Synthesis and Intramolecular Exchange Characteristics of Beryllium Bis(octahydrotriborate), $Be(B_3H_8)_2$

By Donald F. Gaines

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

and John H. Morris

(*Department of Chemistry, University of Strathclyde,* 295 *Cathedral Street, Glasgow* G1 1XL, *Scotland*)

Summary The preparation of $Be(B_3H_8)_2$ from TlB_3H_8 and $BeCl_2$ is reported; a study of its 270 MHz ^1H and 87·6 MHz ^{11}B F.T. n.m.r. spectra over a range of temperatures using spin decoupling and line narrowing techniques has resulted in the identification of its low temperature static configuration and intermediate and high temperature fluxional forms.

Interest in the unresolved problem[1] of the gas phase structure of $Be(BH_4)_2$ has prompted us to extend the scope of beryllium-borane chemistry by seeking analogies in other beryllium derivatives of boranes. Our initial studies indicated that $Be(BH_4)_2$, prepared from $BeCl_2$ and $LiBH_4$,[2] often contains several volatile beryllium–borane impurities. We have identified the most volatile of these impurities as $Be(B_3H_8)_2$, and here we report its characterization, independent synthesis, and fluxional nature.

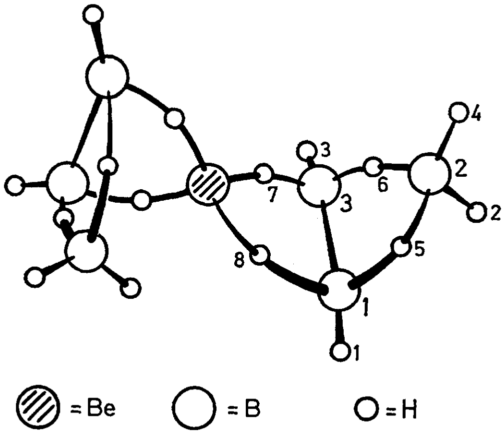

Figure 1. Proposed static structure of $Be(B_3H_8)_2$ (C_2 symmetry).

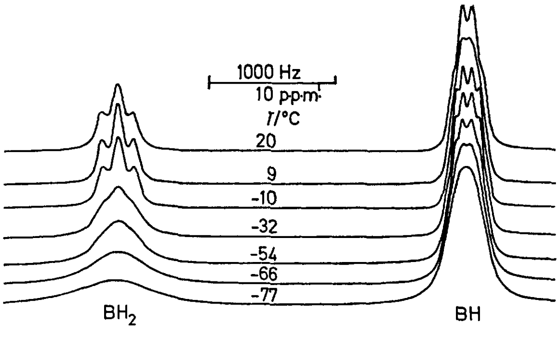

Figure 2. Reversible variable temperature ^{11}B n.m.r. spectra (86·7 MHz) of $Be(B_3H_8)_2$ in [$^2H_8$]toluene (−77 to + 20 °C).

Direct reaction between $BeCl_2$ and TlB_3H_8 at 25—60 °C *in vacuo* produces good yields of $Be(B_3H_8)_2$, which is purified by meticulous high vacuum trap-to-trap distillation. The product is extremely air-sensitive. In contrast to the helical polymeric nature[3] of solid $Be(BH_4)_2$ and the apparent absence of a liquid phase,[4] $Be(B_3H_8)_2$ appears to have a conventional solid phase (m.p. −51 °C) and a normal liquid phase [$\log_{10}(P/\text{Torr}) = -2040{\cdot}8/T + 8{\cdot}2297$; V.p. at 0 °C, 5·7 Torr; b.p. (extrapolated), 108·4 °C; ΔH_{vap}

39·07 kJ mol^{-1}; Trouton's constant, 102·5 J K^{-1} mol^{-1}]. Neat liquid samples decompose slowly at room temperature, but dilute benzene and toluene solutions and low-pressure gas-phase samples, heated to 80 °C for several hours, exhibit <1% decomposition.

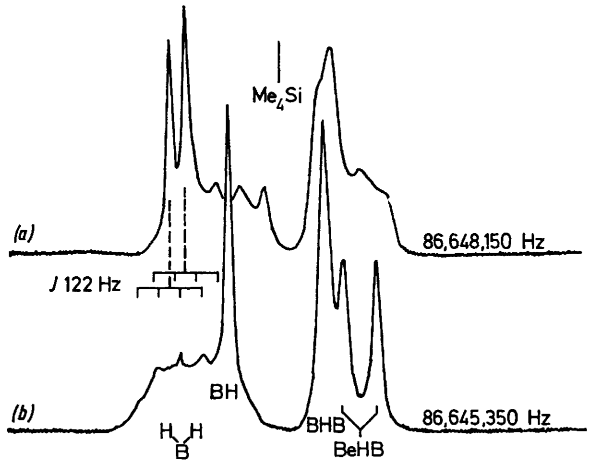

FIGURE 3. The ^{1}H n.m.r. spectra (270 MHz) of $Be(B_3H_8)_2$ in [$^2H_8$]toluene at −10 °C with selective ^{11}B decoupling of B(2) (*a*) and B(1,3) (*b*).

The gas phase i.r. spectrum of $Be(B_3H_8)_2$ exhibits B–H terminal stretching bands at 2570(vs) and 2495(s) cm^{-1} and a broad B–H–B/Be–H–B stretching absorption at 2158(vs), similar to those exhibited by other metal–B_3H_8 compounds.[5]

The mass spectrum of $Be(B_3H_8)_2$ cuts off at *m/e* 91 corresponding to $^9Be(^{11}B_3H_8)_2$. The most intense peak in the group of ions containing six boron atoms occurs at *m/e* 84; calc. for $^9Be^{10}B^{11}B_5H_{10}$, 84·1499; obs., 84·1503.

The temperature dependence of the 270 MHz ^{1}H and 86·7 MHz ^{11}B F.T. n.m.r. spectra indicates three basic molecular forms, one of which is static at temperatures below −10 °C (Figure 1), and the other two are fluxional at higher temperatures. The spectra at −10 °C and below (Figures 2 and 3), consistent with the static structure, indicate two main boron environments, and equal numbers of hydrogens in terminal and bridging regions. Selective decoupling and line narrowing techniques indicate slight non-equivalence of boron atoms 1 and 3, and yield the coupling constants $J_{B(2)-H(2)} = J_{B(2)-H(4)} = 122$; $J_{B(1)-H(1)} = J_{B(3)-H(3)} = 140$; $J_{B(1)-H(8)} = 53$; $J_{B(3)-H(7)} = 65$; $J_{B(1)-H(5)} = J_{B(3)-H(6)} \leqslant 45$; $J_{B(2)-H(5)} = J_{B(2)-H(6)} =$ *ca.* 0 Hz.

At temperatures above −10 °C the appearances of the ^{11}B and ^{1}H spectra alter, and near room temperature indicate that rapid internal exchange occurs within the groups of hydrogen atoms H(1)–H(5)–H(8), H(3)–H(6)–H(7), and H(2)–H(4), although no exchange occurs between these groups. At room temperature the ^{1}H spectrum consists of a single type of terminal hydrogen of area 2 coupled to B(2), and a higher field featureless broad resonance of area 6. The ^{11}B spectrum shows a low field triplet of area 1 and a high field quartet of area 2, both of which collapse to single lines on ^{1}H irradiation.

As the temperature is raised further, the ^{11}B resonances become broad and merge near 80 °C to the weighted average position. This indicates fluxional behaviour which involves exchange of all eight hydrogen atoms and the three boron atoms of each B_3H_8 groups, as has been observed in other octahydrotriborate complexes.[5,6]

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