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HIGH-RESOLUTION CARBON-13 NUCLEAR MAGNETIC RESONANCE SPECTRA OF SOLID D-CAMPHOR

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Abstract. Proton decoupled natural abundance carbon-13 nmr spectra of solid polycrystalline d-camphor have been measured between 275K and 343K. The observed line widths are relatively sharp, making it possible to measure ^{13}C chemical shifts and spin-lattice relaxation times, T_1's, for several of the individual carbon resonances. From the temperature dependence of T_1 an activation energy of 14.2 ± 2 kJ mole^{-1} is calculated. Effective rotational correlation times derived from the ^{13}C T_1's are compared with those obtained for d-camphor using dielectric techniques. Some general advantages of proton decoupled ^{13}C nmr over ^{1}H nmr in studying molecular reorientation in orientationally disordered solids are discussed.

INTRODUCTION

Camphor is a well known example of an orientationally disordered solid.[1-8] d-Camphor has a melting point of 452K and an entropy of fusion of only 1.4R where R is the gas constant. Heat capacity data indicate a solid-solid phase change at approximately 368K, however, both dielectric [2-6] and proton nmr[8] data indicate that the rotational dynamics of d-camphor are approximately continuous through this phase transition. At 246.6K there is a second solid-solid transition ΔS = 3.8R. Both the ^{1}H nmr and dielectric relaxation data indicate that molecular tumbling is completely quenched in this lower temperature phase.

Here we wish to report the preliminary results of a natural-abundance ^{13}C nmr study of solid d-camphor, and point out some advantages of ^{13}C nmr over ^{1}H nmr in studying molecular reorientation in orientationally disordered solids.

EXPERIMENTAL

Proton-decoupled ^{13}C nmr spectra were obtained on a Varian CFT-20 spectrometer equipped with an 8 mm variable temperature probe, and a Bruker WH-90. The RF decoupling field, γH_2, was greater than 3500 Hz.

A coaxial tube containing cyclohexane-d_{12} and TMS provided the necessary deuterium lock and external reference for chemical shift measurements using the CFT-20.

All ^{13}C T_1's were measured on the Varian CFT-20 using the inversion-recovery pulse sequence and calculated from plots of $\ln\{ \langle M_z\rangle_0 - \langle M_z\rangle_t\}$ vs t^{10}. The 90° pulse width was 15 μs.

RESULTS AND DISCUSSION

A typical proton-decoupled carbon-13 nmr spectrum of solid d-camphor at 316K is shown in figure 1. Peak assignments

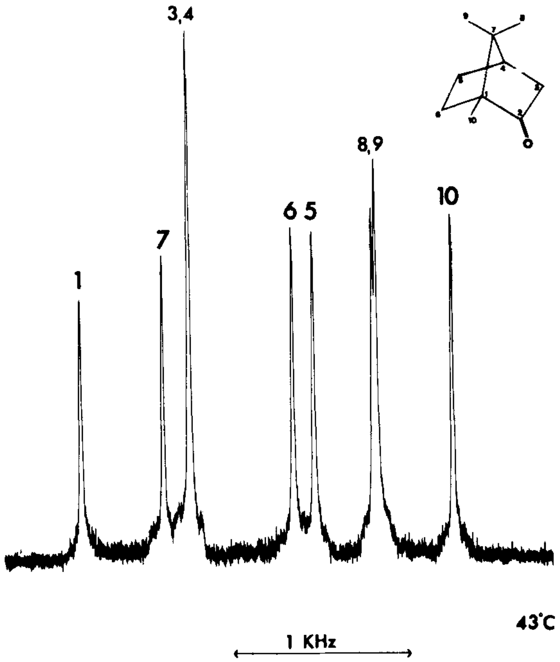

FIGURE 1. ^1H-decoupled 22.6 MHz ^{13}C nmr spectrum of polycrystalline d-camphor at 316K. Line widths at half height are less than 10 Hz. The low field carbonyl resonance is not shown.

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are based on those given in ref. 9. The ^{13}C chemical shifts of solid camphor with respect to external TMS are within 1.0 ppm of those measured for a 1 M solution in benzene.

Carbon-13 T_1's measured as a function of temperature are given in table 1. At 318K the nOe factors for C_5, C_6 and the methyl carbons were 1.8 ± 0.2. This observation together with the observed increase in all measured T_1's as a function of increasing temperature indicates that the dipole-dipole mechanism completely dominates, hence[10-11]

TABLE 1 Carbon-13 Spin-Lattice Relaxation Times for Solid d-Camphor[a]

Temp.	C_5	C_6	C_8,C_9	C_{10}
275K	2.7s	2.9s	3.1s	3.5s
288	4.0	3.5	3.9	3.8
293	4.4	4.5	4.1^5	4.4
303	5.2	6.0	5.1	5.2
318	6.6	7.6	7.1	7.4
333	8.5	8.7	8.8	9.1
343	10.2	10.5	11.1	12.2

[a] estimated experimental error is 10%

$$\frac{1}{T_1(^{13}C)} = \frac{N\hbar^2\,\gamma_H^2\,\gamma_C^2}{r_{CH}^6}\,\tau_{eff} \qquad (1)$$

where N is the number of attached protons, $\hbar$ is Planck's constant divided by 2π, r_{CH} is the C-H bond length, τ_{eff} is the effective rotational correlation time and γ_H and γ_C are the proton and carbon-13 magnetogyric ratios, respectively. τ_{eff} values calculated using equation 1 and the data in table 1 are given in table 2. The shorter values of τ_{eff} for the methyl carbons compared to those of C_5 and C_6 at any given temperature indicate that the methyl carbons are relaxed by internal methyl group rotation as well as by overall molecular tumbling. This behaviour is also observed for benzene solutions of camphor.[12]

TABLE 2 Effective Rotational Correlation Times for Solid d-Camphor from Carbon-13 T_1's.

Temp.	C_5	C_6	C_8, C_9	C_{10}
275K	8.6 ps	8.0 ps	5.0 ps	4.4 ps
288	5.8	6.6	4.0	4.1
293	5.3	5.2	3.7	3.5
303	4.5	3.9	3.0	3.0
318	3.5	3.1	2.2	2.1
333	2.7	2.7	1.8	1.7
343	2.3	2.2	1.4	1.3

Plots of ln τ_{eff} vs 1/T for C_5, C_6 and the methyl carbons are linear within experimental error and have a slope corresponding to $E_a = 14.2 \pm 2$ kJ mole^{-1}. This is within experimental error of the value of 11.7 ± 1.3 kJ mole^{-1} obtained from the temperature dependence of the T_1 for the combined unresolved proton resonance signal of solid d-camphor[8].

For comparison we have also measured the ^{13}C T_1's of 1M solutions of d-camphor in benzene at 303K. The T_1's for C_5, C_6, and C_{10} were 6.3 ± 0.6s, 6.6 ± 0.7s and 7.7 ± 0.8s respectively. The nOe factors were essentially full (1.95 ± 0.15 for C_5 and C_6, 1.9 ± 0.15 for C_{10}) thus the effective correlation times calculated from equation 1 are: 3.5 psec (C_5), 3.7 psec (C_6), and 2.0 psec (C_{10}). These results indicate that molecular reorientation of d-camphor in the plastic crystalline phase is only slightly more hindered than in liquid benzene solution.

It is of interest to compare the rotational correlation times obtained here with those available from dielectric relaxation data[6-7]. At 293K and 333K Williams and Smyth[6] derive τ_d values at 20.6 and 13.0 ps respectively for reorientation of the molecular dipole of d-camphor. Taking the average value of the nmr correlation times for C_5 and C_6 from table 2 as τ_{nmr}, one calculates τ_d/τ_{nmr} values of 3.9

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and 4.8 at 293K and 333K respectively. Values of $\tau_d/\tau_{nmr} > 3$ could be due to:[13–15] (1) non isotropic reorientation, (2) errors in the τ values[16], (3) inadequacy of the rotational diffusion model. Support for the latter possibility is obtained from recent Raman data[17] which indicate highly non-exponential correlation functions for d-camphor.

Finally we would like to point out two advantages of conventional proton decoupled ^{13}C nmr over ^{1}H nmr in studying molecular reorientation in solid d-camphor.

1) The ^{13}C nmr linewidths are much narrower than ^{1}H nmr linewidths[8] in the temperature range considered here[†]. The narrow ^{13}C nmr transition(s) make it possible to monitor the local motion at several positions within a molecule.

2) In general it is much easier to interpret ^{13}C relaxation times because one knows which spins are responsible for dipole-dipole relaxation. For ^{13}C, only directly bonded protons are close enough to produce effective fluctuating magnetic fields necessary for ^{13}C spin-lattice relaxation. In the case of protons, there are contributions to the rate of relaxation from protons on the same molecule as well as those on neighbouring molecules. These general advantages of ^{13}C nmr make it possible to study orientationally disordered solids other than camphor using conventional commercially available high-resolution ^{13}C nmr spectrometers without any special modifications [17–19].

[†] The ^{1}H mean-square width (second-moment) is 0.875 G which corresponds to a $\nu_{\frac{1}{2}} \approx 4$ kHz.

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