.54
AH	109.5	1.12/1.54
AI	109.5	1.15/1.54
AJ	106.6	1.09/1.54
AK	106.6	1.12/1.54

corresponding peak for ethane, which can be satisfactorily interpreted as a representation of two unresolved B-H distances of equal weight at about 1.20 and 1.35 Å., but not as a single B-H distance if

its  $a_{ij}$  value is of the expected order of magnitude (see preceding paragraph). If the 1.20 Å. distance is assigned to the peripheral B-H bonds in the bridge structure (the longer, therefore, to the bridge B-H bonds) and the B-B and longer B...H distances are taken from the remaining strong radial distribution peaks at 1.76 and 2.58 Å., the peripheral H-B-H angle is about 120°. The symmetrical ethane-like structure would account for only a single B-H bond distance, at 1.275 Å., corresponding to an H-B-H angle of about 103°.

Theoretical intensity curves were calculated to cover systematically the following ranges of parameters: Bridge models,  $B-H_{br}/B-H_{bo} = 1.33/1.22$  to  $1.35/1.16$ ,  $B-B/B-H_{av.} = 1.76/1.235$  to  $1.76/1.295$ , and  $\angle H_{bo}-B-H_{bo} = 110$  to  $130^\circ$ ; ethane-like models,  $B-B/B-H = 1.76/1.30$  to  $1.76/1.21$ , and  $\angle H-B-H = 97.2$  to  $112.5^\circ$ . Good agreement with the appearance of the photographs is shown by the better of the curves for the bridge model (curves C, F) but none of the ethane-like curves, including those now shown in Fig. 2, is tolerable in regard to all the following major points, although, to be sure, each except the first is fitted tolerably by some of the curves. The points are: (1) the positions and intensities of the first and second maxima, (2) the shape of the third maximum and fourth minimum, and (3) the intensity relations in the region from  $q = 35$  to  $70$ . The visual curve unfortunately does not show (1) and (2) clearly; (2) may be seen, however, and (1) is definitely implied, inasmuch as the difference between the inner parts of the ethane and diborane patterns, which it was specially desired to estimate, are correctly represented.<sup>16</sup> It must be concluded that the diborane molecule has the bridge structure. The best qualitative agreement with our final interpretation of the photographs (the features which were important for choice of type of model were most important here also) would be given by a model near F, displaced a little toward C, E and H. The final parameter values and limits of uncertainty<sup>17</sup> (see Table I for quantitative comparison) are:  $B-H_{av.}/B-B = 0.716 + 0.008 - 0.013$ ,  $B-H_{bo}/B-H_{br} = 0.890 + 0.020 - 0.016$ ,  $\angle H_{bo}-B-H_{bo} = 121.5 \pm$

(16) The visual curves were drawn by K. H. from his observations only; the diborane curve agrees well with the independent observations and sketches of V. S. except for certain aspects of the first three maxima. The most significant difference concerns the third maximum, which according to the observation of V.S. should be about as indicated by the dotted line, somewhat broader than is indicated by the visual curve and round-topped with more of a suggestion of an outer shoulder near the top rather than down toward the fourth minimum. Re-examination of the photographs and further comparison with the ethane photographs convinced us that the dotted line is indeed substantially correct. The degree of splitting and precise width of the first main feature (maxima 1 and 2) are incorrectly represented by the visual curve but both errors are typical of the actual appearance of features of this type (the same errors were made in the ethane curve) and always have to be allowed for, either before the visual curve is drawn or later, when it is used. In his sketches, which turned out to be in good agreement with the width and split of this feature as shown by the theoretical curves (although uncertain as to whether maximum 1 or maximum 2 is slightly the higher), V.S. tried to make these allowances beforehand. Corresponding allowances have to be made for the St. John effects in judging the measured positions of maxima 1 and 2.

(17) V. Schomaker and J. M. O'Gorman, THIS JOURNAL, **69**, 2642 (1947). The unsymmetrical limits found for the shape parameters  $B-H_{av.}/B-B$  and  $B-H_{bo}/B-H_{br}$  of course imply asymmetrical limits for the derived bond distances narrower than the symmetrical ones which, for simplicity of writing, are given here.

$7.5^\circ$ ,  $B-B = 1.770 \pm 0.013$  Å.,  $B-H_{bo} = 1.187 \pm 0.030$  Å., and  $B-H_{br} = 1.334 \pm 0.027$  Å., in fair agreement with the respective values 0.72, 0.85, 1.20°, 1.79 Å., 1.18 Å., and 1.39 Å. found by Bauer<sup>6b,c</sup> for the bridge model. The  $H_{br}-B-B$  angle is approximately  $48.5^\circ$ .<sup>18</sup>

TABLE I  
COMPARISONS OF OBSERVED AND CALCULATED POSITIONS OF  
MAXIMA AND MINIMA

Min.	Max.	Diborane		Ethane	
		$q_{obs.}^b$	Curve F <sup>a</sup> $q/q_{obs.}$	$q_{obs.}^b$	Curve AH $q/q_{obs.}$
A				7.97	(1.192)
	A			11.33	(1.015)
1		11.31	(1.008)	14.89	(0.940)
	1	17.16	(1.078)	19.73	(1.019)
2		20.00	(1.065)	24.08	(1.047)
	2	23.37	(0.984)	28.32	(1.006)
3		28.84	1.012	34.13	0.996
	3	35.61	(1.011)	40.27	1.000
4		42.83	1.020	49.59	0.990
	4	48.76	1.007	55.93	1.012
5		53.61	1.005	61.90	1.013
	5	59.25	0.999	68.40	1.000
6		64.79	.992	74.43	0.989
	6	71.05	1.002	81.66	.989
7		76.37	1.010	87.66	.994
	7	82.71	1.000	94.90	.991
8		87.69	0.999		
	8	93.40	.998		
9		98.34	1.010		
Average, 13 features			1.006	Average, 10 features	0.997
Average deviation			0.006	Average deviation	0.007

<sup>a</sup> The quantitative comparison was made for all the curves shown in Fig. 2 in order to determine the uncertainties in distance values due to uncertainties in the choice of shape of model. For B-B this effect proves to be almost negligible. The average deviations range from 0.5 to 0.8% and are in agreement with the conclusions from the qualitative comparisons except for Curve B, which, though otherwise unsatisfactory, is alone in having the lowest average deviation. <sup>b</sup> Averages of measurements by K. H. and V. S.

**Ethane.**—The radial distribution curve indicates important interatomic distances at 1.11 Å., 1.54 Å., and 2.20 Å., which must be ascribed to C-H, C-C and C...H interactions, respectively. The corresponding C-C-H angle is 111°.

Theoretical intensity curves, some of which are shown in Fig. 3, were calculated for models having shape parameters in the range  $C-H/C-C = 1.06/1.54$  to  $1.15/1.54$ ,  $\angle C-C-H = 106$  to  $115^\circ$  ( $\angle H-C-H = 112.8$  to  $103.5^\circ$ ). Curves AA, AB, AJ and AK are generally unsatisfactory, and AC, AF, AE and AI have poor intensity relations for the outer rings, with AE and AI also showing the second maximum much too weak, but AD, AG and AH are in good agreement with our interpretation of the photographs, which, as for diborane, is only par-

(18) The shorter B-H distance has been assumed to be the peripheral one, as seems reasonable. No doubt, however, a satisfactory curve would result from some model with the reverse assignment and a correspondingly large (and unlikely?) peripheral bond angle of about  $140^\circ$  which would keep B...H at about 2.58 Å.

tially represented by the visual curves<sup>16,19</sup>; the best agreement would be given by  $C-H/C-C = 1.115/1.54$  and  $\angle C-C-H = 110.5^\circ$ . These considerations and the quantitative comparisons (illustrated in Table I for Model AH) lead in the usual way to the following parameter values and limits of uncertainty:  $C-H/C-C = 0.725 \pm 0.017$ ,  $\angle C-C-H = 110.5 \pm 3.5^\circ$  ( $\angle H-C-H = 108.5 \pm 3.5^\circ$ ),  $C-H = 1.114 \pm 0.027 \text{ \AA.}$ , and  $C-C = 1.536 \pm 0.016 \text{ \AA.}$

**Discussion.**—The choice of model for diborane proved easier and more certain than was anticipated, both because the split of the B-H distances turned out to be favorably large and because the effects of the difference in relative weights of the B-H and B...H terms on the bridge and ethane-like curves proved greater than had been anticipated. Aspects of the determination which did not seem essential to the presentation in the foregoing paragraphs or which particularly depended on the comparison of the ethane and diborane photographs will now be considered.

The average deviations of the quantitative comparisons support the choice of the bridge model, none of the curves shown having a 13-feature average deviation (as in Table I) greater than 0.8%, whereas all the ethane-like curves gave larger values greater than 0.9%, the ones which are perhaps least unsatisfactory qualitatively, moreover, having suspiciously high average deviations of around 1.2%.

According to Bauer<sup>5,6</sup> the weak inner ring of the diborane pattern is about as intense as the inner ring of the ethane pattern and cannot be accounted for by the bridge model. We therefore made especially careful intercomparisons of this region on the photographs and theoretical curves of diborane and ethane; the bridge curves are actually perfectly satisfactory, and the ethane-like curves quite unsatisfactory, in this regard. Direct comparisons, confirmed by several other observers, showed for photographs of approximately equal density that the apparent intensity of the weak inner ring is very much less for diborane than for ethane,<sup>20</sup> about as indicated by the visual curves and in agreement

(19) Points of difficulty appeared in the height of the fifth maximum relative to the fourth and sixth and of the sixth relative to the fifth and seventh. In disagreement with the visual curve, V.S.'s independent sketches would have the fifth maximum somewhat weaker than shown by the visual curve, as required by the theoretical curves which are otherwise to be regarded as the most satisfactory, while showing the sixth about as much too strong as it is too weak on the visual curve. It would be especially desirable to decide on a more precise interpretation of these features since they are sensitive to the  $C-H/C-C$  ratio, the visual curve in this respect favoring a somewhat larger and V.S.'s observations a somewhat smaller value than our final result, but this proved to be impossible because the last two rings (6 and 7) of the photographs are too faint. The original observations are in almost perfect agreement with each other and the best theoretical curves in all other respects.

(20) The heaviest and very lightest photographs are possible exceptions, but they are unsuitable for this purpose because on them the weak inner ring tends to disappear in any case, even if the better marked central region and first main ring can still be seen. It is also true that for both substances the apparent intensity is greater relative to the first main ring than corresponds directly to the best theoretical curves and, further, that the gross appearance of the inner part of the theoretical curves is greatly altered when, as in our calculations in contrast to Bauer's, the factor  $1/s$  of the intensity formula is omitted; neither of these items casts any doubt on our conclusion, however, since our experience with diborane and ethane is entirely consistent with what has been observed in general in the visual interpretation of electron diffraction photographs.

with the theoretical curves for ethane and the bridge model of diborane but in disagreement with the ethane-like curves, which show the inner ring to be about as strong as for ethane.<sup>21</sup>

The narrowness relative to ethane of the first main feature and its lack of any pronounced separation<sup>16</sup> into maxima 1 and 2 are as uniformly characteristic of the bridge model as the weakness of the inner ring, even more clearly visible, we believe, and therefore probably more important; all these effects can be ascribed mainly to the differences in relative numbers of X-X, X-H and X...H distances in the two molecules, the pattern at small  $q$  values being, of course, insensitive to the small variations in the ratios of the distances.<sup>22</sup> Finally, relative areas of radial distribution peaks, although not very reliable in general and in this case subject to the several apparent errors of the visual curves,<sup>16,19</sup> might be expected to give some indication of the relative weights for diborane and ethane. Such comparisons lead to the estimates  $n_{B-B}:n_{B-H}:n_{B...H} = 1:5.8:3.3$ ; two of the three ratios, including the one ( $n_{B-H}/n_{B...H}$ ) which differs most in the suggested structures, favor the bridge model.

Our results for ethane,  $C-C = 1.536 \pm 0.016 \text{ \AA.}$ ,  $C-H = 1.114 \pm 0.027 \text{ \AA.}$ ,  $\angle C-C-H = 110.5 \pm 3.5^\circ$ , are in fair agreement with the respective values  $1.55 \pm 0.03 \text{ \AA.}$  and  $1.52 \pm 0.10 \text{ \AA.}$ ,  $1.09 \pm 0.03 \text{ \AA.}$  and  $1.10 \text{ \AA.}$  (assumed), and  $109.5^\circ$  (ass.) and  $109.5^\circ$  (ass.) reported from the previous electron diffraction studies of Pauling and Brockway<sup>23</sup> and Wierl<sup>24</sup> and with the values  $1.54$  (ass.) and  $1.55$  (ass.),  $1.11 \text{ \AA.}$ , and  $1.098 \text{ \AA.}$ , and  $109.5^\circ$  and  $109.0^\circ$  estimated, respectively, by Smith and Woodward<sup>25</sup> and Smith<sup>26</sup> with the help first of preliminary<sup>25</sup> and then of carefully refined values<sup>26</sup> of the two moments of inertia of the molecule. They are not con-

(21) It may be further noted that according to our measurements (by V.S. only, not shown in Fig. 2 or Table I) the diborane inner ring has a  $q$  value of about 9.5 ( $s = 3$ ) in exact agreement with the position quoted by Bauer. This would place the ring appreciably inside the point  $q \sim 10.7$  suggested by curve F, but we are confident the discrepancy is insignificant: it is always difficult to get reliable measurements of the first feature or two (so much so, in fact, that one cannot readily decide whether, in respect to the measurements, omitting the factor  $1/s$  is empirically adverse or favorable, even for the first minimum where the shift it causes is quite large) and in this case the outer limit measured for the position of the ring was  $q \sim 12.0$  while the indication from the visual curve of Bauer's original publication is about  $q = 11.0$ , both outside the required position.

Although we were unable to form a reliable estimate of the relative "tips" of the inner rings, much less for either substance alone, our consensus would be that the tips are about the same for both substances, in agreement with the best theoretical curves. The better of the ethane-like curves would require that for diborane the inner ring be further toward the inside of the first main maximum than in ethane by a probably detectable amount considerably greater than the shifts which appear to be associated with uncertainties in the treatment of the H...H terms.

(22) Farther out, on the other hand, the pattern variations are less characteristic of the differences in weights, because of the increasing importance of the differences in distances, the severe temperature factor of the X...H terms, and the circumstance that the effect of change in number of X-H terms becomes confused, for intermediate  $q$  values and the bridge structure of diborane, with the effect of the split of the B-H distances.

(23) L. Pauling and L. O. Brockway, *THIS JOURNAL*, **69**, 1223 (1937).

(24) R. Wierl, *Ann. Physik*, **13**, 453 (1932).

(25) L. G. Smith and W. M. Woodward, *Phys. Rev.*, **61**, 386A (1942).

(26) J. G. Smith, *J. Chem. Phys.*, **17**, 130 (1949).

sistent, however, with the results 1.573 Å., 1.093 Å. (ass.) and 106.7° which were obtained by Herzberg<sup>27</sup> on the assumption of the preliminary moment values and the same C-H distance as is found for methane. Nevertheless, the agreement of our results with the moments of inertia is in fact most satisfactory, as may be seen from the excellent agreement (relative to our limits of error) with the model which follows from the reasonable conditions that (1) the completely reliable value  $I_B = 42.234 \times 10^{-40}$  g. cm.<sup>2</sup> be fitted exactly, (2) the indications from the less reliable value  $I_A = 10.81 \times 10^{-40}$  g. cm.<sup>2</sup><sup>28</sup> and our point be averaged, and (3) that with due regard for its likely error as a function of direction in parameter space our point be otherwise adhered to as closely as possible. This model has C-C = 1.533 Å., C-H = 1.110 Å., and  $\angle$ C-C-H = 110.4°; it is fixed by the spectroscopic data to the extent that a change in any one of the electron diffraction parameter values would result in changes of the parameter values of the model of at most about half the change in the electron diffraction value, if distances are expressed in hundredths

(27) G. Herzberg, "Infrared and Raman Spectra of Polyatomic Molecules," D. Van Nostrand and Company, Inc., New York, N. Y., 1945, p. 440.

(28)  $I_A$ , having been revised downward a full 2% from the preliminary value of  $11.03 \times 10^{-40}$  g. cm.<sup>2</sup> on the basis of difficult considerations of complicated perturbations in the  $\perp$  bands, appears still to be somewhat uncertain,<sup>29</sup> and Smith makes no definite claims for its accuracy. The average of the preliminary and final values, it happens, would correspond to our diffraction results.

of an ångström and the angle in degrees.<sup>29</sup> We feel, accordingly, that the indications that C-C is not greater than 1.54, that C-H is considerably greater than in methane, and that  $\angle$ C-C-H is somewhat greater than the tetrahedral value are most probably correct even though the diffraction results alone, because of their large limits of error, would hardly justify this conclusion. It is interesting that values for the C-H distance which have been reported recently for the methyl halides, partly<sup>30</sup> or wholly<sup>31</sup> on the basis of microwave spectra, are also considerably greater than the methane value of 1.094 Å.; the H-C-H angles, however, are reported to be slightly greater than tetrahedral, in disagreement with our finding for ethane. On the other hand, the microwave values for the HCH angle in methyl cyanide<sup>32</sup> and methylacetylene<sup>33</sup> are less than tetrahedral and in methyl isocyanide<sup>32</sup> only a trifle greater than tetrahedral, while in all three molecules the C-H distance is very nearly the same as in methane.

(29) The coefficients of variation due to deviations from our diffraction values respectively of C-C, C-H and  $\angle$ C-C-H are approximately the following: for C-C, +0.5, -0.3 and -0.5; for C-H, -0.2 +0.1 and +0.2; and for  $\angle$ C-C-H, -0.4, +0.2 and +0.4.

(30) See W. Gordy, *Rev. Modern Phys.*, **20**, 712 (1948).

(31) B. P. Dailey, J. M. Mays and C. H. Townes, *Phys. Rev.*, **76**, 136 (1949).

(32) M. Kessler, H. King, R. Trambarulo and W. Gordy, *ibid.*, **79**, 54 (1950).

(33) R. Trambarulo and W. Gordy, private communication.

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## The Relation between the Absorption Spectra and the Chemical Constitution of Dyes XXII. cis-trans Isomerism in Thioindigo Dyes<sup>1</sup>

BY GEORGE M. WYMAN AND WALLACE R. BRODE

The ultraviolet and visible absorption spectra of seven purified thioindigo dyes in benzene and in chloroform were determined under several conditions of temperature and illumination. It was concluded that these compounds exist in solution as two forms (*cis* and *trans*) in equilibrium. The position of the equilibrium is a function of the temperature and the illumination. The approximate spectral absorption curves were calculated for the two isomers of each dye, and the relative amount of each isomer present at the several equilibrium conditions was computed. The two isomers of thioindigo and of 5,5'-dichloro-4,4',7,7'-tetramethylthioindigo were separated chromatographically and their absorption spectra were obtained. Definite configurations were assigned to the two isomers of each dye. Correlations between the absorption spectra and the structures of thioindigo dyes are discussed.

### Introduction

The determination of the spectral absorption curves of purified samples of seven thioindigo dyes in the ultraviolet and visible regions is a part of the National Bureau of Standards research project on the spectrophotometry of pure dyestuffs. Stearns had reported on the reversible change occurring in the absorption spectra of two thioindigo dyes when the dye solutions were exposed to intense white light.<sup>2</sup> Preliminary measurements indicated the existence of such a phototropic effect in the case of the dyes studied in this work; the absorption spectra were found to be a function of the color of the light to which each dye solution had been exposed prior to the measurement. In addition, it was observed that the absorption spectrum of each

dye was also affected by a change in the temperature. It was, therefore, necessary to study the influence of these two variables in order to obtain reproducible spectral absorption curves for this important group of dyestuffs. As a result of this investigation a single explanation has been found for these two related effects.

### Experimental

(a) **Purification of Dyes.**—The dyes used for this investigation were commercial products of known structure. All but one were purified by adsorption on silica gel (Davison Chemical Corp., Commercial Grade, 200-mesh) followed by selective elution. The solvents used were: redistilled carbon tetrachloride, benzene and absolute alcohol. After elution the solution was evaporated to dryness, the residue recrystallized from benzene or chloroform and dried at 60–65°. Bis-4,5-benzothioindigo was purified by recrystallization from benzene due to its low solubility at room temperatures. Table I summarizes the conditions of the chromatographic purifications; the dyes are listed in order of increasing adsorption affinity.

(1) Presented at the 118th Meeting of the American Chemical Society, Chicago, Ill., September, 1950.

(2) E. I. Stearns, *J. Opt. Soc. Am.*, **32**, 282 (1942).