Nuclear Magnetic Resonance Evidence for Bridge Hydrogen Tautomerization (and/or Exchange) in Monocarbahexaborane(7)

By THOMAS ONAK* and JOHN B. LEACH

(*Department of Chemistry, California State College, Los Angeles, California* 90032)

Summary Temperature studies on monocarbahexaborane-(7) show that the two high field doublets in the ^{11}B n.m.r. spectrum taken at 30° collapse into a single doublet at 100°: possible mechanisms are suggested to account for this observation; all involve migration of the single bridge hydrogen.

AN octahedral structure (Figure 1) has been suggested for CB_5H_7[1] by drawing an analogy on the isoelectronic $C_2B_4H_6$ carborane[2] and the $B_6H_6^{2-}$ ion.[3] In support of this assignment the ^{11}B n.m.r. spectrum taken at ambient conditions, indicates that one terminal hydrogen is attached to each boron atom since three B–H$_{\text{terminal}}$ doublets are observed with an area ratio of 1 : 2 : 2 [Figure 2(a)]. Further, an analysis of the ^{1}H n.m.r. spectrum indicates a single hydrogen attached to carbon (slightly broadened singlet) and the presence of one bridge hydrogen (high field broad peak).

A study of the temperature-dependent ^{11}B n.m.r. spectrum of CB_5H_7 reveals that the two upfield doublets, each of area 2, begin to coalesce at *ca.* 70° [Figure 2(b)] and merge into a well-defined single B–H$_{\text{terminal}}$ doublet pattern by 100° [Figure 2(c)]. Also this change is reversible; the new doublet is midway in chemical shift between the two doublets that disappear, and the low field doublet assigned to B-6 is not appreciably affected over this temperature range. Using the structural framework shown in Figure 1, the results can be explained by invoking a bridge tautomerization in which the bridge hydrogen moves rapidly from one triangular face to another. Energetically, all four tautomerized forms are equivalent and it is only necessary for this mechanism that the hydrogen slide around the B_{eq}–B_{ax} 'edges'. Whether the bridge hydrogen in the ground state is situated in the same plane as the equatorial boron atoms or, is pointing down toward B-6 (*i.e.* close to the triangular face defined by B-2, B-3, and B-6) is still in question. The latter situation would be similar to the unique hydrogen in pentaborane(11),[4] which is most probably bridge-bonded to three borons, and is favoured for CB_5H_7 where an intramolecular exchange is invoked.

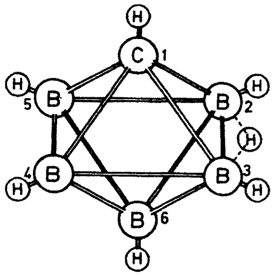

FIGURE 1. *Ball and stick model of* CB_5H_7 *with the bridge hydrogen between equatorial borons but pointing down toward* B-6.

Other explanations are possible for the observed results but are considered less plausible. One such interpretation involves a fast dissociation and recombination of the bridge hydrogen with the transitory formation of a H^+ and the conjugate base of the parent carborane. Such a process may lead to intermolecular bridge exchange and thus result in a loss of B–H_{bridge} coupling with concomitant sharpening of the broad bridge region in the ^1H n.m.r. spectrum at the higher temperature. This sharpening is not observed although, in separate experiments, mechanically-induced heteronuclear ^{11}B decoupling does result in such sharpening. Another explanation which parallels the first-mentioned mechanism, is that the bridge hydrogen is located initially between one equatorial boron and the unique axial boron and moves from edge to edge. However, this would require accidental overlap of two resonances in the ^{11}B n.m.r. spectrum at the lower temperature, and this is unlikely.

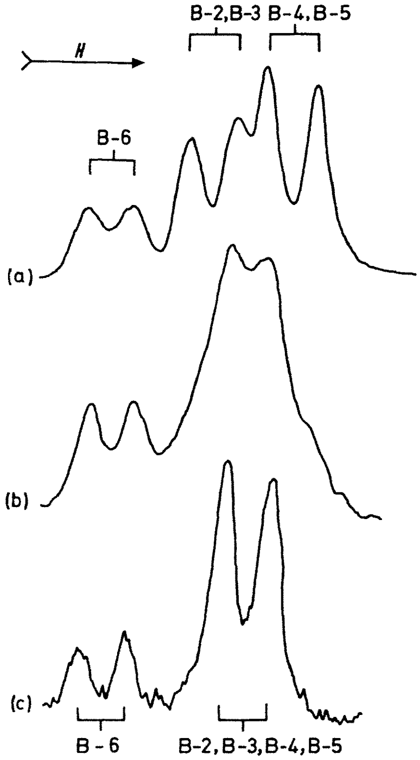

FIGURE 2. ^{11}B *n.m.r. spectra of* CB_5H_7; (a) *at* 30°, *the assignments for* B-2,B-3 *and* B-4,B-5 *are made arbitrarily and may be interchanged*; (b) *at* 70°; (c) *at* 100°.

This work was supported in part by a grant from the Office of Naval Research.

(*Received, November* 19*th*, **1970**; *Com.* 2005.)

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