35Cl NQR in 2,3-dichloroaniline

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^{35}Cl NQR in 2,3-Dichloroaniline+

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Abstract Two resonance lines of ^{35}Cl NQR was observed in 2,3-dichloroaniline from 77 K to the room temperature. The frequencies were exactly assigned by using the empirical equation of Biedenkapp and Weiss. Some anomalous temperature dependence of the resonance frequency was ascribed to the slight departure of the librational axes of the molecule from those estimated from the molecular geometry.

Introduction

In the course of the study on the possibility of the observation of NQR spectrum in the liquid crystal of "anile", an NQR measurement was carried out for chloroanilines, which are the components of anile. The present work is on 2,3-dichloroaniline. The NQR studies on dichloroanilines, such as 2,4-[1], 2,5-[2], and 3,4-[1] dichloroanilines, have already been reported.

Experimental

The sample was a commercial product purified by zone-refining method after vacuume distillation. The methods of the detection of NQR signals and the analysis of the observed data are the same as described in the precceeding paper[3].

Results and Discussion

After searching of the resonance lines in the frequency range of 34-36 MHz at 77 K, two resonance lines of equal intensity were found at 35.800 MHz (ν_1) and 35.400 MHz (ν_2). No splitting of the line due to the crystalline field effect was observed.

Biedenkapp and Weiss[4] found the correlation between the NQR frequency of ^{35}Cl in chlorobenzene derivatives and the substituent parameters:

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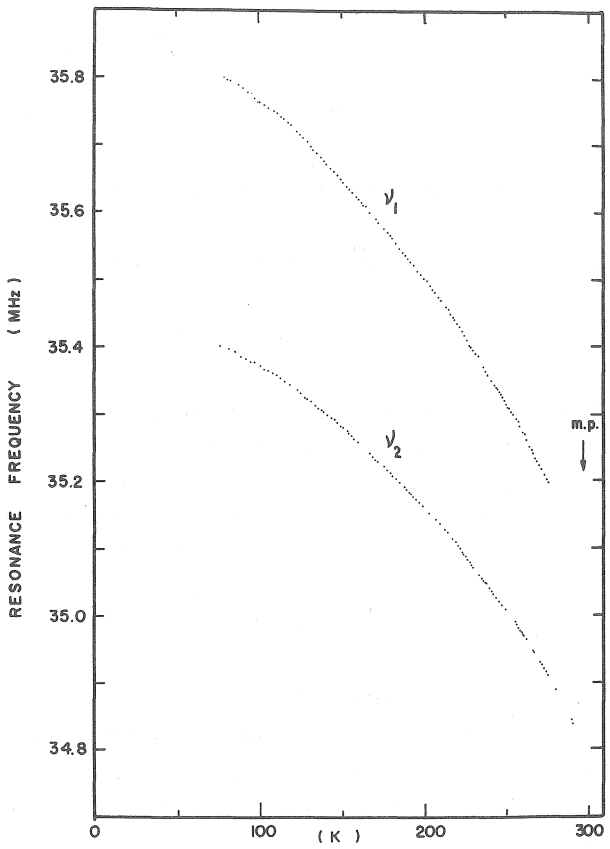

Fig.1. Temperature dependence of ^{35}Cl NQR frequencies in 2,3-dichloroaniline.

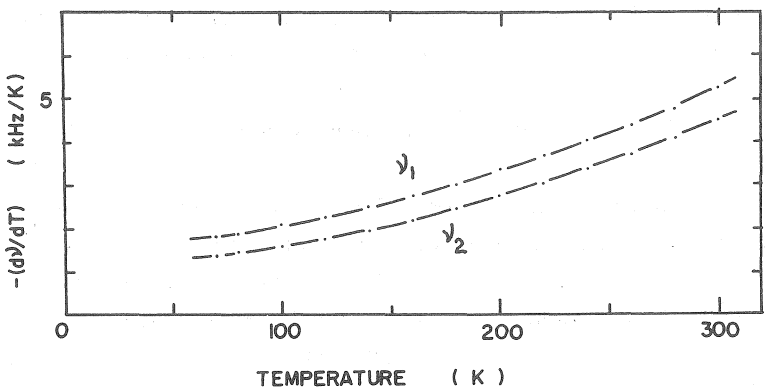

Fig. 2. Temperature dependence of $-(d\nu/dT)$ in 2,3-dichloroaniline.

Table 1. Values of the librational frequency and various fitting parameters.

	Method A	Method B-1			Method B-2			
	ω	ω_{t_0}	α	b_0	ω_{t_0}	α	β	b_0
	cm^{-1}	cm^{-1}	K^{-1}	K^{-1}	cm^{-1}	K^{-1}	K^{-2}	K^{-1}
ν_1	38	44	0.116×10^{-2}	-0.643×10^{-4}	41	0.645×10^{-3}	-0.290×10^{-6}	-0.745×10^{-4}
ν_2	45	54	0.132×10^{-2}	-0.514×10^{-4}	50	0.731×10^{-3}	-0.392×10^{-6}	-0.601×10^{-4}

$t_0=200$ K

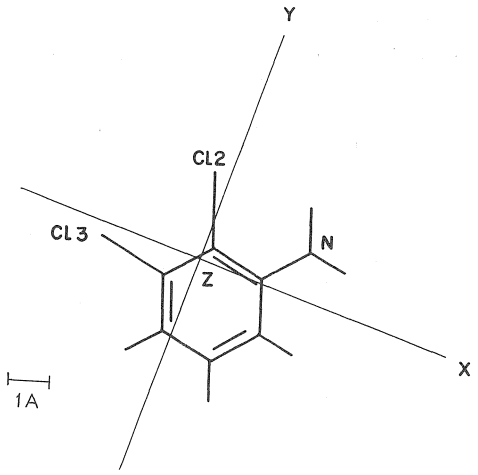

Fig. 3. Assumed molecular geometry of 2,3-dichloroaniline. The values of moment of inertia are $I_X=507\times10^{-40}$ g·cm², $I_Y=664\times10^{-40}$ g·cm², and $I_Z=1170\times10^{-40}$ g·cm².

$$\nu = 34.695+\sum_i \varkappa_i \quad \text{(MHz)}, \tag{1}$$

where $\varkappa_i$ is the best fitted parameters. From the values of $\varkappa_{o\text{-Cl}}=1.206$, $\varkappa_{o\text{-NH}_2}=-0.534$, and $\varkappa_{m\text{-NH}_2}=-0.103$, we obtain that $\nu_{2\text{-Cl}}=35.367$ MHz and $\nu_{3\text{-Cl}}=35.798$ MHz. Hence, ν_1 and ν_2 are assigned to the chlorine atoms of 3- and 2- positions, respectively.

The temperature dependence of the resonance frequencies of the two lines is shown in Fig. 1. In the first grance, no anomalous behavior is seen, but, as shown in Fig. 2, the plots of $-(d\nu/dT)$ against the temperature show the departure from the Bayer's theory,[5] which results in the convergent tendency of $-(d\nu/dT)$.

The librational frequency of the molecule and its temperature coefficients evaluated by using the parameters shown in Fig. 3 are tabulated in Table 1. The coefficients, the values of which were two times as large as those in the "normal" molecular crystals such as tetrachlorothiophene[6], were found. However, the librational frequencies

obtained from the data for the two lines does not coincide with each other. This discrepancy indicates a slight departure of the librational axes in the actual molecular motion from those in the present model of libration due to the crystalline field effect.

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