Two-Dimensional Boron-11–Boron-11 Nuclear Magnetic Resonance Spectroscopy as a Probe of Polyhedral Structure: Application to Boron Hydrides, Carboranes, Metallaboranes, and Metallacarboranes[1]

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Abstract: A general technique has been developed for the direct determination of boron–boron atom connectivities in all types of boron cage compounds, based on *J*-correlated, two-dimensional (2-D) ^{11}B–^{11}B NMR spectroscopy. In this method, which is the first reported demonstration of homonuclear 2-D NMR for a quadrupolar nucleus, a Jeener-type sequence is employed to produce a contour plot in which the x and y axes are ^{11}B chemical shift (at 115.8 MHz) and the z direction is peak intensity. Peaks on the diagonal ($F_1 = F_2$) correspond to the "normal" one-dimensional ^{11}B NMR signals, while the off-diagonal (cross) peaks at δ_A, δ_B arise from spin–spin coupling between ^{11}B nuclei A and B. Since the observable scalar coupling is limited to short-range (adjacent-atom) interactions, the cross peaks reveal the boron connectivity pattern in the framework and routinely yield information about the distribution of electron density that is most difficult to obtain otherwise. Assignment of ^{11}B resonances in conventional 1-D spectra is also greatly facilitated, in many cases allowing a complete assignment in a single experiment usually requiring 10–30 min including generation of the contour plots. Although some discussion of theory is included, this paper is directed to the utilization of the method by the synthetic chemist and describes its application to a variety of boron cage species. A general observation (with two known exceptions) is that boron atoms linked by bridging hydrogen atoms usually do not exhibit mutual coupling, in agreement with earlier theoretical predictions that the electron density in B–H–B bridge bonds is negligible on the B–B vector. A step-by-step procedure for deducing framework structures from 2-D spectra is presented in an appendix.

Since its discovery in 1946,[2] nuclear magnetic resonance spectroscopy has played an increasingly important role in organic, and more recently inorganic, chemistry. Its power as a tool for the study of molecular structure has grown steadily with the introduction of stronger magnetic fields, heteronuclear and multiple-frequency experiments and spin decoupling,[3] and, in very recent years, two-dimensional (2-D) NMR.[4] In the broad area of boron cluster chemistry, NMR utilizing the ^{11}B nucleus has been particularly important in the characterization of polyhedral cage structures;[5] the rapid development of this field in the last 20 years could scarcely have occurred in its absence.

Yet there are serious limitations in ^{11}B NMR as a structural probe for polyhedral clusters, and they are becoming increasingly conspicuous as more complex borane and heteroborane species are synthesized. The two primary problems, well-known to boron chemists, are (1) broad signals (50–150 Hz) arising in part from unresolved ^{11}B–^{11}B coupling[6] and (2) the absence of a broadly applicable theory of ^{11}B shifts. The first of these difficulties, which leads to frequent overlap of resonances, is only partly overcome in high-field (>4 T) instruments; coupling information is normally restricted to first-order boron-terminal hydrogen interactions, as ^{11}B–^{11}B coupling is seldom observable (even with the aid of line-narrowing techniques,[7] ^{11}B–^{11}B coupling is still not resolved in most cases[8]). The presence of the ^{10}B isotope ($I = 3$, 20% abundance) introduces a further complication via coupling with the observed ^{11}B nucleus.

The second problem is intrinsic to boron cage frameworks. Unlike the chemical shifts exhibited by ^1H and ^{13}C nuclei, ^{11}B ($I = {}^3/_2$, 80% abundance) exhibits few general, reliable correlations with molecular structure. The ^{11}B shifts are largely determined by the paramagnetic term σ_0 in Ramsey's equation[9] and can vary considerably with even minor variations in structure.

Consequently, it is frequently the case that the ^{11}B NMR spectrum of a boron cluster of unknown geometry conveys little more than symmetry information, i.e., the presence or absence of mirror planes or rotation axes. When superposition of inequivalent peaks occurs, even this can be misleading. A further perspective on this problem is given by the fact that, even in molecules of established geometry such as $B_{10}H_{14}$, the complete unambiguous assignment of ^{11}B NMR spectra may require laborious studies involving isotopic labeling or single-frequency decoupling.[10]

Confronted with these difficulties, we became intrigued with the possibilities afforded by the recently developed 2-D NMR techniques,[4,11] which involve the detection of a frequency response over two independent time domains. In a 2-D experiment, the data are collected as a t_1, t_2 data matrix followed by a double Fourier transform to yield a frequency spectrum that reveals the presence of connectivity patterns (in this case, *J*-coupling connectivities) between various nuclei. The first 2-D NMR experiments involving the ^{11}B nucleus utilized the *heteronuclear* ^1H–^{11}B interaction and revealed the correlations between the ^{11}B reso-

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[1] Presented in part at the Symposium on New Structural Techniques in Inorganic Chemistry, National Meeting of the American Chemical Society, Seattle, WA, March 1983, Abstract INOR-39.

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[8] Line narrowing in ^{11}B NMR cannot resolve couplings in which $J <$ ~10 Hz or in which the coupled nucleus, S, relaxes so quickly that the observed nucleus "sees" only an average spin state of S.

[9] Ramsey, N. F. *Phys. Rev.* **1950**, *78*, 699; **1953**, *90*, 232.

[10] The complete assignment of the spectrum of $B_{10}H_{14}$ via isotopic labeling experiments over a period of several years is described in ref 5a, pp 164–170.

[11] (a) Aue, W. P.; Bartholdi, E.; Ernst, R. R. *J. Chem. Phys.* **1976**, *64*, 2229. (b) Macura, S.; Huang, Y.; Suter, D.; Ernst, R. R. *J. Magn. Reson.* **1981**, *43*, 259.

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nances and the directly bound protons.[12] This approach is analogous to those involving spin $^1/_2$ nuclei such as ^{13}C and ^{31}P.[13] The *homonuclear* experiment has been successfully applied to the spin $^1/_2$ nuclei ^1H, ^{13}C, and ^{31}P, *all of which typically exhibit resolvable spin–spin coupling in the conventional (1-D) spectrum*.[14] It was not obvious that the homonuclear 2-D experiment involving ^{11}B would be feasible. Not only is ^{11}B–^{11}B coupling normally unresolved in the one-dimensional spectrum but also relaxation times (T_1) for ^{11}B nuclei are 100–1000 times shorter (milliseconds) than are those for protons, suggesting that relaxation would average the spin-coupling interaction between spin pairs to zero. However, we have successfully applied the Jeener 2-D procedure (to be described) to homonuclear ^{11}B–^{11}B systems, representing the first such extension of this technique to a quadrupolar nucleus.

Following our earlier short communication[15] we have refined the method, confirmed its general applicability, and applied it to a variety of boron cage species. In this paper, which is oriented toward the practical utility of the method for the synthetic/structural chemist, we do not deal in depth with the implications of this work for the theory of magnetization transfer through scalar connected energy levels in quadrupolar nuclei. However, qualitative comments on these aspects will be given.

Experimental Section

The compounds utilized in this study were synthesized in this laboratory by previously published procedures or purchased commercially and used as received. Samples of 1,7-$C_2B_{10}H_{12}$ (*m*-carborane) and $B_{10}H_{14}$ [decaborane(14)] were obtained from Alfa Inorganics, and 1,2-$C_2B_{10}H_{12}$ (*o*-carborane) was purchased from the Dexsil Chemical Corp., Hamden, CT 06514. The spectrum of *nido*-2,3-$(C_2H_5)_2C_2B_4H_6$[16] was obtained on a neat sample in a sealed tube, and that of $Na^+(C_2H_5)_2C_2B_4H_5^-$ was recorded in THF solution sealed under vacuum. Tetrahydrofuran (THF) was dried over $LiAlH_4$ and distilled in vacuo. All other compounds are air-stable materials and were dissolved in an appropriate solvent in 10-mm tubes. Solvents were dried prior to use.

Spectra were recorded unlocked in a stable (measured drift rate $<2 \times 10^{-3}$ Hz/h) magnetic field (8.5 T) with a ^{11}B resonance frequency of 115.8 MHz. Referencing was to an external solution of $BF_3 \cdot OEt_2$. Uninterrupted, incoherent ^1H decoupling at low levels ($\sim$2 W) was employed.

The COSY pulse sequence (vide infra) was used to generate the t_1, t_2 data matrix in which t_1 was incremented by the inverse of the sweep width in the F_1 dimension and t_2 has the same meaning as the acquisition time in a 1-D experiment. Typically, the t_1, t_2 matrix was collected as 128 × 256 (reals plus complex) data points. The data were zero-filled once in each dimension after apodization by using a cosine bell function. The final F_1, F_2 matrix was symmetrized[17] prior to plotting the absolute value spectra.

The lower limit for the detection of a reliable cross peak on our spectrometer is $\sim$1% of the height of the tallest diagonal peak. Spectra were obtained on a Nicolet Magnetics Corp. NT-360/Oxford spectrometer, and all data manipulation utilized standard Nicolet software with a 1280/293B data system. Workup of the data including contour plots usually required 10–20 min. By use of the Nicolet MACRO capability the collection and processing of data, including a first contour plot, have been automated for routine analysis.

Results and Discussion

Description of the Technique. The two-dimensional spectra generated by this experiment contain two types of peaks, those lying along the diagonal ($F_1 = F_2$) and the off-diagonal or "cross peaks". The plots are symmetrical about the diagonal so that the cross peaks are found at δ_1, δ_2 and equivalently at δ_2, δ_1. The off-diagonal peaks reveal spin–spin coupling interactions between adjacent boron nuclei and hence disclose the atom connectivities in the polyhedral framework. These coupling patterns are normally clearly observable even when, as is usually the case, no ^{11}B–^{11}B coupling is evident in the routine 1-D spectrum. We emphasize that the method utilizes standard FT NMR equipment together with 2-D software available from the instrument manufacturer or developed by the user.

The pulse sequence COSY (correlated spectroscopy) involves 16 cycles and may be written

$$T_w \rightarrow (\pi/2)_{\phi_1} \rightarrow t_1 \rightarrow (\pi/2)_{\phi_2} \rightarrow t_2(\text{acquisition})_{\psi}$$

where T_w is a time sufficient to ensure that the system is in thermal equilibrium. The first $(\pi/2)$ pulse creates transverse magnetization as in a routine 1-D experiment, and the spins are allowed to process for a time t_1 so that they become frequency labeled. The time t_1 is incremented by the inverse of the sweep width for the first frequency domain F_1 in order to build up a t_1, t_2 data array; at the end of t_1 a second $(\pi/2)$ pulse is applied. This mixing pulse transfers magnetization between coupled spins so that the observed spin now reflects a modulation based on the chemical shift difference ($\delta_A - \delta_B$) of the two scalar coupled spins. At the end of this pulse the transverse magnetization is acquired for t_2, as in any 1-D spectrum. A qualitatively useful analogy for this experiment is to consider each resonance line in a 1-D spectrum as a receiver that is capable of detecting the resonance frequencies of spins that share J-coupling energy levels with the "receiver". The receiver resonance is phase-modulated by the coupled spins as the evolution time is incremented by t_1.

The phase shifts ϕ_2 and ψ, for the second pulse and receiver, respectively, have the dual purpose of suppressing axial peaks and permitting quadrature detection in both dimensions.[18] Extending this cycle by phase shifting the first pulse cancels artifacts that arise from quadrature detection errors.[18] The time domain data matrix $S(t_1, t_2)$ that is collected is then double Fourier transformed to give a frequency domain spectrum $S(F_1, F_2)$.

The resulting spectra can be presented in "stacked" fashion as shown in Figure 1a, but these are time-consuming to produce and are less readily analyzed, although they can be useful in revealing the relative intensities of cross peaks and diagonal peaks. More generally useful, for our purposes, are absolute value contour plots (e.g., Figure 1b) in which the x and y axes represent ^{11}B chemical shifts [measured relative to $BF_3 \cdot O(C_2H_5)_2$ with positive values downfield]. Resonance intensities are represented in the z direction (normal to the page) as a series of contours.

The peaks along the diagonal represent transitions of spins whose precession frequencies were not modulated during the experiment and the chemical shift information they contain is identical with that obtained by normal (1-D) NMR. The cross peaks arise from spin–spin ^{11}B–^{11}B coupling, which for boron-containing clusters is significant only for adjacent nuclei. The connectivities revealed by the cross peaks therefore correspond directly to the framework arrangement of boron atoms within the cluster.

We turn now to a discussion of specific spectra chosen to illustrate both the power of the method in structure elucidation and spectral assignment, as well as its limitations.

Spectra of Boron Clusters: $B_{10}H_{14}$. Figure 1 presents the proton-decoupled 2-D ^{11}B–^{11}B spectrum of $B_{10}H_{14}$ with the conventional $^{11}B\{^1H\}$ 1-D spectrum below. The four peaks along the diagonal correspond to the resonances in the 1-D spectrum and from the pattern of cross peaks it can be seen that the 5, 7, 8, and 10 boron atoms (identified from the unique area-4 signal) are coupled to two of the three other types of boron atoms. The resonance at δ −36 ppm exhibits cross peaks with all other reso-

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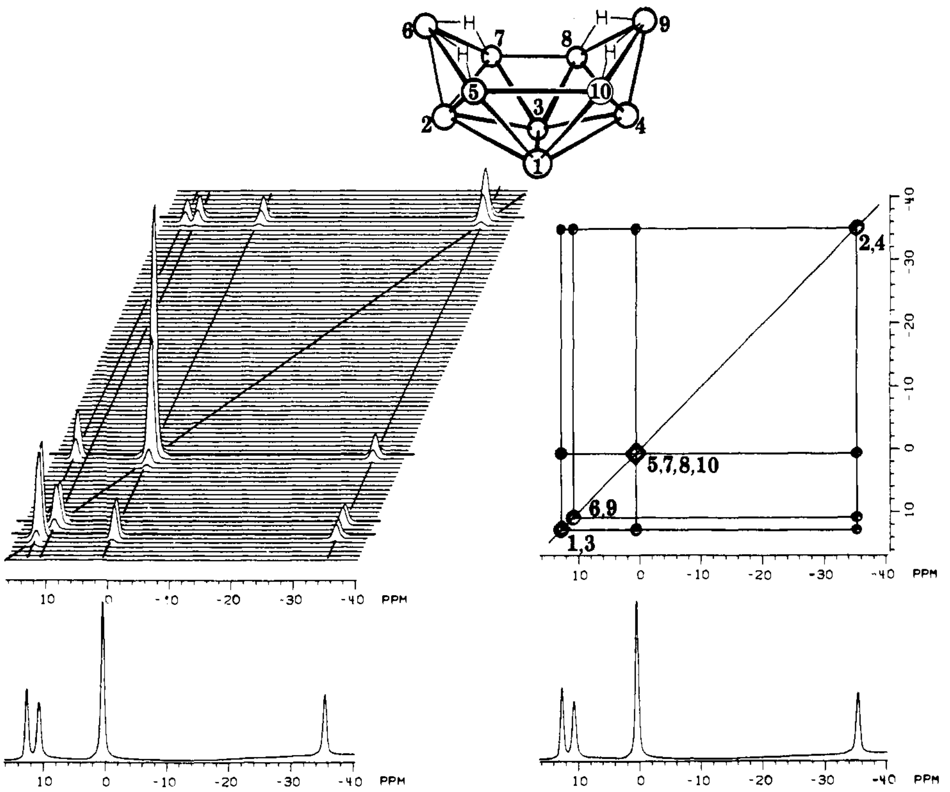

Figure 1. Two-dimensional proton-decoupled $^{11}B-^{11}B$ FT NMR spectra of $B_{10}H_{14}$ in toluene: (a) stacked plot; (b) contour plot. In these and subsequent figures, the conventional one-dimensional ^{11}B spectrum, shown at the bottom, correlates with the peaks on the diagonal. All spectra were recorded at 25 °C except where otherwise indicated.

nances and can therefore be assigned to B(2, 4). It follows that the lowest field peak must arise from B(1, 3) and the remaining resonance from B(6, 9). A complete assignment of the $B_{10}H_{14}$ ^{11}B spectrum[10] is thereby achieved in a single experiment. Even more significantly, the cage structure can be determined from the 2-D NMR data independently of the crystallographically established geometry,[19] if standard electron-counting rules for polyhedra[20] are assumed to hold (see the Appendix).

No cross peak appears between the B(5, 7, 8, 10) and B(6, 9) signals, reflecting a general observation to which we have found only two exceptions thus far: *coupling between boron nuclei linked by bridging hydrogen atoms is usually absent* within the limits of detection of the experiment. This finding is consistent with theoretical calculations[21a–c] on boron hydrides, which show that electron density in B–H–B bridges is negligible along the boron–boron axis,[21d] since the scalar coupling that results in the appearance of a cross peak is dependent on the electron density between the two nuclei (the exceptions mentioned will be discussed later in the paper).

$B_{10}H_{14}^{2-}$. The spectrum of the decaborane(14) dianion, measured as the dicesium salt in aqueous solution, is shown in Figure 2. As in the case of $B_{10}H_{14}$ the 2, 4 resonance is identified from its coupling with all other boron sites in the molecule, but here it lies at the low-field rather than the high-field end of the spectrum. The 5, 7, 8, 10 resonance can be assigned from its 1-D integration, and while the remaining two diagonal peaks exhibit similar cross peak patterns, the one near δ – 36 ppm is a triplet in the proton-coupled 1-D spectrum[22] (not shown) and hence must arise from the BH_2 groups at the 6, 9 positions. The presence of a cross peak between the B(5, 7, 8, 10) and B(6, 9) resonances (in contrast to $B_{10}H_{14}$) is as expected, since these boron–boron connections are not hydrogen bridged in this molecule.

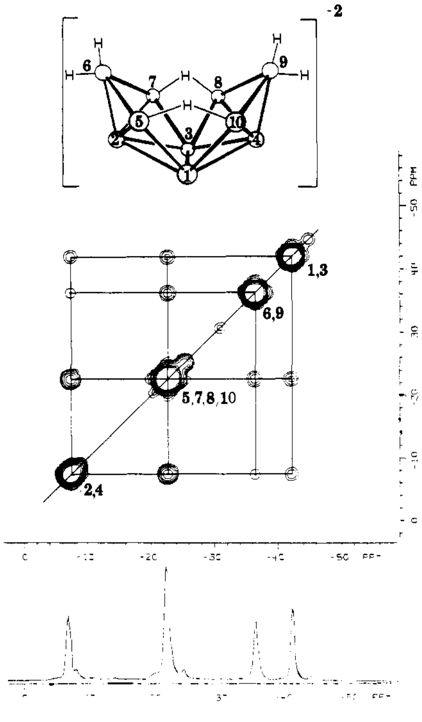

Figure 2. Spectrum of $(2Cs)^{2+}(B_{10}H_{14})^{2-}$ in H_2O at 40 °C.

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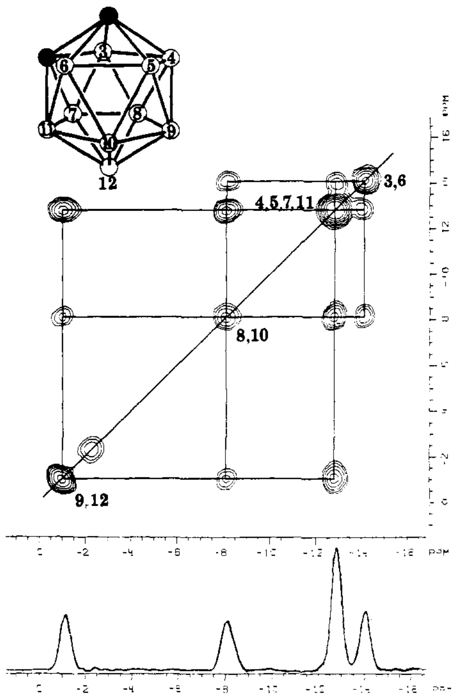

Figure 3. Spectrum of 1,2-$C_2B_{10}H_{12}$ in *n*-hexane.

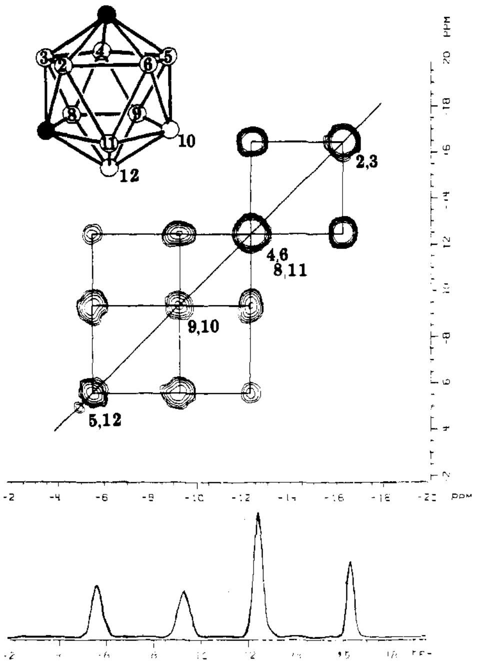

Figure 4. Spectrum of 1,7-$C_2B_{10}H_{12}$ in *n*-hexane.

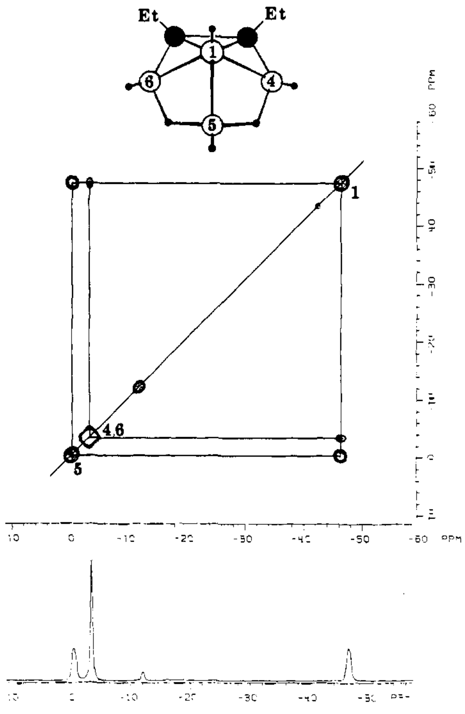

Figure 5. Spectrum of *nido*-2,3-$(C_2H_5)_2C_2B_4H_6$ (neat).

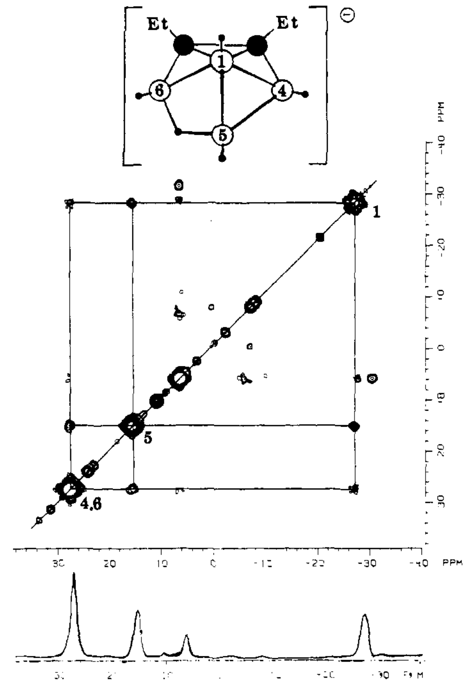

Figure 6. Spectrum of $Na^+[2,3-(C_2H_5)_2C_2B_4H_5]^-$ in THF.

1,2-$C_2B_{10}H_{12}$ and 1,7-$C_2B_{10}H_{12}$ (*o*- and *m*-Carborane). The spectra of the two isomers are presented in Figures 3 and 4, respectively. In each case the 1-D spectrum, shown below, exhibits four signals in a 2:2:4:2 area ratio, consistent with the established structures that have C_{2v} point group symmetry; however, in the 1-D spectra[23] only the area-4 peak can be unambiguously assigned. Moreover, from the 1-D spectra alone it is not possible to differentiate between the two isomers. Analysis of the 2-D spectra, however, clearly identifies the isomers and (with one assumption) permits assignment of all resonances in the spectrum of 1,2-$C_2B_{10}H_{12}$. Thus, only the 1, 2 isomer contains boron atoms (8, 10) that are directly linked to all other boron sites; only in the 1, 7 isomer is there a boron environment (2, 3) that is adjacent to only one other boron type (4, 6, 8, 11). Both features are clearly exhibited by the cross peak correlations in these spectra, so that in each case two of the four boron resonances can immediately be assigned. In the spectrum of the 1, 2 isomer, an ambiguity remains between the lowest and highest field peaks, in that the connectivity indicated by the cross peaks is the same for each resonance. A distinction can be made, however, if one assumes that the 3, 6 boron nuclei, each adjacent to two carbon atoms and hence relatively shielded, will resonate at high field.

For 1,7-$C_2B_{10}H_{12}$ the identification of the B(5, 12) and B(9, 10) resonances is not possible from these data alone; the assignments shown were obtained elsewhere from isotopically labeled derivatives.[24] Thus, in molecules of high symmetry such as the

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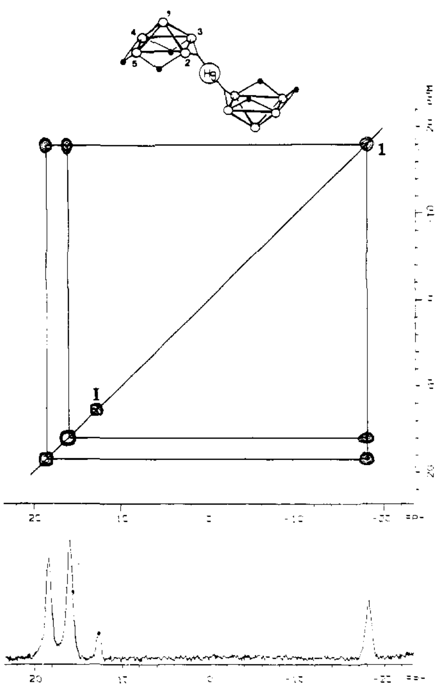

Figure 7. Spectrum of μ,μ'-Hg(B_5H_8)$_2$ in benzene.

icosahedral carboranes, even the 2-D method may not permit complete or unambiguous identification of peaks. In such cases, a simple solution would often be to lower the symmetry by substitution (e.g., by alkylation at one of the carbon vertexes).

***nido*-2,3-(C_2H_5)$_2C_2B_4H_6$ and [2,3-(C_2H_5)$_2C_2B_4H_5$]$^-$.** The 2-D spectrum of the neutral carborane (Figure 5) shows the expected coupling between the apex boron B(1) and the basal boron atoms B(5) and B(4, 6), but coupling between B(4, 6) and B(5) is absent—another manifestation of the bridge hydrogen effect already noted in the $B_{10}H_{14}$ spectrum. On bridge deprotonation with NaH to form the monoanion[25] (Figure 6), a B(4, 6)–B(5) cross peak appears, reflecting the presence of electron density along the B–B vector. (Tautomerism of the remaining bridge proton between two equivalent locations retains the mirror symmetry of the parent molecule on the NMR time scale.) The spectrum of the anion contains extraneous peaks arising from decomposition products, but in the 2-D spectrum these are clearly distinguishable from the resonances of (C_2H_5)$_2C_2B_4H_5^-$ by virtue of the absence of intermolecular cross peaks. This illustrates another general advantage of 2-D spectroscopy: the ability to resolve the spectra of mixtures into their individual components. In our experience this particular feature has been of considerable value in a number of cases.

μ,μ'-Hg(B_5H_8)$_2$ and μ(4,5)-HgCl[1,2,3-C_5(CH_3)$_5$Co-(CH_3)$_2C_2B_3H_4$]. The 2-D spectra of these mercury-bridged complexes[26] (Figures 7 and 8) suggest that the heteroatom bridge does not perturb the electron distribution within the cage. No cross peaks are observed for the cobaltacarborane cage, which contains both a B–H–B and a B–Hg–B bridge, implying that the absence of coupling in B–H–B groups may extend to boron–metal–boron bridges as well. Except for the apical B(1, 1′) resonance in the spectrum of Hg(B_5H_8)$_2$, unique assignments cannot be made without additional information.

***nido*-1,2,3-[C_6(CH_3)$_6$]Fe(C_2H_5)$_2C_2B_3H_5$.** This ferracarborane[27] can be described as a derivative of *nido*-2,3-(C_2H_5)$_2C_2B_4H_6$ (vide supra) in which the apical BH unit is replaced by an isolobal Fe[C_6(CH_3)$_6$] group or, equivalently, as a sandwich complex of C_6(CH_3)$_6$, Fe^{2+}, and the cyclic (C_2H_5)$_2C_2B_3H_5^{2-}$ ligand (an electronic analogue of $C_5H_5^-$). Its 2-D spectrum (Figure 9) clearly contains a cross peak, indicating coupling between the hydrogen-bridged boron nuclei. This observation runs counter to the cases discussed above involving B–H–B and B–Hg–B bridged species and indicates that there are important differences in the basal (ring) bonding in the iron complex in comparison to 2,3-(C_2H_5)$_2C_2B_4H_6$ and other B–X–B bridged compounds. Possibly, the delocalization of electron density about the C_2B_3 ring is greater in the iron complex (resembling its isoelectronic $C_5H_5^-$ counterpart) so that the B–H–B bridges in this compound approach "protonated double bond" character; in the $R_2C_2B_4H_6$ carborane framework[28] the bonding in the B–H–B groups may well be more localized. While such questions are obviously not resolved by this study, 2-D ^{11}B–^{11}B NMR clearly has considerable potential for probing the electron distribution in boron cages and can reveal distinct differences in the bonding of related molecules that may not be apparent from X-ray crystallographic studies.

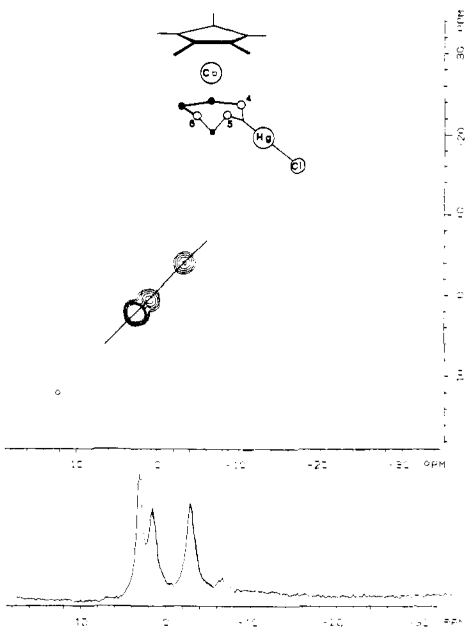

Figure 8. Spectrum of μ(4,5)-HgCl[1,2,3-(C_5[CH_3]$_5$)Co(CH_3)$_2C_2B_3H_4$].

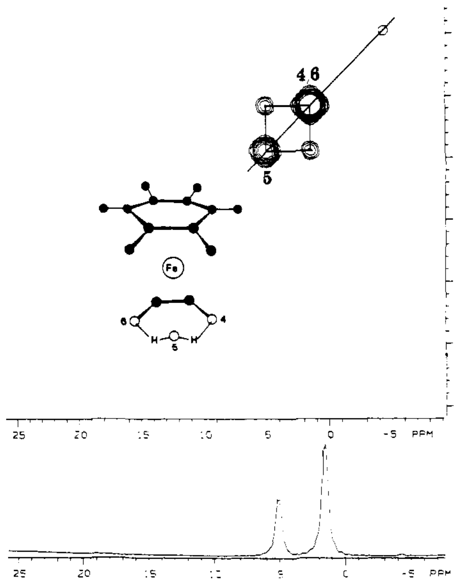

Figure 9. Spectrum of *nido*-1,2,3-[C_6(CH_3)$_6$]Fe(C_2H_5)$_2C_2B_3H_5$ in *n*-hexane.

2-(C_2H_5)CoB$_4H_8$. The 2-D spectrum of this small metallaborane[29] (Figure 10), a B_5H_9 analogue, provides the only other

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(25) Onak, T.; Dunks, G. B. *Inorg. Chem.* **1966**, *5*, 439.

(26) (a) Hosmane, N. S.; Grimes, R. N. *Inorg. Chem.* **1979**, *18*, 2886. (b) Finster, D. C.; Grimes, R. N. *Inorg. Chem.* **1981**, *20*, 863.

(27) Swisher, R. G.; Sinn, E.; Grimes, R. N. *Organometallics* **1983**, *2*, 506.

(28) Boer, F. P.; Streib, W. E.; Lipscomb, W. N. *Inorg. Chem.* **1964**, *3*, 1666.

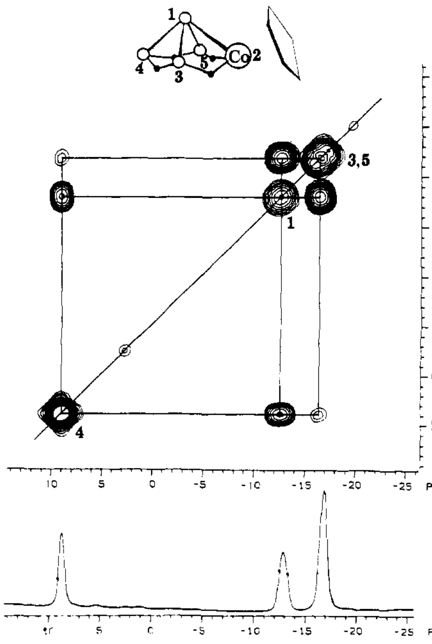

Figure 10. Spectrum of 2-$(C_5H_5)CoB_4H_8$ in heptane.

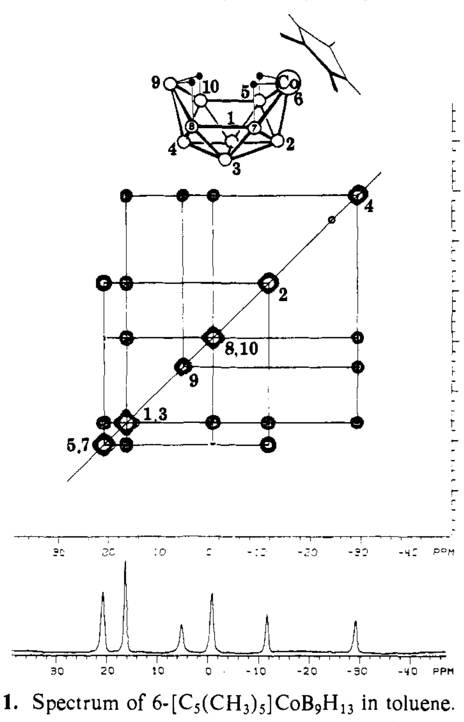

Figure 11. Spectrum of 6-$[C_5(CH_3)_5]CoB_9H_{13}$ in toluene.

example we have encountered of detectable $^{11}B-^{11}B$ coupling between hydrogen-bridged nuclei: a weak, but real, cross peak is observed between the B(3, 5 and B(4) resonances. A rationale for this observation is not readily apparent although one theoretical description[30] of 2-$(C_5H_5)CoB_4H_8$ suggests that the replacement of BH in B_5H_9 by $Co(C_5H_5)$ leads to enhanced boron–boron bonding in the cluster; however, other aspects of that particular study have been challenged recently.[31] It should also be noted that the crystallographically determined[32] B(4)–B(3, 5) bond length [1.757 (2) Å] is slightly shorter than the corresponding bond length in B_5H_9 (1.77 and 1.803 Å from X-ray[33a] and microwave[33b,c] data, respectively). The weak intensity of the B(3, 5)–B(4) cross peak suggests correspondingly weak boron–boron coupling, but such interpretations must be taken with caution (vide infra).

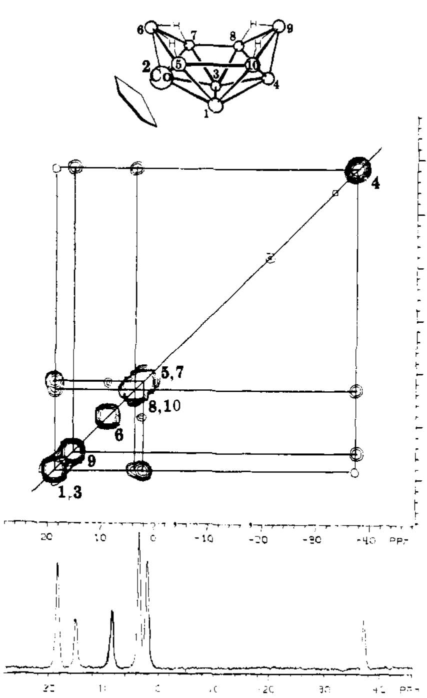

Figure 12. Spectrum of 2-$(C_5H_5)CoB_9H_{13}$ in *n*-hexane.

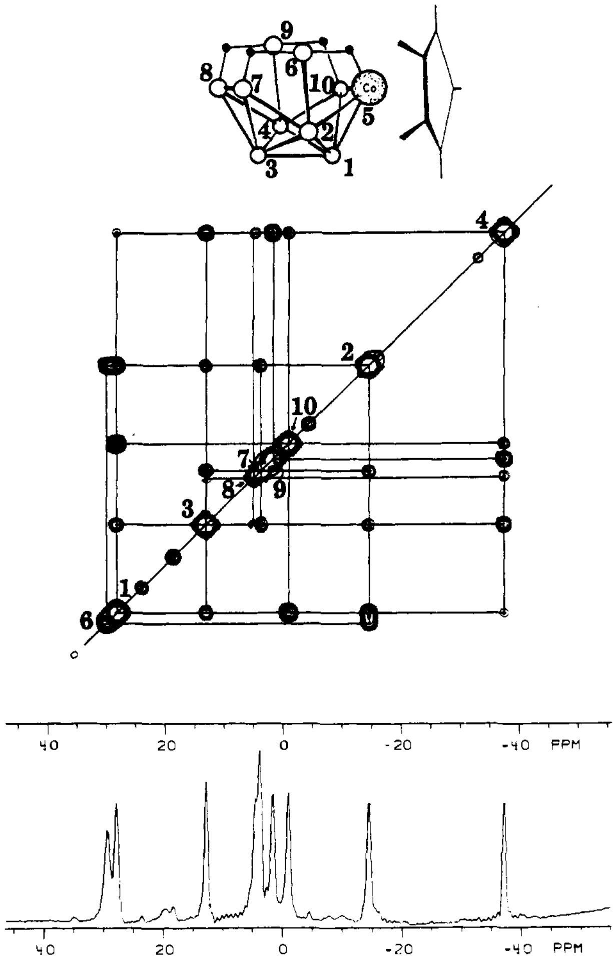

Figure 13. Spectrum of 5-$[C_5(CH_3)_5]CoB_9H_{13}$ in *n*-hexane.

$(C_5R_5)CoB_9H_{13}$ Isomers (R = H or CH_3). Four isomeric cobaltaboranes can be formally generated from the $B_{10}H_{14}$ structure (Figure 1) by the replacement of a BH unit with an isoelectronic $Co(C_5H_5)$ or $Co[C_5(CH_3)_5]$ moiety, and three of these, the 6-,

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[29] Miller, V. R.; Weiss, R.; Grimes, R. N. *J. Am. Chem. Soc.* **1977**, *99*, 5646.

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[31] DeKock, R. L.; Fehlner, T. P. *Polyhedron* **1982**, *1*, 521.

[32] Sneddon, L. G.; Voet, D. *J. Chem. Soc., Chem. Commun.* **1976**, 118.

[33] (a) Dulmage, W. J.; Lipscomb, W. N. *Acta Crystallogr.* **1952**, *5*, 260. (b) Hrostowski, H. J.; Myers, R. J. *J. Chem. Phys.* **1959**, *22*, 262. (c) Schwoch, D.; Burg, A. B.; Beaudet, R. A. *Inorg. Chem.* **1977**, *16*, 3219.

Table I

compound	δ^a (assignment)	$\nu_{1/2}$, Hz^b	T_1, ms^c	"natural line width", Hz^d
6-Cl-5,7-[$C_5(CH_3)_5Co]_2B_8H_{11}$[34e] in toluene	49.9 [B(6)]	149	6.9	46
	24.4 [B(1, 3)]	95	5.9	54
	20.1 [B(2)]	129	5.1	62
	7.9 [B(8, 10)]	175	3.5	91
	−6.1 [B(9)]	146	2.5	127
	−39.8 [B(4)]	78	9.6	33
$(CH_3)_4C_4B_7H_9$[38] in acetone	8.6 [B(9)]	53	31.6	10
	3.1 [B(4)] 2.5 [B(6)] e	134	~28	11
	−3.9 [B(10)]	72	39.6	8.0
	−7.4 [B(1)]	53	28.3	11
	−11.0 [B(11)]	33	26.6	12
	−41.6 [B(5)]	59	86.3	3.7

[a] Shifts in ppm relative to $BF_3 \cdot O(C_2H_5)_2$ with positive shifts downfield. [b] Measured from a least-squares fit of a Lorentzian curve to the observed resonance. [c] T_1 values measured by inversion-recovery using composite pulses.[37] [d] $(\pi T_1)^{-1}$. [e] Insufficiently resolved for clear measurements of $\nu_{1/2}$ and T_1.

2-, and 5-isomers, have been prepared and characterized by X-ray crystallography[34] (the 1-isomer has yet to be reported). Figures 11–13 depict the 2-D ^{11}B spectra of these compounds[35] and are particularly illustrative of the value of the 2-D method in structure determination, since in all three cases the coupling patterns lead to a unique geometry and provide a complete, unambiguous assignment of the spectrum. The only a priori assumptions are (1) a decaborane-like (nido) framework consistent with the skeletal electron count and (2) the absence of coupling between B–H–B bridged nuclei, in accordance with the empirical rule already noted. In the 6- and 2-isomers, a mirror plane is evident from the 2:2:2:1:1:1 pattern of the 1-D spectra, and of the three area-1 peaks in each spectrum (arising from borons on the mirror), one is distinguished by having only one cross peak with other resonances; it is therefore assigned to the 9-vertex, which is directly (i.e., other than B–H–B) linked to only one other boron, B(4), whose resonance in both spectra is thereby identified. Although B(4) is linked to two pairs of boron atoms [B(8, 10) and B(1, 3)], in the 6-isomer these sites are distinguishable by their cross peaks since B(8, 10) is not linked to any unique (area-1) boron other than B(4); B(1, 3) is connected to two unique boron atoms, B(4) and B(2). Thus, the identities of the B(2) and, finally, the B(5, 7) signals fall into place.

The case of the 2-isomer is analyzed similarly (its geometry can also be inferred from the fact that only the 2- and 6-isomers generate a 2:2:2:1:1:1 1-D spectrum). The B(6) resonance has no cross peaks, since it is linked to other borons only via hydrogen bridges. In this spectrum the B(5, 7) and B(8, 10) diagonal peaks are so close that the cross peak, if present, is obscured; however, the B(8, 10) signal is identified from its coupling to the unique boron B(4).

The 5-isomer is the only possible $B_{10}H_{14}$-like $(C_5R_5)CoB_9H_{13}$ structure lacking symmetry and on this basis was identified from its 1-D NMR spectrum[29] prior to X-ray characterization.[34a] Given only the 1-D spectrum, none of the resonances can be assigned, but the 2-D information (Figure 13) readily identifies all nine peaks (see the Appendix). Again, an expected cross peak [B(7)–B(8)] cannot be seen owing to overlap of the two signals along the diagonal. A systematic approach to the analysis of 2-D ^{11}B–^{11}B spectra is given in the Appendix.

Further General Observations. The transitions responsible for cross peaks that appear in 2-D spectra cannot be entirely explained by the classical model of precessing vectors,[14a] and an analysis of the interactions between nuclei is facilitated by a density matrix approach.[11] The contour map is directly related to this mathematical treatment and is, in fact, a pictorial representation of the matrix that describes the J spin–spin coupling network for the observed nuclei. Our concern here is not with these quantitative aspects but with the structural features implied by the presence of a cross peak.

A cross peak will appear when four conditions are met: (1) sufficient electron density exists between the nuclei to permit scalar coupling; (2) the two nuclei are not decoupled by a longitudinal relaxation time (T_1) that is short relative to the reciprocal of the coupling constant (i.e., $2\pi J T_1^s \ll 1$); (3) the transverse relaxation times (T_2) are sufficiently long to prevent the loss of cross peak signals through signal decay (see p 78 of ref 18a); (4) the individual resonances are resolved in the 1-D spectrum. This last requirement underlines the importance of high-field instrumentation in this work; even at 8.5 T (115.8 MHz for ^{11}B), peak overlap is occasionally a problem, as noted in a few examples discussed above.

With respect to condition 1, the fact that scalar coupling is propagated *through the bonding electrons* means that the 2-D technique described herein provides a qualitative picture of the bonding electron density in the framework—a type of information not readily accessible by other structural methods, including X-ray diffraction. Since the electrons are typically delocalized over the cage framework, bond orders between nuclei are variable; even so, coupling is routinely observed in polyhedral systems containing three-center, two-electron bonds,[36] as the number of examples discussed above clearly illustrate.

Condition 2 appeared a priori to be the most likely source of difficulty in developing a 2-D technique for boron, since, as noted in the introduction, T_1 values for ^{11}B are short and one might expect the condition for decoupling, $2\pi J T_1^s \ll 1$, to be frequently satisfied. Indeed, the absence of resolvable coupling in 1-D ^{11}B spectra usually reinforces this idea. However, a previous study on the contributions to line widths of the ^{11}B resonances in B_4H_{10} and B_5H_9 demonstrated that the resonances are broadened by scalar relaxation and unresolved spin–spin multiplets and that *partially collapsed spin–spin multiplets are common.*[6] That we are able to detect cross peaks in almost every case that we have examined to date suggests that significant even if unresolvable coupling must remain.

Measurements of the T_1 values for 6-Cl-5,7-$[C_5(CH_3)_5]$-CoB_9H_{13}[34e] (Table I) have given T_1 = 2.5 ms [B(9)], yet the cross peaks involving this boron atom are clearly detectable. We have measured line widths ($\nu_{1/2}$) and relaxation times (T_1) for representative compounds and *assuming* $T_2 = T_1$ we can calculate a line width based on relaxation alone and compare this to the line widths measured from a least-squares Lorentzian fit (Table I). That the line widths are significantly larger than those calculated

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(34) (a) Pipal, J. R.; Grimes, R. N. *Inorg. Chem.* **1977**, *16*, 3251. (b) Zimmerman, G. J.; Hall, L. W.; Sneddon, L. G. *Ibid.* **1980**, *19*, 3642. (c) Wilczynski, R.; Sneddon, L. G. *Ibid.* **1979**, *18*, 864. (d) Gromek, J. M.; Donohue, J. *Cryst. Struct. Commun.* **1981**, *10*, 871. (e) Venable, T. L.; Sinn, E.; Grimes, R. N. *Inorg. Chem.* **1982**, *21*, 895.

(35) The ^{11}B spectra of the $(C_5H_5)CoB_9H_{13}$ complexes and their $C_5(CH_3)_5$ counterparts are essentially identical.

(36) (a) Lipscomb, W. N. "Boron Hydrides"; Benjamin: New York, 1963. (b) Grimes, R. N. "Carboranes"; Academic Press: New York, 1970.

(37) (a) Cutnell, J. D.; Bleich, H. E.; Glasel, J. A. *J. Magn. Reson.* **1976**, *21*, 43. (b) Freeman, R.; Kempsell, S. P.; Levitt, M. H. *Ibid.* **1980**, *38*, 453.

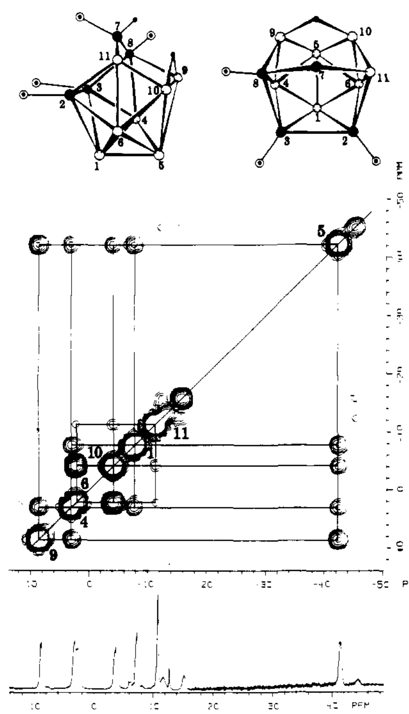


Figure 14. Spectrum of $(CH_3)_4C_4B_7H_9$ in acetone. (●) C; (⊙) CH_3; (○) BH. Two views of the crystallographically determined structure[38] are shown.

from relaxation data alone is further evidence that partially collapsed multiplets are common in these systems.

The question of the proper interpretation of cross peak intensities in 2-D ^{11}B spectra is important. What precisely can we infer about bonding between two nuclei from the apparent strength of the associated cross peak (or, for that matter, the absence of a cross peak)? In some cases, there appears to be a correlation between weak (but observable) coupling and long boron–boron bonds; a case in point is the B(5, 7)–B(8, 10) interaction in 6-$[C_5(CH_3)_5]CoB_9H_{13}$ (Figure 11), whose crystallographically determined distances[34c] are 1.983 (11) Å for B5)–B(10) and 2.023 (11) Å for B(7)–B(8). As of now, we cannot establish a minimum value of J that permits observable cross peaks, since the intensity of a cross peak is not related simply to the magnitude of J but includes the efficiency of magnetization transfer (coherence echo refocusing) between coupled spins[14a,18] and relaxation effects. Condition 3 covers those situations in which significant coupling may be expected although the absence of a cross peak suggests no coupling. Even though spin–spin coupling may be present, if a nucleus loses phase coherence through T_2 relaxation during the course of the experiment, the cross peak intensity may be low or even zero. Also, the single apodization function used for a data set will lead to different cross peak intensities based simply on the variation in line widths of the individual boron resonances.[18a] Although there may well exist compounds exhibiting such a range of line widths that different apodization functions will be required to detect all of the cross peaks, we have not found such a case. Additionally, because ^{11}B–^{10}B interactions do not contribute to the magnitude of cross peaks, intensities are also lowered by the presence of 20% ^{10}B.

This study has disclosed just one example of a missing cross peak for which we presently have no clear explanation. Figure 14 presents the 2-D ^{11}B spectrum of the carborane $(CH_3)_4C_4B_7H_9$, whose structure was established from an X-ray study of its 11-bromo derivative[38] (the ^{11}B NMR spectra of the parent and brominated species are nearly identical). No cross peak is seen for the B(5)–B(6) interaction although the crystallographic distance is 1.806 (6) Å, certainly within normal bonding range. The implication that the electron density between these two boron atoms is abnormally low, while surprising, is difficult to avoid. Alternatively, it is conceivable that the two nuclei are decoupled owing to small T_1 values (i.e., condition 2 above is not satisfied), but this is not supported by measured T_1's and line widths in this molecule.

Conclusion

The obvious power of homonuclear ^{11}B–^{11}B 2D NMR spectroscopy as a *routine* structural tool led us to consider its possible extension to other quadrupolar nuclei, recognizing that since short T_1 and T_2 values and the absence of observable homonuclear coupling in 1-D spectra do not preclude success with ^{11}B, the same may be true for other nuclei as well. Indeed, this is the case; subsequent to our first report,[15] at our suggestion this method was employed elsewhere[39] to record 2-D NMR spectra utilizing ^{51}V, a quadrupole of spin $^7/_2$ whose T_1 values are even shorter than those of ^{11}B and whose 1-D spectra show no detectable homonuclear coupling. (In fact, to our knowledge no ^{51}V–^{51}V coupling has ever been reported.)

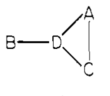
From this evidence it is apparent that the modulation arising from spin–spin coupling can be efficiently transfered by the mixing pulse even though we are unable to observe J coupling in the routine spectrum. The coupling must be obscured by the complex structure of the broad lines. Although we have presented no quantitative or detailed theoretical picture of this experiment, efforts to understand these interactions are in progress.

Appendix

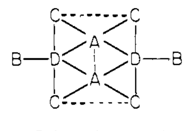
As an aid in utilizing 2-D NMR spectroscopy in structure determination, we show how it can be applied in a logical manner to deduce the cage geometry *without* prior knowledge of the structure. Although this method uses our ^{11}B system, the approach is a general one, applicable to any nucleus, quadrupolar or dipolar. Consider the spectrum of $B_{10}H_{14}$ (Figure 1). Labeling the four peaks in the 1-D spectrum A–D (low to high field), one can construct a connectivity table in which coupled resonances are indicated by X's:

	A	B	C	D
A			X	X
B				X
C	X			X
D	X	X	X	

Since the table is necessarily symmetrical about the diagonal (like the 2-D spectrum itself), only half of the matrix need be written. With no consideration of symmetry, the connectivities can be shown as



which actually is the "asymmetric unit" in the molecule. From the molecular formula (10 boron atoms) and the 2:2:4:2 pattern in the 1-D ^{11}B spectrum, it is clear that atom "C" must have 4-fold weight and A, B, and D 2-fold, in the complete framework. This leads to the diagram



in which the A–A and C–C bonds are shown as dashed lines since they are presumed but not observable (as the method cannot reveal coupling between equivalent nuclei). Since the Wade electron-count rules[20] for $B_{10}H_{14}$ predict a nido (open polyhedral) framework for this $(2n + 4)$-electron system, and any bridging hydrogen atoms will invariably reside on the open face of such a structure, the four "extra" hydrogens can be assumed to bridge

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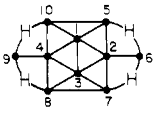
[38] Finster, D. C.; Grimes, R. N. *J. Am. Chem. Soc.* **1981**, *103*, 2675.

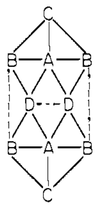
[39] Personal communication from P. J. Domaille, Central Research, E. I. du Pont de Nemours Co., Wilmington, DE. We thank Dr. Domaille for permission to quote his results prior to publication.

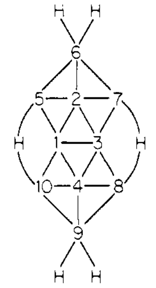
the equivalent C–B positions, giving the pattern



which corresponds to the known structure[19] of $B_{10}H_{14}$ with the standard numbering system in place. It should be clear that no such deduction is possible from the 1-D spectrum alone.

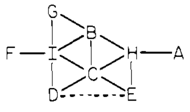
A corresponding approach to the structure of $B_{10}H_{14}^{2-}$ (Figure 2) with the peaks labeled similarly left to right yields the diagram



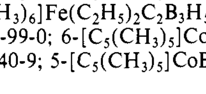


in which the placement of the bridging hydrogen atoms is dictated by the C_{2v} symmetry evident from the spectrum, and the BH_2 groups at the 6, 9 positions are identified from the triplet resonance in the proton-coupled spectrum.[22]

An example of a low-symmetry structure is given by 5-$[C_5(CH_3)_5]CoB_9H_{13}$, whose 1-D spectrum consists of nine peaks of equal area (Figure 13). Once again labeling the peaks alphabetically from left to right, the couplings revealed in the 2-D spectrum yield the connectivity pattern



where the D–E connection must be assumed, since peak overlap prevents observation of a cross peak. Placement of bridging hydrogen atoms on the edges of the nido framework, and filling in the "hole" in the boron skeleton with cobalt, yields a $B_{10}H_{14}$-like structure that conforms to the crystallographically determined geometry.[34a]



It is not necessary to be able to assign all the resonances in a spectrum in order to deduce a unique cage structure. For example, in the spectrum of 1,7-$C_2B_{10}H_{12}$ (Figure 4) the assignment of the B(9, 10) and B(5, 12) peaks is ambiguous, but the only geometry that satisfies both the 2-D coupling information and the electron-count requirement of a closed (icosahedral) framework is the 1, 7 structure shown in the figure. A similar situation obtains for the 1, 2 isomer (Figure 3). Given only the 1-D spectra, no such conclusions could be drawn, and the two isomers could be distinguished only via X-ray crystallography.

Acknowledgment. This research was supported by the National Science Foundation, Grant CHE 81-19936. Purchase of the NT-360 NMR spectrometer system was made possible in part via a major instrumentation grant from the National Science Foundation.

Registry No. $B_{10}H_{14}$, 17702-41-9; $B_{10}H_{14}^{2-}$, 12430-39-6; 1,2-$C_2B_{10}H_{12}$, 16872-09-6; 1,7-$C_2B_{10}H_{12}$, 16986-24-6; *nido*-2,3-$(C_2H_5)_2C_2B_4H_6$, 80583-48-8; *nido*-$[2,3\text{-}(C_2H_5)_2C_2B_4H_5]^-$, 83096-08-6; μ-μ′-$Hg(B_5H_8)_2$, 70850-80-5; μ-(4,5)-$HgCl[1,2,3\text{-}C_5(CH_3)_5Co(CH_3)_2C_2B_3H_4]$, 76081-90-8; *nido*-1,2,3-$[C_6(CH_3)_6]Fe(C_2H_5)_2C_2B_3H_5$, 87862-00-8; 6-$[C_5(CH_3)_5]CoB_9H_{13}$, 43061-99-0; 6-$[C_5(CH_3)_5]CoB_9H_{13}$, 80145-59-1; 2-$(C_5H_5)CoB_9H_{13}$, 68457-40-9; 5-$[C_5(CH_3)_5]CoB_9H_{13}$, 87862-01-9.

Gas-Phase Protonation of Five-Membered Heteroaromatic Rings by $^3HeT^+$ Ions. A Model Reaction for a Theoretical Approach to Heteroaromatic Reactivity[1]

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Contribution from the Istituto di Chimica Nucleare del C.N.R., Area della Ricerca di Roma, C.P. 10, Rome, Italy. *Received March 23, 1983*

Abstract: The results of a study of the reactions of the powerful Brønsted acid, the $^3HeT^+$ ion from the β decay of molecular tritium, with gaseous pyrrole, *N*-methylpyrrole, furan, and thiophene are reported. In all the systems investigated, the tritiated heteroaromatic substrate is the major product, and it is accompanied in the case of furan by very minor amounts (ca. 3%) of tritiated crotonaldehyde. The nature and the yields of the products, and their intramolecular tritium distribution, suggest that the gas-phase protonation reaction on simple five-membered heteroaromatics is regulated by factors related to the electrostatic interactions established within the encounter pair. A close correspondence exists between the gas-phase protonation results and recent theoretical and experimental evidence concerning related substitution processes.

First insight into the behavior of five-membered heteroaromatics toward charged electrophiles in the gas phase was recently allowed by the application of a radiolytic technique[2] that, unlike most conventional mass spectrometric approaches, provides direct information about the site of attack in the heterocyclic molecule and the structure of the resulting ionic intermediate(s). The available radiolytic data indicate that the behavior of a free heteroaromatic molecule toward an alkylating reactant is frequently quite different from that in solution, where solvation and ion pairing may dramatically modify the intrinsic properties of the substrate.[3] Thus, simple heteroaromatics, such as pyrroles

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[1] Gas-Phase Heteroaromatic Substitution. 5. For part 4, see: Margonelli, A.; Speranza, M. *J. Chem. Soc. Perkin Trans. 2* **1983**, 1491–1497.

[2] For comprehensive reviews on the radiolytic technique, see: (a) Ausloos, P. *Annu. Rev. Phys. Chem.* **1966**, *17*, 205–236. (b) Ausloos, P. *Progr. React. Kinet.* **1969**, *5*, 113–179. (c) Ausloos, P.; Lias, S. G. "Ion-Molecule Reactions"; Franklin, J. L., Ed.; Plenum Press: New York, 1972. (d) Cacace, F. "Kinetics of Ion-Molecule Reactions"; Ausloos, P., Ed.; Plenum Press: New York, 1979. (e) Speranza, M. *Gazzetta* **1983**, *113*, 37–60.

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