NOTES

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^{14}N Nuclear Quadrupole Relaxation Near the Plastic Transition Point in the Low-temperature Phase of 1,4-Diazabicyclo[2.2.2]octane

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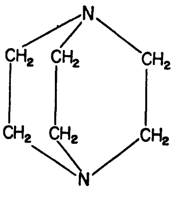
Synopsis. The relaxation mechanism near the plastic transition in the low-temperature phase of 1,4-diazabicyclo[2.2.2]octane is attributed to the overall molecular tumbling. The activation energy is 23.0 kJ mol^{-1}, which is nearly equal to the value of 22.2 kJ mol^{-1} in the proton NMR in the plastic phase.

1,4-Diazabicyclo[2.2.2]octane (triethylenediamine), $(CH_2CH_2)_3N_2$, is known as a globular molecule. In the room-temperature phase, the crystal is hexagonal, with two molecule per unit cell.[1] At 351 K it is transformed into a plastic form. Smith[2] studied the proton NMR of 1,4-diazabicyclo[2.2.2]octane and made a few measurements of the spin-lattice relaxation time (T_1) between 77 and 160 K. Soda and Chihara[3] also studied the proton NMR of 1,4-diazabicyclo[2.2.2]octane and measured the T_1 between 77 K and the melting point. There is no dip of T_1 on approaching the plastic transition point (T_t) from the low-temperature side. The ^{14}N NQR in 1,4-diazabicyclo[2.2.2]octane was discovered by Haigh and Guibé.[4] Zussman and Alexander investigated this resonance from 77 K to the plastic transition and measured the spin-lattice relaxation time (T_1), the linewidth, and the resonance frequency.[5] According to them, T_1 decreases rapidly towards the plastic transition point, but the behavior near T_t has not been clarified in detail. Therefore, we have measured the T_1 near T_t in detail in order to examine the relaxation mechanism thoroughly.



Experimental

The ^{14}N NQR measurements were carried out using a pulsed spectrometer consisting of a Matec gating modulator, Model 5100, a R. F. gated amplifier, Model 515, and a tuned receiver, Model 615, which was designed by Petersen.[6,7] The spin-lattice relaxation times were determined by the repeating 90° pulse method.[8] The pulse width was about 50 μs. The free induction decay signal was averaged in a Nicolet Instrument, Model 527, signal averager. The rf coil containing the sample was enclosed in a cylindrical brass can. This can was placed inside a cylindrical copper container with insulating spacers. The heating wire was wound on this container and connected to a slide-contact voltage regulator. The container was immersed in a large Dewar vessel containing edible oil. The temperature was measured by the use of a copper-constantan thermocouple and stabilized within ± 0.1 K.

1,4-Diazabicyclo[2.2.2]octane of an extra pure reagent grade was purchased from the Katayama Chemical Ind. Co. and was purified by sublimation in an evacuated vessel several times. About a 20-g portion of the reagent was used for the measurements.

Results and Discussion

The temperature dependence of the spin-lattice relaxation time (T_1) is shown in Fig. 1. T_1 falls just below the transition point (T_t). The NQR signal becomes progressively weaker as the temperature approaches T_t, and no signal is observed above T_t, presumably because of the "melting" of the molecular orientation, which averages out the electric-field gradients. The relaxation times in our sample are in good agreement with those of Zussman and Alexander throughout the temperature range studied.

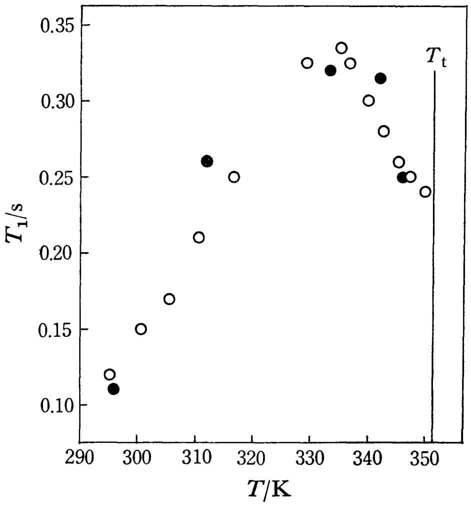


Fig. 1. Temperature dependence of the spin-lattice relaxation times near T_t. Zussman and Alexander's data are shown by the solid circles.

In the room-temperature phase, the N–N axis lies along the hexagonal c axis, and the restricted reorientation of the molecule about the N–N axis is accompanied by a small additional "wobbling" of the N–N axis. In the high-temperature phase above T_t, 351 K, a general molecular reorientation and self-diffusion occur.[2] According to Nimmo *et al.*,[9] molecules at each lattice site undergo hindered reorientations between eight equally weighted orientations at 354 K. It can be said that the "melting" of the molecular orientation or the overall molecular tumbling occurs at T_t. According to the NMR results in the plastic phase reported by Soda and Chihara,[3] the relaxation mechanism is attributable to the overall molecular tumbling near T_t and to the self-diffusion near the melting point (T_m). As the transition temperature, T_t, is approached, this overall molecular tumbling occurs at an increasing rate, which reduces the T_1 of ^{14}N before it affects the T_1 of ^{1}H. A similar phenomenon has been found in the temperature dependence of the T_1 and $T_{1\rho}$ of the protons near T_t for $(CH_3)_3CCOOD$.[10] In this case, the relaxation formula is expressed as follows:[5,11]

$$1/T_1 = C\tau/(1+\omega_Q^2\tau^2) \qquad (1)$$

and

$$\tau = \tau_0 \exp(E_a/RT), \qquad (2)$$

where C is a constant which describes the strength of the interaction, ω_Q is the resonance angular frequency, τ is the correlation time of the motion which changes according to the Arrhenius' relation (2), τ_0 is the inverse frequency factor, and E_a is the activation energy of the motion.

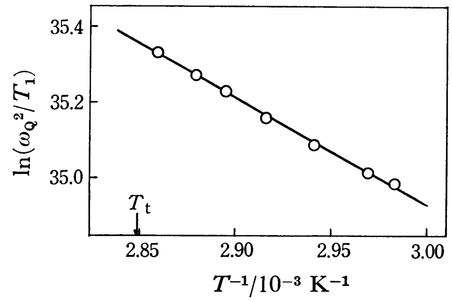


Fig. 2. $\ln(\omega_Q^2/T_1)$ *versus* $10^3/T$.

In the low-temperature region of the T_1 minimum, where $\omega_Q\tau \gg 1$, the following equation is obtained:

$$\ln(\omega_Q^2/T_1) = -E_a/RT + \ln(C/\tau_0) \qquad (3)$$

In the plot of $\ln(\omega_Q^2/T_1)$ *versus* $1/T$, seen in Fig. 2, the slope of the straight line gives the activation energy, E_a. This was found to be 23.0±2.3 kJ mol^{-1}. In the plastic phase, the activation energy of the overall molecular tumbling was found by the proton NMR to be 22.2 kJ mol^{-1}.[3] Accordingly, the reduction of T_1 of ^{14}N is attributed to the overall molecular tumbling.

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