

to the basis set used, but perhaps to the geometry used for the neutral molecule, not indicated in the paper.

It seems that a split-valence basis set produces reliable information on this type of process because it is flexible enough to describe the charge transfer to the proton and lead to accurate values of the protonation energies, even when the electrostatic potential model is used.

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## Sources of Line Width in Boron-11 Nuclear Magnetic Resonance Spectra. Scalar Relaxation and Boron-Boron Coupling in B<sub>4</sub>H<sub>10</sub> and B<sub>5</sub>H<sub>9</sub>

Richard Weiss and Russell N. Grimes\*

Contribution from the Department of Chemistry, University of Virginia, Charlottesville, Virginia 22901. Received July 21, 1977

**Abstract:** The factors responsible for line broadening in <sup>11</sup>B NMR spectra have been investigated by analysis of the spectra of B<sub>4</sub>H<sub>10</sub> and B<sub>5</sub>H<sub>9</sub>. It is demonstrated that unresolved boron-boron spin-spin coupling is not the sole source of extra broadness in <sup>11</sup>B spectra, as scalar relaxation and partially collapsed spin-spin multiplets also play a significant role in broadening <sup>11</sup>B NMR lines. The consequences of these conclusions in spectral simulation and in analysis of boron spectra are discussed.

A characteristic feature of <sup>11</sup>B NMR spectra is the broadness of the peaks, a quality which greatly impairs resolution and is particularly striking when compared to the much narrower lines observed in <sup>1</sup>H and <sup>13</sup>C NMR spectra. Although it might be tempting to attribute these line widths (usually 10-100 Hz) to the short relaxation time of the quadrupolar <sup>11</sup>B nuclei (spin 3/2), this is not a satisfactory explanation since the first measurements of <sup>11</sup>B spin-lattice relaxation times demonstrated that the "natural line width" due to quadrupolar relaxation is generally less than 10 Hz.<sup>1</sup> Consequently, unresolved boron-boron coupling was proposed<sup>1</sup> as the source of the "extra" line width, and this suggestion was shown<sup>2</sup> to be correct for some resonances in selected boron hydrides via a technique which artificially narrows the broad <sup>11</sup>B resonance to reveal the unresolved boron-boron coupling. There are, however, two situations in which line narrowing will not expose the coupling. First, since the experimental lower limit of resolution of the line narrowing technique is about 10 Hz,<sup>2</sup> any coupling smaller than this will probably be unresolvable. The second case arises when, as a result of rapid relaxation of the

coupled nucleus, S, the nucleus under observation, I, "sees" only the average spin state of S and therefore appears as a singlet with no observable coupling (e.g., H-Cl coupling in CHCl<sub>3</sub> is not observed owing to rapid relaxation of <sup>35</sup>Cl and <sup>37</sup>Cl). A further complication is that under certain circumstances, the rapid relaxation of the spin S may act as a spin-spin relaxation mechanism for the spin I, thereby adding broadness to the peak (owing to shortening of T<sub>2</sub>) which may be misinterpreted as unresolved coupling.

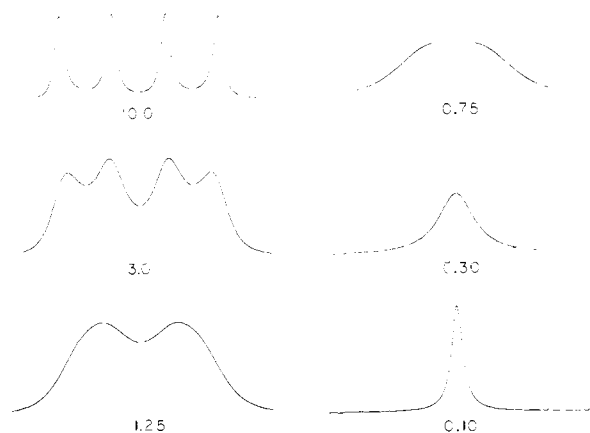
In an attempt to overcome the resolution problem, a recent study<sup>3</sup> employed a line-shape analysis program to extract <sup>11</sup>B-<sup>11</sup>B coupling constants from experimental spectra, such as that of B<sub>4</sub>H<sub>10</sub>, that failed to yield to the line narrowing technique. The program in that work considered only unresolved coupling, neglecting collapsed coupling and scalar contributions to T<sub>2</sub> (and hence line width). The justification offered for this procedure was based on measurements of <sup>10</sup>B spin-lattice and spin-spin relaxation times in <sup>11</sup>B<sub>4</sub>H<sub>10</sub>.

In this paper we examine the origin of line width in the <sup>11</sup>B spectra of B<sub>4</sub>H<sub>10</sub> and B<sub>5</sub>H<sub>9</sub> and demonstrate that (1) scalar

**Table I.** Line Width and Relaxation Data

Sample	Temp, °C	Peak	$T_1$ , ms	Obsd $\nu_{1/2}$ , Hz	"Natural" line width, Hz <sup>b</sup>
<sup>11</sup> B <sub>4</sub> H <sub>10</sub>	-20	B1,3	67.2	8.6	4.7
	-20	B2,4	14.4	26.2	22.1
	-44	B1,3	36.2	11.1	8.8
	-44	B2,4	7.4	42.8	43.0
B <sub>5</sub> H <sub>9</sub> <sup>a</sup>	26.5	B2-5	62.7	Quartet (71.3)	5.1
	26.5	B1	507.0	104	0.6
	-18.5	B2-5	32.8	Quartet (73.1)	9.7
	-18.5	B1	230.0	104	1.4
	-46.5	B2-5	21.8	"Quartet" (75.6)	14.6
	-46.5	B1	141.0	102	2.3
	-62.0	B2-5	14.0	Broad (77.1)	22.7
	-62.0	B1	72.7	101	4.4

<sup>a</sup> Isotopically normal. <sup>b</sup>  $1/\pi T_1$ .



**Figure 1.** Theoretical line shapes for various values of  $2\pi JT_1^S$  when  $S = 3/2$ .

relaxation is a source of line width in <sup>11</sup>B spectra and cannot be neglected, (2) partial or complete collapse of B-B multiplets is a common phenomenon and must also be considered as a possible contribution to line width, and (3) complications due to the presence of <sup>10</sup>B in isotopically normal samples are also possible and hence <sup>11</sup>B-enriched samples are necessary for an accurate analysis. An important general consequence of these results is that the procedure of extracting boron-boron coupling constants and/or relaxation times by matching experimental and calculated spectra is likely to be inaccurate unless *all* sources of line width are included in the analysis. As an aid to the reader in following the discussion we first outline the essential theory.

**Multiplet Collapse.**<sup>4-12</sup> The NMR line shape of a nucleus I spin coupled to a quadrupolar nucleus S with spin  $S \geq 1$  will appear as a multiple of  $2S + 1$  lines of equal intensity, provided that the spin-lattice relaxation time  $T_1$  of the quadrupolar nucleus S is long compared to the reciprocal of the coupling constant  $J$  in rad s<sup>-1</sup>, i.e.,  $2\pi JT_1^S \gg 1$ . When the relaxation time of S is much shorter than  $1/2\pi J$  ( $2\pi JT_1^S \ll 1$ ), the NMR spectrum of I will appear as a sharp singlet, as the nucleus I "sees" only the average spin state of S (e.g., CHCl<sub>3</sub> where I = H and S = Cl). The intermediate case is much more complex and has been treated in detail<sup>5-7</sup> for many situations, including that in which the spin  $S$  is  $3/2$ . The line shapes for some intermediate values of  $2\pi JT_1^S$  are given in Figure 1 and were calculated using eq 11 of ref 5. The important points of interest are (1) the sequence of collapse (quartet → "doublet of doublets" → "doublet" → broad "singlet" → sharp singlet); (2) the general narrowing of the resonance (the total quartet is broader than the doublet of doublets, which in turn is broader than the doublet, and so forth); (3) the value of the product  $2\pi JT_1^S$  vs. the line shape of the resonance of nucleus I.

All three of these features have been experimentally verified a number of times<sup>5,13-16</sup> and thus the theory is a good one upon which conclusions may be based with confidence.

**Scalar Relaxation.**<sup>17,18</sup> As indicated above, if the relaxation time of the nucleus S is short compared to  $1/2\pi J$  ( $2\pi JT_1^S < 1$ ), then the line shape of the resonance of nucleus I will be a single line. The rapid changes in the spin state of S produce a fluctuating local magnetic field which may act as a relaxation mechanism with the contributions to  $T_1^I$  and  $T_2^I$  given in eq 1 and 2,

$$R_1^I = \frac{2}{3}A^2S(S+1) \left\{ \frac{\tau_s}{1 + (\omega_1 - \omega_S)^2\tau_s^2} \right\} \quad (1)$$

$$R_2^I = \frac{1}{3}A^2S(S+1) \left\{ \tau_s + \frac{\tau_s}{1 + (\omega_1 - \omega_S)^2\tau_s^2} \right\} \quad (2)$$

where  $A = 2\pi J$ , the coupling constant in rad s<sup>-1</sup>,  $S$  = the nuclear spin of the rapidly relaxing nucleus S,  $\tau_s = T_1$  of the nucleus S,  $\omega_1 - \omega_S$  = the difference in resonance frequency between the nucleus I and nucleus S, and  $T_1^I$  and  $T_2^I$  are defined by summing all contributions to  $T_1^I$  and  $T_2^I$ :  $1/T_1^I = R_1^I$  (quadrupolar) +  $R_1^I$  (scalar) +  $R_1^I$  (dipole-dipole) + . . . , and  $1/T_2^I = R_2^I$  (quadrupolar) +  $R_2^I$  (scalar) +  $R_2^I$  (dipole-dipole) + . . .

## Results and Discussion

**B<sub>4</sub>H<sub>10</sub>.** Under conditions of complete <sup>1</sup>H decoupling, the <sup>11</sup>B NMR spectrum of B<sub>4</sub>H<sub>10</sub> consists of two singlets of equal area at -41 and -6.7 ppm relative to BF<sub>3</sub>·O(C<sub>2</sub>H<sub>5</sub>)<sub>2</sub>, corresponding to B1,3 and B2,4 respectively (chemical shifts are given with negative sign indicating shift to higher shielding). Early studies<sup>2</sup> were unable to extract any boron-boron coupling constants via the line narrowing technique. A more recent work reported<sup>3</sup> a <sup>11</sup>B-<sup>11</sup>B coupling constant of less than 25 Hz between B1 and B3, and 1.0 Hz between B1 and B2 based on line shape analysis, *neglecting scalar contributions to T<sub>2</sub>*. Another study reported<sup>19</sup> a coupling constant of 20.4 Hz between B1 and B3, based on an estimate of the <sup>11</sup>B-<sup>10</sup>B coupling constant ( $J_{11B10B} = (\gamma_{11B}/\gamma_{10B})J_{11B10B}$ ). We now examine the spectrum and the spin system in detail. In order to remove contributions to the line width from <sup>10</sup>B nuclei and thus simplify the problem, we first discuss the spectrum of a <sup>11</sup>B-enriched sample of B<sub>4</sub>H<sub>10</sub>. The line width and relaxation data for a <sup>11</sup>B-enriched sample of tetraborane (10) at -20 and -44 °C are given in Table I.

**B1,3 Resonance.** The <sup>11</sup>B spin-lattice relaxation time and line width associated with this resonance at -20 °C are 67.2 ms and 8.6 Hz, respectively. The expected natural line width is 4.74 Hz, much less than that observed. This extra broadness *cannot* be due to unresolved B1-B2,4 spin-spin coupling, as the product  $2\pi JT_1^S = 0.09$  (assuming, for the moment, that the reported<sup>3</sup> value of  $J_{B1-B2,4}$  is correct), and this multiplet

is therefore *completely collapsed*. Thus, any resemblance the reported<sup>3</sup> value of  $J_{B1-B2,4}$  might have to the actual value is fortuitous, since it was calculated under the assumption that the multiplet is present. The only other possible source of the "extra" line width is scalar contribution to  $T_2$  from both B2 and B4 (scalar contributions from B3 are not a factor since that nucleus is relaxing more slowly than the reciprocal of the coupling constant). Since we know the  $T_1$  ( $\tau_s$ ) of B2 and B4, we can calculate a new coupling constant from the observed line width based on scalar contributions to  $T_2$  (neglecting inhomogeneity, which should be relatively unimportant for lines this broad) by eq 3,

$$\begin{aligned} \pi\nu_{1/2} = 27.02 = 1/T_2^* &= \frac{1}{T_2} = \frac{1}{T_2} \text{ (quadrupolar)} \\ &+ 2 \frac{1}{T_2} \text{ (scalar)} = \frac{1}{T_1} (B1(3)) \\ &+ 2 \left[ \frac{A^2}{3} S(S+1) \left\{ \tau_s + \frac{\tau_s}{1 + (\omega_1 - \omega_S)^2 \tau_s^2} \right\} \right] \end{aligned} \quad (3)$$

which when solved for the coupling constant yields an upper limit of  $A^2 = 337$  or  $J = 2.9$  Hz, a value which is a factor of 3 larger than that previously reported.<sup>3</sup> Of course, we must now recalculate the product  $2\pi JT_1^s$  to ensure that the multiplet is collapsed; since  $2\pi JT_1^s = 0.27$ , the resonance should be a singlet and our analysis is self-consistent. However, it is important that this interpretation be tested further, as a reasonable alternative explanation is that the coupling constant is even larger than 2.9 Hz and that the broadness is in fact caused by unresolved coupling. A similar analysis at a lower temperature should resolve the dilemma, for if our analysis is correct, we should arrive at the same coupling constant; if not, a much larger value will be obtained. Accordingly, the data at  $-44$  °C were analogously treated and a value of 3.1 Hz was obtained for  $J_{B1-B2,4}$ , confirming the analysis.

**B2,4 Resonance.** The <sup>11</sup>B spin-lattice relaxation time and line width associated with this resonance at  $-20$  °C are 14.4 ms and 26.2 Hz, respectively. The expected natural line width is 22.1 Hz, less than that observed. In this case, the extra broadness *must* be due to unresolved but *partially collapsed* coupling, since  $2\pi JT_1^s = 1.27$ , and therefore there is no significant scalar contribution to  $T_2$ . Figure 1 shows the extent of multiplet collapse expected from theory.

At  $-44$  °C, the product  $2\pi T_1 J$  is 0.68, and the coupling has evidently collapsed. However, the relaxation of B1,3 is apparently not yet fast enough to provide an efficient scalar spin-spin relaxation mechanism, as the observed line width of 43 Hz is identical with the natural line width.

It is clear that the extra broadness in the two resonances in the <sup>11</sup>B NMR spectrum of B<sub>4</sub>H<sub>10</sub> cannot be wholly attributed to unresolved coupling, but includes scalar contributions to  $T_2$  and/or incomplete collapse of the B-B multiplet. In the B1,3 resonance the line width is due to scalar contributions to  $T_2$ , while in the B2,4 signal, incomplete collapse of the multiplet is the major source of broadness. These conclusions are in agreement with the fact that Schaeffer et al. were unable to detect any B-B coupling in the line-narrowed <sup>11</sup>B spectrum of tetraborane (10).<sup>2</sup> However, we must disagree with the statement that "... it has been rigorously shown that  $T_1 = T_2$ " for the <sup>11</sup>B resonances in B<sub>4</sub>H<sub>10</sub>.<sup>3</sup> In fact, no  $T_2$  experiments were conducted on the <sup>11</sup>B signals in B<sub>4</sub>H<sub>10</sub>; the statement quoted is based instead upon the fact that in the <sup>10</sup>B spectrum of <sup>11</sup>B<sub>4</sub>H<sub>10</sub>,  $T_1$  and  $T_2$  were within 4.6% of each other ( $T_2 < T_1$ ) and 5% was the stated experimental uncertainty. An observation is in order: since  $J_{11B11B} = 2.99J_{11B10B}$ , the scalar contributions to  $T_2$  from <sup>11</sup>B-<sup>11</sup>B coupling will be 8.94 times larger than that due to <sup>11</sup>B-<sup>10</sup>B, and therefore the fact that  $T_1$  and  $T_2$  are similar in the <sup>10</sup>B spectrum does not rigorously show

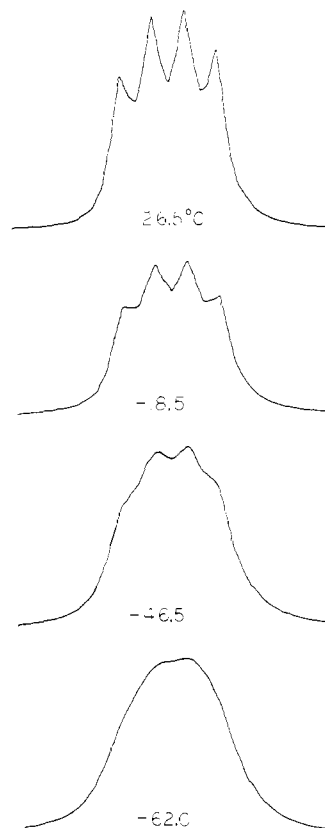


Figure 2. Temperature dependence of the area 4 basal resonance in B<sub>5</sub>H<sub>9</sub>.

that there are no scalar contributions in the <sup>11</sup>B case, as demonstrated by the experiments described above.<sup>20</sup>

**Temperature Dependence of the <sup>11</sup>B NMR Spectrum of B<sub>5</sub>H<sub>9</sub>.** The room temperature <sup>11</sup>B NMR spectrum of an isotopically normal sample of B<sub>5</sub>H<sub>9</sub>, recorded under conditions of complete <sup>1</sup>H decoupling, contains a low-field quartet of area 4 and a high-field singlet of area 1. The quartet arises from the four basal boron nuclei which are coupled to the apex boron nucleus with an observed coupling constant of 19.5 Hz, in excellent agreement with the reported value of 19.4 Hz.<sup>21</sup> The temperature dependence of the area 4 basal peak, shown in Figure 2, has previously been observed and attributed to "thermal decoupling", i.e., collapse of the multiplet due to a decrease in the spin-lattice relaxation time of the apex boron nucleus (S), caused by changes in the correlation time ( $\tau_c$ ) with temperature.<sup>22</sup> This conclusion requires that  $2\pi JT_1^s \approx 1$  at the "coalescence temperature",  $-62$  °C.

However, careful examination of the spectra reveals that in contradiction to theory, the intermediate doublet of doublets, doublet, and subsequent narrowing to a singlet has not been observed; in fact, the "collapsed singlet" is actually broader than the initial quartet (77 vs. 72 Hz, respectively)! In order to ascertain the cause of this seemingly anomalous behavior, we have measured the  $T_1$ 's of both the apex (S) and basal (I) resonances as a function of temperature (Table I) and computed  $2\pi JT_1^s$  at each temperature given. These values are listed in Table II. Examination of the data clearly reveals that

Table II. Values of  $2\pi JT_1^s$  vs. Temperature for Basal <sup>11</sup>B Resonance in B<sub>5</sub>H<sub>9</sub>

Temp, °C	$2\pi JT_1^s$
26.5	61.8
-18.5	28.0
-46.5	17.2
-62.0	8.9

Table III. Line Width and Relaxation Data for  $^{10}\text{B}^{11}\text{B}_4\text{H}_9$ 

Nucleus	Temp, °C	$T_1$ , ms	Coupling	$J$ , Hz	Ref
$^{11}\text{B}1$	26.5	507	$^{11}\text{B}1-^{11}\text{B}2$	19.4	21,25
$^{11}\text{B}2$	26.5	62.7	$^{11}\text{B}1-^{10}\text{B}5$	6.5	19,26
			$^{11}\text{B}2-^{11}\text{B}3$	0	3
			$^{11}\text{B}2-^{11}\text{B}4$	5.0	3
			$^{11}\text{B}2-^{10}\text{B}5$	0	3
$^{11}\text{B}3$	26.5	62.7	$^{11}\text{B}3-^{11}\text{B}4$	0	3
			$^{11}\text{B}3-^{10}\text{B}5$	1.7	26
			$^{11}\text{B}4-^{10}\text{B}5$	0	3
$^{10}\text{B}5$	26.5	95.9			26
$^{11}\text{B}1$	-62.0	72.7	<i>a</i>	<i>a</i>	25
$^{11}\text{B}2-4$	-62.0	14.0	<i>a</i>	<i>a</i>	25
$^{10}\text{B}5$	-62.0	21.4	<i>a</i>	<i>a</i>	26

<sup>a</sup> Same as given for 26.5 °C spectrum.

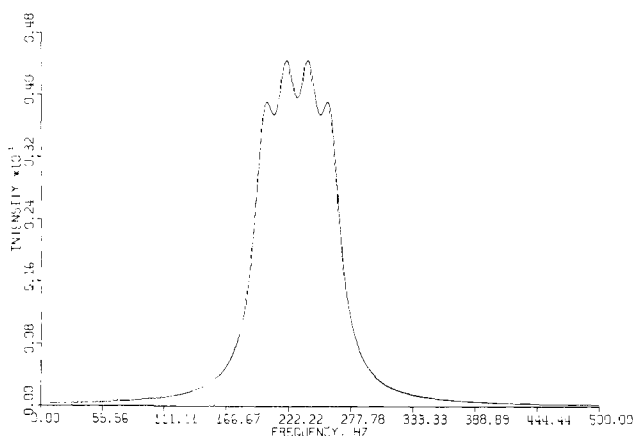


Figure 3. Simulation of basal resonance in  $\text{B}_5\text{H}_9$  at  $-62.0$  °C using the natural line width.

the temperature dependence of the basal resonance is *not* due to thermal decoupling, since at the “coalescence temperature”  $2\pi JT_1^s = 8.9$  and the multiplet should be completely resolved. What in fact is occurring is that each component of the quartet has remained in its original position and simply become broader, obscuring the coupling. Had we accepted the explanation of thermal decoupling on the basis of line shape, assumed  $2\pi JT_1^s = 1$ , and subsequently calculated a value of  $T_1^s$  based on a value of 19.4 Hz for  $J$ , the result would have been inaccurate by more than an order of magnitude. This result clearly demonstrates the need for *all* the spectral information and thorough analysis before calculating spectral parameters on the basis of line shape.

The question which now remains is the source of the broadness of each component of the quartet as the temperature is lowered. The most obvious answer is that as the temperature decreases and changes the correlation time, the spin-lattice relaxation times of *both* the apex and basal resonances decrease, and that therefore the increasing broadness is simply due to an increase in the natural line width. While this phenomenon is certainly a factor in obscuring the coupling at low temperature, it is easily seen that it is not the sole cause, for if one tries to simulate the spectrum at  $-62$  °C by adding four signals of equal intensity with a half-width defined by the observed relaxation time, the multiplet is still observable (Figure 3). In light of the conclusions from our studies of  $\text{B}_4\text{H}_{10}$ , the source of the extra broadness cannot be definitely identified without extensive variable-temperature studies of an isotopically enriched sample of  $\text{B}_5\text{H}_9$ ; however, a good guess may be made from the existing evidence.

Since any unresolved coupling, for example, coupling with a  $^{10}\text{B}$  nucleus in the base, would tend to coalesce with decreasing temperature, such an effect can be ruled out as the

source of broadening in the low-temperature spectra. Scalar relaxation mechanisms contributing to  $T_2$ , then, are the most reasonable explanation, since as the temperature decreases and spin-lattice relaxation times shorten, it is very possible that a relaxation time becomes fast enough to act as a relaxation mechanism for a boron nucleus in the base. Consider, for example, a  $\text{B}_5\text{H}_9$  molecule which consists of  $^{11}\text{B}$  in positions 1-4 and  $^{10}\text{B}$  in position 5. The spectral parameters for such a molecule at 26.5 and  $-62.0$  °C are given in Table III. A quick calculation shows that the coupling between  $^{10}\text{B}5$  and  $^{11}\text{B}3$  is already collapsed at 26.5 °C, as  $2\pi JT_1^s = 1.02$ . Thus, as the temperature decreases and the  $T_1$  of  $^{10}\text{B}5$  shortens, it may act as a spin-spin relaxation mechanism for  $^{11}\text{B}3$ , since  $2\pi JT_1^s$  will now be less than unity. At  $-62$  °C,  $2\pi JT_1^s = 0.229$  and the scalar contribution to  $T_2$  is

$$\begin{aligned} 1/T_2(\text{scalar}) &= \frac{1}{3}(1.7 \times \pi \times 2)^2(3)(4)(21.4 \times 10^{-3}) \\ &= 9.78 \end{aligned}$$

which, when combined with the quadrupolar contribution to  $T_2$ , yields a line width of 25.8 Hz for each component of the quartet, or 3.1 Hz broader than the “natural” line width of each component.<sup>27</sup> Again, confirmation of this suggestion must await extensive studies of isotopically enriched  $\text{B}_5\text{H}_9$ , but it does seem to be a plausible explanation of the experimental facts.

## Conclusions

The major finding of this work is that the broadness of resonance lines in  $^{11}\text{B}$  NMR spectra cannot be wholly attributed to unresolved  $^{11}\text{B}-^{11}\text{B}$  spin-spin coupling, since partially collapsed multiplets and scalar contributions to  $T_2$  also affect line width significantly. An important extension of this observation is that in general, line shape and line width analysis will yield erroneous results unless care is taken to obtain *all* the spectral parameters and to check the results for self-consistency; e.g., one cannot attribute line width to unresolved coupling when  $2\pi JT_1^s < 1$ . Thus, in order to be considered thorough, a comprehensive study of line shape in a  $^{11}\text{B}$  spectrum must include the entire battery of NMR experiments—line narrowing, variable temperature studies, relaxation times, and multiple resonance—separately and in conjunction with both isotopically normal and enriched samples. In short, the spin system is extremely complicated and the resulting spectrum must necessarily be complex.

## Experimental Section

Standard high vacuum techniques were employed where necessary throughout the course of this study. Isotopically normal  $\text{B}_5\text{H}_9$  was obtained from laboratory stock and observed as a 20% solution in toluene- $d_8$ . Isotopically enriched  $^{11}\text{B}_4\text{H}_{10}$  was obtained by the gas-phase photolysis of  $^{11}\text{B}_2\text{H}_6$  in a closed circulating system containing a trap maintained at  $-78$  °C and a hot zone at 120 °C. Isotopically

enriched  $^{11}B_2H_6$  was obtained by the method of Shapiro<sup>23</sup> from  $^{11}BF_3$  and  $LiAlH_4$ . Boron-11 enriched  $^{11}BF_3$  was prepared by the reaction of elemental fluorine with boron-11 enriched amorphous boron (97.15%  $^{11}B$ , Oak Ridge National Laboratory) at 200 °C for 24 h in a stainless steel can, fitted with a Monel stopcock for attachment to the vacuum system. Owing to scarcity of material, the  $^{11}B_4H_{10}$  sample was run as a 10% solution in toluene- $d_6$ .

$^{11}B$  NMR studies were performed at 32.1 MHz on a JEOL PFT-100P/EC 100 FT NMR spectrometer fitted with standard variable temperature equipment.  $T_1$  values were measured accurately ( $\pm 10\%$ ) with the  $180^\circ - \tau - 90^\circ$  pulse sequence.<sup>24</sup> The temperature of each run was determined both before and after each  $T_1$  determination and found to be consistent to within 1 °C. The width of the  $90^\circ$  pulse was typically 15–20  $\mu s$ . For all spectra, the free induction decays contained 8K data points and improvement of signal to noise was achieved by a combination of phase shifting techniques and coherent addition of successive free induction decays. No exponential filter was employed. Typically, 15–20 values of  $\tau$  were used in the  $T_1$  measurements. Reduction of the data was accomplished by an external least-squares fit program utilizing a CDC 6400 computer.

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## References and Notes

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- (20) A referee has raised the question of at what point scalar coupling begins to be important. The answer is not unequivocally given by theory, although it has been implied<sup>17,18</sup> that  $T_1^S$  must be significantly shorter than  $1/A$  in order for scalar relaxation to be a major process. It is clear that in order for scalar relaxation of the second kind<sup>17</sup> to be possible,  $2\pi J T_1^S$  must be less than unity, since the coupling is then collapsed; as to when it becomes important, we can only observe that a sudden "turning on" of a scalar relaxation mechanism is unlikely. A more reasonable expectation is a gradual increase in the importance of the scalar mechanism, analogous to the gradual tapering off of the mechanism as predicted by theory (see eq 2 above). The data in Table I suggest that when  $2\pi J T_1^S = 0.68$  (as is the case at  $-44$  °C for the B<sub>2,4</sub> resonance), scalar relaxation makes no significant contribution to the line width; furthermore, it appears that when  $2\pi J T_1^S = 0.27$  (as at  $-20$  °C), the scalar mechanism has reached its full value as predicted by eq 2. In essence, the intermediate case where either mechanism may be operative is a complex situation whose resolution is beyond the scope of this article. Thus we concentrate on the clear-cut situations in which the existence of scalar coupling can be unambiguously demonstrated.
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- (27) For the reasons given in footnote 20, we shall not attempt to deal with the room temperature spectrum of  $B_5H_9$ , which presents an intermediate situation involving possible contributions for scalar relaxation and/or collapsed coupling. We will, however, comment on the possibility of a "slow" scalar relaxation effect contributing to the line width of each component in the quartet (a referee's suggestion). Such an effect should be important only when  $T_1^S < T_1^I$ ; this is not the case in  $B_5H_9$ , where the S (apex) nucleus has a  $T_1$  about an order of magnitude larger than the I (basal) nuclei. Hence we regard such a phenomenon as unlikely in this case.