

On the Molecular Structure of Beryllium Borohydride, BeB_2H_8

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The electron scattering pattern from gaseous BeB_2H_8 has been recorded from $s = 2.00 \text{ \AA}^{-1}$ to 18.00 \AA^{-1} . The three metal atoms are found to lie at the corners of a roughly equilateral triangle. The scattering pattern is consistent with model II (or IV), Fig. 1, with the bond distances given in Table 2, column c.

Beryllium borohydride was first synthesised by Burg and Schlessinger in 1940.¹ These workers noted that the compound is much less volatile than aluminium borohydride, $\text{Al}(\text{BH}_4)_3$, and that its melting point is at least 180° higher, and concluded that the beryllium compound "may be more highly polar in character than the aluminium compound".¹

The first published attempt to determine the molecular structure was made six years later by Silbiger and Bauer.² They recorded the electron scattering pattern from the gas over the range $s = 1 \text{ \AA}^{-1}$ to 14 \AA^{-1} ; ($s = (4\pi \sin\theta)/\lambda$, where θ is half the scattering angle and λ the electron wave length). The intensities of five maxima and four minima were estimated visually. The data thus obtained were found to be consistent with a model with a linear H—B—Be—B—H skeleton and in which the beryllium atom was surrounded by six hydrogen atoms at the corners of a distorted octahedron.

The IR absorption spectrum of BeB_2H_8 was reported in 1949. The presence of very strong bands around 1500 and 2000 cm^{-1} was interpreted as "very strong evidence for a bridged structure".³

The molecular structure of $\text{Al}(\text{BH}_4)_3$ was determined by Price the same year.⁴ He found each boron atom to be bonded to the aluminium atom through two hydrogen bridge bonds. By analogy and on the basis of the linear B—Be—B skeleton found by Silbiger and Bauer² he then proposed that beryllium borohydride has structure I, Fig. 1.⁴ This model, too, was found to be consistent with the electron diffraction data.⁵

The results of a new attempt to determine the molecular structure, this time by X-ray diffraction, was reported in 1951.⁶ The unit cell contains 16 molecules in general positions, hence no conclusions regarding molecular

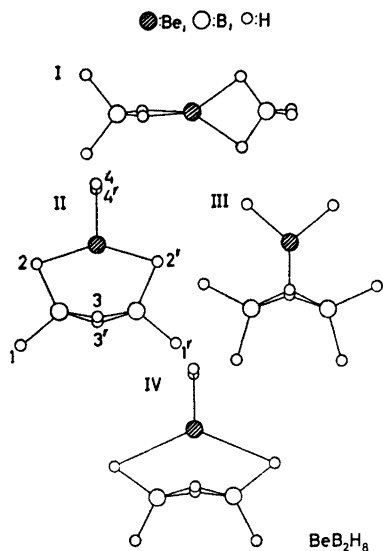


Fig. 1. Molecular models of beryllium borohydride.

symmetry could be reached. A number of Patterson sections, lines, and projections were calculated, but did not suggest a structure.

Since the experimental techniques, and computational methods of electron diffraction both have been greatly improved during the last fifteen years, we have undertaken a new investigation of BeB₂H₆ by this method. A preliminary note on our results has appeared in *Chemical Communications*.⁷

Table 1. Total scattered intensity $\times s^4$. Range $s = 2.00 \text{ \AA}^{-1}$ to 18.00 \AA^{-1} . Increment $\Delta s = 0.25 \text{ \AA}^{-1}$.

138.16	150.72	113.17	126.78
226.38	262.50	168.06	194.44
361.43	381.86	299.01	333.16
388.93	392.24	392.63	390.89
427.33	442.48	402.62	415.33
475.35	477.17	458.14	470.41
484.54	487.31	477.93	480.79
502.04	512.86	489.55	494.68
568.21	585.00	528.16	548.10
612.16	617.34	597.64	606.42
630.52	636.34	621.09	625.25
654.81	663.19	642.94	648.56
695.16	706.13	672.86	683.43
728.14	738.26	712.68	721.65
760.74	767.31	745.92	752.68
800.59	809.49	778.41	789.80
		816.74	

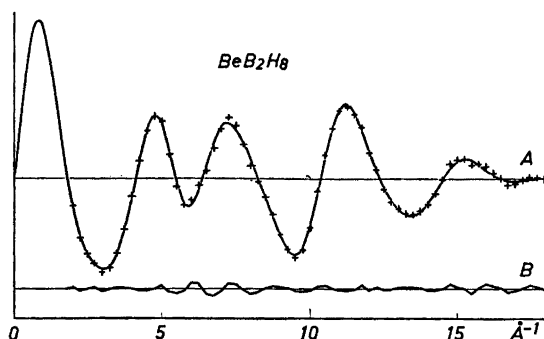


Fig. 2. A. Theoretical modified molecular intensity curve of BeB_2H_8 computed from the parameter values in Table 2, column a with experimental values drawn in. B. Difference curve.

EXPERIMENTAL AND CALCULATION PROCEDURE

The sample of BeB_2H_8 was a gift from Dr. N. A. Bell, Durham. It was redistilled immediately before use. The electron scattering pattern from the gas was recorded on the Oslo electron diffraction unit⁸ with a nozzle to plate distance of 48 cm. The gas reservoir was kept at 35°, the nozzle at 45°C. Burg and Schlessinger report that BeB_2H_8 is stable up to 120°C.¹ Four apparently faultless plates were photometered, the traces read off at $\Delta s = 0.25 \text{ \AA}^{-1}$ intervals, and the data processed in the usual way.⁹ The total corrected intensities times s^4 are listed in Table 1. The modified molecular intensity points from $s = 2.00 \text{ \AA}^{-1}$ to 18.00 \AA^{-1} are shown in Fig. 2. A radial distribution (RD) curve obtained by Fourier inversion of the molecular intensity is shown in Fig. 3 (full line).

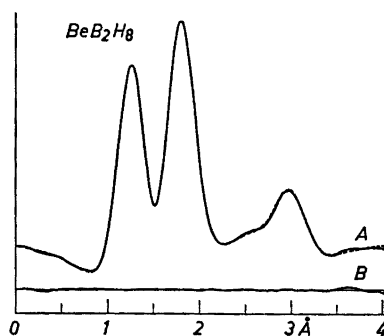


Fig. 3. A. Radial distribution curves for BeB_2H_8 . — experimental, ---- theoretical calculated from the parameter values in Table 2, column a. $k = 0.0025 \text{ \AA}^3$. B. Difference curve.

Theoretical intensity curves were calculated from

$$I^{\text{BeB}}(s) = \text{const} \sum_{i \neq j} \frac{|f_i(s)||f_j(s)|}{|f_{\text{Be}}(s)||f_{\text{B}}(s)|} \cos(\eta_i(s) - \eta_j(s)) \frac{\sin(R_{ij}s)}{R_{ij}} \exp(-\frac{1}{2}u_{ij}^2s^2)$$

$$= \text{const} \sum_{i \neq j} g_{ij/\text{BeB}}(s) \frac{\sin(R_{ij}s)}{R_{ij}} \exp(-\frac{1}{2}u_{ij}^2s^2) \quad (1)$$

The sum extends over all atom pairs i, j in the molecule. R_{ij} is the inter-nuclear distance, u_{ij} the root mean square amplitude of vibration. $f_j(s) = |f_j(s)| \cdot \exp(i\eta_j(s))$ is the complex atomic scattering factor of atom j . It has been computed for H, B, and Be by the partial wave approximation method with a program written by Peacher.¹⁰

Theoretical RD curves were obtained by Fourier inversion of theoretical intensity curves.

STRUCTURE ANALYSIS

A radial distribution (RD) curve obtained by Fourier inversion of the observed intensity is shown in Fig. 3 (full line). It consists of three broad peaks with maxima at 1.25, 1.80, and 3.0 Å with relative areas 3.0:4.0:1.0. The minimum between the first two peaks, falls at 1.50 Å, the minimum between the second and third at 2.2 Å.

In the RD curve each interatomic distance R_{ij} in the molecule is represented by a peak centered at $r = R_{ij}$. The area under the peak is very nearly proportional to $n_{ij}Z_iZ_j/R_{ij}$ where n_{ij} is the number of times the distance occurs in the molecule and Z_i and Z_j are the atomic numbers. The halfwidth of the peak is determined primarily by the root mean square amplitude of vibration, u_{ij} .

In diborane $\text{B}-\text{B} = 1.775 \pm 0.004$ Å.¹¹ In $(\text{Et}_6\text{Be}_2\text{H}_2)\text{Na}_2 \cdot 2\text{Et}_2\text{O}$ where the beryllium atoms are linked by two hydrogen bridge bonds,¹² $\text{Be}-\text{Be} = 2.20 \pm 0.01$ Å.¹³

The peaks in the experimental RD curve must clearly be composite, and the $\text{Be}-\text{B}$ distance peak must be contained in the compound peak with maximum at 1.80 Å. It is then at once clear that the $\text{B}-\text{Be}-\text{B}$ skeleton cannot be linear; this would require a $\text{B} \cdots \text{B}$ distance peak at 3.6 Å where the RD curve is zero. Indeed, the relative area under the peak at 1.80 Å can only be reproduced if it includes the $\text{B}-\text{B}$ distance too. The three metal atoms must therefore lie at the corners of a roughly equilateral triangle.

The highest possible symmetry for such an arrangement of the three metal atoms is C_{2v} . If it is assumed that the hydrogen atoms are placed in such a way that their presence does not lower the molecular symmetry, and if it is assumed that each of the three metal atoms is surrounded by four hydrogen atoms at the corners of a tetrahedron, there are only two possible molecular models, *viz.* II and III in Fig. 1. Each of these may be viewed as an adduct of a BeH_2 fragment to a diborane molecule. They differ in the magnitude of some $\text{Be}-\text{H}$ distances and in the angle ν between the plane of the BeH_2 fragment and the BeBB plane.

In diborane B—H_t = 1.20 ± 0.01 Å, and B—H_b = 1.34 ± 0.01 Å,¹¹ in aluminum borohydride B—H_t = 1.19 ± 0.01 Å and B—H_b = 1.29 ± 0.01 Å.¹⁴ It may therefore be concluded with some confidence that all eight B—H bond distances are shorter than 1.5 Å, *i.e.* that the corresponding peaks are contained in the compound peak with maximum at 1.25 Å in the experimental RD curve.

Only two Be—H bond distances are known. In the shortlived species BeH, Be—H = 1.343 Å,¹⁶ and in (Et₄Be₂H₂) Na₂·2Et₂O where (Et₄Be₂H₂) would appear to be a doubly charged negative ion, Be—H_b = 1.48 ± 0.03 Å.¹³ Even though these bond lengths offer little guidance, it might be expected that in BeB₂H₈ Be—H_t distance peaks should contribute to the peak at 1.25 Å in the experimental RD curve, while Be—H_b distances would fall between it and the peak at 1.80 Å. This, however, is not compatible with the relative areas found under the two peaks. If it is assumed that the former contains eight B—H distances, the area under the latter can only be reproduced if it contains two Be—B, one B—B and *six* Be—H distances.

This means in particular that the Be—H_t distance must be longer than 1.50 Å.

If model II, Fig. 1, is accepted, the large number of short Be—H distances is not as surprising as it may seem: Unless the diborane fragment is very much deformed, the distance from its hydrogen bridge atoms to the beryllium atom must perforce be less than 2.2 Å. The close proximity of these atoms may therefore be a matter of steric necessity as much as the result of direct bonding.

As soon as the atoms are that close, however, same bonding will undoubtedly occur. The beryllium atom therefore appears to be bonded — at least to some extent — to six hydrogen atoms and two boron atoms. This large coordination number may be the reason why the Be—H_t distance is longer than expected.

The area under the peak extending from 2.2 to 3.3 Å in the experimental RD curve corresponds to a total of ten Be...H and B...H distances. This confirms that six BeH distances are shorter than 2.2 Å. If not, the area under the outer peak would have to correspond to twelve Be...H and B...H distances.

The shoulder at 2.5 Å corresponds to two distances, and the main peak at 3.0 Å to eight. In model II the four B...H (4) and the two Be...H (1) distances will automatically be about 3.0 Å. The last two distances in this area might be either B...H(1) or B...H(2) the other being about 2.5 Å.

In model III two of the B...H(4) distances would have to be considerably shorter than 3.0 Å. This model may therefore be discarded.

The molecular structure of beryllium borohydride (model II) is completely determined by ten structure parameters, *e.g.* by the ten following interatomic distances

Be—B (1.8 Å)	B—B (1.8 Å)
Be—H(2) (1.8 Å)	B—H(1) (1.25 Å)
Be—H(3) (1.8 Å)	B—H(2) (1.25 Å)
Be—H(4) (1.6 Å)	B—H(3) (1.25 Å)
Be...H(1) (3.0 Å)	B...H(4) (3.0 Å).

The approximate distances obtained by analysis of the experimental RD curve are given in parenthesis.

The structure parameters may now be refined by least-squares calculations of the intensity data.¹⁶ Since the 24 interatomic vibrational amplitudes (u -values) are not known they should be refined along with the interatomic distances. But since the experimental material consisted of intensities over a rather limited s -range, we chose to reduce the number of adjustable parameters by making the following assumptions: The u -values of the Be—B and B—B distances, of all Be—H and B—H, and of all Be...H and B...H distances were supposed to be equal. All H...H u -values were set equal to 0.20 Å and not refined.

The nature of these assumptions is admittedly rather arbitrary. Moreover, since a number of the interatomic distances of the molecule, for instance Be—B and B—B, are of roughly the same magnitude, they are very strongly correlated with each other and with their u -values. For this reason least-squares calculations cannot be expected to yield much new information.

It was not possible to refine all parameters simultaneously. The calculations were therefore alternated between the simultaneous refinement of all interatomic distances and the simultaneous refinement of the three amplitudes. The computations converged to give the parameter values listed in Table 2 a.

Table 2. Interatomic distances in BeB₂H₈. a and b, parameter values and standard deviations obtained by least-squares refinements of two different start models. c, estimated parameter values with error limits.

	a	b	c
Be—B	1.839 ± 0.015 Å	1.818 ± 0.016 Å	1.83 ± 0.06 Å
B—B	1.74 ± 0.03 Å	1.74 ± 0.02 Å	1.74 ± 0.10 Å
B—H(1)	1.16 ± 0.01 Å	1.16 ± 0.01 Å	1.15 ± 0.10 Å
B—H(2)	1.23 ± 0.02 Å	1.36 ± 0.01 Å	1.30 ± 0.10 Å
B—H(3)	1.31 ± 0.01 Å	1.25 ± 0.01 Å	1.30 ± 0.10 Å
Be—H(2)	1.99 ± 0.03 Å	1.89 ± 0.02 Å	1.85 ± 0.25 Å
Be—H(3)	1.73 ± 0.06 Å	2.04 ± 0.02 Å	1.85 ± 0.25 Å
Be—H(4)	1.61 ± 0.02 Å	1.65 ± 0.03 Å	1.60 ± 0.10 Å
B...H(4)	3.02 ± 0.03 Å	3.04 ± 0.01 Å	3.00 ± 0.10 Å
Be...H(1)	2.99 ± 0.02 Å	2.97 ± 0.02 Å	3.00 ± 0.15 Å
BH...(1')	2.49 ± 0.02 Å	2.46 ± 0.02 Å	*
BH...(2')	2.80 ± 0.03 Å	2.85 ± 0.02 Å	*
$u(M-M)$	0.090 ± 0.002 Å	0.099 ± 0.002 Å	
$u(M-H)$	0.089 ± 0.002 Å	0.089 ± 0.006 Å	
$u(M...H)$	0.126 ± 0.007 Å	0.126 ± 0.021 Å	
R	0.049	0.050	

* One of these distances is 2.50 ± 0.10 Å, the other 2.80 ± 0.15 Å.

They represent a stable minimum as long as distances and amplitudes are refined separately.

It should be noted that because of the way in which they have been obtained, the standard deviations cannot be used as error limits.

A theoretical molecular intensity curve based on the parameter values in Table 2 a is shown in Fig. 2 and a theoretical RD curve in Fig. 3 (stippled line). The agreement with experimental curves is very good.

The parameter values in Table 2 a corresponds to model IV Fig. 1. Be—H (2) is larger than Be—H(3), and the diborane fragment has been folded the other way.

LCAO—MO calculations¹⁷ based on this structure showed that the overlap population ("bond order") of Be—H (2) is roughly twice that of the Be—H (3). This is what one would expect for beryllium with tetrahedrally directed valence, but the opposite of what one would expect from the relative magnitude of the two Be—H distances in the model on which the computations were made.

This prompted us to search for another minimum structure in which Be—H (2) is shorter than Be—H(3).

Such a structure could be obtained if the start model was somewhat modified. The parameter values are given in Table 2 b. They too correspond to a stable minimum as long as distances and *u*-values are refined separately. The reliability factor is only slightly higher than for the parameter values in column a.

It is seen that all *u*-values except for the Be—B and B—B distances are identical in columns a and b. The Be—B and B—B *u*-value has been changed from 0.090 Å to 0.099 Å. This modest change is accompanied with large changes in some of the bond distances.

This suggests that our assumption about the equality of several *u*-values will if uncorrect (which it almost certainly is) lead to considerable errors in the bond lengths obtained. For this reason we have not considered it useful to pursue least-squares calculations any further.

Instead we have, in Table 2, column c, written down what we consider to be the best estimate of the interatomic distances and the error limits. The values are based on the result of the analysis of the RD curve and are the two minimum structures obtained by least-squares calculations.

Even though model III could be ruled out by inspection of the experimental RD curve, this model too was refined by least-squares calculation. The resulting square-error sum was, however, more than three times as high as the one obtained for model II, and when the angle *v* was allowed to vary it changed from 0° to 85° ± 8°.

Conclusion. The electron diffraction data are not consistent with the molecular models I and III in Fig. 1. They are consistent with structures II (or IV) with the interatomic distances given in Table 2, column c.

Note added in proof: We have now investigated two more models of C_{2v} symmetry. In both models there is only one terminal hydrogen atom on beryllium and the boron atoms are joined through a single hydrogen bridge bond. In the first model the beryllium atom is three-coordinated; it is joined to each boron atom through a single hydrogen bridge bond. On each boron atom there are two terminal hydrogens. In the second model the beryllium atom is five-coordinated; it is joined to each boron atom through two hydrogen bridge bonds. On each boron atom there is one terminal hydrogen atom. Neither model was consistent with the electron diffraction data.

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