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COMMUNICATION

THE APPLICATION OF TOCSY TO BORON CHEMISTRY

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Abstract—The use of the two-dimensional TOCSY experiment in the NMR analysis of boron hydrides is demonstrated. Both the ^{11}B and the ^{1}H nuclei have been shown to provide potentially useful results with this technique. The results are compared with those obtained using the well established COSY experiments.

During the last decade the use of two-dimensional techniques in the NMR analysis of boron compounds has progressed rapidly, to the point where such experiments are applied routinely in many laboratories. Both homonuclear ($^{11}B/^{11}B$ and $^{1}H/^{1}H$ COSY) and heteronuclear ($^{11}B/^{1}H$ HETCOR) correlation experiments have been applied successfully to such systems, though there are limitations imposed by the efficient nature of the relaxation of the boron nuclei.[1,2] In general, it has been observed that ^{11}B homonuclear COSY experiments only show correlations (cross peaks) between adjacent boron nuclei, with ^{1}H COSY experiments yielding cross peaks primarily between H nuclei separated by three bonds, though longer range connectivities can be detected. One major problem with ^{11}B COSY experiments is that often cross peaks that would be expected to show are not observed.[1–3] For ^{1}H COSY experiments, possible difficulties are incomplete ^{11}B decoupling, and a narrow chemical shift range for ^{1}H, leading to a high possibility of signal overlap.[4]

In an effort to extend the range of techniques available, the use of the TOCSY (Total Correlation Spectroscopy) sequence in the study of such systems was investigated, looking at results from both the ^{11}B and ^{1}H nuclei. The TOCSY sequence has already been widely used in ^{1}H NMR analyses, particularly in the study of polypeptides/proteins, and is designed to show cross peaks linking all the members of a given spin system.[5] Thus it would be expected that all the proton signals arising from a particular amino acid in a peptide sequence would be correlated to one another. Extending this approach to boranes, one would expect all the ^{11}B signals deriving from a specific borane cluster to exhibit cross peaks to each other in an ^{11}B TOCSY experiment, and similarly all the ^{1}H signals in a ^{1}H TOCSY experiment.

RESULTS AND DISCUSSION

The ^{11}B TOCSY experiment has been performed on both the *closo*-carbaborane 1-Ph-1,2-$C_2B_{10}H_{11}$ and the *nido*-selenaborane 7,9-$Se_2B_9H_9$, the structures of which are shown in Fig. 1, and the results compared with corresponding ^{11}B COSY experiments as shown in Figs 2 (for the carbaborane) and 3 (for the selenaborane). The full analyses of the ^{11}B and ^{1}H spectra of these compounds are reported elsewhere,[3,6] with the results of these assignments being used here to help us to carry out the comparison between the COSY and TOCSY experiments. Tables 1 and 2 show the assignments for these compounds.

Comparison of the ^{11}B TOCSY and COSY results on the carbaborane (Fig. 2), highlight two major features which show up on examination of the spectra. Firstly, the TOCSY experiment shows cross peaks between all the different signals in the

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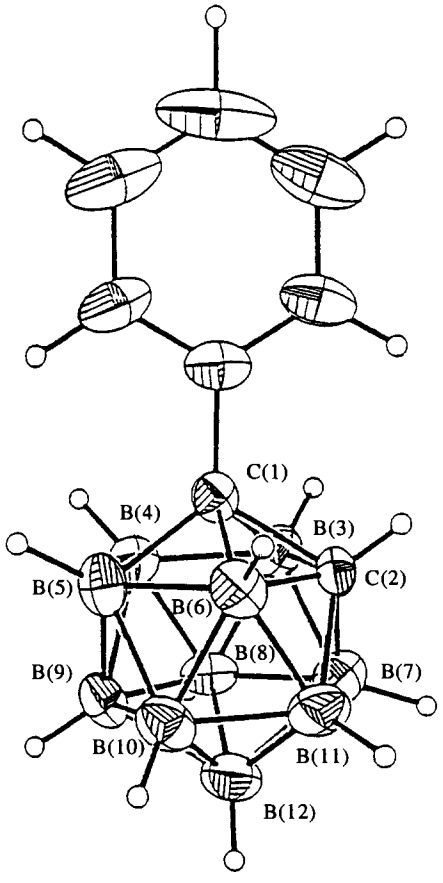

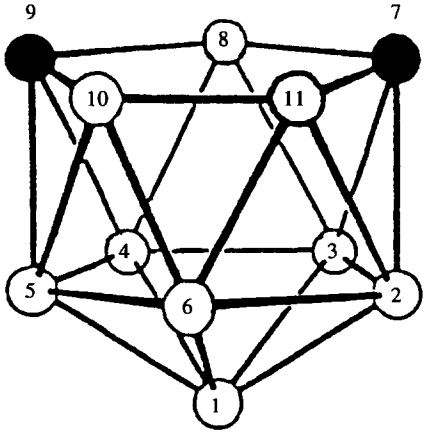

Fig. 1. The structures of *closo*-1-Ph-1,2-$C_2B_{10}H_{11}$ (top) and *nido*-7,9-$Se_2B_9H_9$ (bottom). The selenium atoms are indicated by the filled circles.

Table 1. Assignments for the ^{11}B and ^1H spectra of *closo*-1-Ph-1,2-$C_2B_{10}H_{11}$

B/H Site	$\delta(^{11}B)^a$	$\delta(^1H)^b$
9	−1.1	2.45
12	−3.4	2.36
8, 10	−7.9	2.36
4, 5	−9.7	2.54
3, 6	−10.2	2.62
7, 11	−11.8	2.30

[a] Chemical shifts of ^{11}B referenced to external $BF_3 \cdot OEt_2$ at 0 ppm.
[b] Chemical shifts of ^1H referenced to internal TMS at 0 ppm; $\delta(^1H)$ for cluster CH is 3.99 ppm.

Table 2. Assignments for the ^{11}B and ^1H spectra of *nido*-7,9-$Se_2B_9H_9$

B/H Site	$\delta(^{11}B)^a$	$\delta(^1H)^b$
6	2.1	3.68
2, 5	1.6	3.43
10, 11	−0.6	3.02
3, 4	−1.0	3.24
8	−8.6	2.64
1	−34.6	2.32

[a] Chemical shifts of ^{11}B referenced to external $BF_3 \cdot OEt_2$ at 0 ppm.
[b] Chemical shifts of ^1H referenced to internal TMS at 0 ppm.

spectrum, whereas the COSY shows cross peaks only between signals arising from adjacent boron atoms, as alluded to earlier. The TOCSY experiment has, in this case, provided an ideal result, in that it has provided cross peaks for the complete spin system, for all the signals, in keeping with the results often obtained in proton NMR experiments. The second feature shown up by these experiments is that the cross peaks are more compact in the TOCSY experiment than in the COSY experiment. This is because TOCSY experiments are carried out in the phase sensitive mode, whilst COSY experiments on borane systems are carried out in the absolute value (magnitude) mode. Thus the TOCSY method gives rise to much better resolved two-dimensional results than the COSY techniques adopted for such systems.

The ^{11}B TOCSY experiment performed on the selenaborane produced results which were less comprehensive than those for the carbaborane, but which still extracted several additional correlations compared to the COSY experiment (Fig. 3). The COSY plot, which was used to elucidate the structure of the selenaborane previously,[3] nonetheless had several cross peaks missing which would be expected to show on the basis that adjacent borons are likely to be coupled; these "missing" cross peaks being those between signals B and C, and

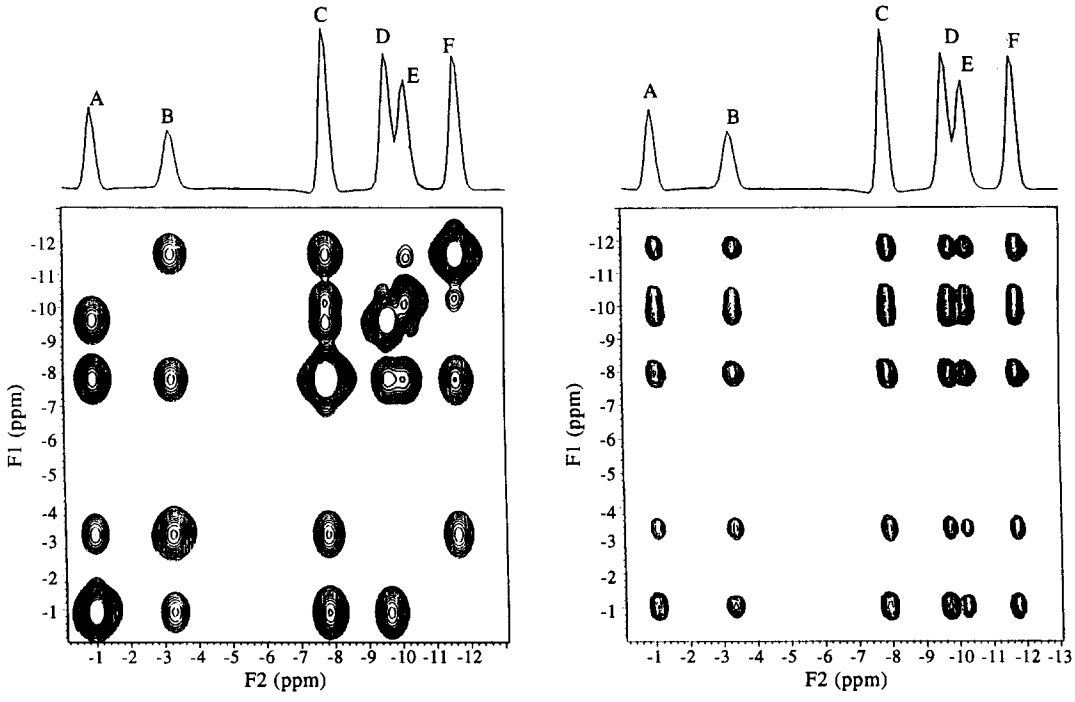

Fig. 2. (a) The absolute value 192.48 MHz ^{11}B COSY plot for 1-Ph-1,2-$C_2B_{10}H_{11}$. The data were acquired using a spectral width of 9363 Hz in both dimensions. There were 128 fids collected, each of 512 data points, which were zero filled to 1024 data points on Fourier transformation. The f1 dimension was also zero filled to 1024 data points. Proton decoupling was applied throughout the experiment. The 90° pulse was 45 μs, and a relaxation delay of 300 ms was used. Data processing involved pseudo echo multiplication in each dimension prior to Fourier transformation. (b) The 192.48 MHz ^{11}B TOCSY plot for 1-Ph-1,2-$C_2B_{10}H_{11}$. The data were acquired using the States–Haberkorn–Ruben method, with 128 t_1 increments. Each fid was of 576 data points and they were zero filled to 2048 points on Fourier transformation. The f1 dimension was zero filled to 1024 data points. Proton decoupling was applied throughout the experiment. The 90° pulse was 45 μs, and a relaxation delay of 300 ms was used. The spin lock mixing time employed was 20 ms.

signals B and D. The TOCSY experiment has brought out these cross peaks, and has also shown a number of other correlations which do not relate to adjacent boron nuclei, namely the cross peaks linking signals E and F, signals D and F, and signals A and D. Most importantly, signal F (from B(1)) displays cross peaks to all other signals in the spectrum, consistent with the signals all deriving from a single spin system.

The two examples discussed thus far highlight some of the types of information that can be obtained using ^{11}B TOCSY experiments. It is clear however that the selenaborane has produced a rather less complete result than did the carbaborane. Possible reasons for this are:

(i) The spectrum width is much larger for the selenaborane, and this will result in the signals at the outside edges of the spectrum receiving pulses which are less than specified in the sequence.

(ii) The COSY experiment for the carbaborane contained all the expected cross peaks, whereas that for the selenaborane did not. It was not surprising therefore to get similar behaviour from the TOCSY.

To further look into TOCSY as a mode of study of boranes, the ^{1}H nucleus was also used, and Fig. 4 shows the comparison between the TOCSY and COSY results for *nido*-7,9-$Se_2B_9H_9$. The COSY experiment shows all the cross peaks arising from ^3J(H,H), and also some correlations from longer range couplings, as evidenced by cross peaks between signals A and E, and between signals C and D. The TOCSY experiment yielded results which showed all the ^{1}H resonances in the spectrum displaying cross peaks to all the others, confirming the potential of this experimental technique for these systems. Again the cross peak areas are much smaller in this experiment than in the corresponding COSY, due to the phase sensitive nature of TOCSY.

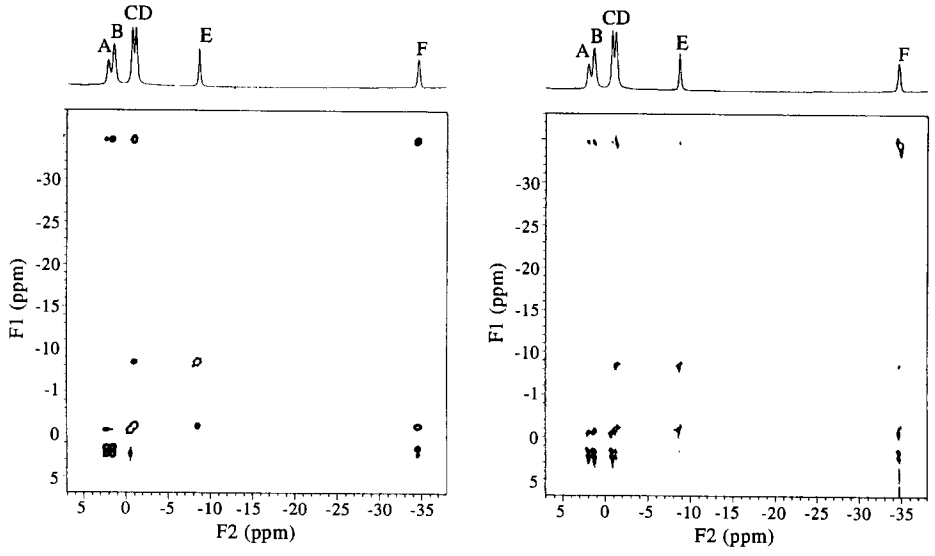

Fig. 3. (a) The absolute value 192.48 MHz ^{11}B COSY plot for 7,9-$Se_2B_9H_9$. The data were acquired using a spectral width of 10,500 Hz in both dimensions. There were 512 fids collected, each of 1280 data points, which were zero filled to 2048 data points on Fourier transformation. The f1 dimension was zero filled to 2048 data points. Proton decoupling was applied throughout the experiment. Data processing involved pseudo-echo multiplication in each dimension prior to Fourier transformation. (b) The 192.48 MHz ^{11}B TOCSY plot for 7,9-$Se_2B_9H_9$. The data were acquired using a spectral width of 10,500 Hz in both dimensions, using the States–Haberkorn–Ruben method, with 256 t_1 increments. Each fid was of 1280 data points, which were zero filled to 2048 data points on Fourier transformation. The f1 dimension was zero filled to 2048 data points. Proton decoupling was applied throughout the experiment. The 90° pulse was 43 μs, and a relaxation delay of 300 ms was used. The spin lock mixing time employed was 30 ms.

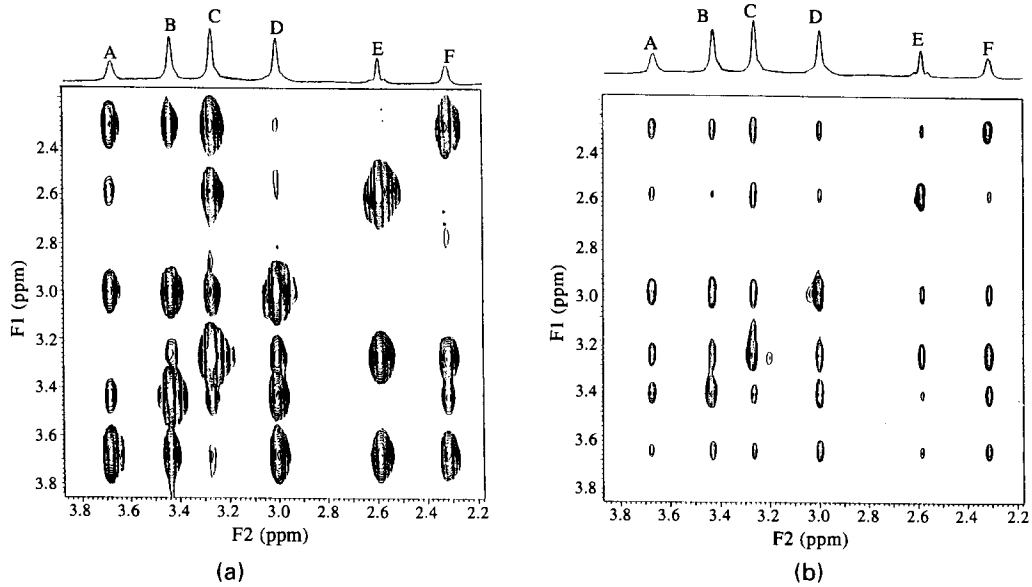

Fig. 4. (a) The absolute value 600 MHz ^{1}H COSY plot for 7,9-$Se_2B_9H_9$. The data were acquired using a spectral width of 4000 Hz in both dimensions. Each fid was of 1024 data points, which were zero filled to 2048 data points on Fourier transformation. The f1 dimension was zero filled to 512 data points. ^{11}B decoupling was applied throughout the experiment. The 90° pulse was 31.7 μs, and a relaxation delay of 1.5 s was used. Data processing involved pseudo-echo multiplication in each dimension prior to Fourier transformation. (b) The 600 MHz ^{1}H TOCSY plot for 7,9-$Se_2B_9H_9$. The data were acquired using a spectral width of 4000 Hz in both dimensions, using the States–Haberkorn–Ruben method, with 128 t_1 increments. Each fid was of 1024 data points, which were zero filled to 2048 data points on Fourier transformation. The f1 dimension was zero filled to 1024 data points. ^{11}B decoupling was applied throughout the experiment. The 90° pulse was 31.7 μs, and a relaxation delay of 1.5 s was used. The spin lock mixing time employed was 50 ms.

CONCLUSIONS

It has been shown that the TOCSY experiment can be successfully applied to boron hydride derivatives, using either ^{11}B and ^{1}H as the observe nuclei. It is likely that the use of ^{11}B as the observe nucleus may be inhibited by its relaxation properties and, in some instances, by its wide chemical shift range, whereas the most probable limiting factors in the use of ^{1}H are likely to be its relatively narrow chemical shift range (with the consequent signal overlap that may result) and the difficulties in getting complete ^{11}B decoupling, though the latter problem is somewhat offset by improvements in decoupling techniques (e.g. GARP[7] etc.). These problems are, of course, equally evident for the COSY experiments. It is most likely that TOCSY will find most use in supplementing results using the COSY sequence, along with heteronuclear correlation experiments. It is also likely that more complex systems (e.g. those with more than one borane cage) will be more readily studied as a result of the increased degree of resolution afforded by this technique. Further investigations are currently in progress to examine the potentials of the various correlation techniques across a wide range of systems containing borane clusters.

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