

infrared absorption at  $1735\text{ cm}^{-1}$ , thin-layer chromatography revealed the presence of a major component, detectable with both spray reagents, and at least two faster moving products in minor amounts. Hydrolysis of the syrup in 0.05 M sulphuric acid at  $60^\circ$  overnight and subsequent treatment of the solution with Dowex 1 ion exchange resin (regenerated with bicarbonate), afforded after evaporation of the solvent a colourless syrup (440 mg). Paper chromatography indicated the presence of only one component, indistinguishable from authentic D-threose, thin-layer chromatography in addition showed the presence of minor amounts of a compound indistinguishable from authentic D-glyceraldehyde.

*1,2-O-Isopropylidene- $\beta$ -L-threofuranose (III)*. The crude L-threose (II) was shaken with acetone (40 ml) containing sulphuric acid (0.3 ml) for 3 h at room temperature. The solution was neutralized with solid sodium bicarbonate, after filtration the solvent was evaporated under reduced pressure, and the residue dissolved in benzene (50 ml). The benzene solution was extracted three times with water (20 ml portions); evaporation of the water under reduced pressure gave chromatographically homogeneous (solvent B) 1,2-O-isopropylidene- $\beta$ -L-threofuranose (III) as a colourless syrup which solidified on standing. The yield was 345 mg (39 % based on L-sorbose). After recrystallization from ether-petroleum ether (b.p.  $40-65^\circ$ ) it had m.p.  $84-85^\circ$  (reported for the D-enantiomer<sup>8</sup>  $84^\circ$ ) and  $[\alpha]_D +13^\circ$  (c 1, acetone) (reported for the D-form<sup>8</sup>  $-15.3^\circ$ ).

*L-Threose (II)*. 1,2-O-Isopropylidene- $\beta$ -L-threofuranose (III) (145 mg) was heated to  $100^\circ$  for 4 h in 30 % aqueous acetic acid. The solvents were evaporated under reduced pressure giving chromatographically homogeneous L-threose (II) as an almost colourless syrup. The yield was 105 mg (96 %), and  $[\alpha]_D +12^\circ$  (c 1, water) (lit.<sup>9</sup>  $+13.2^\circ$ ).

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## On the Molecular Structure of Cyclopentadienylberyllium Borohydride, $C_5H_5BeBH_4$

D. A. DREW, GRETE GUNDERSEN and  
ARNE HAALAND

*Department of Chemistry, University of Oslo,  
Blindern, Oslo 3, Norway*

A series of cyclopentadienyl beryllium compounds,  $C_5H_5BeX$  where  $X = CH_3$ , Cl, Br,  $BH_4$ , has recently been synthesized by Drew and Morgan.<sup>1</sup> The compounds are monomeric in the gas phase and in benzene solution. Infrared absorption spectra show that the cyclopentadienyl rings have  $C_{5v}$  symmetry, *i.e.* that they are of the *penta-hapto* type. The room temperature PMR spectrum of  $(C_5H_5)BeBH_4$  in toluene shows that the four  $BH_4$  protons are equivalent on the NMR time scale, cooling to  $-80^\circ$  did not give separate signals for bridging and terminal hydrogen atoms.

Previously we have determined the molecular structures of  $C_5H_5BeCH_3$  and  $C_5H_5BeCl$  by gas phase electron diffraction;<sup>2</sup> we now report the result of an attempt to determine the molecular structure of  $C_5H_5BeBH_4$ .

Cyclopentadienylberyllium borohydride was supplied by Drew and Morgan. The electron scattering pattern was recorded on Balzers Eldiograph KD-G2. The sample reservoir was maintained at  $60^\circ$  and the

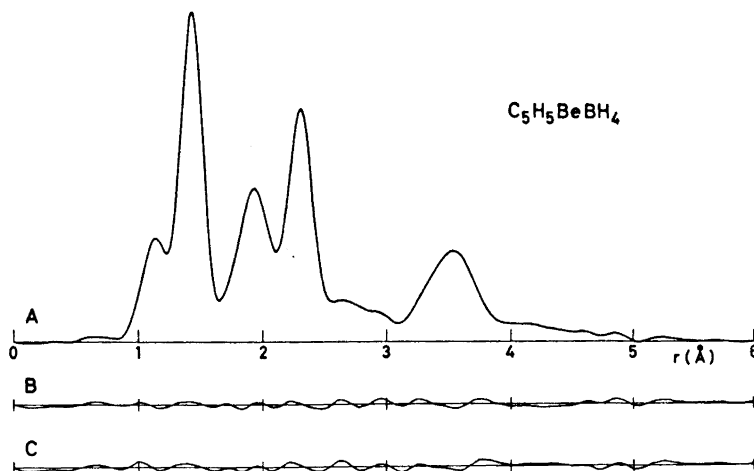
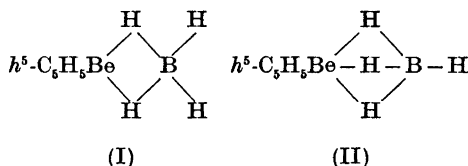


Fig. 1. A. Experimental radial distribution curve for  $C_5H_5BeBH_4$ . The artificial damping constant  $k = 0.002 \text{ \AA}^2$ . B. Difference between the experimental radial distribution curve and a theoretical curve calculated for the best double bridge model. C. Difference between the experimental radial distribution curve and a theoretical curve calculated for the best triple bridge model.

nozzle was heated to about  $80^\circ$ . Exposures were made with nozzle to photographic plate distances of 50 cm and 25 cm. Optical densities of 6 plates from the former and 3 plates from the last set were recorded and processed in the usual way.<sup>3</sup>

Radial distribution curves (see Fig. 1A) confirmed the monomeric nature of the compound and the  $C_{5v}$  (or near  $C_{5v}$ ) symmetry of the  $C_5BeB$  trunk. In gaseous  $Al(BH_4)_3$  the borohydride groups are bound to the metal atom through double hydrogen bridges,<sup>4</sup> in  $Zr(BH_4)_4$  through triple hydrogen bridges.<sup>5</sup>  $Be(BH_4)_2$  is polymeric in the crystalline phase, each beryllium atom is bound to one terminal borohydride group and two bridging borohydride groups through double hydrogen bridges.<sup>6</sup> The structure of gaseous  $Be(BH_4)_2$  has been the subject of some controversy, but the latest and most careful electron diffraction investigation favours a structure where both borohydride groups are bonded to beryllium through triple hydrogen bridges.<sup>7</sup> We have therefore carried out least squares refinements on two models of  $C_5H_5BeBH_4$ : a double bridge model (I) in which the  $BeBH_4$  fragment has  $C_{2v}$  symmetry and a triple bridge model (II) in which the  $BeBH_4$  fragment was assumed to have  $C_{3v}$  symmetry:



The geometry of (I) is determined by eight independent parameters, the geometry of (II) by seven. These parameters and ten rootmean square amplitudes of vibration were refined by least squares calculations on the intensity data with a nondiagonal weight matrix and a separately refined scale factor for each nozzle to plate distance.<sup>8</sup> The final generalized  $R$ -factor<sup>9</sup> was 8.88 % for (I) and 8.94 % for (II). The difference between an experimental radial distribution curve and a theoretical curve calculated for the best double bridge model is shown in Fig. 1B, and the difference between the experimental curve and one calculated for the best triple bridge model is shown in Fig. 1C: Both models can be brought into satisfactory agreement with the electron diffraction data.

Both models gave the same structure parameters for the  $C_5H_5Be$  fragment.

Table 1. Interatomic distances ( $R$ ) and root mean square amplitudes of vibration ( $l$ ) of the  $C_5H_5Be$  fragment with estimated standard deviations in parentheses.  $h$  is the distance from the Be atom to the center of the  $C_5H_5$  ring.

	$R$ (Å)	$l$ (Å)
$C_1-H_1$	1.116(8)	0.054(7)
$C_1-C_2$	1.422(1)	0.054(2)
$Be-C$	1.915(5)	0.101(8)
$C_1 \cdots C_3$	2.301(2)	0.058(3)
$C_1 \cdots H_2$	2.265(7)	0.180(19)
$C_1 \cdots H_3$	3.379(8)	0.098(15)
$Be \cdots H_1$	2.758(9)	0.112(24)
$h$	1.484(7)	

These parameters are listed in Table 1. Structurally this fragment is indistinguishable from the corresponding fragment in  $C_5H_5BeCH_3$ ,<sup>2</sup>  $C_5H_5BeCl$ ,<sup>2</sup> and  $(C_5H_5)_2Be$ .<sup>10</sup>

The structure parameters obtained for the  $BeBH_4$  fragments are listed in Table 2.

Table 2. Interatomic distances and valence angles of the  $BeBH_4$  fragment obtained by refinement on a double bridge model (column I) and a triple bridge model (column II). t = terminal, b = bridge.

	I	II
	$R$ (Å)	$R$ (Å)
$Be-B$	1.88(1)	1.89(1)
$B-H_t$	1.17(3)	1.16(2)
$B-H_b$	1.29(5)	1.28(3)
$Be-H_b$	1.78(9)	1.70(5)
$\angle Be-B-H_b$	65(4)°	62(2)°
$\angle H_t-B-H_b$	123(9)°	

(The vibrational amplitudes refined to reasonable values, but since the standard deviations were very large they are not listed). It is seen that the same value is obtained for the  $Be-B$  bond distances for both models. This bond distance is significantly longer than the mean  $Be-B$  bond distance obtained in the latest electron diffraction investigation of gaseous

$Be(BH_4)_2$ , 1.772(4) Å,<sup>7</sup> but similar to the distance between the beryllium atom and the boron atom in the terminal borohydride group in crystalline  $Be(BH_4)_2$ , 1.92(1) Å.<sup>8</sup>

Similarly the  $Be-Cl$  bond distance in  $C_5H_5BeCl$ , 1.837(6) Å,<sup>2</sup> is significantly longer than the  $Be-Cl$  bond distance in gaseous, monomeric  $BeCl_2$ , 1.72(2) Å.<sup>11</sup> We have previously suggested that the beryllium atom in these compounds may be regarded as ( $sp$ ) hybridized and to be using an ( $sp$ ) hybridized orbital and the two unhybridized  $2p$  orbitals to form bonds to the  $C_5H_5$  ring, and that the lengthening of the  $Be-Cl$  bond in  $C_5H_5BeCl$  relative to  $BeCl_2$  is due to a resulting decrease of dative  $\pi$ -bonding between  $Be$  and  $Cl$ .<sup>3</sup> Similarly the lengthening of the  $Be-B$  bond in  $C_5H_5BeBH_4$  relative to  $Be(BH_4)_2$  may reflect a decrease in the  $\pi$ -component of the  $Be-BH_4$  bonding. Since we have been unable to determine the geometry of this part of the molecule, it is impossible to say whether this weakening is accompanied by reorientation of the  $BH_4$  group or not.

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