On the Molecular Structure of Beryllium Borohydride

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IN 1946 Silbiger and Bauer[1] reported on an electron diffraction study of BeB_2H_8, beryllium borohydride. The intensities of five maxima and four minima had been estimated visually. The i.r. absorption spectrum of the compound was reported in 1949.[2] The presence of very strong bands around 1500 and 2000 cm.$^{-1}$ was interpreted as very strong evidence for a bridged structure like (I) which had first been suggested by Longuet-Higgins and Bell.[3] Bauer[4] found that this structure was compatible with his electron diffraction data, and the model has come to be commonly accepted.

Since the experimental techniques and computational methods of electron diffraction have been greatly improved during the last fifteen years, we have undertaken a new investigation of BeB_2H_8 by this method.

The sample of BeB_2H_8 was a gift from Dr. N. A. Bell, Durham. The scattering pattern from the gas was recorded on the Oslo electron diffraction unit.[5] The gas reservoir was kept at 35°, the nozzle at 45°. Burg and Schlessinger[6] report that BeB_2H_8 is thermally stable up to 120°. Four apparently faultless plates were examined photometrically, the traces read off at $\Delta s = 0{\cdot}25$ Å^{-1} intervals, and the data processed in the usual way.[7] [$s = (4\pi\sin\theta)/\lambda$ when θ is half the scattering angle and λ the electron wavelength]. The resulting modified molecular intensity extended from s = 2·00 Å^{-1} to 18·00 Å^{-1}. Beyond this point it was lost in the background.

Figure 2 shows an experimental radial distribution (R.D.) curve obtained by Fourier inversion of the molecular intensity. It consists of three peaks at 1·25, 1·80, and 3·0 Å of relative areas 3·0 : 4·0 : 1·0. In this curve each interatomic distance R_{ij} in the molecule is represented by a peak centred at $r = R_{ij}$. The area under the peak is (roughly) proportional to $n_{ij}Z_iZ_j/R_{ij}$ where n_{ij} is the multiplicity of the distance and Z_i and Z_j the atomic numbers.

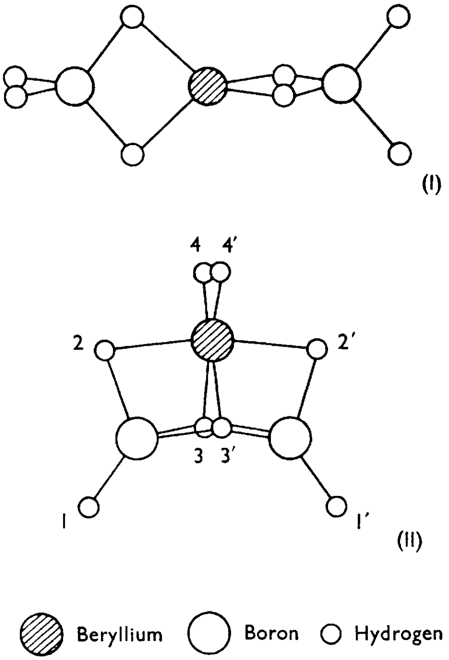

FIGURE 1. *Molecular structure of* BeB_2H_8 *as suggested by Longuet-Higgins and Bell*[3] (I), *and as found in this study* (II).

In diborane, B–H$_t$ = 1·20 ± 0·01, B–H$_b$ = 1·34 ±0·01, and B–B = 1·775 ± 0·004 Å.[8] In Na$_2$-(Et$_4$Be$_2$H$_2$),2Et$_2$O where the beryllium atoms are linked by two hydrogen bridge bonds,[9] Be–H$_b$ (average) = 1·48 ± 0·03 and Be–Be = 2·20 ± 0·01 Å.[10]

Clearly the peaks of the experimental R.D. curve must be composite, the peak at 1·25 Å containing all B–H bond distances and possibly some Be–H bond distances, the peak at 1·80 Å containing the Be–B and probably some Be–H bond distances. It is at once seen that the B–Be–B skeleton cannot be linear; this would require a B · · · B peak at 3·6 Å where the R.D. curve is zero. Indeed, the relative area under the peak at 1·80 Å can only be reproduced if it includes the B–B distance peak, too. The three metal atoms therefore must lie at the corners of a roughly equilateral triangle.

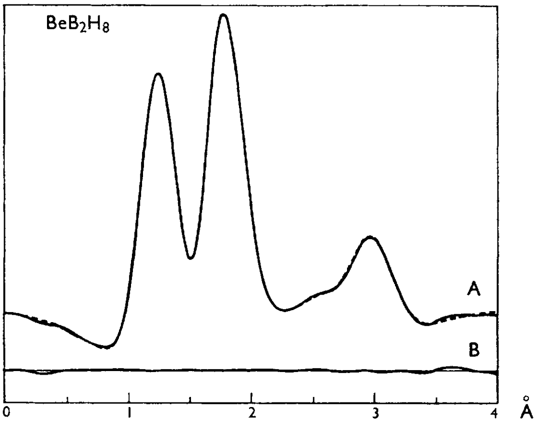

FIGURE 2. (A) *Full line: experimental R.D. curve of* BeB_2H_8. *Broken line: Theoretical curve.* (B) *Difference curve.*

The molecular structure was refined by least-squares calculations on the intensity data on the assumption that the molecular symmetry is C_{2v}. Two different start models were used. Both refinements converged to give structure (II). The bond lengths and valence angles and their standard deviations are given in the Table. The final R-factor was 0·065. The experimental material consisted of 65 intensities and 14 parameters (including the scale factor) were refined. A theoretical R.D. curve is shown in Figure 2. The agreement with the experimental curve is very good.

TABLE. *Bond distances and valence angles in* BeB_2H_8 *with standard deviations*

Be–B	1·839	± 0·005 Å
B–B	1·74	± 0·03 Å
B–H(1)	1·16	± 0·01 Å
B–H(2)	1·23	± 0·02 Å
B–H(3)	1·31	± 0·01 Å
Be–H(2)	1·99	± 0·03 Å
Be–H(3)	1·73	± 0·06 Å
Be–H(4)	1·61	± 0·02 Å
∠ H(1)BH(2).. ..	103·0	± 3·3°
∠ H(3)BH(3′) ..	94·5	± 2·8°
∠ H(2)BeH(2′) ..	131·1	± 4·4°
∠ H(3)BeH(3′) ..	67·4	± 2·5°
∠ H(4)BeH(4′) ..	106·2	± 4·0°

The main features of the molecular structure are consistent with the following simple bonding scheme: the boron atoms are (sp^3) hybridized with an orbital pointing towards each of the four surrounding hydrogen atoms. Two-centre two-electron bonds are formed to H(1) and H(2), and three-centre two-electron bonds are formed through H(3) and H(3′). The beryllium atom is (sp^2) hybridized. Two of the hybrid orbitals point towards the terminal hydrogen atoms and form two-centre two-electron bonds to them. The remaining hybrid orbital points towards the hydrogen-bridge orbitals between the boron atoms and stabilizes the symmetric combination of the latter. The remaining Be *p*-orbital lies in the plane of the paper perpendicularly to the two-fold symmetry axis of the molecule. It stabilizes the antisymmetric combination of the B–H(2) and B′–H(2′) orbitals.

The only feature that has not been adequately accounted for is the great length of the Be–H(4) bonds. These are rather too long for single bonds, which suggests that the bond order is less than one and that the bonding is more delocalized than in this outline.

A full account of this investigation will be submitted to *Acta Chem. Scand.*

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