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6 Two-Dimensional Correlated Nuclear Magnetic Resonance  
of Spin-Coupled  $^{11}\text{B}$ - $^1\text{H}$  Systems.

10 David C. Finster, William C. Hutton, and Russell N. Grimes

Department of Chemistry, University of Virginia  
Charlottesville, Virginia 22901

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

David C. Finster, William C. Hutton, and Russell N. Grimes\*

Department of Chemistry, University of Virginia  
Charlottesville, VA 22901

Abstract. Two-dimensional (2D) Fourier transform nuclear magnetic resonance spectroscopy has been applied for the first time to a  $^{11}\text{B}$ - $^1\text{H}$  spin system. A heteronuclear experiment is performed on the closo-carborane,  $2,4\text{-C}_2\text{B}_5\text{H}_7$ , to give a 2D correlated spectrum in which chemical shift data of  $^{11}\text{B}^*$  and  $^1\text{H}^{**}$  are simultaneously displayed on a three-dimensional map. It is shown that the technique has the potential to resolve broad, overlapped  $^{11}\text{B}^*$  signals via the chemical shift of the protons to which they are scalar-coupled.

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Two-Dimensional Correlated Nuclear Magnetic Resonance  
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Sir:

A common problem in the interpretation of  $^{11}\text{B}$  N.M.R. spectra of polyhedral boron compounds arises when resonances of similar chemical shift are unresolved due to the overlap of intrinsically broad peaks whose width is due to unresolved coupling and rapid relaxation.<sup>1</sup> 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) N.M.R. This method is now commercially available and has been applied to  $^1\text{H}$ ,  $^{13}\text{C}$ , and  $^{31}\text{P}$  nuclei.<sup>2-11</sup> It is the purpose of this Communication to report the successful application of the 2D N.M.R. method to a  $^1\text{H}$ - $^{11}\text{B}$  system, specifically a polyhedral carborane.

The theory of 2D N.M.R. is well-established<sup>2</sup> and details of the basic pulse sequence and many variations of it have appeared,<sup>2-6</sup> including chemical applications.<sup>7-11</sup> The experiment that appears to be most useful for the study of polyhedral boron compounds is analogous to those performed on  $^{31}\text{P}$ - $^1\text{H}$ <sup>7</sup> and  $^{13}\text{C}$ - $^1\text{H}$ .<sup>8</sup> The pulse sequence (Figure 1) begins with the application of a  $90^\circ$  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  $90^\circ$  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  $^{11}\text{B}$  nuclei that are scalar coupled to protons. Finally, a  $90^\circ$  pulse is applied to the  $^{11}\text{B}$  nuclei in order to monitor the  $^{11}\text{B}$  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 is performed on this matrix to give a 2D N.M.R. spectrum having orthogonal frequency axes ( $^{11}\text{B}$  and  $^1\text{H}$ ), simultaneously displaying the chemical shift spectra of both  $^{11}\text{B}$  and  $^1\text{H}$ . 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 axis.

In Figure 2 the spectrum of the closo-carborane  $2,4\text{-C}_2\text{B}_5\text{H}_7$  is shown, which to our knowledge represents the first reported  $^{11}\text{B}\text{-}^1\text{H}$  2D N.M.R. 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  $^{11}\text{B}$  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  $180^\circ$  out of phase, although this is masked in the absolute value spectrum. This effect arises due 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  $^{13}\text{C}$  multiplets of methyl and methylene groups.<sup>5,11</sup>

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

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

It is evident that 2D N.M.R. spectroscopy is capable of resolving heavily overlapped  $^{11}\text{B}$  signals, and of correlating the resonances of individual  $^{11}\text{B}$  and  $^1\text{H}$  nuclei which are scalar-coupled to each other. A further advantage is that  $^1\text{H}$  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.

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David C. Finster, William C. Hutton, and Russell N. Grimes\*  
Department of Chemistry, University of Virginia, Charlottesville,  
Virginia 22901.

References and Notes

- (1) Weiss, R.; Grimes, R.N., J. Am. Chem. Soc., 1978, 100, 1401.
- (2) Aue, W.P.; Bartholdi, E.; Ernst, R.R., J. Chem. Phys., 1976, 64, 2229.
- (3) Maudsley, A.A.; Ernst, R.R., Chem. Phys. Lett., 1977, 50, 368.
- (4) Maudsley, A.A.; Müller, L.; Ernst, R.R., J. Magn. Reson., 1977, 28, 463.
- (5) Bodenhausen, G.; Freeman, R., J. Magn. Reson., 1977, 28, 471.
- (6) Bodenhausen, G.; Freeman, R.; Niedermeyer, R.; Turner, D.L. J. Magn. Reson., 1977, 26, 133.
- (7) Bolton, P.; Bodenhausen, G., J. Am. Chem. Soc., 1979, 101, 1080.
- (8) Freeman, R.; Bodenhausen, G., J. Am. Chem. Soc., 1978, 100, 320.
- (9) Nagayama, K.; Wüthrich, K.; Bachmann, P.; Ernst, R.R., Bioch. Biophys. Res. Comm., 1977, 78, 99.
- (10) Hall, L.D.; Sukumar, S., J. Am. Chem. Soc., 1979, 101, 3120.
- (11) Freeman, R.; Morris, G. A., Bull. Magn. Reson., 1979, 1, 5.
- (12) Morris, G. A., private communication.
- (13) Miller, V.R.; Grimes, R.N., Inorg. Chem., 1977, 16, 15.



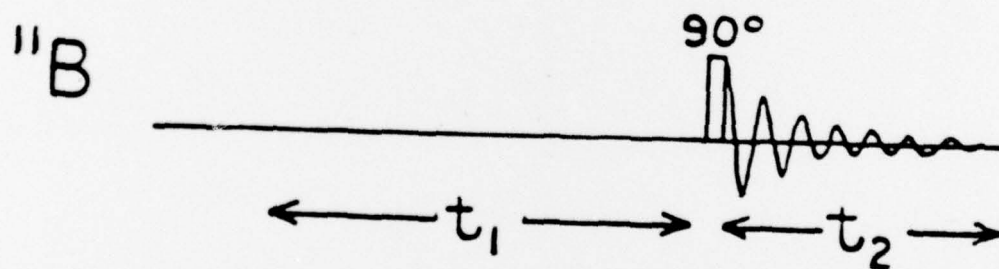
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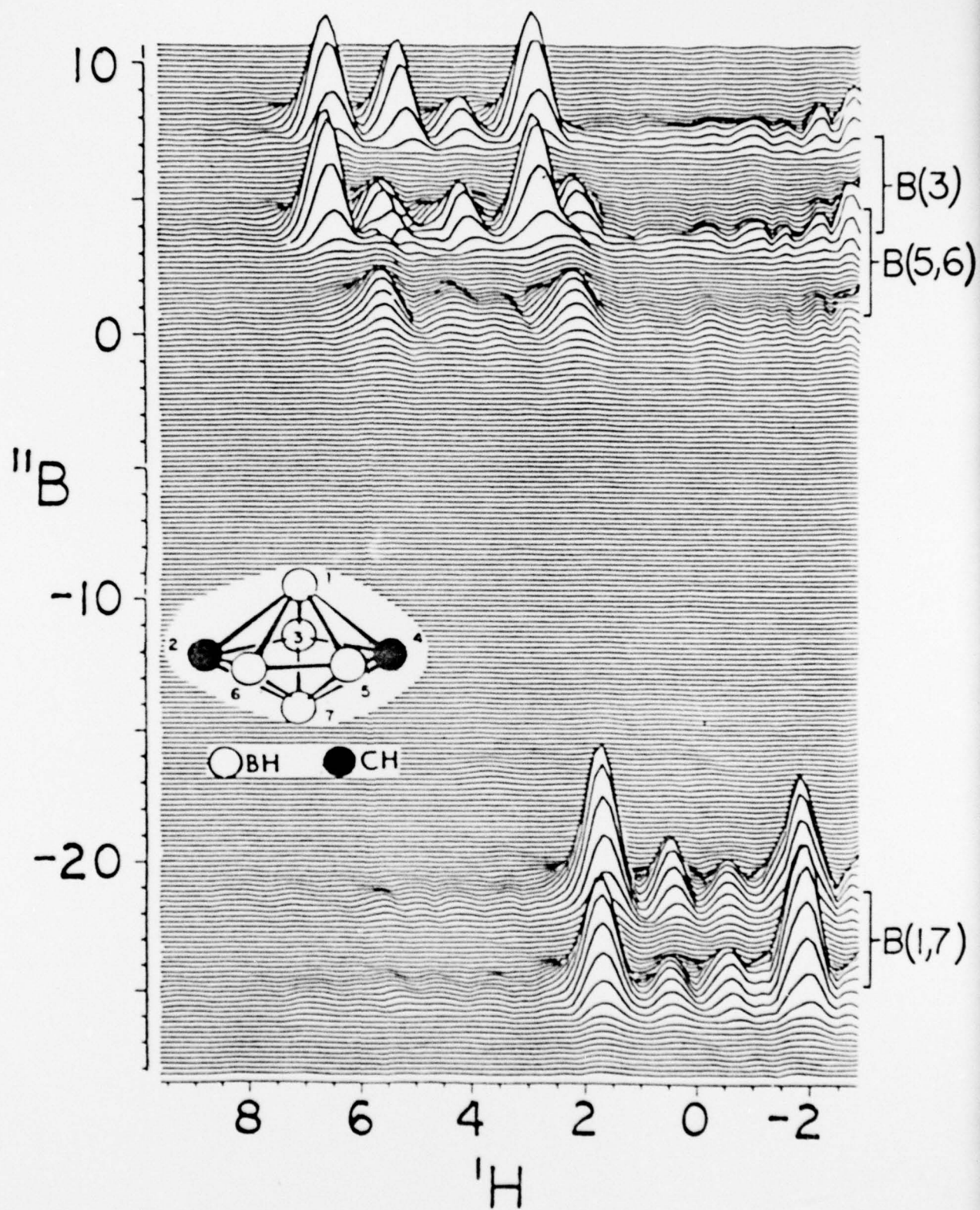
Figure 1. Pulse sequence for the heteronuclear  $^{11}\text{B}$ - $^1\text{H}$  experiment.

Figure 2. Two-dimensional correlated  $^{11}\text{B}$ - $^1\text{H}$  N.M.R. spectrum of  $2,4\text{-C}_2\text{B}_5\text{H}_7$  obtained on an NT-150 spectrometer. The x axis exhibits  $^1\text{H}$  chemical shift,  $\delta$ , in ppm relative to TMS at 150 MHz; the y axis shows  $^{11}\text{B}$  chemical shift in ppm relative to  $\text{BF}_3 \cdot \text{O}(\text{C}_2\text{H}_5)_2$  at 48 MHz. An absolute value spectrum is plotted. The peaks in the upper right are shoulders of unmodulated  $^{11}\text{B}$  signals not included in the plot.<sup>5</sup>

Figure 3. Projection on the y axis of Figure 2 showing the  $^{11}\text{B}$  doublets due to  $^{11}\text{B}$ - $^1\text{H}$  coupling.

Figure 4. Proton N.M.R. spectra of  $2,4\text{-C}_2\text{B}_5\text{H}_7$ . (a) 1D spectrum at 200 MHz. (b) Projection on the x axis of Figure 2. For assignments see reference 13.





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$B(3)$

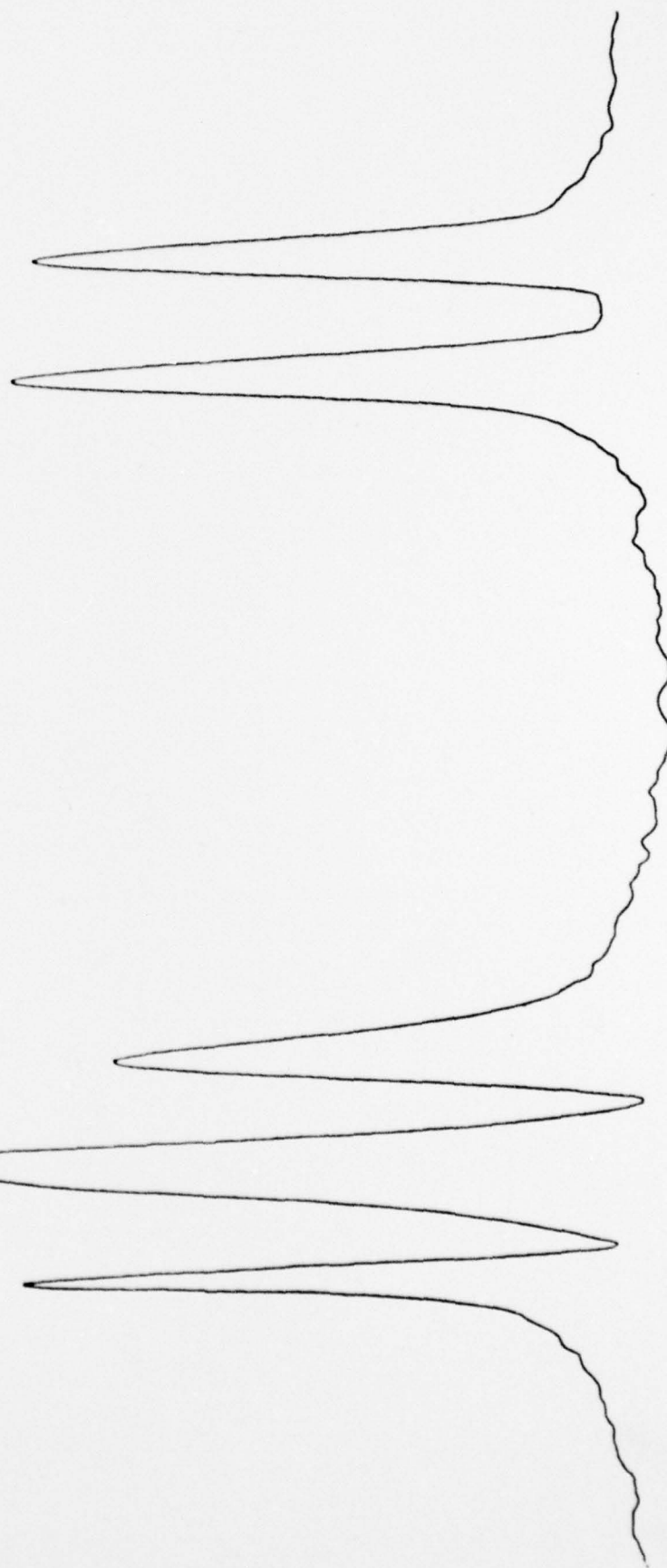
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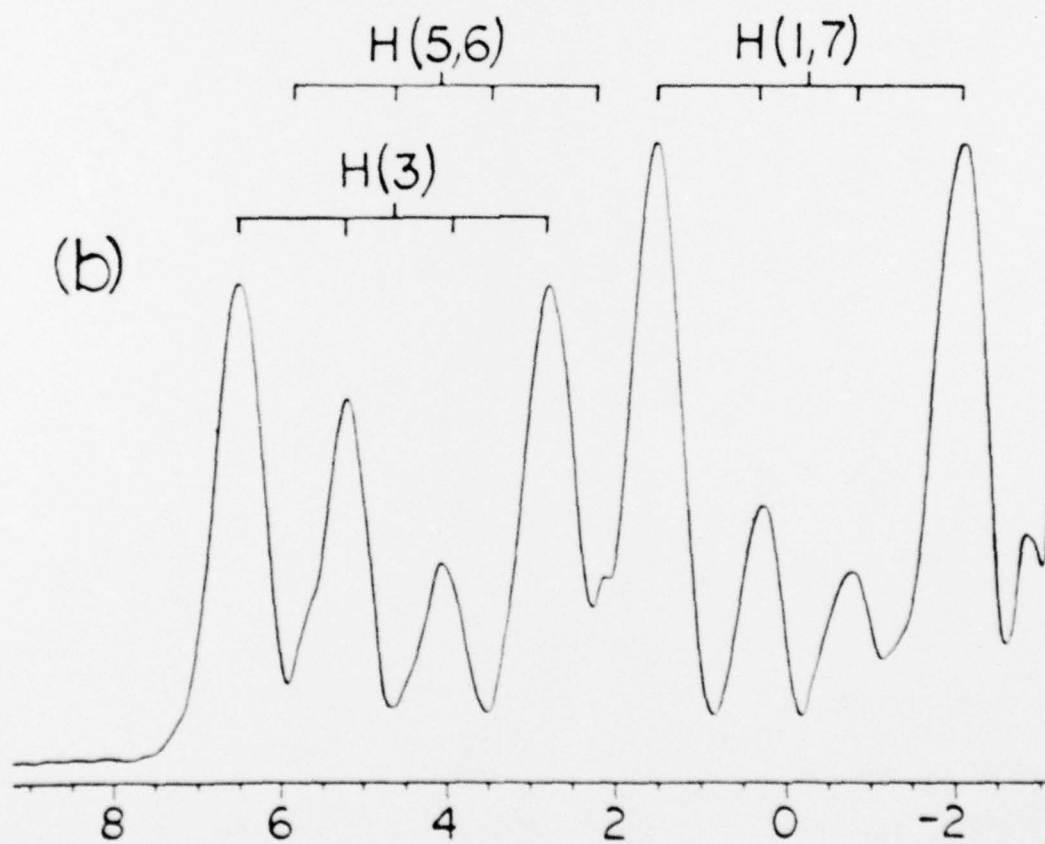
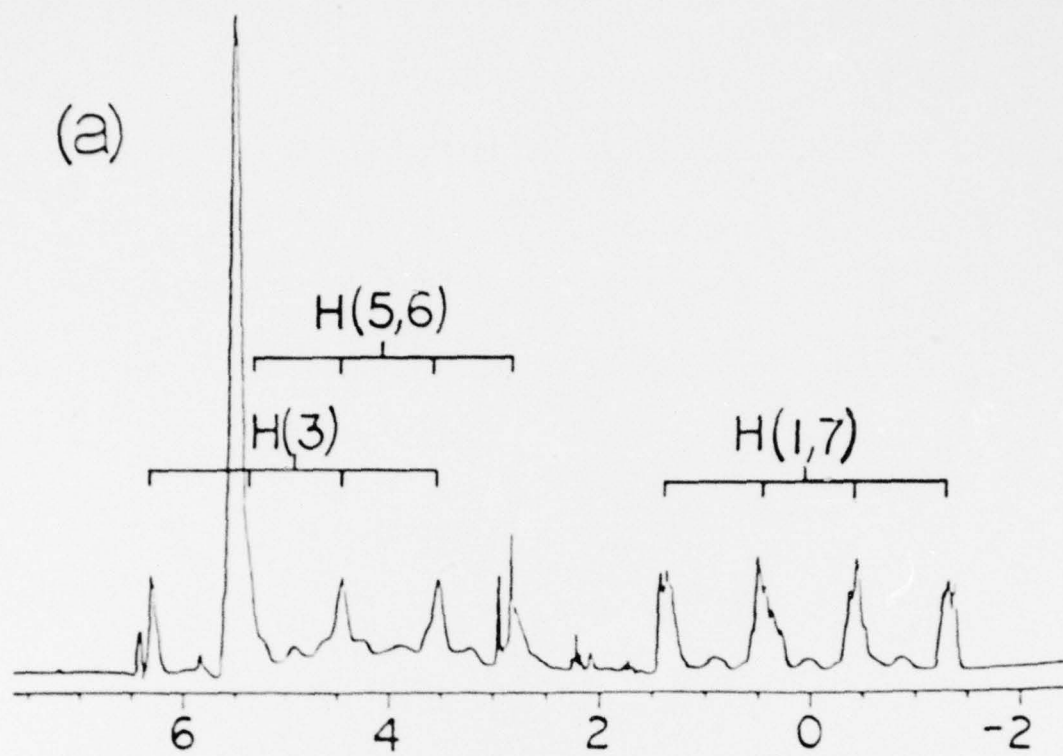
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