NQR of the 1 : 2 Molecular Complex of 1,4-Diazabicyclo[2.2.2]-octane with Chloroform

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The ^{14}N and ^{35}Cl NQR and ^{14}N spin-lattice relaxation have been studied at various temperatures on the 1:2 molecular complex of 1,4-diazabicyclo[2.2.2]octane (DABCO) with $CHCl_3$. Two transitions have been observed near 123 K and 138 K. In the lowest temperature phase a minimum in the T_1 was observed and attributed to the axial reorientation of DABCO molecules. The activation energy for this motion was determined to be 12.1 ± 1.2 kJ mol^{-1}. The electron population is discussed for the DABCO complexes with $CHCl_3$ and $CDCl_3$ using the Townes-Dailey treatment.

DABCO has been known to form a molecular complex with chloroform by charge transfer from the former to the latter. The crystal structure of this complex has not been determined as yet. DABCO itself is well known as a plastic crystal and its motions have been studied in detail by NMR and NQR.[1,2] Since DABCO is globular, its motion in the complex will offer information about intermolecular interactions and, consequently, a clue to the molecular structure. Lucus and Guibé have already measured ^{14}N and ^{35}Cl NQR of this complex.[3] They reported the average ^{14}N NQR frequency and three ^{35}Cl NQR lines at liquid nitrogen temperature. We observed the temperature dependence of the ^{14}N and ^{35}Cl NQR lines and the ^{14}N spin-lattice relaxation times of the complex in order to examine the molecular motions and intermolecular interactions.

Experimental

The molecular complex was prepared by adding chloroform to DABCO purified by sublimation in an evacuated vessel and then cooling the mixture gently below 250 K. ^{14}N NQR measurements were carried out using a pulsed NQR spectrometer.[4] On the other hand, ^{35}Cl NQR spectra were observed using a superregenerative spectrometer. The temperature was measured by the use of a copper-constantan thermocouple. The frequency was checked by means of a frequency counter.

Results and Discussion

Temperature Dependence of ^{14}N and ^{35}Cl NQR Lines.

TABLE 1. ^{14}N NQR PARAMETERS IN DABCO COMPLEXES AT LIQUID NITROGEN TEMPERATURE

Complex	ν_-/kHz[a]	ν_+/kHz[a]	η/%	(e^2Qq/h)/kHz
$C_6H_{12}N_2 \cdot 2CHCl_3$	3551.0		0	4734.7
	3545.8	3583.9	1.603	4753.1
	3532.7	3567.5	1.470	4730.9
	3528.9	3562.2	1.409	4734.7
$C_6H_{12}N_2 \cdot 2CDCl_3$	3553.1		0	4737.5
	3551.1	3587.6	1.534	4759.1
	3535.9	3571.9	1.519	4738.5
	3532.8	3564.5	1.340	4731.5

a) Experimental error is within ±0.1 kHz.

Tables 1 and 2 show the NQR frequencies for the DABCO complexes at liquid nitrogen temperature. Seven ^{14}N and eleven ^{35}Cl resonance lines were observed for the complex of DABCO with $CHCl_3$ whereas seven ^{14}N and ten ^{35}Cl resonance lines were observed for the complex of DABCO with $CDCl_3$.

In the complex of DABCO with $CHCl_3$, the average frequency of four ^{14}N NQR lines (except three ν_+ lines) is 3.5396 MHz and agrees well with the value of 3.5397 MHz reported by Lucus and Guibé.[3] For ^{35}Cl NQR lines, frequencies of three among eleven resonance lines coincide approximately with the three frequencies, 37.666, 37.853, and 37.955 MHz, reported by Lucus and Guibé.[3] It is not possible at present to interpret the discrepancy in the number of ^{35}Cl resonance lines between the present study and Ref. 3.

Figure 1 shows the temperature dependence of ^{14}N NQR frequencies in the $CHCl_3$ complex. Seven resonance lines at liquid nitrogen temperature are denoted as (a), (b), (c), ···, and (g) as shown in Fig. 1. (a) and (b) as well as (e) and (f) approached each other with increasing temperature and coincided at about 123 K. The intensity of (d) was about twice as strong as those of the rest at liquid nitrogen temperature. As the temperature was raised, (d) became weak from 115 K and faded out near 123 K. Therefore, the seven resonance lines reduced to four near 123 K. These lines disappeared at 138 K but one broad line 50 kHz wide appeared just above this temperature as shown by the solid line in Fig. 1. As the temperature was raised, the

TABLE 2. ^{35}Cl NQR FREQUENCIES OF DABCO COMPLEXES AT LIQUID NITROGEN TEMPERATURE

Complex	ν/MHz[a]		
$C_6H_{12}N_2 \cdot 2CHCl_3$	37.122	37.360	37.402
	37.491	37.642	37.728[b]
	37.818	37.831	37.917
	37.932	38.059	
$C_6H_{12}N_2 \cdot 2CDCl_3$	37.135	37.368	37.412
	37.498	37.648	37.737[c]
	37.833[b]	37.923	37.942
	38.059		

a) Experimental error is within ±0.005 MHz. b) Double intensity line. c) Doublet.

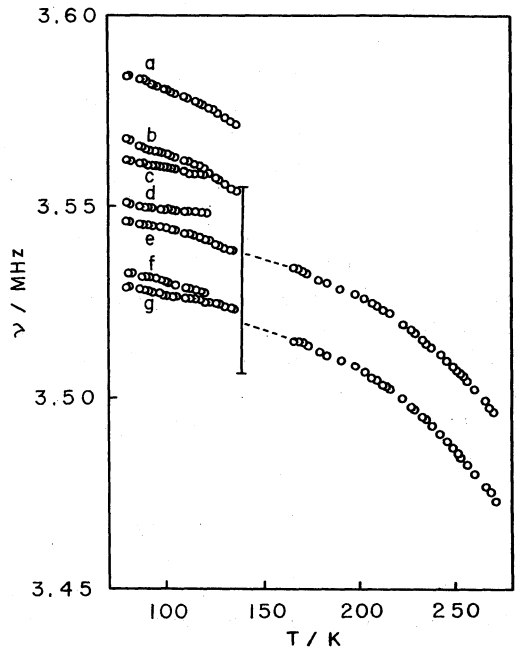

Fig. 1. Temperature dependence of ^{14}N NQR frequencies in $C_6H_{12}N_2 \cdot 2CHCl_3$.

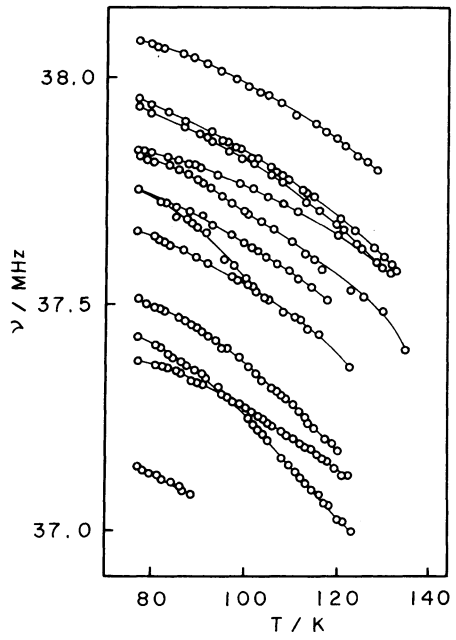

Fig. 2. Temperature dependence of ^{35}Cl NQR frequencies in $C_6H_{12}N_2 \cdot 2CHCl_3$.

linewidth decreased gradually and near 165 K the broad line split into two components. Since it was impossible to determine the resonance frequency with accuracy over the temperature range from 138 K to 165 K, the resonance lines are shown by the dotted lines in Fig. 1.

On the other hand, the temperature dependence of ^{35}Cl NQR frequencies in the $CHCl_3$ complex is shown in Fig. 2. Eleven resonance lines were observed at liquid nitrogen temperature, indicating that there are at least four $CHCl_3$ molecules in this complex. By analogy with ^{14}N resonance lines, the number of ^{35}Cl resonance lines decreased to half near 123 K and faded out

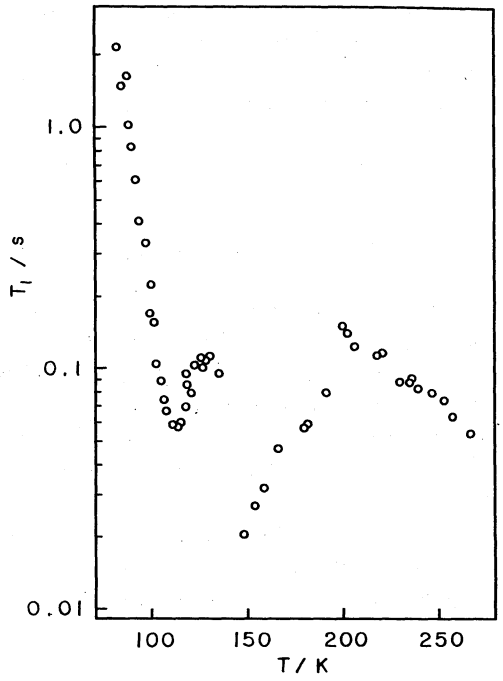

Fig. 3. Temperature dependence of ^{14}N spin-lattice relaxation times in $C_6H_{12}N_2 \cdot 2CHCl_3$. The spin-lattice relaxation times were measured for the (e) line between 80 K and 138 K and for the higher resonance line above 138 K.

near 138 K. However, no ^{35}Cl resonance lines appeared above 138 K up to the melting point (*ca.* 273 K).

^{14}N Spin-Lattice Relaxation Time. Figure 3 shows the temperature dependence of ^{14}N spin-lattice relaxation time in the complex of DABCO with $CHCl_3$. In the temperature range from 80 K to 123 K, the most remarkable feature is the appearance of the T_1 minimum at about 115 K. This process can be attributed to the reorientation of the DABCO molecule about its three-fold axis. The activation energy for this motion was calculated. In this case, the dominant relaxation mechanism can be regarded as magnetic dipole-dipole interaction between ^{14}N and nearby protons. Then, the relaxation time is given by the following equation:[1]

$$1/T_1 = C\tau/(1+\omega_Q{}^2\tau^2), \quad (1)$$

where C is a constant related to the intrinsic nature of the molecular motion. τ is the correlation time of the motion, and ω_Q is the resonance angular frequency. Assuming that the Arrhenius' relation for the correlation time, the following equation holds:

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

where τ_0 is the inverse frequency factor and E_a is the activation energy for the motion. E_a was calculated to be 12.1±1.2 kJ mol^{-1} for this motion from Eqs. 1 and 2 and the observed T_1 values. In the case of DABCO itself, the activation energy about the N-N axis was found to be 34.2±1.3 kJ mol^{-1} by Zussman *et al.*[1] This

value is nearly three times as large as that of the present complex. This finding suggests that the packing of the molecules is somewhat loose in the complex because the DABCO molecule lies between two bulky chloroform molecules.

At T_1 minimum, $\omega_Q\tau=1$ and the following equation holds:[1]

$$T_1^{min} = (8/81)(\omega_Q r_{NH}^6/\gamma_N^2\gamma_H^2\hbar^2), \quad (3)$$

where r_{NH} is the N-H distance in DABCO. γ_N and γ_H are the gyromagnetic ratio of nitrogen and hydrogen, respectively. Assuming that the structure of DABCO in the complex is the same as that in the pure DABCO crystal,[1] the value of T_1 minimum was calculated to be 60 ms. This is in good agreement with the observed value, 63 ms.

Bond Nature. In the case of the ^{14}N resonance, a pair of resonance lines, ν_- and ν_+, are observed and their frequencies are expressed as follow:

$$\nu_\pm = (e^2Qq/4h)(3\pm\eta), \quad (4)$$

where e^2Qq/h and η are the quadrupole coupling constant and the asymmetry parameter, respectively. In the complex of DABCO with $CHCl_3$, two ^{14}N resonance lines at temperatures above 138 K were found to be one pair of ν_- and ν_+ by measuring their Zeeman effect. Below 138 K the small intensity and small spacing of the multiple resonance lines make the measurement of the Zeeman effect unavailable. However, the temperature dependence of the ^{14}N and ^{35}Cl resonance frequencies makes their assignment to resonance lines possible. Since there are at least four crystallographically nonequivalent $CHCl_3$ molecules at liquid nitrogen temperature as described above, four nonequivalent nitrogen atoms should exist: There are seven ^{14}N resonance lines consisting of three pairs of ν_- and ν_+ and one single line. Between 123 K and 138 K, there are four ^{14}N and six ^{35}Cl resonance lines, indicating the presence of two nonequivalent nitrogen and chloroform. Since (b) and (f) lines coincided to (a) and (e) lines, respectively, at the first transition point as shown in Fig. 1, (a) and (e), (b) and (f), and (c) and (g) are paired. The asymmetry parameters and quadrupole coupling constants obtained by this pairing are listed in Table 1.

^{14}N resonance lines of the complex of DABCO with $CDCl_3$ are also listed in Table 1 together with the asymmetry parameters and quadrupole coupling constants evaluated by the same pairing as that of the $CHCl_3$ complex. The ^{14}N resonance frequencies of the $CDCl_3$ complex shift to the higher frequency region than those of the complex with $CHCl_3$ in the same manner as the ^{35}Cl resonance frequencies. In both complexes the nitrogen atoms are considered to form sp^3 hybrid orbitals. Three hybrid orbitals form N-C sigma bonds and the rest is a lone pair nonbonding orbital. Therefore, the quadrupole coupling constant is given by,[6]

$$e^2Qq/h = (3/4)(m-n)e^2Qq_0/h, \quad (5)$$

where m and n are the electron population in the lone pair and sigma bond orbitals, respectively, and e^2Qq_0/h is the quadrupole coupling constant by a 2p electron of nitrogen and is assumed to be 11.3 MHz.[7] From Eq. 5 and the average coupling constant, the value of $(m-n)$ is computed to be 0.5599 and 0.5595 for the $CHCl_3$ and $CDCl_3$ complexes, respectively. This indicates that the electron population in the lone pair nonbonding orbital in the $CDCl_3$ is larger by 0.0004 than those in the $CHCl_3$ if the frequency difference is taken to arise only from hydrogen bonding formation.

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