Carbon-13 Nuclear Magnetic Resonance Studies on Hexamethylethane

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Hexamethylethane, $(CH_3)_3CC(CH_3)_3$, referred to hereafter as HME, is the most symmetrical of the octane molecules. The high-temperature plastic phase exists from the transition point at 152.5 K to the melting point at 374 K.[1] The crystal structure of the plastic phase is a body-centered cubic lattice with two molecules per unit cell.[2] At atmospheric pressure the liquid phase exists for a range of only 6 K.

Molecular motion studies carried out by ^1H NMR on the brittle and plastic phases of HME have shown the existence of a variety of motions such as reorientation of methyl and *t*-butyl groups, overall molecular tumbling and self-diffusion.[3-5] However, ^{13}C relaxation measurements are particulary suited to studies of molecular rotations in plastic crystals since intermolecular contributions and dipolar interaction between like spins do not generally complicate the interpretation, unlike the situation for ^1H and ^{19}F.[6] It should also be remembered that the ^1H and ^{13}C NMR techniques are complementary in the sense that they monitor the rotations of different vectors. For these reasons, we have chosen to examine in a direct fashion the NMR spectrum of the dilute ^{13}C nuclei in HME.

The half linewidth, $\Delta\nu_{1/2}$, of the ^{13}C methyl peak has been measured throughout the plastic phase. The line from the quaternary carbon appeared about 212 Hz downfield for the methyl signal. This line exhibited a shoulder on the methyl peak, and thus contributed somewhat to the half linewidth of the main peak, when $\Delta\nu_{1/2} \gtrsim 160$ Hz. The half linewidth of the methyl peak was about 200 Hz from the transition temperature (152 K) to 280 K. A further increase in the temperature resulted in a gradual decrease in $\Delta\nu_{1/2}$ to about 3 Hz in the liquid phase. It is interesting to note that a similar line narrowing has been reported to occur in the same temperature range for the methyl proton signal of HME.[4,5] That line narrowing was attributed to translational self-diffusion of the molecules.

In succinonitrile [7] the ^{13}C linewidth has also been found to increase with decreasing temperature from 4 Hz at 318 K (13 K below the melting point) to a maximum value of 75 Hz. Similarly, in the plastic phase of adamantane [8] a ^{13}C linewidth of about 49 Hz has been reported.

For a unique motional process $\Delta\nu_{1/2}$ is an inverse measure of the spin-spin relaxation time T_2 for the system.[9] In the high-temperature plastic phase this can also be regarded as the equivalent of the spin-lattice relaxation time in the local field $T_{1\rho}$. Whereas T_1 is controlled by the intramolecular dipole-dipole relaxation mechanism in the studied temperature range (*vide infra*), it seems that T_2 (and $T_{1\rho}$) also get significant contributions from intermolecular relaxation processes.

The observed melting point of HME was not sharp and the melting took place over a few degrees. At about 370 K it was possible to observe both a liquid and a solid (plastic) component in the ^{13}C NMR spectrum. The methyl and quaternary ^{13}C signals in the plastic phase were, respectively, 0.57 and 0.45 ppm downfield for the corresponding signals in the liquid phase. In pivalic acid a chemical shift difference of 1.4 ppm between the liquid and solid has been reported.[10] Although the ^{13}C linewidth of the liquid component of HME was distinctly smaller than that of the plastic component, a large change, like that reported to occur in the proton spectrum,[4] was not observed.

The T_1 values of the methyl carbon have been measured in the temperature range 152 to 378 K. It was difficult to obtain accurate values of T_1 just below the melting point due to the presence of the liquid component. A semilog plot of T_1 *versus* the inverse temperature is shown in Fig. 1. It is seen that there is no discontinuity in T_1 in going from the plastic to the liquid phase, indicating a similar mechanism for rotation in both phases. Similar behaviour has been observed for other spherical or approximately spherical molecules.[11,12]

We belleve that the methyl carbon relaxation is dominated by the dipole-dipole (DD) relaxation mechanism throughout the liquid and plastic phases. This assumption is supported by measurements of the nuclear Overhouser enhancement (NOE) factor η which gave maximal NOE within experimental error ($\eta = 1.8 \pm 10\%$ and $\eta = 2.0 \pm 10\%$ in the liquid and plastic phases, respectively). A negligible contribution from the spin-rotation mechanism is consistent with the reported highly hindered correlated reorientation of the methyl and *t*-butyl groups in HME.[4,5] In most organic solids, however, the barriers hindering methyl group rotation are small.[12]

A minimum in T_1 is not reached with falling temperature since the transition point intervenes. However, the temperature variation of T_1 shows an Arrhenius behaviour with an activation enthalpy E_a of 10.3 kJ mol^{-1}. This value is somewhat higher than the value obtained from ^1H NMR studies of HME in the plastic phase (9.2 kJ mol^{-1}).[4,5] Our value is, however, not unusually high for isotropic reorientation in a plastic crystal [12] (for example, 12.9

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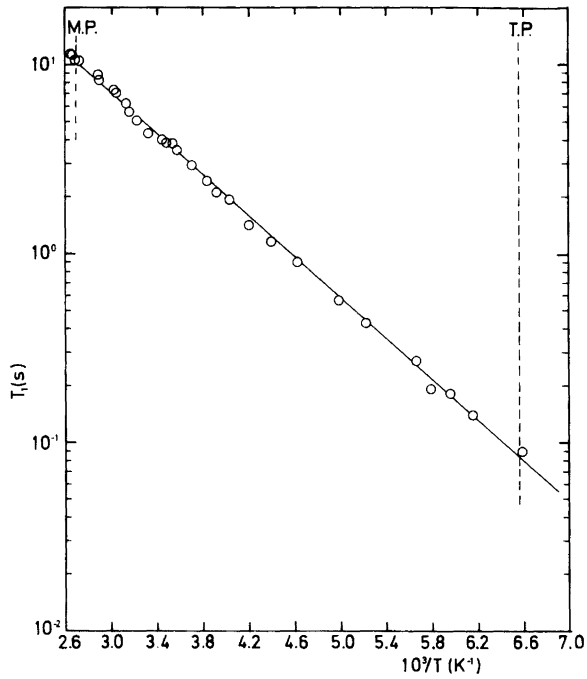

Fig. 1. Carbon-13 spin-lattice relaxation times at 22.63 MHz in hexamethylethane plotted *versus* $10^3/T$.

and 11.7 kJ mol^{-1} in adamantane[11] and *d*-camphor,[13] respectively).

The measured T_1 values are well within the high temperature side of the T_1 minimum, that is, the extreme narrowing condition applies, $(\omega_H + \omega_C)\tau_c \ll 1$ where τ_c is the appropriate correlation time. If contributions from non-bonded protons are ignored, the ^{13}C relaxation time due to the intramolecular C–H dipolar interaction, T_1^{DD}, is given by eqn. (1),[6] where n_H is the number of protons directly attached to the carbon in question, r_{CH} is the C–H bond length and τ_c is the effective isotropic correlation time for molecular reorientation. Assuming that $r_{CH} = 1.10$ Å, as found for ethane, it follows from eqn. (1) that T_1 for the methyl carbon is given by eqn. (2). However, if there is internal

$$1/T_1^{DD} = \hbar^2 \gamma_H^2 \gamma_C^2 n_H r_{CH}^{-6} \tau_c^{eff} \quad (1)$$

$$1/T_1^{DD}{}_{Me} = 6.097 \times 10^{10} \tau_c^{eff} \quad (2)$$

rotation of specific groups, such as a methyl group attached to an isotropically tumbling molecule, one must take into account two correlation times, τ_r for overall rotation and τ_i for internal rotation.[14,15] For $\tau_i \ll \tau_r$ it can be shown that $\tau_c^{eff} = \tau_r/9$. When $\tau_r \ll \tau_i$, however, $\tau_c^{eff} = \tau_r$. Thus, in either limit the dipolar relaxation time is related to the overall tumbling motion alone, whereas for intermediate cases both motions contribute.

By using eqn. (2) it is found that $\tau_c^{eff} \approx 1.5 \times 10^{-12}$ s at the melting point ($T_1 \approx 11.0$ s). On the basis of the above discussion, however, it is reasonable to expect a somewhat larger value for τ_r. Values of τ_r have not been measured for many plastic organic solids, however, according to Boden[12] a value of $\tau_r \simeq 2 \times 10^{-12}$ s at the melting point seems to be a characteristic property of these materials. At the transition point $T_1 \simeq 8.5 \times 10^{-2}$ s, thence $\tau_c^{eff} \simeq 1.9 \times 10^{-10}$ s. This value is quite close to those reported for succinonitrile (*ca.* 2.4×10^{-10} s)[7] and adamantane[8] (*ca.* 1.4×10^{-10} s) at the solid-plastic phase transition temperature.

The proton-coupled methyl carbon quartet has been observed at a series of different temperatures in the plastic and liquid phases of HME. The one-bond proton-carbon coupling constant $^1J_{CH} = 126$ Hz in the liquid phase. The four peaks of the quartet remained quite sharp with a separation of 124 – 126 Hz for temperatures down to about 335 K. When the temperature was reduced further the quartet became rapidly broader with partly overlapped lines and reduced peak separation. At 326 K only the two major peaks of the quartet with a separation of 100 Hz, were observed. The quartet collapsed into a single very broad peak at 320 K. A similar

temperature dependence has also been observed for the corresponding methyl quartet of pivalic acid[10,16] and *t*-butyl chloride.[16] This temperature effect is probably the result of hindered reorientations of the *t*-butyl groups or cooperative intermolecular (medium) effects in the plastic phase. This problem is at present being pursued by means of CNDO/2 calculations in an attempt to elucidate the physical nature of the phenomenon.

Experimental. The sample of HME obtained commercially from EGA-Chemie was purified by sublimation. The ^{13}C NMR spectra were measured at 22.63 MHz on a Bruker CXP 100 spectrometer equipped with external deuterium lock. The sample temperature was regulated and stabilized to within 0.5 K by means of a Bruker B-ST 100/700 c temperature control unit. The longest T_1 values were measured by fast inversion-recovery $(180°-\tau-90°-T)_n$ with T (10–12 s) significantly shorter than $5T_1$,[17] whereas the shorter T_1 values were measured using ordinary inversion-recovery $(180°-\tau-90°-T)_n$ with $T \gtrsim 5T_1$.[6] Short and long τ values were alternated in order to minimize errors in T_1 due to systematic spectrometer performance problems like degrading resolution. The 90° pulse length was 12.4 μs. Throughout the experiment the number of scans varied from 50 to 200, depending on the linewidth.

The T_1's were calculated by means of iterative nonlinear least squares methods[18,19] using 7–18 pairs of experimental points. The estimated accuracy of the T_1 values ranges from ±4 to ±10% depending on the numer of τ values and the signal-to-noise ratio.

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