

Made available courtesy of Royal Society of Chemistry: <http://www.rsc.org/>

Reprinted with permission. No further reproduction is authorized without written permission from the Royal Society of Chemistry. This version of the document is not the version of record. Figures and/or pictures may be missing from this format of the document.

View Online

Gas-phase Nuclear Magnetic Resonance Spectroscopic Study of the Molecular Structure of Beryllium Borohydride, Be(BH₄)₂

By DONALD F. GAINES,* JERRY L. WALSH, and DAVID F. HILLENBRAND

(Department of Chemistry, University of Wisconsin, 1101 University Avenue, Madison, Wisconsin 53706)

Summary Gas-phase and solution n.m.r. spectral studies of beryllium borohydride, Be(BH₄)₂, indicate that it contains magnetically equivalent BH₄ groups which undergo rapid internal hydrogen exchange; previously postulated triangular boron-beryllium-boron molecular configurations are inconsistent with the n.m.r. data.

THE gas-phase structure of beryllium borohydride, Be(BH₄)₂, has been a subject of some controversy. As many as nine different structures have been proposed for the gas-phase monomer¹ with varying degrees of supporting evidence based primarily on vibrational,¹⁻⁵ electron diffraction,⁶⁻¹⁰ and dipole moment^{5,11} studies. Several theoretical studies have also been undertaken.¹²⁻¹⁶ The solid-state structure of Be(BH₄)₂ has been shown to be a helical polymer by a single-crystal X-ray diffraction study.¹⁷ In spite of these efforts, unambiguous experimental evidence defining the gas-phase structure of Be(BH₄)₂ has not been reported. We report here the results of ambient gas-phase and solution ¹¹B and ¹H n.m.r. spectral studies of Be(BH₄)₂.

Beryllium borohydride was prepared by the method of Schlesinger, Brown, and Hyde¹⁸ and was handled using standard high-vacuum techniques. ¹¹B and ¹H n.m.r. spectra (86.7 and 270 MHz, respectively) of Be(BH₄)₂ were obtained on a Bruker WH-270 F.T.n.m.r. spectrometer. For the gas-phase spectra, the boron probe was modified to

and/or argon] to effect collision narrowing of the spectral lines. Solution-phase spectra were obtained using [²H₆]benzene and [²H₂]dichloromethane solvents.

The gas-phase ¹¹B and ¹H n.m.r. spectra of Be(BH₄)₂, shown in Figure 1, indicate the presence of a single species. The ¹¹B spectrum consists of a 1:4:6:4:1 quintet that arises from equivalent boron atoms, each of which is coupled to four equivalent hydrogen nuclei [$J(^{11}\text{B}-\text{H}) = 87 \text{ Hz}$]. The ¹H spectrum is a 1:1:1:1 quartet indicating that all hydrogen atoms are equivalent and are coupled to a single ¹¹B (80%, $I = 3/2$) nucleus [small resonances due to coupling to ¹⁰B (20%, $I = 3$) are also present]. The ¹¹B spectrum shows the presence of a small amount of diborane(6) [58.0 p.p.m. downfield from the Be(BH₄)₂ signal], a decomposition product which accumulates during the course of the spectral acquisition (*ca.* 12 h). No line-shape features of the ¹¹B or ¹H spectra require the invocation of ⁹Be ($I = 3/2$) coupling, nor have such couplings been identified in the spectra of alkyl beryllium hydrides.¹⁹ The solution spectra exhibit the same patterns and the same coupling constants as are observed for the gas-phase spectra (¹¹B: $\delta +36.2 \text{ p.p.m. (BF}_3\text{OEt}_2 = 0)$, $J = 86 \text{ Hz}$, in [²H₆]benzene; ¹H: $\delta +0.4 \text{ (Me}_4\text{Si} = 0)$, $J = 86 \text{ Hz}$ in [²H₆]benzene).

Downloaded by University of North Carolina at Greensboro on 02 March 2011
Published on 01 January 1977 on <http://pubs.rsc.org/> | doi:10.1039/C39770000224

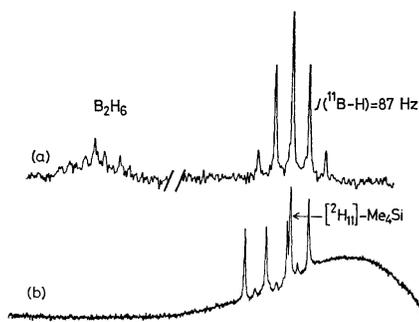


FIGURE 1. Gas-phase n.m.r. spectra of Be(BH₄)₂. (a) ¹¹B spectrum at 86.6 MHz. (b) ¹H spectrum at 100 MHz.

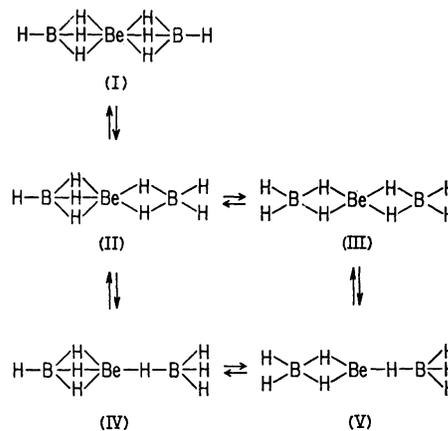


FIGURE 2

eliminate borosilicate glass, and the samples were contained in 5 mm quartz tubes in order to eliminate background boron signals. ¹H spectra were also obtained on a Varian XL-100 F.T.n.m.r. spectrometer using a 12 mm o.d. Pyrex sample tube. The ¹H spectra showed significant probe backgrounds unique to each instrument. Spectra were obtained at ambient temperature (*ca.* 23 °C) on saturated-vapour samples containing partial pressures of *ca.* 6 Torr of Be(BH₄)₂ and 2-5 atm of inert gas [(CD₃)₄Si

The n.m.r. spectra can be interpreted only in terms of a Be(BH₄)₂ structure containing magnetically equivalent borohydride groups. Within each borohydride group rapid internal hydrogen exchange takes place on the n.m.r. time scale. None of the previously postulated (see refs. 2, 3, and 6) or remotely possible *triangular* Be(BH₄)₂ structures are consistent with these spectra, regardless of the mechanism of hydrogen exchange. However, an exchange mechanism

involving rapid transformation from one linear B–Be–B configuration to another, such as that depicted in Figure 2, is consistent with the observed n.m.r. spectral data.

All uncontroversial Be–BH₄ interactions [solid, polymeric Be(BH₄)₂,¹⁷ (MeBeBH₄)₂,^{20,21} and solid B₅H₁₀BeBH₄,²²] indicate the presence of double hydrogen bridges between beryllium and the borohydride boron. Theoretical studies have favoured either double or triple hydrogen bridges and a linear B–Be–B framework.^{14–16} Most recent i.r. spectral studies suggest either double or triple hydrogen bridges.^{1,3}

Thus, gas-phase monomeric Be(BH₄) is highly fluxional on the n.m.r. time scale and, based on the present as well as previous studies,^{1,9,12,15,16} undoubtedly has a linear B–Be–B framework in which local configurational interchange results in rapid hydrogen exchange within each borohydride group.

We thank the National Science Foundation for financial support.

(Received, 20th December 1976; Com. 1384.)

¹ J. W. Nibler, *J. Amer. Chem. Soc.*, 1972, **94**, 3349.

² T. H. Cook and G. L. Morgan, *J. Amer. Chem. Soc.*, 1969, **91**, 774.

³ T. H. Cook and G. L. Morgan, *J. Amer. Chem. Soc.*, 1970, **92**, 6493.

⁴ W. C. Price, H. C. Longuet-Higgins, B. Rice, and T. F. Young, *J. Chem. Phys.*, 1949, **17**, 217.

⁵ J. W. Nibler and J. McNabb, *Chem. Comm.*, 1969, 134.

⁶ A. Almennigen, G. Gundersen, and A. Haaland, *Acta Chem. Scand.*, 1968, **22**, 859.

⁷ G. Silbiger and S. H. Bauer, *J. Amer. Chem. Soc.*, 1946, **68**, 312.

⁸ S. H. Bauer, *J. Amer. Chem. Soc.*, 1950, **72**, 622.

⁹ G. Gundersen, L. Hedberg, and K. Hedberg, *J. Chem. Phys.*, 1973, **59**, 3777.

¹⁰ K. Brendhaugen, A. Haaland, and D. P. Novak, *Acta Chem. Scand.*, 1975, **29**, 801.

¹¹ J. W. Nibler and T. Dyke, *J. Amer. Chem. Soc.*, 1970, **92**, 2920.

¹² R. Ahlrichs, *Chem. Phys. Letters*, 1973, **19**, 174.

¹³ G. Gundersen and A. Haaland, *Acta Chem. Scand.*, 1968, **22**, 867.

¹⁴ D. R. Armstrong and P. G. Perkins, *Chem. Comm.*, 1968, 352.

¹⁵ D. S. Marynick and W. N. Lipscomb, *J. Amer. Chem. Soc.*, 1973, **95**, 7244.

¹⁶ D. S. Marynick, *J. Chem. Phys.*, 1976, **64**, 3080.

¹⁷ D. S. Marynick and W. N. Lipscomb, *Inorg. Chem.*, 1972, **11**, 820.

¹⁸ H. I. Schlesinger, H. C. Brown, and E. K. Hyde, *J. Amer. Chem. Soc.*, 1953, **75**, 209.

¹⁹ N. A. Bell, G. C. Coates, and J. W. Emsley, *J. Chem. Soc. (A)*, 1966, 1360.

²⁰ T. H. Cook and G. L. Morgan, *J. Amer. Chem. Soc.*, 1970, **92**, 6487.

²¹ L. J. Allamandola and J. W. Nibler, *J. Amer. Chem. Soc.*, 1976, **98**, 2096.

²² D. F. Gaines and J. L. Walsh, *J.C.S. Chem. Comm.*, 1976, 482.