somewhat larger SSO angle of 112.7° was observed[11] for the SO dimer.

Acknowledgment. Equipment for this research was funded by the National Science Foundation. Acknowledgement is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this research. I thank Bob Feltham for helpful discussions on this project.

Registry No. Nitric oxide dimer, 16824-89-8.

---

(11) F. J. Lovas, E. Tiemann, and D. R. Johnson, *J. Chem. Phys.*, **60**, 5005 (1974).

Atom Connectivities in Polyhedral Boranes Elucidated via Two-Dimensional *J*-Correlated ^{11}B–^{11}B FT NMR: A General Method

T. Leon Venable, William C. Hutton, and
Russell N. Grimes*

Department of Chemistry, University of Virginia
Charlottesville, Virginia 22901

Received May 28, 1982

The application of ^{11}B nuclear magnetic resonance spectroscopy to molecular structure determination in boron clusters is limited in practice by two inherent problems: signal broadness (10–100 Hz), which frequently causes peak overlap and masks coupling information, and the scarcity of general, reliable correlations between chemical shift and structure. The first of these difficulties is mitigated in strong magnetic fields, which resolve resonances sufficiently to eliminate much of the overlap. The advent of two-dimensional (2-D) NMR spectroscopy during the past 6 years has provided a powerful new approach for eliciting structural information from NMR spectra. Although a variety of 2-D techniques has been applied primarily to ^{1}H, ^{13}C, and ^{31}P nuclei,[1] our group has reported the use of heteronuclear 2-D NMR of spin-coupled ^{11}B–^{1}H systems[2] wherein resonances that are overlapped in the ordinary (1-D) ^{11}B or ^{1}H spectrum are effectively resolved in the 2-D experiment.

We now report the utilization of a *homonuclear* ^{11}B–^{11}B 2-D NMR procedure to reveal spin–spin coupling (and hence direct bonding) interactions in borane frameworks and its successful application to a wide variety of borane and heteroborane species. This extension of the Jeener 2-D NMR experiment[3] to ^{11}B systems is, to our knowledge, the first demonstration of homonuclear *J*-correlated 2-D FT NMR of a quadrupolar nucleus and holds promise of developing into a routine structural tool.

The theory underlying this procedure has been presented elsewhere,[4] and the experimental details *for spin-$^1/_2$ systems* have been described.[5] In our work, results are given via three-dimensional plots in which the *x* and *y* coordinates are ^{11}B chemical shift (at 115.8 MHz) in ppm relative to $BF_3 \cdot O(C_2H_5)_2$ (positive shifts to low field) and the *z* direction, normal to the page, is peak intensity. Figure 1 presents two examples that are typical of the ~30 compounds studied thus far. In each spectrum, the peaks on the diagonal ($F_1 = F_2$) correspond to the normal one-dimensional ^{11}B FT NMR spectrum; these peaks represent resonances whose precession frequencies are unchanged by the mixing pulse. The off-diagonal or cross peaks, located at δ_A, δ_B (and equivalently at δ_B, δ_A, so that each spectrum exhibits mirror symmetry relative to the diagonal) are a consequence of spin–spin coupling between $^{11}B_A$ and $^{11}B_B$. Since such coupling is significant only for adjacent nuclei, this information relates directly to the boron–boron connectivity in the framework.

In the spectrum of the small carborane 2,3-$(C_2H_5)_2C_2B_4H_6$ (Figure 1a), the cross peaks P and Q indicate coupling between the apex boron, B(1), and the basal boron nuclei B(4, 6) and B(5), respectively. Peak R arises from an impurity in the sample; the absence of any cross peaks involving R illustrates the value of this technique in analyzing mixtures.[6,7]

A significant feature in Figure 1a is the *absence* of a cross peak between the basal boron resonances B(4, 6) and B(5). We have noted, in general, that *coupling is absent between boron atoms in B–H–B bridge bonds*; this observation is consistent with molecular orbital calculations on boranes such as B_2H_6, B_5H_9, and $B_{10}H_{14}$ which indicate that the electron density in B–H–B bridges is centered on hydrogen and is negligible along the B–B vector.[8] In contrast, the 2-D ^{11}B–^{11}B spectrum of the 2,3-$(C_2H_5)_2C_2B_4H_5^-$ anion, obtained by bridge deprotonation of the neutral carborane, *does* contain a B(4, 6)–B(5) cross peak, as expected since these nuclei are directly bonded when the bridging proton between them is removed.

Figure 1b presents the spectrum of the cobaltaborane 6-$[C_5(CH_3)_5]CoB_9H_{13}$, which contains six boron environments in a 2:2:2:1:1:1 ratio. The cross peaks establish B–B connectivities and permit the assignment of the six resonances to specific framework borons (again the absence of coupling between the hydrogen-bridged atoms B(9) and B(8, 10) is notable). The unique topology revealed by these data is entirely consistent with the structure established by X-ray crystallography.[9]

The success of this technique rests on the clear detection of scalar ^{11}B–^{11}B coupling, whose significance as a contributor to line width was demonstrated earlier in our laboratory.[10] Although $J_{^{11}B-^{11}B}$ is small relative to the resonance line width and is not normally resolved (usually, $2\pi JT_1 < 1$, and the nuclei are partially decoupled), it is nevertheless sufficient to generate significant cross peaks in the 2-D experiment. Such peaks result from a magnetization transfer process that is more efficient than the *J* modulation of the free induction decay by the scalar coupling. This phenomenon has been quantitatively analyzed for $I = {}^1/_2$ systems.[5a]

The power of 2-D ^{11}B–^{11}B *J*-correlated FT NMR spectroscopy in structure elucidation is twofold: in a relatively fast experiment, it can reveal the coordination of each boron nucleus with respect to its boron neighbors, and it provides unambiguous assignments of ^{11}B resonances without resort to isotopic labeling or extensive decoupling experiments. In addition the method can be utilized to study mixtures, as noted above, as well as reactive species. Moreover, extension of this approach to other quadrupolar nuclei may be feasible.

---

(1) For a summary of leading references, see ref 2, ref 2–11.

(2) Finster, D. C.; Hutton, W. C.; Grimes, R. N. *J. Am. Chem. Soc.* **1980**, *102*, 400.

(3) Jeener, J. Ampere International Summer School, Basko Polje, Yugoslavia, 1971, unpublished results.

(4) (a) Aue, W. P.; Barthodi, 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.

(5) (a) Bax, A.; Freeman, R. *J. Magn. Reson.* **1981**, *44*, 542. (b) The pulse sequence $(\pi/2)_x$–t_1–$(\pi/2)_\phi$–t_2 (acquisition) where $\phi = +x, +y, -x, -y$ is used to generate the t_1, t_2 data matrix in which t_1 is incremented by the inverse of the sweep width of the F_1 dimension and t_2 has the same meaning as the acquisition time in a normal (1-D) experiment. The phase shifting of the second transmitter pulse relative to the receiver has the dual purpose of eliminating axial peaks and permitting the use of quadrature detection in both dimensions. Samples were run unlocked in a stable magnetic field (8.5 T) with a ^{11}B resonance frequency of 115.8 MHz. Uninterrupted, incoherent ^{1}H decoupling at low levels was employed. The carborane sample was neat, and the t_1, t_2 matrix of 128×256 data points required less than 5 min for accumulation. The cobaltaborane sample (0.29 mmol, 74 mM) involved a 1-h accumulation time in which 400 transients were collected for each of the 128 t_1 values. 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 required 20–30 min.

(6) (a) Bax, A.; Freeman, R.; Morris, G. *J. Magn. Reson.* **1981**, *42*, 164. (b) Bain, A. D.; Bell, R. A.; Everett, J. R.; Hughes, D. W. *Can. J. Chem.* **1980**, *58*, 1947. (c) Nagayama, K.; Wüthrich, K.; Ernst, R. R. *Biochem. Biophys. Res. Commun.* **1979**, *90*, 305. (d) Kumar, A.; Wagner, G.; Ernst, R. R.; Wüthrich, K. *Biochem. Biophys. Res. Commun.* **1980**, *96*, 1156. (e) Wagner, G.; Kumar, A.; Wüthrich, K. *Eur. J. Biochem.* **1981**, *114*, 375.

(7) Van Divender, J. M.; Hutton, W. C. *J. Magn. Reson.* **1982**, *48*, 272.

(8) (a) Switkes, E.; Stevens, R. M.; Lipscomb, W. N. *J. Chem. Phys.* **1969**, *51*, 2085. (b) Switkes, E.; Epstein, I. R.; Tossell, J. A.; Stevens, R. M.; Lipscomb, W. N. *J. Am. Chem. Soc.* **1970**, *92*, 3837. (c) Laws, E. A.; Stevens, R. M.; Lipscomb, W. N. *Ibid.* **1972**, *94*, 4467.

(9) Venable, T. L.; Sinn, E.; Grimes, R. N. *Inorg. Chem.* **1982**, *21*, 895.

(10) Weiss, R.; Grimes, R. N. *J. Am. Chem. Soc.* **1978**, *100*, 1401.

(11) Baumann, R.; Wider, G.; Ernst, R. R.; Wüthrich, K. *J. Magn. Reson.* **1981**, *44*, 402.

0002-7863/82/1504-4716$01.25/0

J. Am. Chem. Soc. **1982,** *104,* 4717-4718

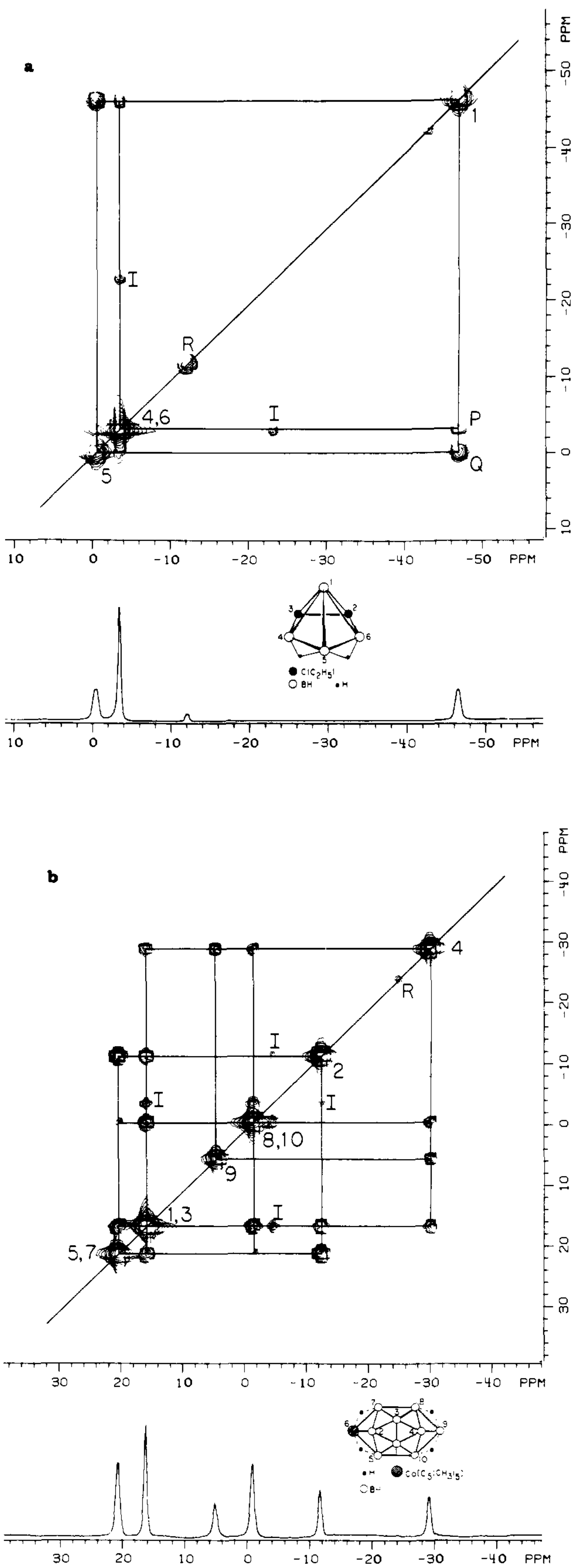

Figure 1. Symmetrized,[11] absolute value contour plots of the *J*-correlated 2-D spectra of (a) 2,3-$(C_2H_5)_2C_2B_4H_6$ and (b) 6-$[C_5(CH_3)_5]CoB_9H_{13}$. In each spectrum, peaks on the diagonal correspond to the conventional proton-decoupled ^{11}B NMR spectrum shown below; numerals by the diagonal peaks correspond to framework boron positions as shown. Boron-boron couplings (hence connectivities) are indicated by horizontal and vertical lines linking the diagonal and cross peaks. Peaks R and I are, respectively, impurities and artifacts at the transmitter frequency.

We are examining a series of boranes, carboranes, and metalla derivatives via the 2-D method and will present a detailed report at a later date.

Acknowledgment. Support of this research by the National Science Foundation, Grant No. CHE 81-19936, is gratefully acknowledged. The NMR spectrometer was obtained in part via a departmental major instrument grant from the National Science Foundation.

Registry No. 2,3-$(C_2H_5)_2C_2B_4H_6$, 80583-48-8; 6$[C_5(CH_3)_5]CoB_9H_{13}$, 80145-59-1; boron-11, 14798-13-1.

Ge-H Bond Strengths in Germanes

Matthew J. Almond, Alan M. Doncaster, Paul N. Noble,[†] and Robin Walsh*

Department of Chemistry, University of Reading
Whiteknights, Reading RG6 2AD, England

Received April 26, 1982

In a recent review[1] we have summarized our measurements of Si-H bond-dissociation energies. This work has helped to provide a fundamental basis for discussion of kinetics and mechanism in the area of silane, and in particular organosilane, chemistry. We now report results pertinent to germane chemistry that indicate that, while absolute values of bond strengths are different from those of silanes, there are several aspects of striking similarity.

Some years ago,[2] we measured $D(Me_3Ge-H)$ and obtained a value of 340 kJ mol^{-1} (81 kcal mol^{-1}). At that time the benchmark reference bond strength, $D(H_3Ge-H)$ was, and has remained until now, rather uncertain, with values spanning the range 326-386 kJ mol^{-1} (78-92 kcal mol^{-1}).[3-5] Thus, it has not been possible from absolute measurements to say whether methyl substitution strengthens or weakens Ge-H bonds. The parallel of Si-H bonds would suggest little effect,[1] but on the other hand methyl groups are well-known to weaken C-H bonds in organic compounds. This point has been given added pertinence by the recent work of McKean et al.[6] who claim that methyl substitution *does* significantly weaken both Si-H and Ge-H bonds. We report here a new measurement of $D(H_3Ge-H)$ that throws light on this and other questions.

This study employs the thoroughly tested and reliable technique pioneered by Golden and Benson[7] and applied by us already to silanes[1] and Me_3GeH,[2] viz., the investigation of the kinetics of the gas-phase iodination process. The reaction between I_2 and GeH_4 takes place conveniently at 445 K and may be monitored spectrophotometrically. The principal products formed are HI and two or more iodinated germanes. At low ratios of GeH_4 to I_2 there is a sequential development of three UV peaks at 240, 270, and 350 nm. From comparison with known UV spectra and from independent corroboration by IR spectra, the initial product is GeH_3I, followed by GeH_2I_2, while the third product is as yet unidentified. This evidence is consistent with the occurrence of reaction 1 in the early stages.

$$I_2 + GeH_4 \rightarrow GeH_3I + HI \qquad (1)$$

At high $[GeH_4]_0/[I_2]_0$ ratios this reaction predominates throughout, since $[GeH_4]$ is always much greater than $[GeH_3I]$. At lower ratios the secondary UV absorptions develop quickly, and this is consistent with GeH_3I reacting with I_2 to form GeH_2I_2

[†] On leave from California State University, Sacramento.

(1) R. Walsh, *Acc. of Chem. Res.*, **14**, 246 (1981).

(2) A. M. Doncaster and R. Walsh, *J. Phys. Chem.*, **83**, 578 (1979).

(3) K. C. Kim, D. W. Setser, and C. M. Bogan, *J. Chem. Phys.*, **60**, 1837 (1974).

(4) F. E. Saalfeld and H. J. Svec, *J. Phys. Chem.*, **70**, 1753 (1966).

(5) K. J. Reed and J. I. Brauman, *J. Chem. Phys.*, **61**, 4830 (1974).

(6) D. C. McKean, I. Torto, and A. R. Morrisson, *J. Phys. Chem.*, **86**, 307 (1982).

(7) D. M. Golden and S. W. Benson, *Chem. Rev.*, **69**, 125 (1969).