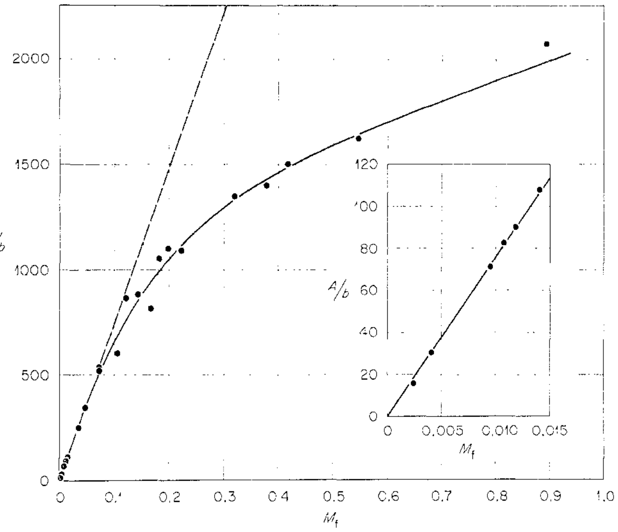

Figure 2.—Beer's law plot of A/b vs. M_t for values of A at the band maximum and at 240°. Inset shows the dilute, linear range and the dashed line represents limiting Beer's law behavior.

To compare this work with recent measurements of lower oxidation states of bismuth in NaX–AlX_3 for X = Cl or Br, it was necessary to extend the spectrum of the proposed Bi^+ ion in pure molten $BiCl_3$ into the near-infrared region as shown in Figure 1 (curve A). Also shown are spectra for Bi^+ in NaBr–$AlBr_3$[10] and NaCl–$AlCl_3$.[7] Similar changes in spectrum occur in both solvent systems as chloride is replaced by bromide. The bands shift to lower energies and become somewhat more intense. A comparison of the main band maxima for all four solvents is given in Table I, and the similarities are obvious. The most striking difference between solvent systems, as seen in Figure 1, is in the intensities which are 10 times greater in BiX_3 than in NaX–AlX_3 mixtures. This absorptivity intensification in BiX_3 solvents may arise from a Bi(I)–Bi(III) intervalence-transfer absorption similar to that observed in the Ti(III)–Ti(IV) system.[11] Such an effect has been suggested for these ions in molten NaCl–$AlCl_3$.[7] If one assumes this explanation for the large intensity differences, then the spectra are otherwise fairly similar, lending support to the presumption that Bi^+ exists in $BiCl_3$ and $BiBr_3$ melts and that curves A and C, respectively, represent its spectrum in these media.

Table I

Energies (cm^{-1}) of Band Maxima in AlX_3–NaX and BiX_3 Solvents

X	AlX_3–NaX	BiX_3
Br	16,400	16,300
	13,900	
Cl	18,200	17,900
	14,500–15,100	13,300

As pointed out earlier the exact equilibria occurring in BiX_3 melts cannot be specified. However, if one makes the reasonable assumption that Bi^+ is present in equilibrium with a polymeric species as in eq 1 and 2, constants for such equilibria can be calculated from the spectrophotometric data and a comparison of these constants for Bi–$BiCl_3$ and Bi–$BiBr_3$ will then show the relative tendency for Bi^+ formation in the two systems. Thus, the exact equilibrium need not be known as long as it is of the general type

$$n\mathrm{Bi}^+ = \mathrm{Bi}_m{}^{(3m-2n)+} + (n - m)\mathrm{Bi}^{3+} \qquad (4)$$

Since a mass action constant for eq 1 has already been calculated for the chloride system, this same constant was calculated for Bi–$BiBr_3$ using the same procedures.[3] The value compared reasonably well with the equilibrium constant obtained by Topol and Osteryoung[5] from emf measurements on the Bi–$BiBr_3$ system. The mass action constant, K_M, based on molarity, was converted to K_N, based on mole fraction using the density data of Keneshea and Cubicciotti.[9] At 240°, $K_N = 1.16 \times 10^3 K_M$ so that the spectrophotometric K_N is 2.4×10^4. K_N, calculated from emf data at this temperature, is 1.9×10^4. In the chloride case K_N's of 3.8×10^6 and 2.7×10^6 were obtained at 264° by spectrophotometric[3] and emf[5] methods, respectively. The agreement between emf and spectrophotometric results in both systems is quite good considering the experimental uncertainty in determining these constants.

The equilibrium constant for reaction 1 is about 100 times larger for chloride than bromide indicating that the replacement of chloride by bromide favors the formation of Bi^+. Electrical conductivity measurements[12] indicate that the tendency for Bi^+ formation is even greater in BiI_3 so that the order of increasing stability of Bi^+ in BiX_3 melts appears to be X = Cl < Br < I.

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Studies of Boranes. XXVII. Boron-11 Nuclear Magnetic Resonance Spectrum of *n*-Nonaborane(15) at 64.16 MHz[1]

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We have recently had the opportunity to obtain the ^{11}B nmr spectra of a number of compounds at 64.16 MHz,[2] and since the published literature contains only

[1] For paper XXVI of this series see R. Maruca, J. D. Odom, and R. Schaeffer, *Inorg. Chem.*, **7**, 412 (1968).

[2] The spectra were obtained with the cooperation of Mr. Eugene Pier, Varian Associates, Palo Alto, Calif.

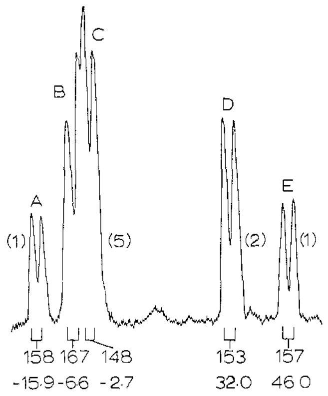

Figure 1.—The ^{11}B nmr spectrum of n-B_9H_{15} at 64.16 MHz. Coupling constants (top line) are in Hz; chemical shifts (bottom line) are in ppm relative to $(C_2H_5)_2O\cdot BF_3$.

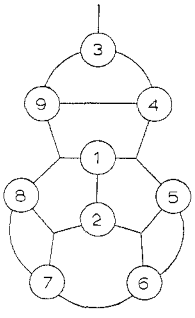

Figure 2.—The boron arrangement in n-B_9H_{15}.

a 12.8-MHz[3] spectrum of n-B_9H_{15} and 19.3-MHz[4] spectra of partially deuterated n-B_9H_{15}, we felt it worthwhile to examine the high-resolution spectrum of this material.

The spectrum in Figure 1 represents a fivefold improvement in resolution over the 12.8-MHz spectrum published by Burg and Kratzer.[3] Five of the six magnetically distinguishable boron environments are clearly represented. The signal from the sixth boron is obscured by the two overlapping doublets B and C, since the integrated area of this set of peaks is five-ninths that of the total spectrum.

Although it is still not possible to interpret the spectrum of n-B_9H_{15} unambiguously, it seems reasonable to make a tentative assignment using a suggestion by Lipscomb[5] based on the similarity of environment between many of the boron atoms in n-B_9H_{15} and those in B_4H_{10} and B_5H_{11}. Figures 2 and 3 illustrate the boron arrangement in n-B_9H_{15} and in B_4H_{10} and B_5H_{11}, respectively. The configuration of the 3-, 4-, and 9-boron atoms in n-B_9H_{15} bears a strong resemblance to the arrangement of the 1-, 2-, and 3-boron atoms in B_4H_{10}, while the 2-, 5-, 6-, 7-, and 8-boron atoms in n-B_9H_{15} are similar to the apical and basal borons in B_5H_{11}.

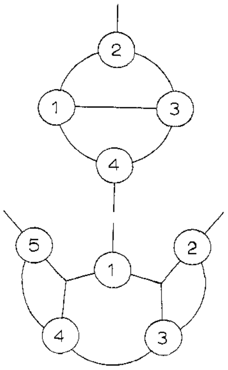

Figure 3.—The boron arrangement in B_4H_{10} and B_5H_{11}.

The doublet E of unit intensity at highest field may be assigned to the B(2) atom on the basis of its similarity to the apical position in B_5H_{11}. Proceeding to lower field, one might assign doublet D to the 4- and 9-boron atoms, corresponding to the BH groups in B_4H_{10}. The overlapping set of peaks, B and C, of intensity 5 may be correlated with the 5-, 6-, 7-, and 8-boron atoms, which resemble the basal atoms in B_5H_{11}, and the B(3) atom, obscured by the other peaks, which resembles the BH_2 groups in B_4H_{10}. By process of elimination the extreme low-field signal A may be assigned to the boron atom in position 1.

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A Proton Magnetic Resonance Hydration Study of Scandium, Yttrium, and Thorium Perchlorates in Water–Acetone Mixtures

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The value of the direct proton magnetic resonance (pmr) method for measuring cation hydration numbers has been demonstrated for a variety of systems.[1–14] In a pmr investigation of the nitrate solutions of diamagnetic Sc^{3+}, Y^{3+}, and Th^{4+} in water–acetone mixtures, hydration numbers of about 3.9, 2.4, and 2.9, respectively, were obtained for these ions, and the results

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