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^{14}N Nuclear Quadrupole Relaxation in *N*-Methylpiperidine

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Synopsis. Two crystal modifications of *N*-methylpiperidine were found by means of the nuclear quadrupole resonance (NQR) of Nitrogen-14. From the temperature dependence of the ^{14}N spin-lattice relaxation times (T_1), it is deduced that the α-form has a lower activation energy for the reorientation of the methyl group than the β-form.

The ^{14}N nuclear quadrupole resonance (NQR) spectrum of *N*-methylpiperidine was first reported by Colligiani *et al.*[1] In the present research we have attempted to obtain further information on the dynamical properties of this compound from the ^{14}N nuclear quadrupole relaxation. The spin-lattice relaxation time (T_1) was measured by the pulse method, and the molecular motions in this compound will be discussed.

Experimental

^{14}N NQR measurements were carried out using a pulse spectrometer described previously.[2] The resonance lines were observed by means of the spin-echo signals, using a 90°—180° pulse sequence series. The spin-lattice relaxation time (T_1) was determined by the repeating-90°—180°-pulse method.[3] The pulse width of a 90° pulse was about 50 μs. The spin-echo signal was averaged by means of a Nicolet Instrument Model 527 signal averager. The temperature was controlled by the method of Abe.[4] The temperature was stabilized within ±0.1 K. The frequency was measured by means of a frequency counter, TR-5104, from the Takeda Riken Co.

N-Methylpiperidine of an extra-pure reagent grade was purchased from the Wako Pure Chemical Ind. Co. and was purified by distillation. About 20 g of the reagent was used for the measurement.

Results and Discussion

In the case of the nitrogen-14 resonance, a pair of NQR absorption lines, ν_- and ν_+, are observed, and the frequencies are expressed as follows:

$$\nu_\pm = \frac{|e^2Qq|}{4h}(3\pm\eta), \qquad (1)$$

where $|e^2Qq/h|$ and η are the quadrupole coupling constant and the asymmetry parameter respectively. Table 1 shows the results at the temperature of liquid nitrogen. The α-form, the ^{14}N NQR spectrum of which was observed by Colligiani *et al.*,[1] is obtained by cooling the compound to the temperature of liquid nitrogen. This form is transformed to the β-form at about 157 K by rapid warming, but remains the same upon slow warming and melts at about 163 K. The data for the α-form were checked again and are listed for comparison.

TABLE 1. ^{14}N NQR PARAMETERS IN α- AND β-FORMS OF *N*-METHYLPIPERIDINE

	ν_-/MHz	ν_+/MHz	$(\lvert e^2Qq/h\rvert)$MHz	η/%
α-Form	3.6898	3.7803	4.9801	3.63
β-Form	3.7674	3.8262	5.0624	2.32

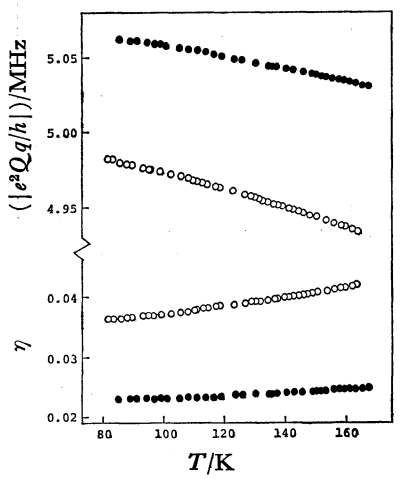

Fig. 1. The temperature dependence of the quadrupole coupling constant and asymmetry parameter in the α-form (○) and β-form (●) of *N*-methylpiperidine.

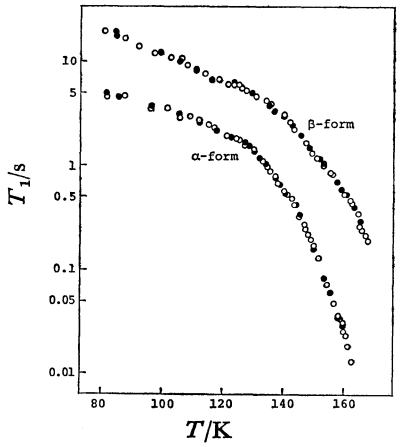

Fig. 2. The temperature dependence of the spin-lattice relaxation times in *N*-methylpiperidine. ●: ν_- line; ○: ν_+ line.

The temperature dependences of the quadrupole coupling constant and the asymmetry parameter in *N*-methylpiperidine in the temperature range from the temperature of liquid nitrogen to the melting point are shown in Fig. 1. The temperature coefficient of the quadrupole coupling constant in the α-form (denoted by the open circle) is slightly smaller than that in the β-form (denoted by the filled circle). This may indicate that the packing of the molecules in the β-form is closer than that in the α-form.

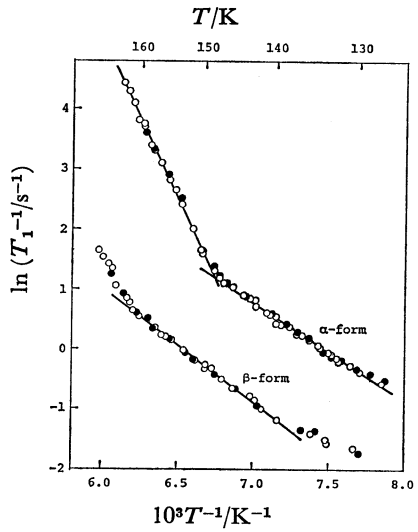

Fig. 3. $\ln(1/T_1)$ *vs.* $10^3/T$ in *N*-methylpiperidine. ●: ν_- line; ○: ν_+ line.

The temperature dependences of the spin-lattice relaxation times (T_1) for the ν_- and ν_+ lines in the α-form and β-form of *N*-methylpiperidine are shown in Fig. 2. In each form, the T_1's for both ν_- and ν_+ lines are coincident within the limits of experimental error. This suggests that the molecular motions equally contribute to T_1 for both resonance lines.

In the case of the α-form, up to 115 K the spin-lattice relaxation time decreases monotonously as the temperature rises. In this region, T_1 is determined by the torsional lattice vibration and is dominated by two indirect phonon processes, so that $1/T_1 \propto T^2$. In the temperature range from about 130 K to the melting point, T_1 drops exponentially as the temperature rises. This process can be attributed to the reorientation of the methyl group around the N–C bond. In this case, the relaxation formula is expressed as follows:

$$1/T_1 = C\tau/(1+\omega^2\tau^2), \quad (2)$$

and:

$$\tau = \tau_0 \exp(E_a/RT), \quad (3)$$

where C is a constant which describes the strength of the interaction; ω is the resonance angular frequency; τ is the correlation time of the motion, which changes according to the Arrhenius relation (Eq. 3); τ_0 is the inverse frequency factor, and E_a is the activation energy of the motion. In the low-temperature region of the T_1 minimum, where $\omega\tau \gg 1$, the following equation is obtained:

$$\ln(1/T_1) = -E_a/RT + f(\omega), \quad (4)$$

where $f(\omega)$ is a function of ω, the temperature dependence of which is negligible. In Fig. 3, the $\ln(1/T_1)$ value is plotted as a function of $1/T$. A break point is found near 150 K; T_1 values below 150 K are dominated by different molecular motions. That is, the dominant relaxation mechanism below 150 K is considered to be caused by the reorientation of the methyl group around the N–C bond, whereas that above 150 K is brought about by the reorientation of the molecule. In fitting Eq. 4 to the experimental T_1 values, the activation energies for these motions are determined to be 12.6 kJ/mol for the former motion and 51.2 kJ/mol for the latter.

The ^{14}N spin-lattice relaxation times (T_1) in *N,N'*-dimethylpiperazine were measured in the temperature range from 77 K to the melting point by Tzalmona and Kaplan.[5] T_1 drops exponentially above 200 K. It is considered that this is caused by the switching between the two chair configurations. The activation energy for this motion is calculated to be 56.5 kJ/mol. Therefore, we consider that the molecular motion with the barrier of 51.2 kJ/mol in *N*-methylpiperidine is the switching motion between the two chair configurations.

In the case of the β-form, below 130 K the spin-lattice relaxation time is determined by the torsional lattice vibration. On the other hand, in the temperature range from 140 K to the melting point (about 168 K), T_1 drops rapidly as a function of the temperature. This may be caused by the reorientation of the methyl group. In Fig. 3, the $\ln(1/T_1)$ value is plotted as a function of $1/T$. In fitting Eq. 4 to the experimental T_1 values, the activation energy for this motion is evaluated to be 15.8 kJ/mol. This value is larger than that in the α-form. This indicates that the methyl group in the β-form is slightly more suppressed than is the α-form. That is, the packing of the molecules in the α-form is less compact than that in the β-form. This is parallel to the finding of the temperature dependence of the quadrupole coupling constant.

References

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