the replacement of H^+ by Na^+ should lower Q (salt in HF) by 0.09 log unit. We estimate that replacing BF_4^- by Cl^- should produce a further reduction of Q by about 0.09 log unit. This is based on the difference in the salting effects reported for 1 M NaCl and 1 M $NaClO_4$,[18] and the assumption that BF_4^- will have the same salt effect as ClO_4^-.

Figure 3 shows the relative amounts of the fluoroborates formed at pH values of 3 and 6 plotted as a function of the free fluoride concentration. At the higher pH the amounts of $BF_2(OH)_2^-$ and $BF(OH)_3^-$ which are formed are greater and the fluoride concentrations at which these species appear are higher. The distribution data in Figure 3 represent the metastable system in which tetrafluoroborate has not formed. At equilibrium (Figure 4) the predominant product at high fluoride concentrations is BF_4^-.

Since there was no significant improvement in the fit to the data by the assumption that the undissociated acids HBF_3OH and $HBF_2(OH)_2$ are formed, we may conclude that in the present measurements these species could have reached concentrations no higher than ~5 and ~25%, respectively, of the concentration of the corresponding ion. From this the acid dissociation constants are judged to have the following lower limits: HBF_3OH, 0.2; $HBF_2(OH)_2$, 10^{-4}. These are consistent with the values (~0.2 and ~0.03, respectively) estimated from conductance measurements by Wamser.[3b]

These results provide very strong evidence in support of the existence of $BF_3(OH)^-$ and $BF_2(OH)_2^-$ in water as well as evidence for $BF(OH)_3^-$. They have also permitted the evaluation of equilibrium quotients relating all the species BF_4^-, $BF_3(OH)^-$, $BF_2(OH)_2^-$, $BF(OH)_3^-$, and $B(OH)_3$. Recent ^{19}F nmr studies in our laboratory will be reported soon which have confirmed the conclusions from these potentiometric results.

Registry No. $B(OH)_4^-$, 15390-83-7; $BF(OH)_3^-$, 32554-53-3; $BF_2(OH)_2^-$, 32554-52-2; $BF_3(OH)^-$, 18953-00-9; BF_4^-, 14874-70-5; $B(OH)_3$, 10043-35-3; F^-, 16984-48-8.

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High-Resolution Boron-11 Nuclear Magnetic Resonance. III. Diborane(6) and Tetraborane(10)[1,2]

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The upper limits for the ^{11}B-^{11}B nuclear spin coupling constant, J_{BB}, have been obtained for a three-center, two-electron BHB bond in diborane(6)-^{11}B (<1.1 Hz) and in tetraborane(10)-^{11}B (<0.3 Hz) under conditions of double and triple resonance, respectively. The efficiency of the triple-resonance technique, used for the first time in ^{11}B nmr studies, is discussed for pentaborane(9). The value of J_{BB} in a three-center, two-electron BHB bond is compared with that found for the boron-boron coupling constant in pentaborane(9).

Since the first determination of a ^{11}B-^{11}B coupling constant (J_{BB})[4] in our laboratories,[5] we have been engaged in a systematic investigation of the factors which influence the value of J_{BB}. This has included a study of substituent effects on the magnitude of J_{BB} in pentaborane(9) derivatives in which various groups are substituted for hydrogen in the apex position.[6] In addition, studies have been conducted to determine boron-boron coupling constants in which boron is engaged in different bonding situations (*i.e.*, two-center, two-electron BB bonds, three-center, two-electron BBB bonds, and three-center, two-electron BHB bonds).[7] A molecule of fundamental importance and also one in which the value of J_{BB} has been reported is diborane(6). Recent studies by Farrar, *et al.*,[8] resulted in a "best fit" value of $|J_{BB}| = 5 \pm 2$ Hz. Similarly, Hopkins, *et al.*,[9] inferred from a detailed spectral analysis of the ^1H and ^{11}B nmr spectra of B_4H_{10} that the value of J_{BB} (*i.e.*, B_1-B_2[10]) was equal to zero.

In this study we have examined the B_2H_6 and B_4H_{10} molecules in an attempt to determine experimentally the value of J_{BB} in these compounds. Comparisons of the spin coupling constants for these molecules with that determined for B_5H_9 provide the opportunity to attempt a correlation between J_{BB} and the nature of the bonding between the two boron atoms under consideration.

Experimental Section

Nmr Measurements. Boron-11 nmr measurements were made on a Varian XL-100-15 nmr spectrometer operating at 32.1 MHz. Field/frequency lock was employed by locking to either ^2H or ^{19}F. The double-resonance experiments were conducted using the Varian Gyrocode decoupler. The triple-resonance experiments (observing ^{11}B, homonuclear decoupling ^{11}B, and heteronuclear noise decoupling ^1H) were accomplished with the Gyrocode decoupler in conjunction with a Varian V-3512-1 heteronuclear spin decoupler. For

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[2] Presented in part at the 163rd National Meeting of the American Chemical Society, Boston, Mass., April 1972. This paper is based, in part, on the thesis submitted by D. W. L. to the Graduate School of the University of South Carolina in partial fulfillment of the requirements for the M.S. degree.

[3] (a) University of South Carolina. (b) Varian Associates.

[4] Unless stated otherwise, J_{BB} is used to represent a ^{11}B-^{11}B spin coupling constant.

[5] J. D. Odom, P. D. Ellis, and H. C. Walsh, *J. Amer. Chem. Soc.*, 93, 3529 (1971).

[6] P. D. Ellis, J. D. Odom, and D. W. Lowman, submitted for publication.

[7] W. N. Lipscomb, "Boron Hydrides," W. A. Benjamin, New York, N. Y., 1963.

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[10] The numbering system employed here is that set forth in *Inorg. Chem.*, 7, 1945 (1968).

those experiments employing a ^{19}F lock and ^1H noise decoupling, a comb-line band-pass filter was used to prevent the decoupler from interfering with the lock channel.[11,12] Standard low-temperature accessories were employed.

All chemical shifts are reported in ppm with respect to external $BF_3 \cdot O(C_2H_5)_2$. The estimated *maximum* error in the measurement of the chemical shifts is 0.1 ppm. The concentrations employed were approximately 20% by volume. Spectra were run at −65° (B_2H_6) and −30° (B_4H_{10}).

Synthesis of Compounds. Standard high-vacuum techniques were used throughout this investigation.[13] All vacuum lines were equipped with greaseless stopcocks. The isotopically enriched diborane(6) was prepared by lithium aluminum hydride reduction of $^{11}BF_3$ which was obtained from Oak Ridge National Laboratory as the dimethyl ether complex. The isotopic purity was stated to be 96.8%. The $^{11}B_2H_6$ was separated from dimethyl ether by fractionation on a low-temperature vacuum distillation column similar in design to that reported by Dobson and Schaeffer.[14] Purity of the material was checked by vapor pressure measurement[13] and a comparison of its infrared spectrum with that reported in the literature.[15] The $^{11}B_4H_{10}$ was prepared by pyrolysis of $^{11}B_2H_6$ in a gas circulation system using a pyrolysis bath temperature of 135° and a trapping temperature of approximately −120°. This pyrolysis produced a mixture of $^{11}B_4H_{10}$, $^{11}B_5H_{11}$, and $^{11}B_{10}H_{14}$ which was fractionated on a low-temperature vacuum distillation column.[14]

Results and Discussion

Upper Limit of J_{BB} in Diborane(6). In the previous work on B_2H_6,[8] an upper limit for J_{BB} was determined by observing the ^{11}B nmr spectrum while irradiating at the ^2H resonance frequency of a sample whose composition was approximately 50% $^{10}B^{11}BD_6$. When the ^2H resonance frequency was applied, the broad (75 Hz) ^{11}B resonance narrowed to a line width of 18 Hz. This line width was assumed to have arisen from unresolved ^{10}B-^{11}B spin coupling. In the resulting analysis the line width was set equal to $6J_{^{10}B\,^{11}B}$, and, thus, an *upper limit* of J_{BB} was determined to be approximately 9 Hz. From a comparison of the experimental and computer-simulated ^1H nmr spectra of B_2H_6, a value of $|J_{BB}| = 5 \pm 2$ Hz was obtained.

There are several problems associated with the determination of an upper limit to J_{BB} by the procedure outlined above. Although the spin coupling of deuterium to boron is removed by irradiation at the proper frequency (assuming that the decoupling power was sufficient), it does not necessarily follow that the effect of the deuterium quadrupole upon the relaxation processes of the boron nucleus has been removed. That is, even with ^2H decoupling, broadened lines due to the presence of ^2H may occur. In addition, it appears that the "natural line width" of boron was not included in the determination of an upper limit of $|J_{BB}|$. The ambiguities mentioned above can be removed by the experimental procedure described below.

An estimate of the natural line width of the ^{11}B nucleus in $^{11}B_2H_6$ can be obtained by measuring the line width, $\Delta^{11,11}$, of the ^{11}B resonance under conditions of complete ^1H decoupling. Under these conditions the two ^{11}B nuclei become equivalent and, thus, J_{BB} cannot be observed. If the line width, $\Delta^{10,11}$, of $^{10}B^{11}BH_6$ (determined under identical conditions) is then measured and compared to $\Delta^{11,11}$, the difference between these two line widths can be ascribed to a more realistic upper limit of J_{BB}:$6J_{^{10}B\,^{11}B} \leqslant \Delta^{10,11} - \Delta^{11,11}$. In the preceding analysis, other factors that may contribute to the experimental line width have been neglected. These factors are additional quadrupole broadening of the ^{11}B nucleus by the ^{10}B nucleus and an isotope shift in the ^{11}B resonance of $^{11}B_2H_6$ and $^{10}B^{11}BH_6$. Therefore, the above expression represents a "true" upper limit of $J_{^{10}B\,^{11}B}$.

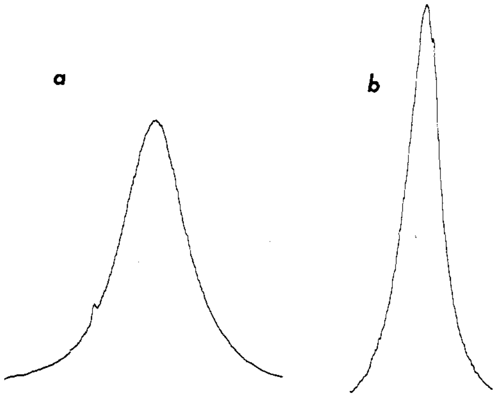

Figure 1. The ^1H noise decoupled 32.1-MHz nmr spectrum of $^{11}B_4H_{10}$ in *sym*-$C_2F_4Br_2$: (a) borons 2 and 4 ($W_{1/2}$ = 14.6 Hz); (b) borons 1 and 3 ($W_{1/2}$ = 8.2 Hz).

Using the complete ^1H decoupling method described previously,[5] a value of 6.2 Hz was obtained for $\Delta^{11,11}$ and 8.4 Hz for $\Delta^{10,11}$. The upper limit of $|J_{BB}|$ in B_2H_6 obtained by such a procedure results in a value of 1.1 Hz. The value of $|J_{BB}| \cong 5$ Hz is considerably outside our experimental error, which is at worst 0.2 Hz. This difference clearly points out the difficulties that can arise from fitting calculated spectra of quadrupolar nuclei that contain unresolved spin coupling to experimental spectra. However, one can only speculate as to the exact cause for the difference between the "calculated" and experimental results.

Upper Limit of J_{BB} in Tetraborane(10). As an extension of the work on B_2H_6, it was desirable to examine boron-boron spin coupling in a similar bond in another boron hydride. For this reason the completely ^1H-decoupled ^{11}B nmr spectrum of $^{11}B_4H_{10}$ was obtained. The spectrum consisted of two relatively narrow lines separated by 35.0 ppm. The line width corresponding to borons 1 and 3 was 8.2 Hz and that corresponding to borons 2 and 4 was 14.6 Hz (Figure 1). The difference in line width of these two resonances is presumably due to a difference in the relaxation times of the two types of magnetically different borons. If the observed line width arises solely from unresolved boron spin coupling, then an upper limit of J_{B1B2} in $^{11}B_4H_{10}$ (derived from the B1(3) resonance line) is approximately 1.4 Hz. However, as mentioned in the preceding section, an analysis of this type ignores the contribution to the line width from intrinsic properties of the nucleus in that molecule and hence is somewhat unsatisfactory.

To avoid this ambiguity, the following triple-resonance experiment was performed: observe B1(3), noise decouple the ^1H's, and irradiate at the B2(4) frequency. The B1(3) resonance was observed because it is the narrower of the two resonances in $^{11}B_4H_{10}$, under conditions of complete ^1H decoupling and thus, presumably, has a narrower intrinsic line width. It should therefore be easier to detect a change in line width due to a change in boron spin coupling. If the residual line width after ^1H decoupling is caused by ^{11}B-^{11}B spin coupling, then there should be a corresponding change in the line width of the boron being observed in the triple-resonance experiment. It is, however, important to check that the experimental arrangement furnishes enough decoupling power to perturb the boron spin system in B_4H_{10}.

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(12) V. J. Bartuska, T. T. Nakashima, and G. E. Maciel, *Rev. Sci. Instrum.*, **41**, 1458 (1972).

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(15) J. J. Kaufman, W. S. Koski, and R. Anacreon, *J. Mol. Spectrosc.* **11**, 1 (1963).

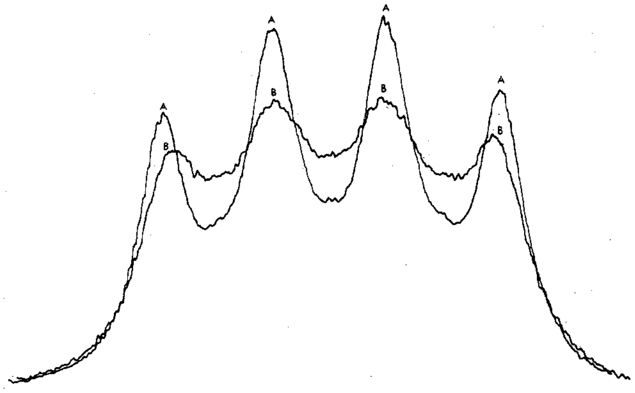


Figure 2. The 32.1-MHz ^{11}B nmr spectrum of the basal borons in isotopically normal B_5H_9 in toluene-d_8: (a) ^1H noise decoupled (J_{BB} = 19.4 Hz); (b) ^1H noise decoupled with irradiation of the apex boron at the appropriate frequency.

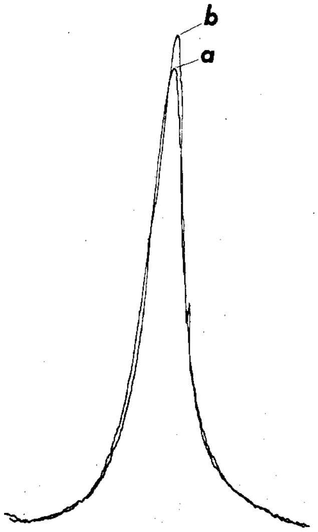
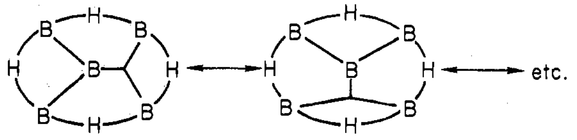


Figure 3. The 32.1-MHz ^{11}B nmr spectrum of B1(3) in $^{11}B_4H_{10}$ in *sym*-$C_2F_4Br_2$: (a) ^1H noise decoupled ($W_{1/2}$ = 8.2 Hz); (b) ^1H noise decoupled with irradiation of B2(4) at the appropriate frequency ($W_{1/2}$ = 6.4 Hz).

Since from previous work it is known that the value of J_{BB} in B_5H_9 is 19.4 Hz,[5] the ^{11}B nmr spectrum of B_5H_9 was observed under triple-resonance conditions (Figure 2). The basal borons are split into a quartet from spin coupling to the apex boron, indicating that the system has enough ^1H decoupling power. When the second radiofrequency is applied, a significant line shape change is observed. It is obvious from Figure 2 that the decoupling system employed can perturb, but not decouple, a 19.4-Hz spin coupling. However, in B_4H_{10} the upper limit of J_{BB} is 1.4 Hz and it is assumed that the present system can decouple, or at least *significantly* reduce, boron–boron spin coupling in B_4H_{10}.

The results from the analogous experiment on $^{11}B_4H_{10}$ are shown in Figure 3. The resonance corresponding to B1(3) was observed while ^1H noise decoupling and irradiating at the B2(4) frequency. There is a noticeable change in line shape in the triple-resonance experiment compared to the double-resonance experiment. This change is due to unresolved coupling to borons 2 and 4. As was mentioned previously, the line width for B1(3) was 8.2 Hz in the double-resonance experiment. Under conditions of triple resonance the B1(3) line width narrowed to 6.4 Hz. In the absence of a detailed line shape analysis the change in line width was equated to $6J_{BB}$, since there are two magnetically equivalent borons coupled to B1(3). This gives rise to an upper limit of 0.3 Hz to J_{BB} in $^{11}B_4H_{10}$. This result is in excellent agreement with the implications of Hopkins, *et al.*,[9] mentioned in the Introduction.

In comparing the upper limits of J_{BB} in B_4H_{10} to the value of J_{BB} in B_5H_9, the question of what is causing the large differences in J_{BB} in these systems arises. The answer, in all probability, lies in the difference in the bonding between the borons of interest in these molecules. In pentaborane(9) the bonding between the apex boron and the basal borons can be described as a linear combination of two-center, two-electron bonds and "closed" three-center, two-electron bonds,[16] *i.e.*



Previous work on boron-carbon coupling constants has shown that when boron is involved in a two-center, two-electron bond the coupling constant varies from 45 to 75 Hz.[17] The bonding scheme postulated for B_5H_9 may be responsible for the reduced value of J_{BB} in this molecule compared to the value of J_{BB} in a pure two-center, two-electron bond. Research designed to measure J_{BB} in a two-center, two-electron bond and a three-center, two-electron BBB bond is currently in progress. It is not presently known if such a three-center bond will cause a reduction in the coupling constant. However, in B_2H_6 and B_4H_{10}, for the borons of interest, there is *no* significant two-center, two-electron bonding character between the two borons. A tentative hypothesis could be brought forward—namely, that the exceptionally small values for J_{BB} in B_2H_6 and B_4H_{10} are due to properties of the BHB bridge bond. Supporting evidence for this hypothesis can be obtained by examination of qualitative molecular orbital theories of nuclear spin coupling constants.[18]

Registry No. B_2H_6, 19287-45-7; B_4H_{10}, 18283-93-7; B_5H_9, 19624-22-7; $^{10}B^{11}BH_6$, 36534-01-7; $^{11}B_2H_6$, 12068-64-3; $^{11}B_4H_{10}$, 34269-30-2.

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