Gas-phase Nuclear Magnetic Resonance Spectroscopic Study of the Molecular Structure of Beryllium Borohydride, $Be(BH_4)_2$

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Summary Gas-phase and solution n.m.r. spectral studies of beryllium borohydride, $Be(BH_4)_2$, indicate that it contains magnetically equivalent BH_4 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, $Be(BH_4)_2$, has been a subject of some controversy. As many as nine different structures have been proposed for the gas-phase monomer[1] 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 $Be(BH_4)_2$ 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 $Be(BH_4)_2$ has not been reported. We report here the results of ambient gas-phase and solution ^{11}B and ^1H n.m.r. spectral studies of $Be(BH_4)_2$.

Beryllium borohydride was prepared by the method of Schlesinger, Brown, and Hyde[18] and was handled using standard high-vacuum techniques. ^{11}B and ^1H n.m.r. spectra (86·7 and 270 MHz, respectively) of $Be(BH_4)_2$ were obtained on a Bruker WH-270 F.T.n.m.r. spectrometer. For the gas-phase spectra, the boron probe was modified to 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 $Be(BH_4)_2$ and 2—5 atm of inert gas $[(CD_3)_4Si$ and/or argon] to effect collision narrowing of the spectral lines. Solution-phase spectra were obtained using $[^2H_6]$-benzene and $[^2H_2]$dichloromethane solvents.

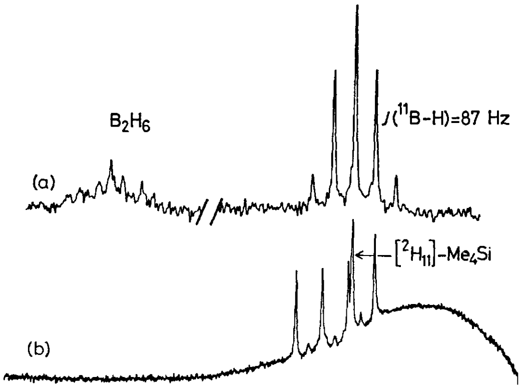

FIGURE 1. Gas-phase n.m.r. spectra of $Be(BH_4)_2$. (a) ^{11}B spectrum at 86.6 MHz. (b) ^1H spectrum at 100 MHz.

The gas-phase ^{11}B and ^1H n.m.r. spectra of $Be(BH_4)_2$, shown in Figure 1, indicate the presence of a single species. The ^{11}B 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 [$J(^{11}B\text{–}H) = 87$ Hz]. The ^1H spectrum is a 1:1:1:1 quartet indicating that all hydrogen atoms are equivalent and are coupled to a single ^{11}B (80%, $I = 3/2$) nucleus [small resonances due to coupling to ^{10}B (20%, $I = 3$) are also present]. The ^{11}B spectrum shows the presence of a small amount of diborane(6) [58·0 p.p.m. downfield from the $Be(BH_4)_2$ signal], a decomposition product which accumulates during the course of the spectral acquisition (*ca.* 12 h). No line-shape features of the ^{11}B 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 {^{11}B: δ +36·2 p.p.m. ($BF_3\cdot OEt_2 = 0$), $J = 86$ Hz, in $[^2H_6]$benzene; ^1H: δ +0·4 ($Me_4Si = 0$), $J = 86$ Hz in $[^2H_6]$benzene}.

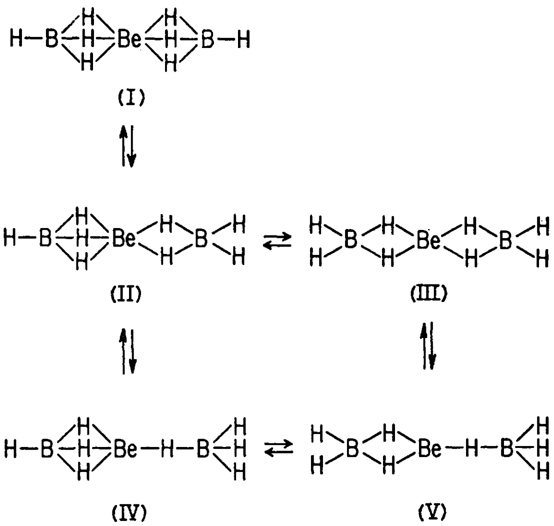

FIGURE 2

The n.m.r. spectra can be interpreted only in terms of a $Be(BH_4)_2$ 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* $Be(BH_4)_2$ 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–BH_4 interactions [solid, polymeric $Be(BH_4)_2$,[17] $(MeBeBH_4)_2$,[20,21] and solid $B_5H_{10}BeBH_4$[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 $Be(BH_4)$ 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.

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