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 n-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 $T_1$ 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°–τ–90°–τ–180° pulse se-
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) $v_4$, $v_6$, and $v_7$, b) $v_1$, $v_2$, and $v_9$, c) $v_3$, $v_5$, and $v_8$. 
sequence, while at higher temperatures the $90^\circ - \tau - 90^\circ$ pulse method was applied. $T_2$ was measured with the usual $90^\circ - T - 180^\circ$ 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 $90^\circ$ pulses were from 20 to 25 $\mu$s.

**Results**

The temperature dependence of the $^{35}$Cl NQR frequencies is shown in Figure 1. The frequency vs. $T$ relations were approximated by $v(35$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 $v_4$ are difficult because $v_5$ is located very closely to $v_4$ 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 $v_4$. The sharp decrease of $T_1$ with increasing temperature obeys equation

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

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 $\mu$s 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.

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-

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Table 1. Coefficients of the power series $v(35$Cl$) = A + BT + CT^2$. For numbering of $v$ see Figure 1.

<table>
<thead>
<tr>
<th>$v_i$</th>
<th>$A$ (MHz)</th>
<th>$B \cdot 10^4$ (MHz/K)</th>
<th>$C \cdot 10^5$ (MHz/K$^2$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$v_1$</td>
<td>39.761</td>
<td>-7.7245</td>
<td>-1.2121</td>
</tr>
<tr>
<td>$v_2$</td>
<td>39.558</td>
<td>-9.5371</td>
<td>-1.2454</td>
</tr>
<tr>
<td>$v_3$</td>
<td>39.531</td>
<td>-20.275</td>
<td>-0.48289</td>
</tr>
<tr>
<td>$v_4$</td>
<td>39.482</td>
<td>-10.219</td>
<td>-1.3588</td>
</tr>
<tr>
<td>$v_5$</td>
<td>39.476</td>
<td>-21.857</td>
<td>-0.45226</td>
</tr>
<tr>
<td>$v_6$</td>
<td>39.414</td>
<td>-18.488</td>
<td>-1.2287</td>
</tr>
<tr>
<td>$v_7$</td>
<td>39.142</td>
<td>-17.110</td>
<td>-1.7066</td>
</tr>
<tr>
<td>$v_8$</td>
<td>38.906</td>
<td>-20.241</td>
<td>-0.48892</td>
</tr>
<tr>
<td>$v_9$</td>
<td>38.457</td>
<td>-12.631</td>
<td>-1.0033</td>
</tr>
</tbody>
</table>

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

<table>
<thead>
<tr>
<th>$-$CCl$_3$ group</th>
<th>$-$CCl(x) ($x$ = 14, 15, 16)</th>
<th>$-$CCl(y) ($y$ = 21, 22, 23)</th>
<th>$-$CCl(z) ($z$ = 11, 12, 13)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$V_0$ (kJ/mol)</td>
<td>$v_4$ ~ 36</td>
<td>$v_5$ ~ 42</td>
<td>$v_6$ ~ 42</td>
</tr>
<tr>
<td>$V_0$ calc (kJ/mol) $^a$</td>
<td>$E$</td>
<td>$E$</td>
<td>$4.5 E$</td>
</tr>
<tr>
<td>$\left[\frac{1}{V_Q} \frac{dv}{dT}\right]_{calc}$ (K$^{-1}$)</td>
<td>$8.50 \times 10^{-5}$</td>
<td>$7.08 \times 10^{-5}$</td>
<td>$6.07 \times 10^{-5}$</td>
</tr>
<tr>
<td>$\left[\frac{1}{V_Q} \frac{dv}{dT}\right]_{obs}$ (K$^{-1}$)</td>
<td>$13.5 \times 10^{-5}$</td>
<td>$10.7 \times 10^{-5}$</td>
<td>$11.2 \times 10^{-5}$</td>
</tr>
<tr>
<td>$B_{eq}$ (Å$^2$) $^b$</td>
<td>Cl(14) 6.89(2)</td>
<td>Cl(21) 6.19(2)</td>
<td>Cl(11) 5.40(2)</td>
</tr>
<tr>
<td></td>
<td>Cl(15) 7.55(4)</td>
<td>Cl(22) 5.77(2)</td>
<td>Cl(12) 6.23(3)</td>
</tr>
<tr>
<td></td>
<td>Cl(16) 7.11(3)</td>
<td>Cl(23) 6.52(4)</td>
<td>Cl(13) 6.20(3)</td>
</tr>
<tr>
<td>Average 7.18(3)</td>
<td>Average 6.16(3)</td>
<td>Average 5.94(3)</td>
<td></td>
</tr>
</tbody>
</table>

$^a$ $E$ ~ 70 kJ/mol; $^b$ see [1].
Molecule 1 (symmetry 1)

\[
\begin{align*}
\alpha' &= 109.1^\circ \\
\beta' &= 112.4^\circ \\
\gamma' &= 112.7^\circ \\
\alpha &= 109.4^\circ \\
\beta &= 113.0^\circ \\
\gamma &= 111.6^\circ 
\end{align*}
\]

Molecule 2 (symmetry \(\overline{1}\))

\[
\begin{align*}
\alpha &= 109.2^\circ \\
\beta &= 112.7^\circ \\
\gamma &= 112.5^\circ 
\end{align*}
\]

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

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The values of \(V_0\) obtained for the CCl₃ groups in bisTMB are consistent with those reported for the reorientation of CCl₃ groups in a number of molecular crystals [4–11]. The \(V_0\) value and the fade out temperature of \(v_3\), \(v_5\), and \(v_8\) 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 \(v_x\) (\(x = 1 \sim 9\)) that the nine NQR lines can be divided into three sets of lines, \((v_1, v_2, v_9)\), \((v_3, v_5, v_8)\), and \((v_4, v_6, v_7)\). The intensities of \(v_1\) and \(v_2\) are much stronger than the other ones, and hence the set \(v_1\), \(v_2\), and \(v_9\) 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 \(v_4\), \(v_6\), and \(v_7\) is assignable to CCl(14–16), and \(v_3\), \(v_5\), and \(v_8\) 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 CCl₃ groups, and this confirms that \(v_3\), \(v_5\), and \(v_8\) belong to CCl(11–13). It will be seen that these assignments are supported by the discussion given below.

\(^{35}\text{Cl} \) NQR Spectra and Molecular Structure

In each of the NQR spectra of the three CCl₃ 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, \(v_7\), \(v_8\), and \(v_9\) correspond to Cl(14), Cl(11) and Cl(22), respectively.
The same splitting pattern of the Cl NQR spectrum of the CC13 group has been found for TMB [11]. It has been correlated to the orientation of the CC13 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).

The shortest intermolecular H···Cl distances of Cl(11) (v8) and Cl(22) (v9) are ca. 310 pm, while Cl(14) (v7) has no intermolecular H···Cl contact shorter than 400 pm. This seems to be responsible for the fact that T2 of v7 is considerably longer than T2 of v8 and v9.

**The temperature dependence of the 35Cl NQR frequencies**

The temperature dependence of the NQR frequency of the CC13 group due to the oscillation around the C−C axis is given by the equation

\[
v(T) = v_0 \left( 1 - \frac{3h \sin^2 \alpha}{16 \pi^2 I_r \cosh \frac{h v_r}{2kT}} \right),
\]

where \(v_0\), \(v_r\), \(I_r\), and \(\alpha\) 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 CC13 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

\[
v_r = \frac{3}{2\pi} \sqrt{\frac{V_0}{2I_r}}.
\]

Using the magnitude of \(I_r\), estimated from the geometry of the molecule, we obtained \(v_r = 1.7 \times 10^{12}\) Hz. Then \(kT > h v_r\), and hence the following simple relation results [15]:

\[
\frac{1}{v_0} \frac{dv(T)}{dT} = -\frac{k}{3v_0}.
\]

The temperature coefficients calculated from the observed values of \(V_0\) are listed in Table 2. The contribution of the reorientation of the CC13 group explains part of the observation, and hence the excess of the temperature coefficient should be attributable to other modes of molecular motions. For CC1(11−13) and CC1(21−23), the libration around the C···CC13 axis appears to be responsible, because the three NQR lines in each of the CC13 groups exhibit identical temperature coefficients.

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