[CONTRIBUTION FROM THE RESEARCH LABORATORY, OLIN MATHIESON CHEMICAL CORPORATION]

N.m.r. Spectra of B_4H_{10}: Correlation of Boron Hydride Spectra

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RECEIVED JUNE 1, 1959

The B^{11} n.m.r. spectrum of tetraborane at 12.8 mc. exhibits a completely resolved doublet (representing the BH groups) and triplet at lower field (representing the BH_2 groups). Observed fine structure is attributed to bridge proton coupling and B^{10}–B^{11} coupling. The H^1 n.m.r. spectrum at 40 mc. shows that the BH quartet is at higher field than the BH_2 quartet. Various features of the n.m.r. spectra of tetraborane make possible the correlation of the spectra of the other boron hydrides. Such correlations are discussed in detail.

The n.m.r. spectra of tetraborane have been published previously[2] and portions of these spectra interpreted on the basis of established structure of tetraborane[3–5]; the previous B^{11} n.m.r. spectrum was obtained at 6 mc., and the H^1 n.m.r. spectrum at both 30 and 40 mc. The B^{11} spectrum at 6 mc. consisted of an "apparent quartet" and was correctly interpreted as a low field triplet (BH_2 groups) overlapped by a higher field doublet (BH groups). Recently we obtained the B^{11} spectrum at 12.8 mc. which completely resolves the triplet and doublet; in addition, boron^{10}–boron^{11} coupling is observed at 12.8 mc. which was undetected at 6 mc. An improved H^1 n.m.r. spectrum has been obtained at 40 mc. in sufficient detail to establish that the terminal (BH_2 group) protons are represented by a quartet centered at low field relative to the quartet representing the terminal (BH group) protons.

The previous H^1 spectra at 30 and 40 mc. contained a small peak at high field which probably represented an impurity. Interpretation of this peak as arising from tetraborane required exaggeration of the bridge proton-boron^{11} coupling constants and rendered the previous B^{11} and H^1 spectra[2] mutually incompatible.

Experimental

Tetraborane was purified by standard high vacuum techniques. One portion (liquid) was transferred into a 5 mm. o.d. tube while the second (gas phase) was placed in a 15 mm. o.d. tube.

The B^{11} and H^1 n.m.r. spectra were obtained using a Varian Associates High Resolution Nuclear Magnetic Resonance Spectrometer operating at 12.8 and 40 mc., respectively.

Discussion

Interpretation of the N.m.r. Spectra of Tetraborane.—The B^{11} n.m.r. spectrum of tetraborane (Fig. 1) contains a triplet representing the BH_2 groups at low field. The shoulders on each member of the triplet represent the coupling of the (BH_2 group) boron atoms with two additional bridge protons. The complexity of the high field doublet (BH groups) results from a greater number of interactions. The "basic doublet" results from the coupling of the single terminal proton; however, the fine structure is best explained by the combined influence of the coupling of two bridge protons to all of the (BH group) B^{11} nuclei and the coupling of B^{10} nuclei (BH group) to 20% of the B^{11} (BH group) nuclei.

The H^1 n.m.r. spectrum of tetraborane (Fig. 2) obtained at 40 mc. does not contain the peak at highest field observed in the previous spectra.[2] Repeated "trial and error" adjustments and subtractions of the bridge proton component (dotted line, Fig. 2) from the total H^1 n.m.r. spectrum resulted in an acceptable terminal proton spectrum of tetraborane. The two types of terminal protons are sufficiently resolved to show that the center of the quartet representing the BH_2 groups (at lower field in the B^{11} n.m.r. spectrum) is also at lower field in the H^1 spectrum. The lowest field members of both quartets are approximately superpositioned whereas the highest field members of the quartets are separated; the ratio of the spin-spin coupling constants of the two quartets necessarily agrees with the ratio of the spin-spin couplings of the triplet and doublet in the B^{11} spectrum.

Correlation of Spectra.—Certain relationships become apparent when comparing the spectra of tetraborane with those of the other common boron hydrides.

Chemical Shifts of BH_2 Groups and BH Groups.—In tetraborane the BH_2 group is represented at lowest field (Fig. 3) in the B^{11} n.m.r. spectrum. The base BH_2 groups in B_5H_{11}[6] also occur at lowest field within the B^{11} n.m.r. spectrum and the BH_2 resonance in diborane occurs at a low field within the spread covered by the various boron hydrides.[7] However, in an "intermolecular sense" the chemical shifts of BH and BH_2 groups are not mutually exclusive.

Chemical Shifts of Boron Nuclei and their Associated Terminal Protons.—The n.m.r. spectra of tetraborane provide another example where terminal protons attached to "higher field" borons appear at higher field; and conversely, those protons attached to "lower field" borons appear at lower field. This condition has also been noted in B_5H_9,[8] B_5H_{11},[6] B_6H_{10},[9] and $B_{10}H_{14}$[8,10–12] where the "apex" borons and protons occur at high field. It is also true that in many cases the base boron chemical shifts are quite similar and the lack of resolution prevents stating that this relationship is general. Lack of resolution at 40 mc. prevents

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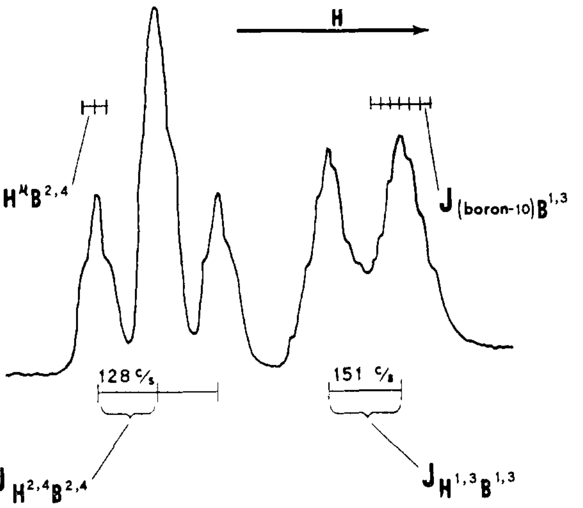

Fig. 1.—B^{11} n.m.r. spectrum of tetraborane.

the observation of differences among the base terminal protons in B_5H_{11},[6] B_6H_{10},[9] and $B_{10}H_{14}$.[8,10–12]

Boron^{10}–Boron^{11} Coupling (Single Bond).—The multiplicity of the high field doublet in the B^{11} n.m.r. spectrum is explained on the basis of B^{10} and bridge-proton interaction with the B^{11} nuclei; however, many other possibilities were considered. The liquid and vapor phase B^{11} n.m.r. spectra of tetraborane were equivalent; therefore, the multiplicity cannot be caused by intermolecular association.

Another possibility assumed that the four tetraborane bridge hydrogens were equivalent to the unique bridge hydrogen in B_5H_{11}, which is "some times" considered to be coupled with three boron atoms.[6,13–15] If the BH group boron atoms were identically coupled with all four bridge hydrogens, quintets would result. If the BH boron atoms were coupled to the adjacent pair of bridge hydrogens exactly two times as strongly as the remaining pair, a septet is possible; however, the degree of coupling when applied to the proton spectrum would require a broader bridge hydrogen multiplet than is observed. Several other less plausible combinations of interactions were considered and eliminated for comparable reasons.

The only presently acceptable explanation is that the two adjacent bridge protons change the "basic" doublet into (unresolved or semi-resolved) triplets and each member of the triplets in one-fifth of the B^{11} nuclei (coupled to B^{10} nuclei) are further split by the spin-3 of B^{10} into septets. It is possible that the coupling constants are comparable (B^{11}–H bridge and B^{11}–B^{10}) and that overlapping nonets result (the smallest components might not be observed).

A similar phenomenon is observed when a proton is connected with one to three borons. A terminal proton (connected to single B^{11}) has a J of 80–190 c./s., a bridge proton (connected to two B^{11}'s) has a J value of *ca.* 35–40 c./s., and a unique bridge proton (as in B_5H_{11}) associated with three borons probably has a much smaller J.[6] The J = 35–40 c./s. for "normal" bridges has been observed in B_2H_6, B_4H_{10}, B_5H_9, $B_{10}H_{14}$ and derivatives.

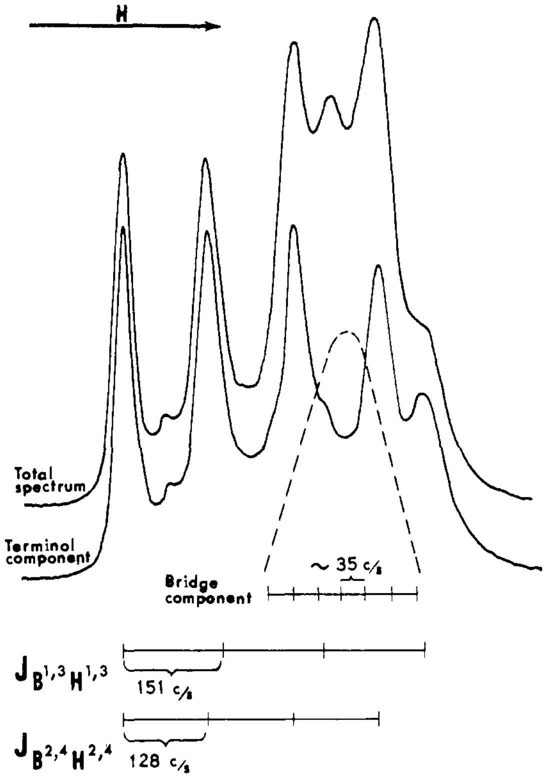

Fig. 2.—H^1 n.m.r. spectrum of tetraborane.

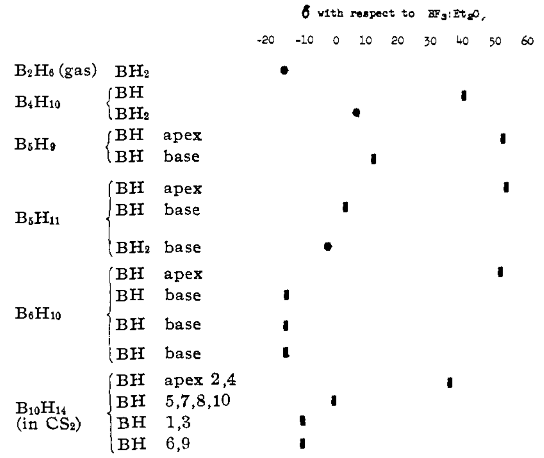

Fig. 3.—Comparison of B^{11} n.m.r. chemical shifts in boron hydrides: ●, refers to BH_2; ■, refers to BH.

Coupling in BH_2 Groups (B$''$n.m.r.).—Diborane, tetraborane and pentaborane-11 contain BH_2 units which are associated with two bridge protons. Only in the BH_2 groups of diborane and tetraborane are secondary triplets caused by coupling with two identical bridges partially resolved. Although there is disagreement on the structure of B_5H_{11}[13–15] we feel that the base BH_2 groups in B_5H_{11} are coupled to two non-equivalent bridge protons thus creating secondary quartets which defy resolution despite the fact that the line width of the primary

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BH_2 triplet is relatively narrow, thus indicating little or no boron–boron coupling. This interpretation would favor the structure of B_5H_{11} wherein the unique proton is a "bridge" rather than a terminal proton.

Observations Regarding "Saturation."—There is evidence that terminal protons are coupled with non-adjacent atoms such as bridge protons and non-identical terminal protons. When the proton spectrum of pentaborane, for example, is obtained when sweeping from low field to high (at high power), the spectrum is substantially different from that observed when sweeping in the reverse direction. When sweeping from low field to high, components of the base terminal protons are first encountered followed by apex terminal and bridge protons; in this case the amplitude of the bridge proton component is reduced significantly and the apex quartet slightly reduced. Sweeping in the reverse direction produces an opposite effect; the base terminal proton components are reduced relative to the apex. The bridges are much more sensitive to saturation with power. This "telegraphing" to other parts of the molecule is believed to result primarily from visually unresolved coupling between non-adjacent protons.

Only in tetraborane is a boron–boron single bond thought to exist between identical boron atoms uncomplicated by bonds to other non-identical boron nuclei, and only in tetraborane has resolved boron–boron coupling been observed. This would suggest that fine structure resulting from B^{10}-B^{11} coupling should be observed in simple compounds or compounds where pairs of boron atoms are isolated.

The observation of boron^{10}-boron^{11} coupling in tetraborane implies that both B^{10}-B^{11} and B^{11}-B^{11} coupling should at least broaden the lines in boron hydrides wherein two boron atoms are connected by a single bond; such broadening is not observed in the higher boron hydrides. Thus, although multiple boron bonding (see below) might reduce the coupling constants, we believe that depicting the boron skeleton of the higher boron hydrides as containing *any* localized single bonds should be suspect. The actual structures are probably hybrids of several canonical forms (*i.e.*, the several ways in which the boron skeleton can be portrayed using two centered and three centered[16] bonds) and no true localized single bonds actually exist in the boron framework of the higher boron hydrides.

Boron–Boron Coupling (Multiple Bonds).—Two explanations accounting for the broadness in certain B^{11} n.m.r. spectra, *i.e.*, pentaborane-9 apex boron, have been suggested. These two are: nuclear quadrupole broadening due to lack of symmetry around the boron nucleus and/or boron–boron coupling which is not resolved. It has been pointed out that nuclear quadrupole broadening would not be important in the spectrum of the borohydride ion and as a result its B^{11} n.m.r. spectrum is composed of narrow peaks.

On the other hand after observing several other compounds[17] which contain boron nuclei in environments analogous to the apex of pentaborane, but which have narrow resonance lines, it becomes necessary to conclude that the apex broadening in pentaborane-9 is characteristic of the molecule and not of the B^{11} nucleus. Therefore, unresolved boron–boron coupling and not nuclear quadrupole broadening plays the most important role. In isotopically normal pentaborane-9 the apex B^{11} nuclei are associated with five "kinds of bases": 41% $B_4{}^{11}$, 41% $B_3{}^{11}B^{10}$, 15.5% $B_2{}^{11}B_2{}^{10}$, 2.5% $B^{11}B_3{}^{10}$ and 0.2% $B_4{}^{10}$. Considering only the 41% of the apex borons connected to four B^{11} nuclei in the base (which would account for the greatest spread in the apex B^{11} n.m.r. spectrum), each member of the apex doublet would be expected to be split into thirteen peaks in the ratio of 1:4:10:20:31:40:44:40:31:20:10:4:1; these thirteen peaks are spaced with a zone of about 160 c./sec.; thus the B^{11} apex to B^{11} base coupling constant is $< 13 +$ c./sec. Although B^{11}-B^{11} single bond coupling cannot be observed in tetraborane, its value can be calculated. The B^{10}-B^{11} coupling constant (Fig. 1) is approximately 23 c./sec.; the B^{11}-B^{11} coupling would be 2.98 times that or about 70 c./sec. as opposed to 13 c./sec. In contrast to a single boron–boron bond the B^{11}-B^{11} coupling has diminished when multiple boron bonding is involved. This decrease in coupling constant ("J") with multiplicity of bonding is also observed when comparing boron and hydrogen coupling constants.

Boron Hydrogen Coupling Constants.—A decrease in J with multiplicity is noted also when comparing borons connected with 1 to 4 protons. A boron with one terminal proton has a J value of 140–190 c./sec.; with two protons, 120–130 c./sec.; three protons, 90–100 c./sec.; and finally in borohydride ion, 80-90 c./sec. A similar trend has been observed in the C^{13}-H (180–210 c./sec.) and C^{13}-H_2 (140–170 c./sec.) spin–spin coupling constants.[18] Similar observations have been made in the proton spectra of tetraborane and other boron hydrides.

Acknowledgment.—The authors wish to acknowledge the assistance of Mr. Max Lustig and Mrs. June Gray for their assistance in obtaining these and many other n.m.r. spectra and preparing them for publication.

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