Nuclear Magnetic Resonance Relaxation in Complex Spin Systems. Proton and Boron-11 Spin–Lattice Relaxation Studies of Carboranes and Metallocarboranes[1]

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Abstract: The nuclear magnetic resonance relaxation behavior of complex spin systems containing both quadrupolar and spin ½ nuclei was investigated. Direct measurements of spin-lattice relaxation times for both ^{11}B and ^{1}H nuclei in carboranes and metallocarboranes were obtained and found to be useful in assigning spectra and elucidating structures. Boron-11 relaxation times were determined to be a function of both field gradient and molecular motion. Unexpectedly, T_1 values of protons bound to cage carbon atoms were found to be strongly affected by decoupling of ^{11}B nuclei, indicating a heteronuclear cross-relaxation effect whose origin was demonstrated to be scalar.

The proliferation of commercially available Fourier transform nuclear magnetic resonance (FT NMR) spectrometers has greatly broadened the scope and power of the NMR technique as a structural tool, particularly for relatively complex molecules such as the polyhedral boron cage compounds. In this laboratory, recent efforts to exploit FT NMR structural capabilities have concentrated in two areas: the study and measurement of long-range proton-proton coupling by triple resonance NMR, presented elsewhere,[2] and the correlation of ^{11}B and ^{1}H spin-lattice relaxation times with molecular structure. The latter investigation is the concern of this paper.

Although spin-lattice and spin-spin relaxation times of ^{1}H, ^{13}C, and other nuclei have found wide use in structural assignment,[3] relaxation effects are particularly important in molecules containing quadrupolar nuclei such as ^{11}B, often obscuring couplings and producing broad lines. In some cases, modulation of the spin-spin coupling by the rapid relaxation of the quadrupolar nucleus may act as a relaxation mechanism for a spin ½ nucleus such as ^{1}H or ^{19}F. This behavior has been treated[4-20] both theoretically and experimentally by many authors and for many sets of coupled nuclei, including ^{14}N–^{1}H, ^{11}B–^{1}H, ^{11}B–^{19}F, ^{10}B–^{1}H, and ^{10}B–^{19}F. The experimental exploitation of this phenomenon, sometimes labeled "thermal decoupling", has been used, together with relaxation theory, to calculate T_1 values for quadrupolar nuclei and/or spin coupling constants.[4,7]

One difficulty with this technique is that there are usually too many variables to unequivocally characterize the interaction. In an attempt to reduce the number of unknowns, some authors[7,9] have used the line width of the resonance of the quadrupolar nucleus as a measure of T_1. While this approach is valid for an isolated quadrupole, it cannot be used for a molecule containing more than one such nucleus since, due to quadrupolar spin-spin coupling, the line width in this case is *not* entirely determined by relaxation effects. The boron hydrides furnish a good example of this effect, in that the ^{11}B line widths and relaxation times of B_2H_6 and B_5H_9 do not correlate. Allerhand, Odom, and Moll[18] suggested that this was due to unresolved ^{11}B–^{11}B spin-spin coupling, a hypothesis which has been supported recently by an application[19,20] of line-narrowing techniques to the ^{11}B spectra.

For molecules containing spin-coupled quadrupolar nuclei, a direct measurement of the spin-lattice relaxation time of the quadrupolar nucleus is necessary in order to thoroughly understand the behavior of the spin system. In this work, multiple resonance and relaxation techniques were used to probe the systematics of a complex system of quadrupolar and spin ½ nuclei. Direct relaxation time measurements of both ^{11}B and ^{1}H nuclei were conducted under a variety of conditions in order to identify the salient relaxation mechanisms involved in spin systems of this type, the ultimate goal being structural correlation. Although motional differences prevented direct comparison of T_1 values in different molecules, structural correlations with both ^{11}B and ^{1}H relaxation times were possible within individual samples. The quadrupolar T_1 values of ^{11}B nuclei were found to be dependent upon local symmetry, reflecting the dominance of the quadrupolar interaction as a relaxation mechanism. Quite unexpectedly, *relaxation studies of ^{1}H nuclei revealed a significant heteronuclear cross-relaxation mechanism between ^{11}B and ^{1}H.* This interaction was found to be scalar in origin and very useful in interpreting spectra.

Description of the Spin System, Spectral Features, and General Theory

The compounds under investigation in this study—carboranes and metallocarboranes—are stable, diamagnetic, polyhedral cage systems whose structures and ^{11}B chemical shifts are presented in Figure 1 and Table I, respectively. In each instance, the primary concern was the central metallocarborane or carborane cage exclusive of exo-polyhedral ligands such as C_5H_5. These cages contain many dissimilar nuclei including ^{11}B ($S = \frac{3}{2}$), ^{10}B ($S = 3$), ^{59}Co ($S = \frac{7}{2}$), ^{1}H ($S = \frac{1}{2}$), and ^{13}C ($S = \frac{1}{2}$), all of which are dipolar and/or scalar coupled to each other as demonstrated both in this work and in recent multiple resonance studies.[2] However, this investigation was restricted to ^{11}B (80% abundance) and ^{1}H.

The ^{11}B spectra contain doublets arising from ^{11}B–^{1}H spin coupling between directly bonded nuclei. Spin-spin ^{11}B–^{11}B or ^{11}B–^{59}Co coupling is unobservable, as is long-range ^{11}B–^{1}H coupling, but line widths (50–200 Hz) are usually too broad to be attributed to relaxation alone. In the ^{1}H spectra both resolved and unresolved ^{11}B–^{1}H couplings are observed, as are ^{1}H–^{1}H couplings. Terminal protons attached to boron-11 (spin $\frac{3}{2}$) show the expected quartet, while protons linked to carbon exhibit signals broadened by long-range ^{1}H–^{11}B coupling.

Since calculations for spin systems of this size are themselves very complex, we will assume, as a first approximation, that each molecule in this study may be described by a number of two-spin subsystems which, when combined, generate the characteristics of the entire system. The behavior of the longitudinal magnetization vectors of a two-spin system of coupled nuclei may be represented[21] by a set of coupled differential

Table I. ^{11}B NMR Chemical Shifts Relative to $BF_3 \cdot O(C_2H_5)_2$[a]

Compd	^{11}B chemical shift[b] (relative intensity)
$2,4\text{-}C_2B_5H_7$, I[c]	−12.5 (1), −9.2 (2), 16.4 (2)
$2,3\text{-}C_2B_4H_8$, II[d]	1.9 (3), 53.0 (1)
$1,2,3\text{-}(\eta^5\text{-}C_5H_5)CoC_2B_3H_7$, III	−2.7 (2), −2.0 (1)
$2\text{-}CH_3\text{-}1,2,3\text{-}(\eta^5\text{-}C_5H_5)CoC_2B_4H_5$, IV	−13.1 (1), −8.0 (1), −3.0 (2)
$1,2,4\text{-}(\eta^5\text{-}C_5H_5)CoC_2B_4H_6$, V	−6.7 (3), −1.4 (1)
$1,4,5\text{-}(\eta^5\text{-}C_5H_5)CoC_2B_6H_8$, VI	−66.7 (1), −4.1 (1), 3.7 (1), 9.6 (1), 16.4 (1), 21.0 (1)
$1,7,2,3\text{-}(\eta^5\text{-}C_5H_5)_2Co_2C_2B_3H_5$, VII	−53.3 (1), −5.7 (2)
$2\text{-}CH_3\text{-}1,7,2,3\text{-}(\eta^5\text{-}C_5H_5)_2Co_2C_2B_3H_4$, VIII	−54.7 (1), −7.5 (2)
$1,7,2,4\text{-}(\eta^5\text{-}C_5H_5)_2Co_2C_2B_3H_5$, IX	−21.2 (2), −12.0 (1)
$1,2,3,5\text{-}(\eta^5\text{-}C_5H_5)_2Co_2C_2B_3H_5$, X	−48.7 (1), −8.0 (2)
$1,2,4,5\text{-}(\eta^5\text{-}C_5H_5)_2Co_2C_2B_3H_5$, XI	−44.7 (2), −11.4 (1)
$1,7,5,6\text{-}(\eta^5\text{-}C_5H_5)_2Co_2C_2B_5H_7$, XII	−80.3 (1), 2.9 (2), 12.3 (2)
$1,8,5,6\text{-}(\eta^5\text{-}C_5H_5)_2Co_2C_2B_5H_7$, XIII	−116.3 (1), −4.0 (2), 11.6 (2)

[a] In $CDCl_3$ except where otherwise indicated. [b] Positive signs denote shifts to higher field. [c] Acetone-d_6 solution. [d] Benzene-d_6 solution.

Table II. Boron-11 Spin-Lattice Relaxation Times for $2,4\text{-}C_2B_5H_7$ in CD_3COCD_3

^{11}B signal chem shift[a] (rel area)	Assignment	Nondecoupled T_1, ms	Decoupled T_1, ms	% difference
−12.5 (1)	B(3)	38.5	38.8	1
−9.2 (2)	B(5,6)	50.9	45.8	10
16.4 (2)	B(1,7)	69.1	67.6	2

[a] Parts per million relative to $BF_3 \cdot O(C_2H_5)_2$.

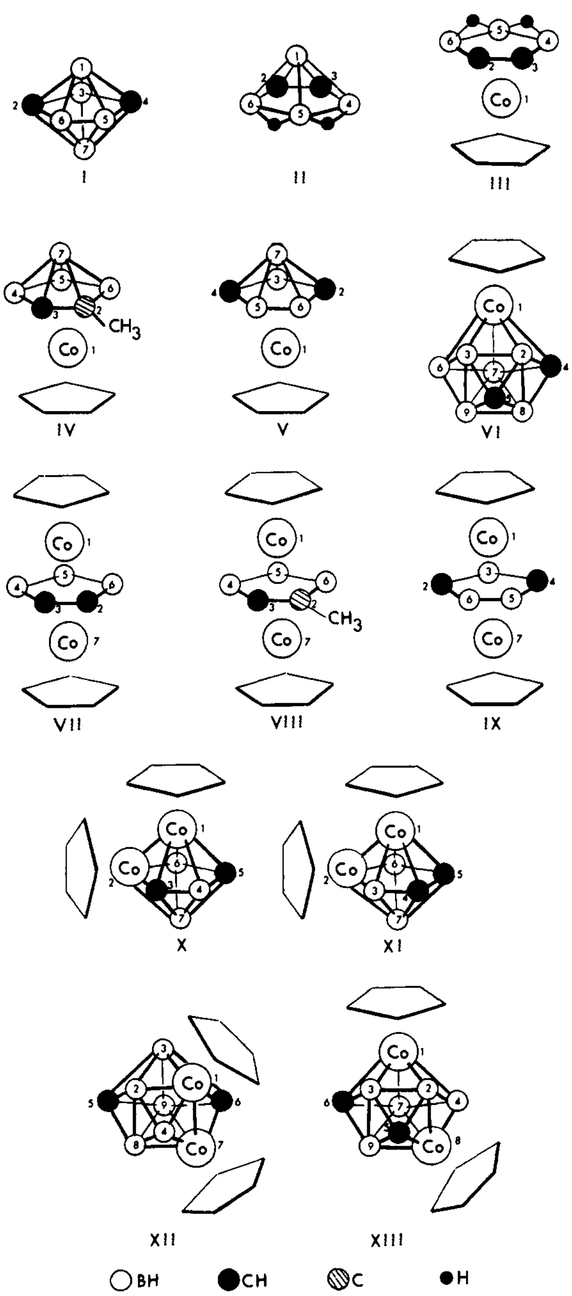

Figure 1. Structures and numbering systems of carboranes and metallocarboranes studied in this work. Connecting lines depict geometry only and have no bonding significance.

equations first given by Solomon.[22] These relations predict that the relaxation of either nucleus is in general *not* describable by a single exponential, but rather by a sum of exponentials due to cross-relaxation.[23-26] A semilog plot of the experimental data, however, often fails to reveal the nonlinearity because of experimental error.[23] Saturation of either spin removes these cross-relaxation mechanisms, and the relaxation of the unsaturated spin reverts to a single exponential,[27] although the intensity of the resonance may change due to the nuclear Overhauser effect.[28] Consequently, in studying the relaxation behavior of complex spin systems, it is important to examine the system under conditions of multiple resonance in order to determine the extent of cross-relaxation and/or nuclear Overhauser effect (NOE). For ^{13}C, decoupling all protons in the molecule may increase the intensity of a ^{13}C resonance by as much as a factor of 3,[28] but the observed relaxation time does not usually change significantly.[29]

Theory, Results, and Discussion

Boron-11 Spin-Lattice Relaxation Times. Since for nuclei with spins greater than ½ the magnitude of the quadrupolar interaction is generally much larger than internuclear couplings, there should be no effective cross-relaxation mechanisms or Overhauser effects to complicate the relaxation. This expectation was demonstrated experimentally, as T_1 values obtained while noise decoupling all protons in the sample were usually identical with those obtained in the absence of decoupling. Differences were in all cases within experimental accuracy (estimated at 10%) and of a random nature. Table II gives the T_1 values for both decoupled and nondecoupled spectra for $2,4\text{-}C_2B_5H_7$ (Figure 1, compound I).

Thus, for the ^{11}B resonances the observed time constant will be an accurate estimate of T_1, uncomplicated by cross-relaxation. For nuclei with spins greater than ½, the dominant contribution to T_1 will be the quadrupole interaction, caused by modulation of the tensor coupling I·A·I between the nuclear spin and the electric field gradient at the nucleus by the reorientation of the molecule in solution:[21,30]

$$\frac{1}{T_1} = \frac{1}{T_2} = \frac{3}{40}\left(\frac{2I+3}{I^2(2I-1)}\right)\left(\frac{e^2Qq}{\hbar}\right)^2 \tau_c$$

where $e^2Qq/\hbar$ is the nuclear quadrupole coupling constant, dependent on the field gradient, I is the nuclear spin of the quadrupole nucleus, and τ_c is the molecular correlation time,

Table III. ^{11}B Spin-Lattice Relaxation Times

Compd	δ, ppm[a]	Relative area	Assignment[b]	T_1, ms
I	−12.5	1	B(3)	38.6
	−9.2	2	B(5,6)	47.7
	16.4	2	B(1,7)	68.3
II	1.9[c]	3[c]	B(4,5,6)	47.0
	53.0	1	B(1)	93.9
III	−2.7	2	B(4,6)	13.9
	−2.0	1	B(5)	16.0
IV	−13.1	1	B(5) or B(7)	6.60
	−8.0	1	B(7) or B(5)	5.83
	−3.0	2	B(4,6)	5.91
V	−6.7[c]	3[c]	B(3,5,6)	9.70
	−1.4	1	B(7)	14.7
VI	−66.7	1	see text	16.6
	−4.1	1		12.1
	3.7	1		14.5
	9.6	1		14.4
	16.4	1		16.8
	21.0	1		11.8
VII	−53.3	1	B(5)	4.47
	−5.7	2	B(4,6)	3.19
IX	−21.2	2	B(5,6)	3.61
	−12.0	1	B(3)	2.86
X	−48.7	1	B(6)	5.60
	−8.0[c]	2[c]	B(3,7)	9.08
XI	−44.7	2	B(3,6)	6.39
	−11.4	1	B(7)	6.64
XII	−80.3	1	B(4)	7.01
	2.9	2	B(2,8) or B(3,9)	8.00
	12.3	2	B(3,9) or B(2,8)	9.72

[a] Relative to $BF_3 \cdot O(C_2H_5)_2 = 0$. [b] See Figure 1. [c] Overlapped nonequivalent ^{11}B signals.

describing molecular reorientation. Hence, alterations in the spin-lattice relaxation time may be attributed to changes in the nuclear quadrupole coupling constant and/or the correlation time.

Boron-11 spin-lattice relaxation times determined for a number of carboranes and metallocarboranes are presented in Table III. Examination of the data reveals some interesting systematics. First, the carboranes examined (compounds I and II) have longer T_1 values than analogous monometallocarboranes, which in turn have longer T_1 values than the corresponding dimetallocarboranes. This trend is exemplified by the B(3) and B(5,6) T_1 values in 2,4-$C_2B_5H_7$ (I), 1,2,4-(η^5-C_5H_5)$CoC_2B_4H_6$ (V), and 1,7,2,4-(η^5-C_5H_5)$_2Co_2C_2B_3H_5$ (IX). It will be seen that the T_1 values of the B(3) and B(5,6) resonances are progressively shorter as (η^5-C_5H_5)Co units are introduced into the molecule, formally replacing BH units. Similar progression is shown by the series 2,3-$C_2B_4H_8$ (II), 1,2,3-(η^5-C_5H_5)$CoC_2B_3H_7$ (III), and 1,7,2,3-(η^5-C_5H_5)$_2$-$Co_2C_2B_3H_5$ (VII).

A second trend observed is the fact, previously reported[18,31] for a number of boron hydrides and some carboranes, that the T_1 values of apical boron atoms are generally longer than those of nonapical boron nuclei. This is demonstrated clearly in the pentagonal pyramidal and pentagonal bipyramidal structures where apex and equatorial borons are quite distinct, in contrast to a regular icosahedron in which no such variance exists. Table IV summarizes some of the details of this effect. It is evident that in each case the apex boron T_1 value is the longest in the molecule, although for 1,2,4,5-(η^5-C_5H_5)$_2Co_2C_2B_3H_5$ (XI) the difference is not striking.

As we indicated earlier, the trends discussed above can be ascribed to differences in the field gradients and/or correlation times (motion) between the various boron nuclei. Allerhand, et al., have suggested[18] that the difference in the T_1 values of the apex and equatorial boron nuclei in B_5H_9 is a manifestation of field gradient differences, as the apex boron has a more symmetric environment than the equatorial borons. Thus, the apex boron should experience a smaller field gradient and hence show a longer T_1. We agree with this interpretation and feel that, more generally, the differences in the T_1 values of apical and nonapical borons observed both in this work and in previous studies[18,31] are a consequence of this nonuniformity of field gradients. Furthermore, the symmetry-field gradient-T_1 relationship may in some cases be expanded to include comparisons between nonapical borons *in the same molecule.* This restriction negates any motion differences, as all borons may be considered to have identical correlation times (accepting, for the present, isotropic reorientation). Estimates of the degree of symmetry may be obtained via a simple model and then compared to the observed T_1 values. The method we employ is to consider the ^{11}B nucleus in question as the origin of a coordinate system and then to draw vectors to all bonded, neighboring nuclei. The direction of the vector can be simply obtained from relevant crystal structures, and the magnitude taken to be the atomic number of the bonded atom. These vectors are then added and the magnitude of the resultant vector is taken as a measure of the field gradient of the ^{11}B nucleus in question. Although crude, the model works surprisingly well for the compounds studied in this work, as illustrated in Table V. In 2,4-$C_2B_5H_7$, for example, the expected order of ^{11}B T_1 magnitudes (remembering that the apex T_1 is longest) is B(1,7) > B(5,6) > B(3), in agreement with observation. Similarly, the model implies that in the triple-decker sandwich species VII the T_1 of the area 2 resonance [B(4,6)] should be shorter than that of the area 1 signal [B(5)], while the reverse should be true in the isomeric triple-decker IX, i.e., T_1 [B(5,6)] > T_1 [B(3)]. The results in Table V are in accord with this prediction.

Table IV. Apical and Nonapical Spin-Lattice Relaxation Times for Some Polyhedral Molecules

Compd[a]	I	II	V	X	XI
Apex T_1, ms	68.3	93.9	14.7	9.08	6.64
Longest nonapex T_1, ms	47.7	47.0	9.70	5.60	6.39

[a] See Figure 1 for identification of compounds.

Some precautionary notes are in order. First, the apical-nonapical separation can be applied to systems where such a distinction is obvious, e.g., pyramidal and bipyramidal structures, but a more general correlation between high coordination numbers and high T_1 values has not been established. Second, the symmetry considerations break down when comparing two atoms of different coordination number. Third, field gradient arguments are generally invalid for comparison of *individual* boron nuclei in two different molecules, as differences in molecular motion may enhance or negate any differences in field gradients (this does not, of course, preclude the comparison of *trends* between molecules as in the cases of VII and IX above).

The effect of motion is best seen by analysis of the previously described shortening of the ^{11}B T_1 when a boron atom is replaced by cobalt, as in the series I, V, and IX. It is perhaps tempting to attribute the shortening of T_1 values to an increase in the field gradient due to the presence of cobalt. However, the order of magnitude change in T_1 is too large to be attributed solely to an increase in the field gradient, as T_1 values in the same molecule, where motion differences should be minimal, differ at most by a factor of 2 in this series of compounds despite the variety of molecules studied. Consequently, the decrease in T_1 upon addition of (η^5-C_5H_5)Co is probably due

Table V. Boron-11 Field Gradient Estimates and Spin-Lattice Relaxation Times for Equatorial Boron Atoms in Pentagonal Bipyramidal Systems

Compd	Resonance	Magnitude of vector sum	T_1, ms
I	B(3)	13.13	38.6
	B(5,6)	12.57	47.7
VII	B(5)	43.06	4.5
	B(4,6)	43.66	3.2
IX	B(3)	44.24	2.9
	B(5,6)	43.66	3.6

to a combination of motion and field gradient effects; this is reasonable, since the addition of the bulky (η^5-C_5H_5)Co moiety must certainly slow the molecular motion, increasing τ_c and therefore shortening T_1. This interpretation is further supported by the fact that ^{1}H T_1 values also decrease significantly upon addition of (η^5-C_5H_5)Co.

While generalizations about motional differences between molecules can be made (as above), they seem inherently unreliable, as anisotropic rotation may be present, invalidating the concept of a single correlation time. Indeed, anisotropic motion has been shown[34] to be particularly important for quadrupolar nuclei. Consequently, correlations between different samples are at best doubtful even if motion has been considered. This may be illustrated by attempting to predict the T_1 of the area 2 resonance in the ^{11}B spectrum of 1,2,4,5-(η^5-C_5H_5)$_2$$Co_2C_2B_3H_5$ (XI) by comparison with an analogous monocobalt system, 2-CH_3-1,2,3-(η^5-C_5H_5)-$CoC_2B_4H_5$ (IV), whose area 2 resonance has a T_1 value of 5.91 ms. Addition of another (η^5-C_5H_5)Co moiety should (a) increase the field gradient and (b) slow the molecular tumbling, both of which should result in a substantial shortening of T_1, yet the observed T_1 for this signal, 6.39 ms, is comparable to (actually longer than) that obtained for the monocobalt system. This type of behavior is probably due to anisotropic reorientation and exemplifies the problems associated with generalizations between different molecules. In principle it is also possible for anisotropic motion to complicate field gradient effects within a single sample. However, we have not seen any experimental evidence requiring the use of more than one effective correlation time for individual molecular systems.

Proton Relaxation Times. Numerous experimental studies on ^{13}C relaxation have been published, primarily demonstrating the predominance of the dipole-dipole interaction with protons as a relaxation mechanism,[3a,b] but also noting exceptional cases and recognizing the importance of the spin rotation, scalar, and chemical shift anisotropy relaxation mechanisms in many instances.[35-41] Proton relaxation is also believed[3c] to be dominated by dipole-dipole interactions with other protons, but multiple resonance studies have not in general been attempted, since the spin system is usually much more complex and there is no convenient test such as the NOE with which to judge the relative importance of the dipolar mechanism. This is not to say that there would be no theoretical NOE for the proton-proton case, but rather that the number of instances where a meaningful NOE measurement could be obtained is at best small. Thus, testing for the presence of other relaxation mechanisms is in general more difficult for protons than for carbon-13, not only due to the absence of a quick reference such as the NOE, but also due to the myriad "second-order" effects such as strong couplings,[42] cross-correlations,[43-46] intermolecular dipole-dipole contributions,[47,48] "saturation" arising from sampling a nonequilibrium state,[49] chemical exchange,[21,27,50,51] and other phenomena. While the dipolar and/or scalar coupling of protons with quadrupolar nuclei in a large molecule will certainly further complicate the system, heteronuclear decoupling should allow the determination of the relative importance of these effects.

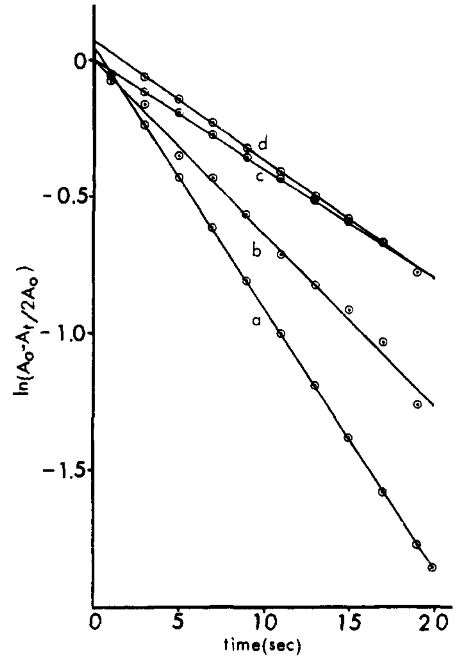

Figure 2. Semilog plots of ^{1}H relaxation in 2,4-$C_2B_5H_7$ with and without ^{11}B decoupling: (a) no decoupling; (b) saturating B(1,7); (c) saturating B(5,6); (d) saturating B(3).

In the molecules examined here, the *H*-B protons appear as broad quartets which are observed with difficulty, if at all. Therefore, in order to compare the relaxation before and after heteronuclear decoupling and/or observe any NOE, one must use the C-*H* resonances, readily observable in all the spectra obtained. The greater distance between these C-*H* protons and any boron coupled to them attenuates both the dipolar and scalar coupling, resulting in many ramifications. First, $2\pi T_1 J < 1$ and hence the C-*H* resonance is not split into a quartet by the scalar ^{11}B-^{1}H coupling, but rather appears as a broad singlet. Second, the boron-proton separation is now so large that heteronuclear dipole-dipole contributions to both T_1 and T_2 are negligible at the correlation times encountered in this study.[52] Third, since the T_1 of the quadrupolar nucleus is now short compared to the reciprocal of the coupling constant in radians/second, the rapid relaxation of the ^{11}B nucleus, which the proton "sees" as a rapidly fluctuating magnetic field, may act as a relaxation mechanism with contributions[21,27] to $1/T_1$ and $1/T_2$. The scalar contribution to T_2 is significant (one of the reasons the C-*H* singlet is broad), but the scalar contribution to T_1 is small due to the large difference in the Larmor frequencies of ^{11}B and ^{1}H ($\omega_I - \omega_S \approx 10^8$ rad s^{-1}).

These considerations suggested that the heteronuclear decoupling of ^{11}B would not significantly alter the ^{1}H spin-lattice relaxation, as the combination of the long internuclear distance and large difference in the Larmor frequencies of ^{11}B and ^{1}H results in very inefficient relaxation mechanisms and therefore small contributions to T_1 and cross-relaxation. Narrowing of the C-*H* resonance would be expected due to the collapse of unresolved coupling and the attenuation of the scalar contribution to T_2, but ^{11}B decoupling could be anticipated to have no measurable effect on T_1. This expectation, to our considerable surprise, proved altogether wrong. Table VI compares the T_1 values of the C-H protons with and without irradiation of selected boron nuclei; in each instance a substantial lengthening of T_1 is noted on decoupling. Figure 2 presents semilog plots of the proton relaxation for 2,4-$C_2B_5H_7$, in which the effect was particularly dramatic. The magnitude of in-

Table VI. Double Resonance ^1H Relaxation Data

Compd	^{11}B Signal decoupled[a]	T_1 of cage C–*H* resonance,[b] s	
I	None	10.5	
	−12.5	25.1	
	−9.2	23.1	
	16.4	15.8	
II	None	11.4	
	1.9	19.2[c]	
	53.0	19.3	
IV	None	3.14	
	−13.1	8.61[c]	
	−8.0	8.01[c]	
	−3.0	8.78[c]	
V	None	3.15	
	−6.7	3.72[c]	
	−1.4	2.72[d]	
VI	None	2.62	1.77
	−66.7	4.70	2.25
	−4.1	4.40	2.74
	3.7	5.52	3.17
	9.6	4.70	3.50
	16.4	5.27	2.71
	21.0	5.29	2.23
VIII	None	2.32	
	−54.7	3.30	
	−7.5	3.63	
IX	None	2.75	
	−21.2	3.58	
	−12.0	3.51	
X	None	4.91	2.49
	−48.7	5.16	2.10[d]
	−11.4	5.35	3.40
XI	None	2.43	
	−44.7	3.41	
	−11.4	3.24	
XII	None	4.72	1.80
	−80.3	6.43	1.65[d]
	2.9	9.19	1.77[d]
	12.3	4.75	1.54[d]
XIII	None	2.28	
	−116.3	2.05[d]	
	−4.0	1.51[d]	
	11.6 (2)	2.59[d]	

[a] Parts per million relative to $BF_3{\cdot}O(C_2H_5)_2$. [b] Where two values are given, the first corresponds to the downfield C–H resonance. [c] This value is ambiguous due to overlap of ^{11}B signals. [d] This value is ambiguous due to overlap of B–*H* and C–*H* resonances.

crease in T_1 was found to be a function of the decoupler power applied to the resonance, which is not unreasonable considering the large power requirement for saturation of a ^{11}B signal.[21]

$$H_1^2 \gg 1/\gamma_S^2(T_1)_S(T_2)_S$$

The exact response of the observed C–*H* time constant to the decoupler power applied to the apex ^{11}B resonance is given in Table VII.

These observations suggested that heteronuclear cross-relaxation was occurring to a significant degree, notwithstanding the large internuclear separation and difference in Larmor frequencies. The exact relaxation mechanism appeared to be a scalar interaction, since "saturation" of the three different ^{11}B signals produced *different* changes in the observed C–*H* spin–lattice relaxation time, yet the boron atoms associated with these signals are all at a comparable distance from the proton(s) in question. As a test of this hypothesis, the T_1 of the apex proton in $2,4\text{-}C_2B_5H_7$ was measured with and without saturation of the *directly bonded* ^{11}B nucleus, and found to be 5.93 s without irradiation and 6.40 s when the boron was saturated. This finding rules out a dipolar mechanism (which would have produced an enormous lengthening of T_1 due to the short internuclear distance) and indicates that the lengthening of the C–*H* T_1 value on irradiation of boron is a scalar effect.[53] The observed small increase in T_1 in the experiment just described is probably real, and may arise from an effective dipolar mechanism at this shorter internuclear separation. The longer range mechanism, however, is clearly demonstrated to be scalar in origin.

Table VII. Observed T_1 as a Function of Decoupler Power, H_1

T_1, s	Decoupler power, W	T_1, s	Decoupler power, W
10.5	0	12.1	10
10.8	2	15.8	20
11.1	5		

Two questions now arise: (1) Why does the large difference in Larmor frequencies fail to "insulate" the ^{11}B and ^1H spin systems from each other as predicted? (2) What is the functional form of the scalar contribution to cross-relaxation? While these problems must ultimately be resolved by a detailed theoretical treatment of the spin system, we propose the following qualitative assessment. The eigenfunctions used in previous theoretical treatments of scalar relaxation are of the type $|m_I m_S\rangle$, where m_I and m_S are the spin quantum numbers of the I and S nuclei, respectively. The use of these functions, however, *specifically neglects the mixing of wave functions due to scalar coupling.* Thus, in the completely accurate representation of the system, including all couplings, the eigenfunctions will be complex linear combinations of the $|m_I m_S\rangle$ wave functions, and the net result will be an increase in the numbers of eigenstates and allowed transitions. Some of these "new" transitions may be between states sufficiently close in energy to "short circuit" the "insulation" formerly provided by the difference in Larmor frequencies. While the exact functional form of the interaction cannot be stated a priori, it should be somewhat similar to the scalar contribution to T_1, in that there should be a dependence upon both the coupling constant J and the quadrupolar spin–lattice relaxation time τ.

Application of Double Resonance T_1 Measurements in Structure Determination. For ^{11}B nuclei with similar relaxation times, the magnitude of the interaction between boron and a C–H proton, just described, should be dependent only on the coupling constant; hence the change in T_1 for that proton (ΔT_1) induced by saturation of a given ^{11}B nucleus will be indicative of J_{BH} and, therefore, in a general sense, distance. In the case of $2,4\text{-}C_2B_5H_7$ (I), saturation of each equatorial ^{11}B resonance (δ −12.5 and −9.2) produces comparable ΔT_1's (Table VI) in accordance with the fact that all equatorial BH groups are adjacent to CH. The isomers 1,7,2,3-, 1,7,2,4-, and $1,2,4,5\text{-}(\eta^5\text{-}C_5H_5)_2Co_2C_2B_3H_5$ (VII, IX, and XI) provide further examples. In IX, saturation of either ^{11}B resonance has nearly the same effect on the T_1 of the cage CH proton, as expected since both BH units are adjacent to CH. In VIII (the $C\text{-}CH_3$ derivative of VII) and XI, however, saturation of the area 1 ^{11}B resonance induces a smaller increase in the cage CH T_1 than does saturation of the area 2 ^{11}B signal. In VIII this is a consequence of the fact that B(5) is not adjacent to (and hence further from) either cage CH group; in XI, the coupling constant for the interaction of the CH proton with the apex boron is undoubtedly small, as was seen in $2,4\text{-}C_2B_5H_7$.

Finally, we shall illustrate the use of this effect to elucidate the structure of a metallocarborane, $(\eta^5\text{-}C_5H_5)CoC_2B_6H_8$ (VI), whose structure was not previously established. Several different geometries are compatible with the chemical shifts, coupling constants, and signal area ratios of the ^{11}B and ^1H NMR spectra; two possibilities[54] are shown in Figure 3 (in both

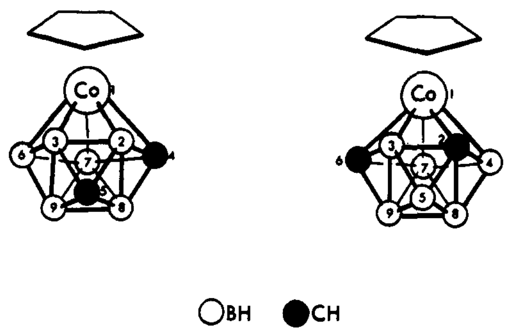

Figure 3. Two proposed geometries[54] for (η^5-C_5H_5)$CoC_2B_6H_8$: structure A, left; structure B, right.

cases, the gross geometry of a tricapped trigonal prism was assumed for these nine-vertex cage systems). The ^{11}B and ^1H spectra do little to resolve the problem of which structure, if either, is correct as both A and B will produce NMR spectra consistent with complete absence of symmetry.

The multiple resonance ^1H relaxation data (Table VI), however, distinguishes the two isomers. Saturation of four resonances, δ −4.1, 3.7, 9.6, and 16.4, results in a substantial change in the T_1 of the upfield C-*H*, while a large change in the T_1 of the downfield C-*H* is produced upon saturation of three signals, δ 3.7, 16.4, and 21.0. This implies that in the correct geometry one carbon is directly bonded to four boron atoms, while the other carbon is adjacent to only three borons. Both proposed structures fulfill this requirement. However, in structure A, saturation of the signals corresponding to B(2) and B(8) should produce a significant change in the T_1 of *both* C-*H* resonances, while in structure B, only B(3) is bonded to both carbons. The experimental observation that upon saturation of *two* signals, δ 3.7 and 16.4, the T_1 of *both* C-*H* resonances is significantly lengthened suggests that structure A is correct. Additional confirmation is provided by the T_1 behavior of the C-*H* resonances upon saturation of the ^{11}B signal at δ −66.7. This signal can be assigned to B(6) in structure A and B(4) in structure B, on the basis of the well-established observation[54] that four-coordinate BH groups adjacent to Co or Fe in polyhedra of eight or more vertices exhibit low field (<−40 ppm) ^{11}B chemical shifts. In the present case, saturation of the signal at δ −66.7 causes only a small change in the T_1 of either C-*H* resonance, again consistent with structure A, but incompatible with structure B.

In implicating structure A as the correct one, we have also partially assigned the ^{11}B and ^1H spectra. We now attempt to complete this assignment on the basis of relaxation studies. From double resonance T_1 values, the upfield and downfield C-*H* signals may be attributed to the protons bonded to C(5) and C(4), respectively. As discussed previously, B(6) may be assigned to the ^{11}B signal at δ −66.7. Of the three resonances which upon saturation cause a large change in the T_1 of the downfield, C(4)-*H* signal, the resonance at δ 21.0 must correspond to B(7), as upon saturation of this signal, no large change in the T_1 of the upfield C(5)-*H* resonance is observed. The two ^{11}B resonances at δ 3.7 and 16.4, which upon saturation result in significant lengthening of both C-*H* signals, must correspond to B(2) and B(8). Boron-11 relaxation times permit the further assignment of the resonances at δ 3.7 (T_1 = 14.5 ms) to B(2) and δ 16.4 (T_1 = 16.8 ms) to B(8) on the basis of symmetry arguments, as B(2) has a less uniform environment (due to its proximity to cobalt) than B(8), and hence should have a shorter T_1. Exactly analogous arguments result in the assignment of the remaining two boron atoms; the ^{11}B signal at δ −4.1 (T_1 = 12.1 ms) corresponds to B(3) and the final resonance at δ 9.6 (T_1 = 14.4 ms) can be assigned to B(9).

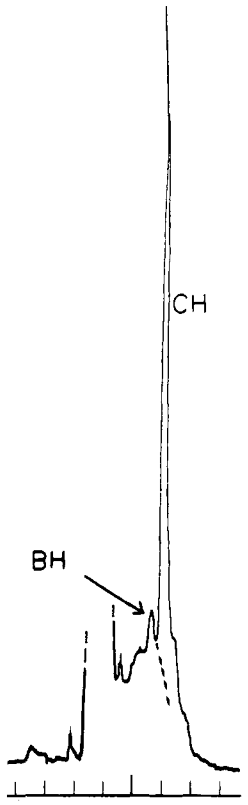

Figure 4. A portion of the ^1H NMR spectrum of 1,8,5,6-(η^5-C_5H_5)$_2Co_2C_2B_5H_7$, recorded while selectively decoupling the ^{11}B resonance at 11.6 ppm. Due to the band width of the decoupler, the ^{11}B resonance at −4.0 ppm is also partially saturated, causing the directly bonded proton to appear as a broad peak which is seen to be overlapping the cage C-*H* resonance. The C_5H_5 ^1H singlet has been omitted for clarity.

Several limitations and difficulties inherent in the double resonance T_1 measurements will be briefly mentioned. In 32.1-MHz ^{11}B spectra, saturation of a given signal may result in partial saturation of a different resonance if the two peaks are overlapped. In proton spectra, a problem encountered occasionally is the overlap of B-*H* and C-*H* signals, producing an observed T_1 value which does not accurately describe the relaxation rate of either nucleus. An example is 1,8,5,6-(η^5-C_5H_5)$_2Co_2C_2B_5H_7$ (XIII): in the absence of decoupling, there is no overlap of C-*H* and B-*H* resonances, and the observed T_1 of the C-*H* proton is 2.28 s. However, on decoupling the area 2 ^{11}B signal at −4.0 ppm, overlap of B-*H* and C-*H* signals (Figure 4) results in an observed time constant of 1.51 s. Similar problems are encountered with the upfield C-*H* resonances of 1,7,5,6-(η^5-C_5H_5)$_2Co_2C_2B_5H_7$ (XII) and 1,2,3,5-(η^5-C_5H_5)$_2Co_2C_2B_3H_5$ (X). The downfield C-*H* resonances of these two compounds, however, are not plagued by this problem and yield useful information consistent with the known structures.

Summary

In this work we have attempted to develop correlations between ^{11}B and ^1H-C spin-lattice relaxation times and molecular geometry, and to reconcile the observed T_1 values with existing theory as far as practicable for these complicated spin systems. The results suggest that T_1 measurements can be profitably employed as a routine structural technique for carboranes and metallocarboranes, augmenting the conventionally observed NMR parameters such as chemical shift and signal area ratios as well as the more recently exploited measurements of proton-proton spin coupling constants.[2,62] The entirely unexpected observation of variation of T_1 for CH protons on ^{11}B decoupling, indicating heteronuclear cross-relaxation, has been utilized empirically as an additional structural probe, but the full implications of this finding in the development of NMR theory for polyhedral cluster molecules remain to be determined.

Experimental Section

Materials. 2,4-Dicarba-*closo*-heptaborane(7) ($C_2B_5H_7$) was obtained from Chemical Systems, Inc. and purified by GLC (30% Apiezon L on Chromosorb W at 35 °C). 2,3-Dicarba-*nido*-hexaborane(8) ($C_2B_4H_8$) was prepared by the method of Onak.[55] The remaining metallocarboranes studied in this work were prepared by previously described methods.[54b,56-58]

Spectra. Boron-11 and proton magnetic resonance studies were performed on a JEOL PFT-100 P/EC 100 FT NMR spectrometer at 32.1 and 100 MHz, respectively. T_1 values were measured accurately (±10%) with the $180°-\tau-90°$ pulse sequence[59] at 25 °C. The width of the 90° pulse was typically 15-20 μs for boron and 25-30 μs for proton nuclei. For the T_1 spectra, the free induction decays contained 8K data points and improvement of signal to noise was achieved by a combination of phase shifting techniques, exponential filter, and coherent addition of successive free induction decays. Typically, ten values of τ were obtained for proton T_1 measurements, while 15-20 values of τ were used for boron-11 runs. Reduction of the data was accomplished by an external least-squares fit program and plotting routine utilizing a CDC 6400 computer.

In scattered samples during the ^{11}B studies, some phase difficulties arose for short values of τ, due to spin-echo effects. These phase errors have been previously described[59-61] and manifest themselves when the pulse interval is short compared to the spin-spin relaxation time, T_2. The difficulty can be eliminated[59-61] by the application of a homospoil pulse immediately following the 180° pulse (this technique prevents the buildup and refocusing of any transverse magnetization, which is the cause of the problem). However, our instrument is not equipped for this procedure and an alternate solution had to be found. Since the magnitude of this effect varies in a cyclic manner as a function of offset from resonance,[60] the frequency of the exciting pulse was set as close as possible to resonance without distorting the transformed spectrum. This procedure was found to minimize and nearly eliminate any phase errors for those peaks near the pulse frequency. Peaks which were offset far from the exciting frequency, however, still exhibited the phase errors. The problem was overcome in the following manner. If a sample contained two groups of resonances which were spaced relatively far apart such that the phase problem could only be eliminated for one set of resonances, then the pulse frequency was first set below the lowest frequency peaks and a T_1 determination was performed, yielding T_1 values without phase errors for the low-frequency resonances. The pulse frequency was then set above the highest frequency peaks and the entire spectrum "folded over",[27] rephased, and another T_1 determination performed, yielding accurate T_1 values for the high-frequency peaks. While this procedure is admittedly more time consuming than the homospoil technique, it does reduce or eliminate the phase problem and could be of use to those lacking homospoil capabilities.

Acknowledgment. We are grateful to Dr. A. S. DeReggi and Dr. D. L. Vanderhart of the National Bureau of Standards and Dr. V. R. Miller and Mr. W. C. Hutton of this department for many enlightening discussions. This work was supported in part by the Office of Naval Research, and the pulse Fourier transform NMR equipment was obtained in part via a departmental instrument grant from the National Science Foundation.

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