Long-Range Magnetic Resonance Coupling between the Apical and Basal Hydrogens in Pentaborane(9)

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Summary Using double resonance techniques a multiplet is observed for the apical hydrogen of pentaborane(9) which is interpreted in terms of coupling of equal magnitude, 5·7 Hz, to both the basal-terminal and bridging hydrogens.

Nuclear magnetic resonance coupling between proton nuclei separated by at least two boron atoms in the polyboron compounds is unknown. This may be attributed largely to the experimental difficulties of simultaneously, and effectively, decoupling all the boron nuclei in such compounds. Thus, previously reported ^{11}B decoupled proton spectra of these systems have exhibited limited fine structure for each kind of proton nucleus, sufficient to assign coupling for nearest and/or for next nearest neighbours solely.[1,2]

With the use of a sufficiently broad frequency band[3] it is possible to irradiate all of the boron nuclei of pentaborane(9) and obtain the proton spectrum as shown in the Figure (b). With sufficient r.f. decoupling power fine structure emerges from the resonance attributed to the apical hydrogen, Figure (c). Seven peaks are observed with equal spacing of 5·7 Hz between adjacent resonances. Long-range coupling of either base-terminal or bridging hydrogens can account for a five-membered multiplet at most; moreover, the peak heights as well as the relative areas of the inner five peaks of the observed spectrum do not fit the required 1:4:6:4:1 ratio expected for such a coupling pattern.

It is suggested, therefore, that the observed multiplet are the visible members of a nontuplet with theoretical relative intensities of 1:8:28:56:70:56:28:8:1. This would demand that the apical hydrogen be coupled to all four base-terminal hydrogens as well as all four bridging hydrogens, and additionally, that the magnitude of coupling constants for both of these be, coincidentally, the same to within *ca.* 0·1 Hz. The measured intensities of the seven visible members of this nontuplet are 9:29:55:70:56:28:11 which agree well with the theoretical ratio when a noise

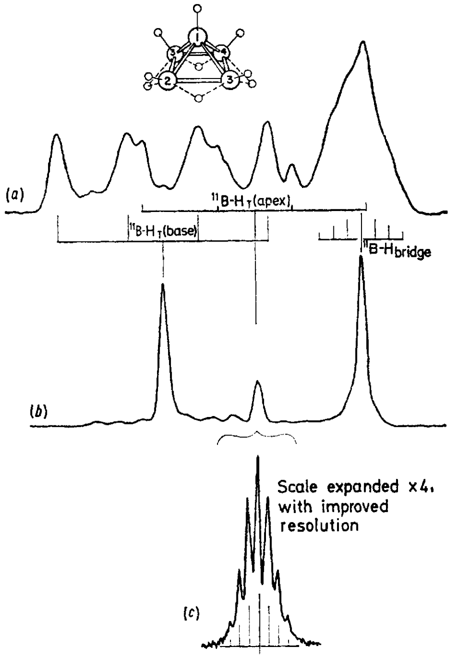

Figure ^{1}H *n.m.r. spectrum* (100 *MHz*) *of pentaborane*(9): (a) *undecoupled;* (b) *noise decoupled;* (c) *apex proton,* ^{11}B *noise decoupled.*

level of *ca.* 1—2 on this arbitrary scale is taken into account. Furthermore, the magnitude of the noise level adequately accounts for the difficulty in observing the two outer members of the nontuplet.

It is somewhat surprising that coincidental values for $J(\mathrm{H_{apex}}–\mathrm{H_{bridge}})$ and $J(\mathrm{H_{apex}}–\mathrm{H_{base-terminal}})$ should be found; however, this should not imply the possibility of base–terminal and bridge equivalency through a tautomerization mechanism such as found in the $B_3H_8^-$ ion and B_6H_{10}.[1] It must be remembered that both the base-terminal and bridging hydrogens are found as two distinct resonances in the proton spectrum of pentaborane(9), and that a fast tautomeric equilibration would give rise to only one resonance for these two types of hydrogens.

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[1] For pertinent references see: G. R. Eaton and W. N. Lipscomb, "NMR Studies of Boron Hydrides and Related Compounds," Benjamin, New York, 1969.

[2] J. B. Leach and T. Onak, *J. Magnetic Resonance*, 1971, **4**, 30; J. B. Leach, C. B. Ungermanns, and T. Onak, *ibid.*, 1972, **6**, 74.

[3] R. R. Ernst, *J. Chem. Phys.*, 1966, **45**, 3845.