Bridge Proton Exchange in B_6H_{10} and $2\text{-}CH_3B_6H_9$; Low Temperature Nuclear Magnetic Resonance Spectra of Static Structures

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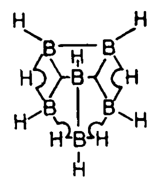
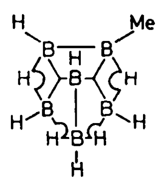
Summary Low temperature ^1H and ^{11}B n.m.r. spectra of B_6H_{10} and $2\text{-}MeB_6H_9$ demonstrate: (1) the bridge proton exchange rate is slow on the n.m.r. time scale; (2) the spectra of B_6H_{10} thus obtained are consistent with the known solid state structure; and (3) the static structure of $2\text{-}MeB_6H_9$ is without a mirror plane of symmetry.



I



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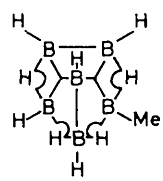

III

Correlating the ^1H [1] and ^{11}B n.m.r.[2] data for B_6H_{10} (consistent with C_{5v} symmetry) with the known *X*-ray crystal structure (I)[3] (*Cs* symmetry) has long been a problem. One rationale assumes coincidental overlap of basal resonances,[4] while another assumes a rapid tautomerism of bridge hydrogen atoms thereby averaging the magnetic environment of the basal atoms.[2] We have resolved this problem in favour of the latter explanation.

Variable temperature ^1H n.m.r. spectra (with ^{11}B spin decoupling) of B_6H_{10}, (Figure 1) and $2\text{-}MeB_6H_9$,[5] (Figure 2) have been obtained. At temperatures at which the exchange rate is slow on the n.m.r. time scale, resonances that can be related to static structures are observed. The appropriate weighted averages of the chemical shifts of the resonances observed for the systems (Figures 1b and 2b) agree within experimental error with the chemical shifts of the corresponding resonances at higher temperature (Figures 1a and 2a). This confirms the suggestion of rapid bridge hydrogen exchange at higher temperatures as the reason for the magnetic equivalence observed.

The spectrum of B_6H_{10} thus obtained (Figure 1b) is fully consistent with *X*-ray structure in that three types of basal

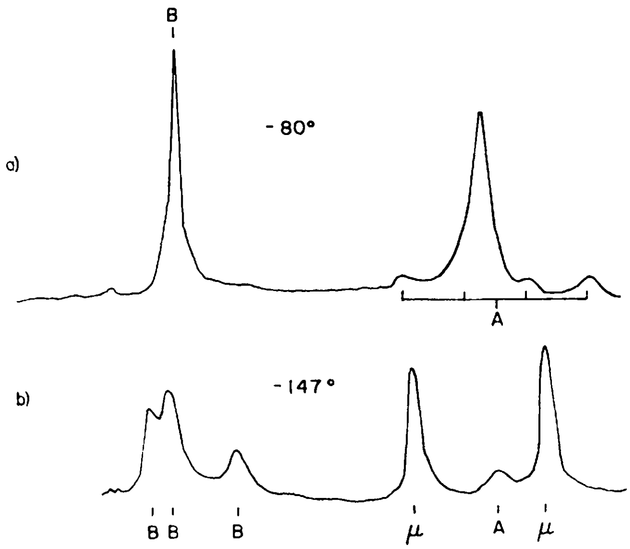

Figure 1. ^{1}H *n.m.r. spectra at* 100 MHz *of* B_6H_{10} (B = *basal terminal hydrogens*, A = *apical terminal hydrogens*, μ = *bridging hydrogens*); (a) *basal* ^{11}B *atoms spin-decoupled*, (*b*) *all* ^{11}B *atoms spin-decoupled.*

terminal hydrogen and two types of bridge hydrogen atoms are observed.

By irradiating individual boron atoms as well as various combinations while observing the ^{1}H n.m.r. spectra of B_6H_{10}, we find that the highest field basal terminal proton and the lower field bridge protons are apparently spin-coupled to the highest field basal boron which is opposite the B–B bond. The higher field bridge protons are therefore adjacent to the B–B bond.

The four different basal terminal resonances observed for 2-MeB_6H_9 together with the four bridge resonances (Figure 2b) indicate that the static structure cannot have a mirror plane as in (I). Two possible structures are (II) and (III).

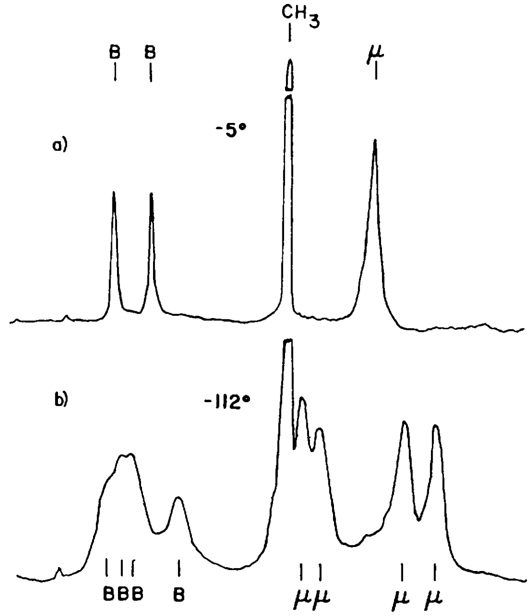

Figure 2. ^{1}H *n.m.r. at* 100 *MHz of* 2-MeB_6H_9 *with* ^{11}B *spin decoupling:* B = *basal terminal hydrogens*, μ = *bridging hydrogens. Note that the apical boron is not decoupled and the apical proton is not visible in these spectra.*

Neither the methyl boron resonance nor the methyl proton resonance of 2-MeB_6H_9 shifts significantly as the temperature is lowered. We therefore believe that the B–B bond in the static structure is not adjacent to the methyl boron, as in structure (II). We favour structure (III), and have obtained data on 2-$MeB_5H_7^-$ [6] which support this choice.

^{11}B n.m.r. spectra of B_6H_{10} and 2-MeB_6H_9 are fully consistent with the ^{1}H n.m.r. spectra presented above and further demonstrate the quenching of bridge proton exchange in each case.

In continuing studies, we find that at −40 to −60°, the ^{1}H n.m.r. spectra of 2-MeB_6H_9 and 2-BrB_6H_9 show some, though no longer all, of the bridge protons to be static on the n.m.r. time scale.

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