Heteronuclear Two-dimensional Nuclear Magnetic Resonance: Decaborane

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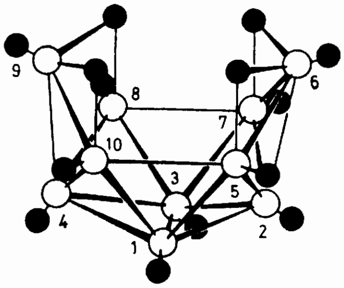
Boron-11/proton two-dimensional n.m.r. spectroscopy with heteronuclear decoupling in both frequency dimensions has been used to study decaborane. The chemical-shift correlation map shows clearly how resonances from the various boron and proton sites are related, and in particular demonstrates the association of the bridging protons with B^{5,7,8,10} and with B^{6,9}.

NUCLEAR magnetic resonance experiments designed to achieve dispersion in two separate frequency dimensions are now established as an important technique for the study of complex organic molecules,[1-3] and can yield, for example, two-dimensional (2D) J- and δ-correlated spectra, and can provide broad-band decoupling in homonuclear spin systems. The main area of application of heteronuclear δ-correlated spectra has been to relate ^{13}C and proton shieldings *via* the one-bond C–H coupling,[4,5] although some work [6] has also been done on ^{31}P/^{1}H correlation. There are many other nuclei for which such experiments are potentially valuable. If full heteronuclear decoupling is used in both dimensions the resultant spectrum is uncomplicated by line splittings due to J coupling, and has the chemical shifts of the different nuclear species as its two frequency axes, so that it forms a *chemical-shift correlation map*.[5]



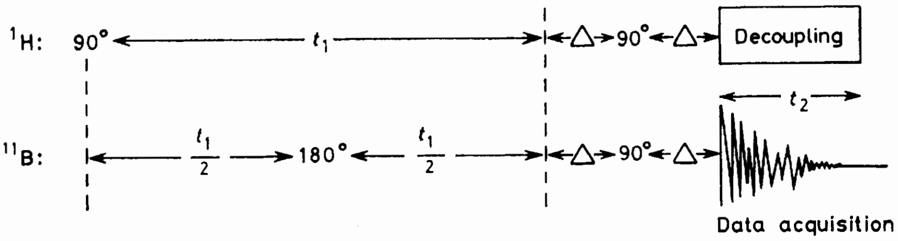
(I)

This technique is of considerable promise in boron hydride chemistry where the nuclear quadrupole moment of ^{11}B ($I = \frac{3}{2}$, natural abundance = 82%) normally leads to substantial line broadening and extensive overlapping in the proton and boron one-dimensional n.m.r. spectra of even relatively simple molecules. For particular problems various forms of ^{11}B-{^{1}H} and ^{1}H-{^{11}B} decoupling can be invaluable, but these lack the generality of the two-dimensional approach, and we report here the ^{11}B/^{1}H 2D n.m.r. spectrum of decaborane, $B_{10}H_{14}$ (I), obtained with full decoupling in both dimensions.

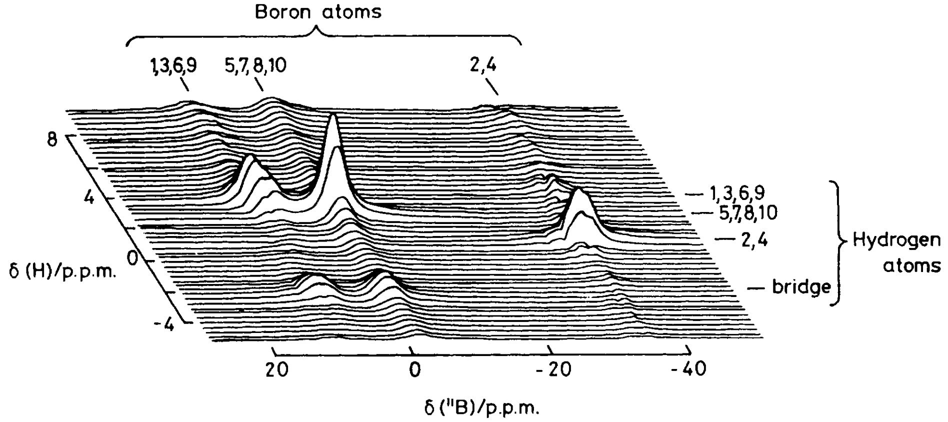
RESULTS AND DISCUSSION

Previously, Grimes and co-workers [7] have obtained 2D spectra from two small carboranes, but as they did not use decoupling in either dimension the resulting traces were considerably complicated by splittings due to the $^{1}J(^{11}B-^{1}H)$ coupling constants. For very simple molecules these extra splittings can be an advantage since they contribute to the information content of the spectrum, but in molecules of any complexity their presence can lead to difficulties of interpretation. For example, in the absence of any decoupling even a single BH_3 group gives a 16-line 2D ^{11}B/^{1}H spectrum with repeated spacings in either dimension of $^{1}J(^{11}B-^{1}H) \approx 100$ Hz which is comparable with the linewidth. Decoupling in *either* the ^{11}B or the ^{1}H dimension reduces this to four lines, and simultaneous ^{11}B and ^{1}H decoupling gives just a single peak with co-ordinates $\delta(^{11}B)$, $\delta(^{1}H)$. For a molecule with several boron sites the undecoupled spectrum is therefore extremely complex, whereas the fully decoupled spectrum will constitute a chemical-shift correlation map with peaks at positions corresponding to the shieldings of the various boron atoms and their associated protons.

The pulse sequence [5] used to obtain the 2D spectrum of (I) is as shown below. Fourier transformation of each free induction decay as a function of t_2 yields a set of modulated spectra each showing frequency dispersion in the f_2 or ^{11}B dimension, and a second set of Fourier transformations of corresponding points in each spectrum as a function of t_1 then produces the frequency dispersion in the f_1 or proton dimension.[2] Proton decoupling is



achieved in the normal way by switching on the proton decoupler during data acquisition, and the effect of boron decoupling is produced by a 180° ^{11}B pulse at the middle of the t_1 time interval, although it should be noted that this does not remove the line broadening brought about by the ^{11}B quadrupolar relaxation. To prevent mutual cancellation of antiphase signals when two-dimensional decoupling is desired, it is necessary [4] to include two extra delays each of length Δ, related to the coupling constant J used to correlate the boron and proton spectra by $\Delta = 1/2J$. In the case of (I) the couplings $^1J(^{11}\mathrm{B}-^1\mathrm{H})$ for the terminal hydrogen atoms are *ca.* 140 Hz corresponding to $\Delta = 3.6$ ms, while those for the bridging hydrogens are probably *ca.* 50 Hz, corresponding to $\Delta = 10$ ms. Furthermore, for the bridging protons it is necessary to take into account simultaneous coupling to *two* ^{11}B nuclei in about 67% of the molecules of (I), and for these species the optimum value of Δ will be close to $1/4J$, *i.e. ca.* 5 ms. Thus in principle several separate 2D experiments should be needed to display with full intensity all signals resulting from one-bond coupling relationships in the chemical-shift correlation map. In practice a value of $\Delta = 4.0$ ms was found to represent a satisfactory compromise, giving very nearly full intensities for the terminal protons, and acceptable intensities for the bridging ones. Thus for this kind of experiment the exact value of Δ is not at all critical, and, when necessary, phasing anomalies can be avoided by using the absolute-value mode of presentation. It should be noted however, that in a doubtful case it will generally be better to use a value of Δ which is somewhat shorter than optimum rather than one which is too long.



Absolute-value display of the 2D ^{11}B/^{1}H n.m.r. spectrum of decaborane with decoupling in both frequency dimensions. Forty free induction decays were accumulated at intervals of 6 s in 256 data points for each of 128 values of t_1 ranging from 0.25 to 32 ms corresponding to a frequency range of $\pm 2\,000$ Hz in the f_1 (^{1}H) dimension. Quadrature detection was used, and each free induction decay was acquired for 51.2 ms which was equivalent to a frequency range of 2 500 Hz in the f_2 dimension. In view of the quadrupolar-induced broadening it was permissible to apply an exponential weighting equivalent to an additional line broadening of 20 Hz to the free induction decays prior to the first $[S(t_1, t_2) \longrightarrow S(t_1, f_2)]$ set of Fourier transformations; however, in order to improve the line shape the interferograms were weighted with a line-narrowing exponential before the second $[S(t_1, f_2) \longrightarrow S(f_1, f_2)]$ set of Fourier transformations. The absolute-value 2D spectrum is symmetrical with respect to the radio-frequency pulse frequency in the f_1 dimension and so only one half need be displayed; in fact, only 50 traces farthest from and on one side of the pulse frequency are reproduced here. The chemical-shift scales are to high frequency of the references: $\mathrm{Et_2O{\cdot}BF_3}$ for ^{11}B, and $\mathrm{SiMe_4}$ for ^{1}H

The Figure shows the 2D fully decoupled spectrum of (I) with the boron and proton shieldings as axes, and the positions of the peaks fully confirm the literature [8,9] assignments derived from 1D spectra. Thus there are resonances at $\delta(^{11}\mathrm{B}) = -36$, $\delta(^1\mathrm{H}) = 0.7$ p.p.m. (corresponding to $\mathrm{B^2}$ and $\mathrm{B^4}$ and their terminal protons); at -2, 2.7 p.p.m. ($\mathrm{B^5}$, $\mathrm{B^7}$, $\mathrm{B^8}$, and $\mathrm{B^{10}}$); and at 14, 3.2 p.p.m. ($\mathrm{B^1}$, $\mathrm{B^3}$, $\mathrm{B^6}$, $\mathrm{B^9}$). The quadrupolar-induced broadening prevents full resolution of the $\mathrm{B^1}$, $\mathrm{B^3}$ from the $\mathrm{B^6}$, $\mathrm{B^9}$ resonances for which the shielding differences are very small in both dimensions, but close examination of the structure of the peak at 14, 3.2 p.p.m. shows that the pair with the larger boron chemical shift also has a larger δ(H). Selective deuteriation experiments have previously shown [9] these to be $\mathrm{B^1}$, $\mathrm{B^3}$. It is clear from the Figure that boron and hydrogen atoms not connected by a single-bond coupling do not give any response, *e.g.* there is no peak at -36, 2.7 p.p.m. which would have corresponded to an interaction of $\mathrm{B^2}$, $\mathrm{B^4}$ with $\mathrm{H^5}$, $\mathrm{H^7}$, $\mathrm{H^8}$, $\mathrm{H^{10}}$. However, there are definite signals at -2, -2.1, and 14, -2.1 p.p.m. and the presence of these demonstrates unequivocally that the bridging hydrogens are associated with $\mathrm{B^5}$, $\mathrm{B^7}$, $\mathrm{B^8}$, $\mathrm{B^{10}}$ and with two (presumably $\mathrm{B^6}$ and $\mathrm{B^9}$) of $\mathrm{B^1}$, $\mathrm{B^3}$, $\mathrm{B^6}$, $\mathrm{B^9}$, the reduced intensities of these signals being due in part to the use of a shorter than optimum value of Δ as discussed above. Although selective decoupling had already confirmed [10] the spectral assignments [8] in respect of the terminal protons, it has not until now been possible to relate the bridging protons with specific boron sites, even though the resonances of these protons in the 1D spectrum are considerably broadened by the ^{11}B quadrupolar relaxation. Thus ^{11}B/^{1}H fully decoupled two-dimensional n.m.r. spectra can be important in boron hydride chemistry both by providing increased spectral resolution since peaks which overlap in one dimension may not do so in the other, and by correlating 1D boron and proton spectra in a way which can be difficult or even impossible using conventional decoupling methods.

EXPERIMENTAL

The sample was a *ca.* 20% solution of decaborane in C_6D_6 contained in a 10-mm outside diameter spinning tube. Spectra were recorded on a JEOL FX90Q spectrometer with a multinuclear probe tuned to a detecting frequency of 28.7 MHz for ^{11}B with a proton irradiating frequency of 89.8 MHz. The ^{11}B and proton 90° pulse lengths were 51 and 44 μs respectively; all data manipulation was performed using prototype software provided by JEOL, and the pulse sequence was generated using a PG200 programmable multipulser unit.

We thank Dr. J. D. Kennedy for the sample of decaborane and for many helpful discussions, and the S.R.C. for financial support.

[1/187 *Received, 6th February*, 1981]

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