All ΔH_i values reported here were based on at least two completely independent series of calorimetric measurements using freshly prepared samples of all components. Each such set of measurements included at least five replica determinations of the enthalpy terms reported.

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(4) Brown, H. C. "The Nonclassical Ion Problem"; Plenum Press: New York, 1977. Brown, H. C. *Tetrahedron* **1976,** *32,* 179. This test for extra stabilization is based on the idea that, if the norbornyl nucleus is abnormally stable, it will place less electron demand on a methyl group attached to the cation center than will a normal secondary carbonium ion.
(5) Thus, although *tert*-butyl chloride is ~5 kcal/mol more stable than *sec*-butyl chloride, cyclohexyl chloride is 5 kcal/mol *more stable* than its tertiary isomer, 1-methylcyclopentyl chloride.[3] We regret that this comparison was stated incorrectly (in italics) on page 5411 of ref 3, although it was stated correctly in the abstract of that article and is shown correctly in Figure 3 on page 5412.
(6) Schleyer, P. v. R.; Allinger, N. L., private communication.
(7) Calorimetric techniques and conditions used here were mostly identical with those described in ref 2. The calorimeter was rebuilt, however, to permit higher precision at lower temperatures. Also special measures were required to deal with the reduced solubility of the alkyl chloride precursors at low temperature.
(8) The kinetic stability of the 4-methyl-2-norbornyl ion at this temperature is a consequence of the relatively slow 3,2 hydride shift[9] which precedes the 5,3 Wagner-Meerwein rearrangement that produces the final tertiary ion.
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(16) Supportive evidence for preparation of the 4-methyl-2-norbornyl ion was also provided by Dr. G. K. Surya Prakash of the Hydrocarbon Research Institute of the University of Southern California using ^{13}C NMR at −130 °C in a solution of SbF_5/SO_2ClF. During the time required for spectra accumulation with the Fourier transform experiment some rearrangement to the 2-methyl cation occurred even at this low temperature.

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Two-Dimensional Correlated Nuclear Magnetic Resonance of Spin-Coupled ^{11}B–^{1}H Systems

Sir:

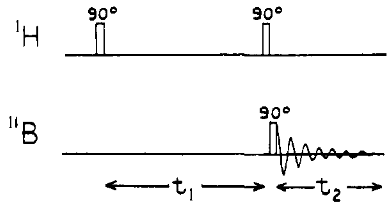

Figure 1. Pulse sequence for the heteronuclear ^{11}B–^{1}H experiment.

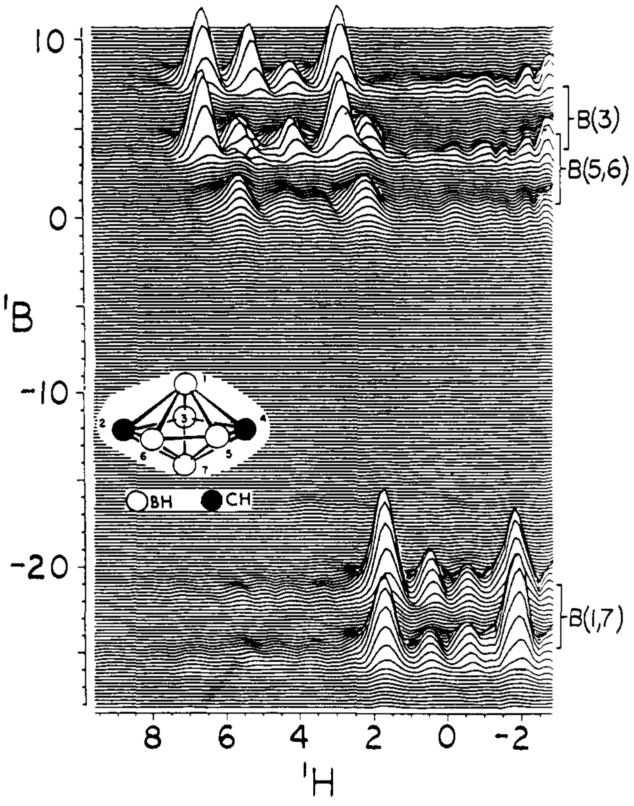

Figure 2. Two-dimensional correlated ^{11}B–^{1}H NMR spectrum of 2,4-$C_2B_5H_7$ obtained on an NT-150 spectrometer. The *x* axis exhibits ^{1}H chemical shift, δ, in parts per million relative to Me_4Si at 150 MHz; the *y* axis shows ^{11}B chemical shift in parts per million relative to $BF_3 \cdot O(C_2H_5)_2$ at 48 MHz. An absolute value spectrum is plotted. The peaks in the upper right are shoulders of unmodulated ^{11}B signals not included in the plot.[5]

A common problem in the interpretation of ^{11}B NMR spectra of polyhedral boron compounds arises when resonances of similar chemical shift are unresolved owing to the overlap of intrinsically broad peaks whose width is due to unresolved coupling and rapid relaxation.[1] Although the use of higher polarizing magnetic fields certainly mitigates this problem, a powerful new technique which has the potential to circumvent resolution difficulties is two-dimensional (2D) NMR. This method is now commercially available and has been applied to ^{1}H, ^{13}C, and ^{31}P nuclei.[2-11] It is the purpose of this communication to report the successful application of the 2D NMR method to a ^{1}H–^{11}B system, specifically a polyhedral carborane.

The theory of 2D NMR is well established[2] and details of the basic pulse sequence and many variations of it have appeared,[2-6] including chemical applications.[7-11] The experiment that appears to be most useful for the study of polyhedral boron compounds is analogous to those performed on ^{31}P–^{1}H[7] and ^{13}C–^{1}H.[8] The pulse sequence (Figure 1) begins with the application of a 90° pulse to a proton population at thermal equilibrium, thus generating transverse magnetization. After an evolution period t_1, the transverse magnetization vectors of differing frequencies (e.g., the two components of a doublet) will then occupy different orientations in the rotating frame. A second 90° pulse is then applied in order to rotate the dephased vectors out of the *x*–*y* plane which produces corresponding vectors of differing M_z values. The second pulse results in selectively "pumping" the spin populations of ^{11}B nuclei that are scalar coupled to protons. Finally, a 90° pulse is applied to the ^{11}B nuclei in order to monitor the ^{11}B free induction decay during t_2. The experiment is repeated many times, systematically varying t_1 and thus establishing a two-dimensional data matrix over t_1 and t_2. A double Fourier transformation

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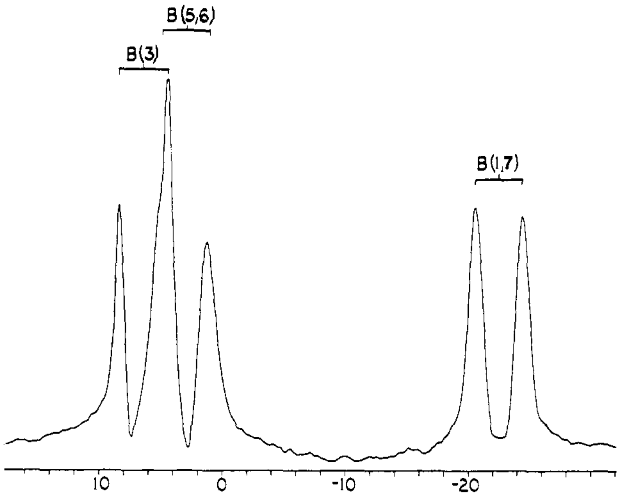

Figure 3. Projection on the *y* axis of Figure 2 showing the ^{11}B doublets due to ^{11}B–^{1}H coupling.

is performed on this matrix to give a 2D NMR spectrum having orthogonal frequency axes (^{11}B and ^{1}H), simultaneously displaying the chemical-shift spectra of both ^{11}B and ^{1}H. A peak in the "map" will correspond to a BH pair (or part of a BH pair if no decoupling is employed) with chemical shifts indicated on the appropriate axes.

In Figure 2 the spectrum of the *closo*-carborane 2,4-$C_2B_5H_7$ is shown, which to our knowledge represents the first reported ^{11}B–^{1}H 2D NMR experiment. The compound selected is typical of boron cage systems in that it exhibits large terminal B–H scalar coupling and minor long range (>1 bond) coupling. The resolution of ^{11}B signals over two distinct axes is clearly visible; since no decoupling is employed, the BH pairs appear as three doublets of quartets having relative areas of 2:2:1 corresponding to the three distinct boron environments in the molecule.

The two components of each of the doublets appearing in the boron dimension are 180° out of phase, although this is masked in the absolute value spectrum. This effect arises owing to the progressive and regressive nature of the modulation by the protons which allows no net transfer of magnetization between the spin systems. The 1:−1 intensity pattern can be explained by classical spin pumping arguments used previously to account for the ^{13}C multiplets of methyl and methylene groups.[5,11]

One striking feature of the spectrum is the approximate 3:1:1:3 intensity pattern for the ^{11}B-coupled ^{1}H quartets, which differs from the familiar 1:1:1:1 pattern ordinarily seen for a nucleus coupled to a single spin $I = \frac{3}{2}$ nucleus. Density matrix analysis[12] predicts a 3:1:−1:−3 pattern for a coupled ^{11}B–^{1}H pair of spins if 90° pulses are applied to both ^{11}B and ^{1}H nuclei.

Projection of the 2D spectra on the ^{11}B axis (Figure 3) and the ^{1}H axis (Figure 4b) produce 1D spectra which resemble the normal NMR spectra. However, an important difference exists between the proton projection and the normal 1D NMR of the same sample (Figure 4a): the 2D projection has eliminated the C–H protons (δ 5.5), organic impurities in the sample (1.5–3.0), and multiplets due to ^{10}B–^{1}H decoupling; the reason, of course, is that only ^{11}B–^{1}H pairs are observed in this type of experiment.

It is evident that 2D NMR spectroscopy is capable of resolving heavily overlapped ^{11}B signals and of correlating the resonances of individual ^{11}B and ^{1}H nuclei which are scalar-coupled to each other. A further advantage is that ^{1}H spectra are simplified by elimination of resonances of protons (e.g., in organic substituents and in solvents) that are not coupled to boron. Modifications of this procedure, such as decoupling experiments, are expected to increase still further the information that can be extracted by this technique.

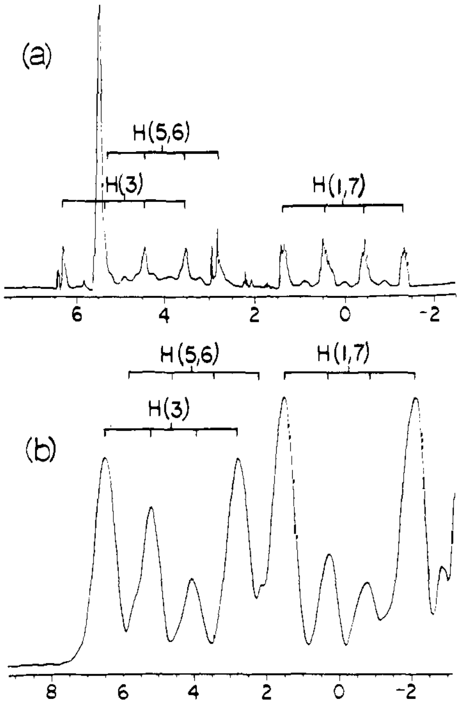

Figure 4. ^{1}H NMR spectra of 2,4-$C_2B_5H_7$: (a) 1D spectrum at 200 MHz; (b) projection on the *x* axis of Figure 2. For assignments see ref 13.

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Preferential Anion Binding to the Lactim Tautomers of 2-Hydroxypyridines

Sir:

Considerable attention has been devoted to the lactim-lactam tautomeric equilibria;[1-3] in part this is because the Watson–Crick model for nucleic acid structure and function involves specific base pairing of the *lactam* forms of the hydroxypyrimidines and hydroxypurines. Indeed, these are

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