Inequivalent Reorientation of the Trichloromethyl Groups in 1,4-Bis(Trichloromethyl) Benzene as Studied by Pulsed ^{35}Cl NQR *

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The temperature dependence of T_1 of ^{35}Cl NQR of the title compound evidenced that the three crystallographically inequivalent CCl_3 groups have different potential barriers against reorientation (about 30, 36, and 42 kJ/mol). An intramolecular interaction between π-electrons on the benzene ring and the C–Cl bond is proposed to interpret the characteristic frequency splitting common to the ^{35}Cl NQR spectrum of each of the three inequivalent CCl_3 groups. The magnitude of T_2 of each Cl atom is interpreted by intra- and intermolecular H ⋯ Cl interactions. It was found that only part of the temperature dependence of the NQR frequency can be interpreted by reorientation.

Key words: Chlorine NQR; Spin lattice relaxation; Transeverse relaxation; Molecular structure.

Introduction

The crystal structure of the title compound, 1,4-bis(trichloromethyl)benzene (bisTMB), shows that there are three crystallographically independent trichloromethyl (CCl_3) groups in the asymmetric unit of the crystal [1]. In accord with the crystal structure, a nine line ^{35}Cl NQR spectrum has been observed for bisTMB [2–3]. It is interesting that the nine NQR lines are spread over a frequency range of 38.3–39.6 MHz; this splitting of ca. 1.3 MHz seems to be too large to be accounted for only by the effect of the intermolecular crystal field and hence indicative of certain intramolecular interactions.

Lattice vibrations and the reorientation of CCl_3 in bisTMB were previously studied by means of the pulsed ^{35}Cl NQR method [4, 5]. In these investigations, however, the measurements of the spin lattice relaxation times T_1 (^{35}Cl) were carried out only for a part of the NQR lines. In this work we measured the relaxation time of eight ^{35}Cl NQR lines in detail for further study on the thermal motions of the three inequivalent CCl_3 groups.

The relationship between the frequency splitting and the molecular structure was also examined. To carry out this investigation, it was inevitable to divide the nine NQR lines into three sets of lines and to assign the individual one of these three sets to each of the three CCl_3 groups in the crystal. It will be shown in this paper that the dynamic properties of the inequivalent CCl_3 groups, as found by pulsed ^{35}Cl NQR, are useful to sort the NQR lines.

Experimental

^{35}Cl NQR signals were detected by a frequency modulated super-regenerative spectrometer. A pulsed NQR spectrometer (Matec 5100-525) was employed for the measurements of the spin-lattice relaxation time (T_1), the spin-spin relaxation time (T_2), and the apparent inverse line width parameter (T_2^*). In the low temperature range, where T_1 was longer than T_2, T_1 was determined by the 90°$-\tau-$90°$-\tau'-$180° pulse se-

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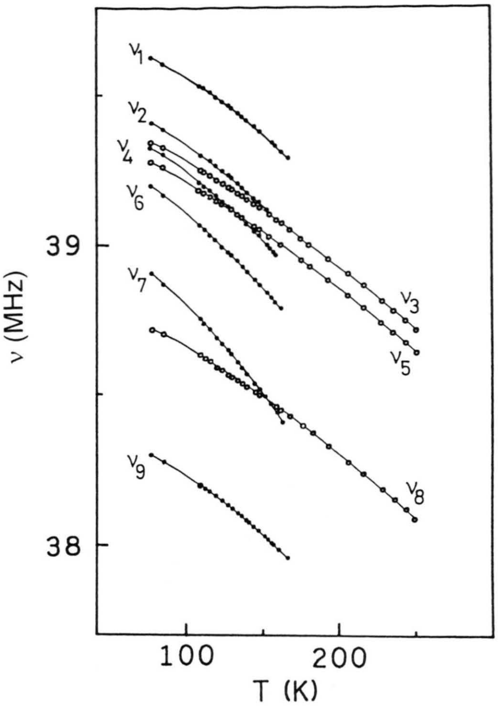
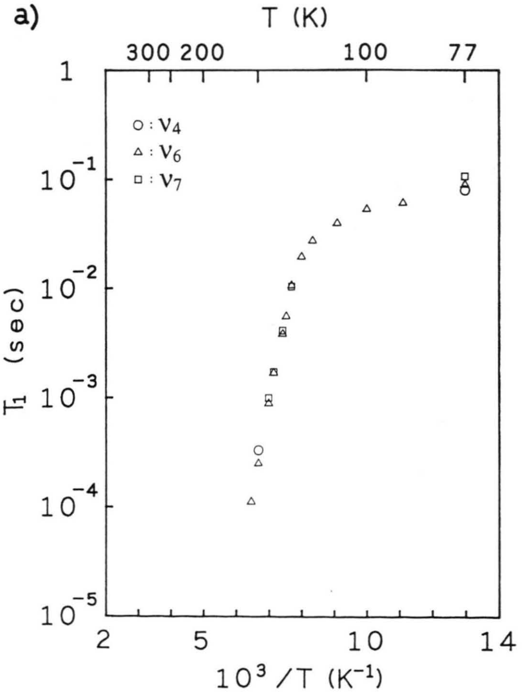
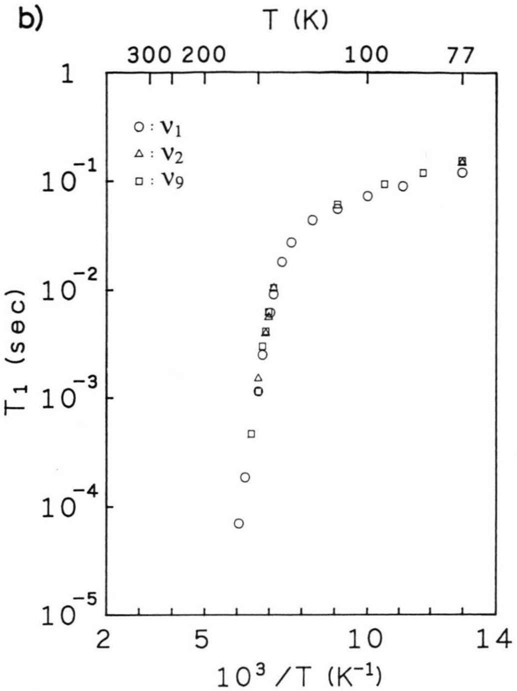


Fig. 1. Temperature dependence of the ^{35}Cl NQR frequencies of 1,4-bis(trichloromethyl)benzene.





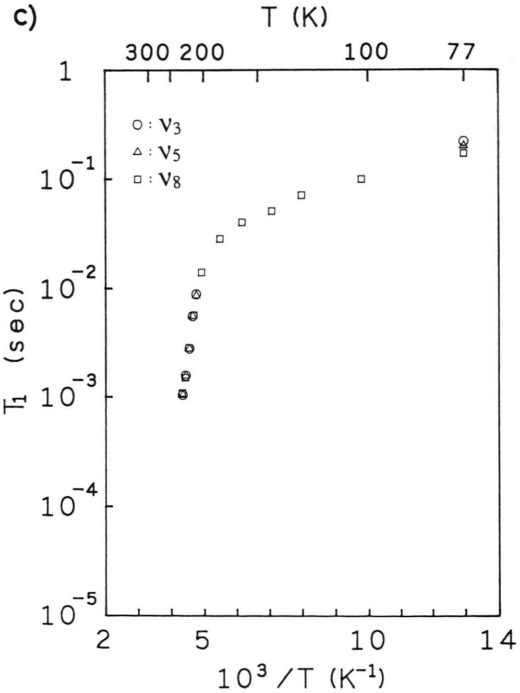


Fig. 2. Temperature dependence of the spin-lattice relaxation time T_1 of ^{35}Cl NQR in 1,4-bis(trichloromethyl)benzene. a) ν_4, ν_6, and ν_7. b) ν_1, ν_2, and ν_9. c) ν_3, ν_5, and ν_8.

quence, while at higher temperatures the $90°-\tau-90°$ pulse method was applied. T_2 was measured with the usual $90°-\tau-180°$ pulse sequence. T_2^*, defined as the time required for a given induction signal to decay to $1/e$ of its maximum value, was obtained from the shape of free induction decay or from that of echo signals. The widths of 90° pulses were from 20 to 25 μs.

Results

The temperature dependence of the ^{35}Cl NQR frequencies is shown in Figure 1. The frequency vs. T relations were approximated by $\nu(^{35}\mathrm{Cl}) = A + BT + CT^2$. The coefficients A, B, and C are listed in Table 1. The measurements of T_1 and T_2 of ν_4 are difficult because ν_5 is located very closely to ν_4 at temperatures above ca. 100 K. Figure 2 shows the T_1 vs. $1/T$ curves of the eight ^{35}Cl NQR lines. Only two points are plotted for ν_4. The sharp decrease of T_1 with increasing temperature obeys equation

$$T_1^{-1} = b \exp\left(-\frac{V_0}{RT}\right), \tag{1}$$

where V_0 is the height of the potential barrier hindering the reorientation of the CCl_3 group [6]. The values of V_0 obtained from the slopes of T_1 vs. $1/T$ curves are listed in Table 2. The values of T_2 at 77 K are also summarized in this table. T_2^* was about 100 μs for each resonance line in the temperature region in which the reorientation of CCl_3 is not exited. It is evident that the line width of ^{35}Cl NQR is governed by inhomogeneous electric field gradients (EFG) owing to lattice imperfections.

Table 1. Coefficients of the power series $\nu(^{35}\mathrm{Cl}) = A + BT + CT^2$. For numbering of ν see Figure 1.

ν_i	A (MHz)	$B \cdot 10^4$ (MHz/K)	$C \cdot 10^5$ (MHz/K^2)
ν_1	39.761	− 7.7245	−1.2121
ν_2	39.558	− 9.5371	−1.2454
ν_3	39.531	−20.275	−0.48289
ν_4	39.482	−10.219	−1.3588
ν_5	39.476	−21.857	−0.45226
ν_6	39.414	−18.488	−1.2287
ν_7	39.142	−17.110	−1.7066
ν_8	38.906	−20.241	−0.48892
ν_9	38.457	−12.631	−1.0033

The magnitudes of V_0 were estimated for the three CCl_3 groups by the atom-atom potential method described in [7]. The results of the calculations of V_0 are given in Table 2.

Discussion

Assignment of the NQR lines

The unit cell of the bisTMB has two crystallographically independent molecules [1]. One of them (molecule 1) is located at a general position, while the center of the other molecule (molecule 2) is at an inver-

Table 2. Selected characteristic parameters of 1,4-bis(trichloromethyl) benzene.

$-CCl_3$ group Set of lines	$-CCl(x)$ (x=14, 15, 16) ν_i (i=4, 6, 7)	$-CCl(y)$ (y=21, 22, 23) ν_j (j = 1, 2, 9)	$-CCl(z)$ (z= 11, 12, 13) ν_k (k = 3, 5, 8)
V_0 (kJ/mol)	ν_4 $\nu_6 \sim 30$ $\nu_7 \sim 30$	$\nu_1 \sim 36$ $\nu_2 \sim 36$ $\nu_9 \sim 36$	$\nu_3 \sim 42$ $\nu_5 \sim 42$ $\nu_8 \sim 42$
$V_{0\,\mathrm{calc}}$ (kJ/mol) [a]	E	E	$4.5\,E$
$\left[\frac{1}{\nu_Q}\frac{d\nu}{dT}\right]_{\mathrm{calc}}$ (K^{-1})	8.50×10^{-5}	7.08×10^{-5}	6.07×10^{-5}
$\left[\frac{1}{\nu_Q}\frac{d\nu}{dT}\right]_{\mathrm{obs}}$ (K^{-1})	ν_4 13.5×10^{-5} ν_6 13.2×10^{-5} ν_7 17.7×10^{-5}	ν_1 10.7×10^{-5} ν_2 10.7×10^{-5} ν_9 10.7×10^{-5}	ν_3 11.2×10^{-5} ν_5 11.3×10^{-5} ν_8 11.4×10^{-5}
B_{eq} (Å^2) [b]	Cl (14) 6.89 (2) Cl (15) 7.55 (4) Cl (16) 7.11 (3) Average 7.18 (3)	Cl (21) 6.19 (2) Cl (22) 5.77 (2) Cl (23) 6.52 (4) Average 6.16 (3)	Cl (11) 5.40 (2) Cl (12) 6.23 (3) Cl (13) 6.20 (3) Average 5.94 (3)
T_2 at 77 K (μs)	ν_4 520 ν_6 670 ν_7 950	ν_1 600 ν_2 580 ν_9 720	ν_3 600 ν_5 530 ν_8 710

[a] $E \sim 70$ kJ/mol; [b] see [1].

sion center. Then, as shown in Fig. 3, the unit cell contains three independent CCl_3 groups; CCl (i) ($i=11$, 12, and 13), CCl (j) ($j=14$, 15, and 16), and CCl (k) ($k=21$, 22, and 23). Since there is no phase transition between 77 K and room temperature, the crystal structure is consistent with the nine line ^{35}Cl NQR spectrum observed between 77 and about 250 K. Since the multiplicity of CCl (21–23) is two, the ^{35}Cl NQR lines of this group are expected to be 2 times as strong as the other six NQR lines.

The values of V_0 obtained for the CCl_3 groups in bisTMB are consistent with those reported for the reorientation of CCl_3 groups in a number of molecular crystals [4–11]. The V_0 value and the fade out temperature of ν_3, ν_5, and ν_8 are in good agreement with those reported for a related compound, *p*-chlorobenzotrichloride (TMB) [11].

It is clear from the values of V_0 and the temperature dependence of $\nu_x (x=1\sim9)$ that the nine NQR lines can be divided into three sets of lines, (ν_1, ν_2, ν_9), (ν_3, ν_5, ν_8) and (ν_4, ν_6, ν_7). The intensities of ν_1 and ν_2 are much stronger than the other ones, and hence the set ν_1, ν_2, and ν_9 is assigned to the trichloromethyl group in molecule 2 (CCl(21–23). As can be seen in Table 2, the equivalent temperature factors (Beq) determined in the X-ray work for the chlorine atoms in CCl (14–16) in molecule 1 are significantly larger than those in CCl (11–13) in the same molecule [1]. This means that the former group has larger amplitudes of thermal vibration and hence smaller V_0. Then ν_4, ν_6, and ν_7 is assignable to CCl (14–16), and ν_3, ν_5, and ν_8) to CCl (11–13). As can be seen in Table 2, V_0 calculated for CCl (11–13) is considerably higher than those of the other CCl_3 groups, and this confirms that ν_3, ν_5, and ν_8 belong to CCl (11–13). It will be seen that these assignments are supported by the discussion given below.

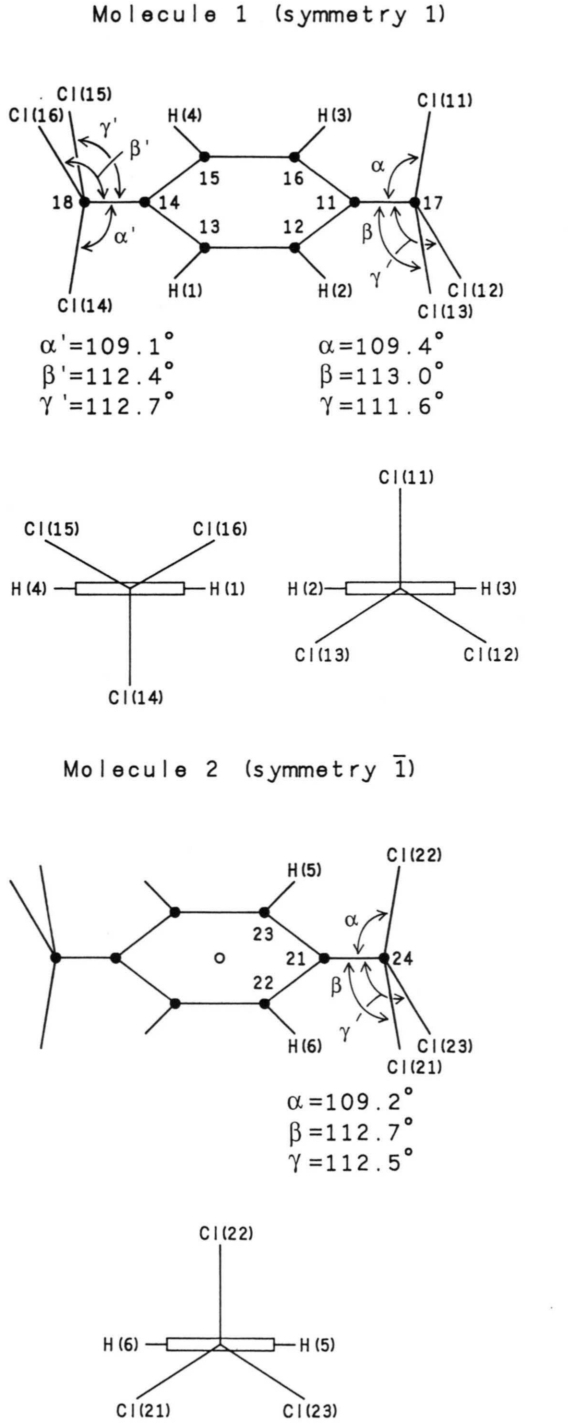


Fig. 3. Molecular structures of molecules 1 and 2 of 1,4-bis(trichloromethyl) benzene.

^{35}*Cl NQR Spectra and Molecular Structure*

In each of the NQR spectra of the three CCl_3 groups (Fig. 4), one can see a characteristic splitting pattern common to the three sets of lines: one NQR line at a lower frequency and two at higher frequencies. This splitting is consistent with the pseudo mirror symmetry of molecules 1 and 2 confirmed by the X-ray work [1]. Then the lowest frequency line of each set can be assigned to the chlorine atoms on the pseudo mirror planes. Thus, ν_7, ν_8, and ν_9 correspond to Cl (14), Cl (11) and Cl (22), respectively.

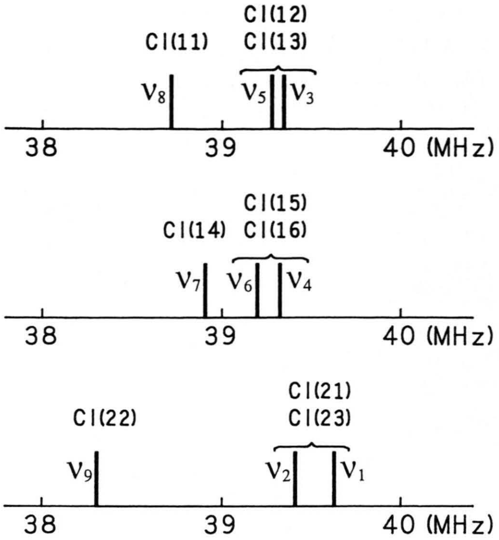


Fig. 4. Stick diagrams showing the locations of the nine ^{35}Cl NQR lines of the three different CCl_3 groups in 1,4-bis(trichloromethyl)benzene at $T=77$ K.

The same splitting pattern of the Cl NQR spectrum of the CCl_3 group has been found for TMB [11]. It has been correlated to the orientation of the CCl_3 group relative to the benzene ring. Namely, the C–Cl (2) bond of TMB which is perpendicular to the benzene ring when seen from the C–C bond, interacts most effectively with the π-electron of the benzene ring to result in a decrease of the NQR frequency of the chlorine atom. The angle of C–C–Cl (2) in TMB was estimated to be 102°, and this value, which is lower than the tetrahedral angle, was considered to be an indication of the interaction [11]. The same mechanism can be used to explain the observed splitting patterns of bis TMB, because the geometries of molecules 1 and 2 are similar to that of TMB (see the angles α, β and γ, shown in Figure 3).

T_2 of ν_3 and ν_5 is significantly shorter than that of ν_8. The same tendency can be seen in the other two sets of lines (see Table 2). In molecule 1, the distances between the chlorine atom on the pseudo mirror plane (Cl (11)) and the hydrogen atoms bonded to the two para-positions of the CCl_3 group (H(2) and H(3)) are ca. 340–360 pm, while the distances Cl (12) $\cdots$ H(3) and Cl (13) $\cdots$ H(2) are 260–270 pm. Similar geometrical relations are seen for the other two CCl_3 groups. If the magnetic dipole moment of the hydrogen atom contributes dominantly to T_2, it is reasonable that T_2 of the chlorine atom on the pseudo mirror plane of a molecule is longer than those of the other two chlorine atoms. Thus the value of T_2 seems to reflect the pseudo mirror symmetry of the bis TMB molecules in the crystal.

The shortest intermolecular H $\cdots$ Cl distances of Cl(11) (ν_8) and Cl (22) (ν_9) are ca. 310 pm, while Cl (14) (ν_7) has no intermolecular H $\cdots$ Cl contact shorter than 400 pm. This seems to be responsible for the fact that T_2 of ν_7 is considerably longer than T_2 of ν_8 and ν_9.

The temperature dependence of the ^{35}Cl NQR frequencies

The temperature dependence of the NQR frequency of the CCl_3 group due to the oscillation around the C–C axis is given by the equation

$$\nu(T)=\nu_Q\left(1-\frac{3h\sin^2\alpha}{16\pi^2 I_r \nu_r}\coth\frac{h\nu_r}{2kT}\right), \tag{2}$$

where ν_Q, ν_r, I_r, and α are the resonance frequency for the rigid lattice, the frequency of the oscillation, the moment of inertia corresponding to the oscillation, and the angle between the C–C and C–Cl bonds in a CCl_3 group, respectively [12–14].

If we assume a sinusoidal potential function $V=\frac{1}{2}V_0(1-\cos 3\theta)$ for the oscillation, then

$$\nu_r=\frac{3}{2\pi}\sqrt{\frac{V_0}{2I_r}}. \tag{3}$$

Using the magnitude of I_r estimated from the geometry of the molecule, we obtained $\nu_r=1.7\times10^{12}$ Hz. Then $kT>h\nu_r$, and hence the following simple relation results [15]:

$$\frac{1}{\nu_Q}\frac{d\nu(T)}{dT}=-\frac{k}{3V_0}. \tag{4}$$

The temperature coefficients calculated from the observed values of V_0 are listed in Table 2. The contribution of the reorientation of the CCl_3 group explains part of the observation, and hence the excess of the temperature coefficient should be attributable to other modes of molecular motions. For CCl (11–13) and CCl (21–23), the libration around the C $\cdots$ CCl_3 axis appears to be responsible, because the three NQR lines in each of the CCl_3 groups exhibit identical temperature coefficients.

Acknowledgements

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