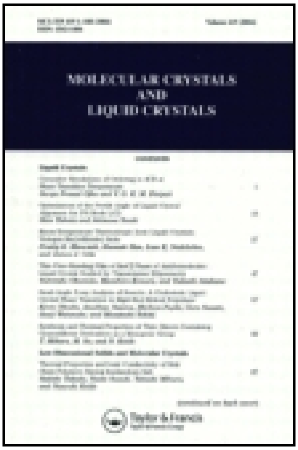

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# Natural Abundance 13-Carbon High-Resolution Magnetic Resonance in Solid 1-Vinyl-o-Carborane

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# Natural Abundance 13-Carbon High-Resolution Magnetic Resonance in Solid 1-Vinyl-*o*-Carborane

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The proton decoupled 13-carbon NMR spectrum of solid 1-vinyl-*o*-carborane has been examined over the temperature range of its plastic phase. At the higher end of the temperature range, high resolution proton coupled 13-carbon spectra have been obtained. A study of the temperature dependence of the $T_1$ values obtained for the individual protonated carbons allows a determination of the activation energy for rotation in the solid phase to be 13.3 KJoule/mole.

Recently, the observation of high-resolution $^{13}C$ spectra of several liquid crystals and adamanate in the room temperature phase[1] as well as solid pivalic acid has been reported[2] along with the determination of spin-lattice relaxation times for the individual carbon atoms in pivalic acid.[3] This report concerns the observations of high-resolution $^{13}C$ spectra of 1-vinyl-*o*-carborane in the solid state, the measurement of spin-lattice relaxation times of the individual nuclei and the interpretation of the temperature dependence of the relaxation times in terms of activation energies for in site rotation of 1-vinyl-*o*-carbonate molecules.

1-Vinyl-*o*-carborane, VOC, belongs to a class of materials known as plastic crystals and shows solid-solid phase transitions at 208°K and 284°K and a melting point of 352°K.[4] The natural abundance $^{13}C$ spectrum has been examined over the temperature range of 301°K to 333°K. At 333°K the completely decoupled $^{13}C$ spectrum of solid 1-vinyl-*o*-carborane shows resonances at 131.4, 123.2, 73.6 and 60.0 ppm relative to external $d_6$-benzene as 128.0 ppm (Figure 1). The spectrum with inverse-gated-decoupling shows the line at 123.2 ppm as 1:2:1 triplet with a 161 Hz coupling constant, the line at 131.4 ppm as a doublet with a coupling constant of 171 Hz, the line at 73.6

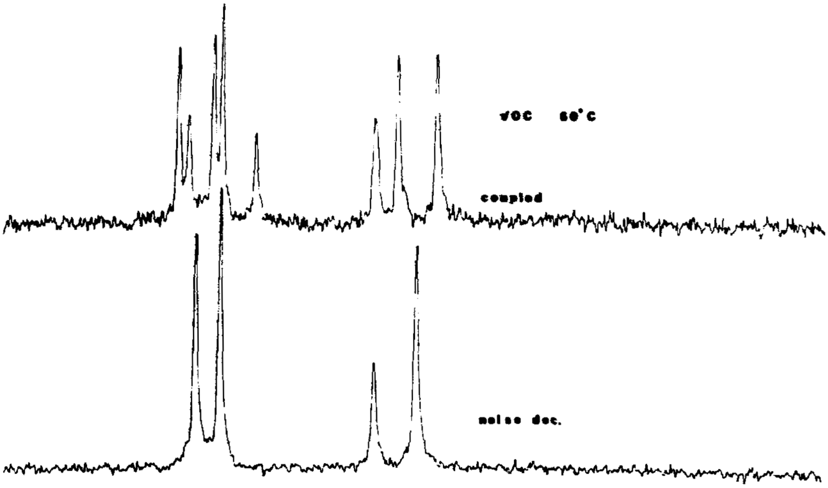

FIGURE 1 Upper trace: The $^{13}C$ spectrum of solid 1-vinyl-*o*-carborane with proton couplings included. Lower trace: The $^{13}C$ spectrum of 1-vinyl-*o*-carborane with 1KHz width noise decoupling.

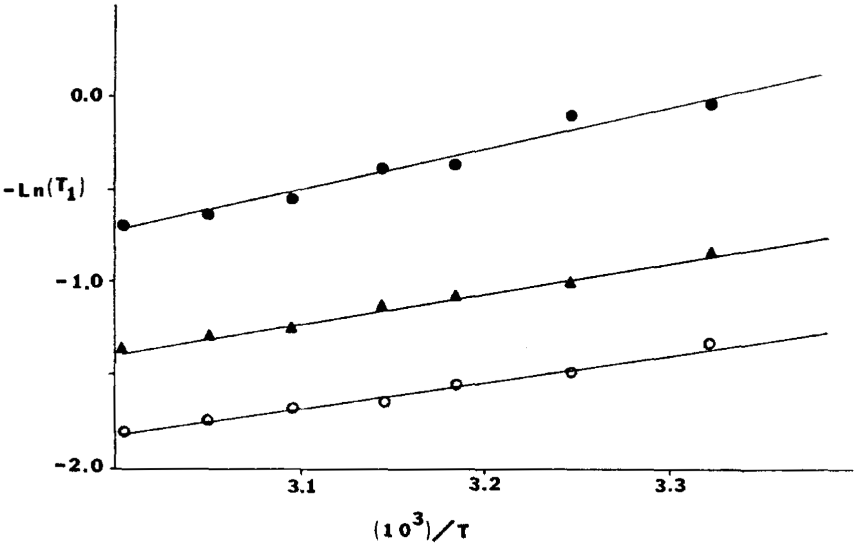

FIGURE 2 Temperature dependence of the relaxation times for the carbon atoms in 1-vinyl-*o*-carborane. ● (*—CH=CH$_2$); ▲ (*CH$_2$=CH—); ○ (cage C—H).

ppm as a singlet and the line at 60.0 ppm as a doublet with a coupling constant of 190 Hz. This data allows the assignment of the carbon resonances as the terminal methylene carbon at 123. 2 ppm and the remaining vinyl carbon as the resonance at 131.4 ppm, the latter assignment based primarily upon the chemical shift. The protonated cage carbon is then assigned as the resonance at 60.0 ppm and the unprotonated cage carbon is assigned as the resonance at 73.6 ppm. Linewidths are on the order of 20 Hz, and the spectrum was independent of spinning rate up to 50 Hz.

The spectra were obtained using a JEOL FX–60Q spectrometer on a sample that has been melted into a 10 mm sample tube. The completely decoupled spectra were obtained on 48 pulses using a 6 $\mu$sec (45°) pulse, 1KHz broadband proton decoupling, and a 5 sec pulse repetition time. Relaxation time measurements were made under the control of the JEOL Auto-Stacking program with 12 $\mu$sec (90°) and 24 $\mu$sec (180°) pulse widths. The results of the spin-lattice relaxation time measurements as a function of temperature are shown in Figure 2. NOE values were measured by comparing the intensities of the spectral lines obtained under gated-decoupling and cw-noise-decoupling conditions. The values obtained for the NOE were 2.39, 2.64, 1.79 and 2.25 for the resonances listed in order of decreasing chemical shift.

The analysis of the temperature dependence of the spin-lattice relaxation times were made using the equations of Allerhard *et al.*,[5] Eq. 1.

$$\frac{1}{T_1} = \left(\frac{1}{10}\right) K^2 r^{-6} \chi$$

$$\chi = \frac{\tau_R}{1 + (\omega_H - \omega_c)^2 \tau_R^2} + \frac{{}^3\tau_R}{1 + \omega_c^2 \tau_R^2} + \frac{{}^6\tau_R}{1 + (\omega_H + \omega_c)^2 \tau_R{}^2} \qquad [1]$$

$$K_2 = h^2 \gamma_c^2 \gamma_H^2$$

Values in the range of 1–3 sec for $T_1$ could be obtained from two different correlation times, approximately $10^{-10}$ sec for the exchange narrowing, fast exchange, region or approximately $10^{-6}$ sec for the slow exchange region. Because the measured Nuclear Overhauser Enhancement is larger than that expected for correlation times of $10^{-6}$ sec, 1.153,[6] the correct choice of correlation times is probably on the fast exchange branch of the curve. Furthermore, the measured $T_1$ values increase with temperature and if the correct correlation times were on the slow exchange branch, they should decrease with increasing temperature. The activation energies for tumbling were determined by plotting $\ln(1/T_1)$ vs $10^3/T$ to give an activation energy of 12.8 KJoule/mole from the data for the resonance at 131 ppm, 15.7 KJoule/mole from the data for the resonance at 123.2 ppm and 11.5 KJoule/mole for the data from the resonance at 60.0 ppm. The average value for the activation energy for rotation is then 13.3 KJoule/mole.

## References

1. C. A. Fyfe, J. R. Lyel, and C. S. Yannon, *J. Mag. Res.*, **31**, 315 (1978).
2. J. D. Graham and J. S. Darby, *J. Mag. Res.*, **23**, 369 (1976).
3. J. D. Graham and J. S. Darby, *J. Mag. Res.*, **23**, 287 (1976).
4. T. J. Klingen and J. R. Wright, *Mol. Cryst. Liq. Cryst.*, **16**, 283 (1972).
5. D. Doddrell, V. Glushko, and A. Allerhand, *J. Chem. Phys.*, **56**, 3683 (1972).
6. K. F. Kuhlman, D. M. Grant, and R. K. Harris, *J. Chem. Phys.*, **52**, 3439 (1970).