Reorientational Motion of Trihalogenomethyl Groups in Organic Compounds as Studied by $^{35}$Cl NQR and $^{19}$F NMR Spectroscopy

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Trihalogenomethyl derivatives of 4-chloroacetanilide, 4-CIC$_6$H$_4$NHCOCCl$_3$, 4-CIC$_6$H$_4$NHCOCF$_2$Cl, and 4-CIC$_6$H$_4$NHCOCF$_3$ were prepared. The $^{35}$Cl NQR and $^{19}$F NMR spin-lattice relaxation times $T_{10}$ and $T_{1F}$, respectively, of these compounds were measured at various temperatures. On heating, $T_{10}$ of the CCl$_3$ and CF$_2$Cl groups decreased rapidly above ca. 110 and 150 K, respectively, showing the onset of reorientation of the trihalogenomethyl group about the pseudo-triad axis. The activation energies were determined to be 27 and 13 kJ mol$^{-1}$ for the CCl$_3$ and CF$_2$Cl reorientation, respectively. The temperature dependences of the $^{19}$F NMR $T_{1F}$ of the CF$_3$Cl and CF$_3$ groups lead to activation energies of 13 and 4.3 kJ mol$^{-1}$, respectively, for the same reorientations. $T_{1F}$ of the CF$_3$ group observed above ca. 200 K was attributed to the spin-rotational interaction. The $T_{2N}$ law of the onset of reorientation of the trihalogenomethyl group about the pseudo-triad axis. The activation energies were determined to be 27 and 13 kJ mol$^{-1}$ for the CCl$_3$ and CF$_2$Cl reorientation, respectively. The temperature dependences of the $^{19}$F NMR $T_{1F}$ of the CF$_3$Cl and CF$_3$ groups lead to activation energies of 13 and 4.3 kJ mol$^{-1}$, respectively, for the same reorientations. $T_{1F}$ of the CF$_3$ group observed above ca. 200 K was attributed to the spin-rotational interaction. The $T_{2N}$ law with $n = 2.2$ and 1.1, respectively, whereas that of 4-CIC$_6$H$_4$NHCOCF$_3$Cl by the sum of two contributions: $T_{2N}$ law ($n = 2.0$) and the modulation mechanism due to the CF$_2$Cl reorientation.

Key words: Spin-lattice relaxation, NQR, NMR, Reorientational motion.

Introduction

$^{35}$Cl nuclear quadrupole resonance (NQR) signals of CCl$_3$ groups in organic compounds have been reported to disappear far below the melting point [1–11]. This fade-out phenomenon has been interpreted in terms of the onset of reorientation of CCl$_3$ groups. The activation energy and the correlation time of this motion can be determined by the measurements of the spin-lattice relaxation time. The motional parameters so far reported are summarized in [1].

In the present investigation, the reorientation of trihalogenomethyl groups of different sizes and symmetries is studied for trichloro-, difluorochloro-, and trifluoromethyl derivatives of 4-chloroacetanilide. Since mixed trihalogenomethyl groups like CF$_3$Cl contain nuclei with magnetic moments, both $^{35}$Cl NQR and $^{19}$F NMR techniques can be applied to investigate reorientations of mixed trihalogenomethyl groups.

Analyzing the combined data of the spin-lattice relaxation times of $^{35}$Cl NQR and $^{19}$F NMR, we intend to reveal which potential model, symmetric or asymmetric, can be applied for the trihalogenomethyl reorientation. The asymmetric potential model is expected for the mixed CF$_3$Cl group but would be possible also for the CCl$_3$ or CF$_3$ group if the halogen atoms are nonequivalent in the crystal, as reported for 4-CIC$_6$H$_4$NHCOCCl$_3$ [6].

Experimental

Preparations and Chemical Analysis: The chloro- and fluoro-substituted acetanilides were prepared by mixing 4-chloroaniline, trichloroacetonic acid, and phosphorus oxychloride [12]. The products were recrystallized from ethanol several times. 4-CIC$_6$H$_4$NHCOCCl$_3$, 4-CIC$_6$H$_4$NHCOCF$_2$Cl, and 4-CIC$_6$H$_4$NHCOCF$_3$ were all colorless with melting points 128 °C (126–129°C were reported in [6, 12]), 121 °C, and 124 °C (123–124°C in [13]), respectively. Difluorochloro- and trifluoro-4-chloroacetanilide crystallized in needles, trichloro-4-chloroacetanilide in prisms. For the last compound, large single crystals

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Table 1. Elementary analysis of trihalogenomethyl derivatives of 4-chloroacetanilide (in weight %). The calculated values are given in parentheses.

<table>
<thead>
<tr>
<th>Compounds</th>
<th>Found (Calcd.) in weight %</th>
<th></th>
</tr>
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<tbody>
<tr>
<td></td>
<td>C</td>
<td>H</td>
</tr>
<tr>
<td>4-ClC₆H₄NHCOCCl₃</td>
<td>35.3</td>
<td>1.8</td>
</tr>
<tr>
<td></td>
<td>(35.2)</td>
<td>(1.8)</td>
</tr>
<tr>
<td>4-ClC₆H₄NHCOCF₂Cl</td>
<td>40.1</td>
<td>2.0</td>
</tr>
<tr>
<td></td>
<td>(40.0)</td>
<td>(2.1)</td>
</tr>
<tr>
<td>4-ClC₆H₄NHCOCF₃</td>
<td>43.0</td>
<td>2.1</td>
</tr>
<tr>
<td></td>
<td>(42.9)</td>
<td>(2.2)</td>
</tr>
</tbody>
</table>

could easily be grown from a saturated ethanol solution by slow evaporation of the solvent at room temperature. The prepared compounds were identified by elementary analysis (see Table 1).

$^{35}$Cl NQR: The NQR spectra were recorded with a modified Dean-type super-regenerative spectrometer [14] at 77 K. A pulsed NQR spectrometer was used for the spin-lattice relaxation time, $T_{1\varphi}$ measurements [15, 16]. The $180^\circ - \tau - 90^\circ - \tau_e - 180^\circ$ pulse sequence was applied, where the spacing time, $\tau$, was varied while $\tau_e$ was set constant (ca. 150 $\mu$s). The error of $T_{1\varphi}$ measurements is estimated to be ca. ± 10%. The sample temperature was controlled within ± 1 K by a temperature controller (Oxford DTC2) equipped with a gold(0.07% Fe)-chromel thermocouple.

$^{19}$F NMR: A pulsed NMR spectrometer [17] was employed to determine the temperature dependence of the spin-lattice relaxation time, $T_{1F}$. For 4-ClC₆H₄NHCOCF₃, the usual $180^\circ - \tau - 90^\circ$ method was applied at Larmor frequencies of 19 and 42 MHz. For 4-ClC₆H₄NHCOCF₂Cl, the saturation $- \tau - 90^\circ$ method was employed because of a long $T_{1F}$ (ca. 50 s) at room temperature. To obtain the second moment $M_2$ of the absorption line, $^{19}$F NMR spectra were recorded at 40 MHz using a JEOL JNM-MW-40S broadline NMR spectrometer. The error of $T_{1F}$ and $M_2$ measurements is estimated to be ca. ± 10%. The sample temperature was controlled by the previously reported gas flow system [18]. The temperature was determined with copper-constantan thermocouples within ± 1 and ± 3 K for the pulsed and broadline NMR experiments, respectively.

Least-Squares Fitting Calculation: The observed data were compared with the theoretical curves calculated using the least-squares program SALS reported by Oyanagi and Nakagawa [19] at the Nagoya University Computation Center.

Results

$^{35}$Cl NQR:

NQR frequencies of 4-ClC₆H₄NHCOCCl₃, 4-ClC₆H₄NHCOCF₂Cl, and 4-ClC₆H₄NHCOCF₃ at 77 K are listed in Table 2. The data for 4-ClC₆H₄NHCOCCl₃ are in accordance with the literature values [6]. The fact that a single $^{35}$Cl NQR frequency attributable to the ring-chlorine was observed for each compound suggests that all molecules are crystallographically equivalent. For the CCl₃ group three NQR lines $\nu_1$, $\nu_2$, and $\nu_3$ were observed. The temperature dependence of the NQR signals is shown in Figures 1–3. Signals of the CCl₃ group in 4-ClC₆H₄NHCOCCl₃ “bleached out” at ca. 150 K, while those of the CF₂Cl group in 4-ClC₆H₄NHCOCF₂Cl at ca. 220 K. On the other hand, a smooth temperature dependence of the NQR frequency was observed for the ring-chlorine of each compound up to room temperature.

In Figs. 4–6, the temperature dependences of $T_{1\varphi}$ of the three compounds are shown. $^{35}$Cl $T_{1\varphi}$ of the CCl₃ group in 4-ClC₆H₄NHCOCCl₃ decreased rapidly above ca. 110 K, while that of the ring-chlorine showed a weak temperature dependence up

Table 2. $^{35}$Cl NQR frequencies observed for trichloro-, difluorochloro-, and trifluoromethyl derivatives of 4-chloroacetanilide at 77 K. Accuracy ± 1 kHz.

<table>
<thead>
<tr>
<th>Compounds</th>
<th>$\nu$/MHz</th>
<th></th>
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<tbody>
<tr>
<td>4-ClC₆H₄NHCOCCl₃</td>
<td>$\nu_1$</td>
<td>39.902</td>
</tr>
<tr>
<td></td>
<td>$\nu_2$</td>
<td>39.562</td>
</tr>
<tr>
<td></td>
<td>$\nu_3$</td>
<td>39.400</td>
</tr>
<tr>
<td></td>
<td></td>
<td>34.564 (ring-Cl)</td>
</tr>
<tr>
<td>4-ClC₆H₄NHCOCF₂Cl</td>
<td>36.221</td>
<td></td>
</tr>
<tr>
<td></td>
<td>34.826   (ring-Cl)</td>
<td></td>
</tr>
<tr>
<td>4-ClC₆H₄NHCOCF₃</td>
<td>35.015</td>
<td></td>
</tr>
</tbody>
</table>
Fig. 1. Temperature dependences of the $^{35}$Cl NQR frequencies $v$ of 4-ClC\textsubscript{6}H\textsubscript{4}NHCOCCl. •: Ring-chlorine; v, o, α: CCl\textsubscript{3} group.

to room temperature (Figure 4). The “bleaching out” of the CCl\textsubscript{3} signals can be ascribed to the shortening of $T_{1Q}$. The $T_{1Q}$ values for the three chlorines in the CCl\textsubscript{3} group coincided above ca. 110 K within experimental errors. In 4-ClC\textsubscript{6}H\textsubscript{4}NHCOCF\textsubscript{2}Cl, a steep temperature dependence of $T_{1Q}$ was observed for both ring-chlorine and CF\textsubscript{3}Cl chlorine (Figure 5). $T_{1Q}$ of 4-ClC\textsubscript{6}H\textsubscript{4}NHCOCF\textsubscript{3} was slightly temperature dependent (Figure 6).

$^{19}$F NMR: The temperature dependence of $^{19}$F NMR $T_{1F}$ of 4-ClC\textsubscript{6}H\textsubscript{4}NHCOCF\textsubscript{2}Cl measured at 19 MHz is shown in Figure 7. A long $T_{1F}$ (ca. 50 s) at room temperature exponentially increased with decreasing temperature. Figure 8 shows the temperature

Fig. 2. Temperature dependences of the $^{35}$Cl NQR frequencies $v$ of 4-ClC\textsubscript{6}H\textsubscript{4}NHCOCF\textsubscript{2}Cl. •: Ring-chlorine; o: CF\textsubscript{3}Cl group.

Fig. 3. Temperature dependence of the $^{35}$Cl NQR frequency $v$ of 4-ClC\textsubscript{6}H\textsubscript{4}NHCOCF\textsubscript{3}.
Fig. 4. Temperature dependences of the $^{35}$Cl NQR spin-lattice relaxation times $T_{1Q}$ of 4-ClC$_6$H$_4$NHCOCl. •: Ring-chlorine; ◊: CF$_2$Cl group. Solid lines represent the best-fitted theoretical values.

Fig. 5. Temperature dependences of the $^{35}$Cl NQR spin-lattice relaxation times $T_{1Q}$ of 4-ClC$_6$H$_4$NHCOCl. •: Ring-chlorine; ◊: CF$_2$Cl group. Solid lines represent the best-fitted theoretical values.

maximum temperature. The second moment $M_2$ of 4-ClC$_6$H$_4$NHCOCl was independent of temperature and became ca. 2.4 $T^2$ (1 $G = 10^{-4}$ T) above ca. 100 K, as shown in Figure 9.

Discussion

4-ClC$_6$H$_4$NHCOCl: $T_{1Q}$ of the CCl$_3$ group can be attributed to the following two mechanisms: At temperatures lower than ca. 100 K, $T_{1Q}$ is mostly determined by the lattice vibrations. The steep $T_{1Q}$ decrease observed above ca. 110 K is due to the onset of...
Fig. 7. Temperature dependence of the $^{19}$F NMR spin-lattice relaxation time $T_{1F}$ of 4-ClC$_6$H$_4$NHCOCF$_2$Cl measured at 19 MHz.

Fig. 8. Temperature dependences of the $^{19}$F NMR spin-lattice relaxation times $T_{1F}$ of 4-ClC$_6$H$_4$NHCOCF$_3$, measured at 19 and 42 MHz. Solid line represents the best-fitted theoretical values.

Fig. 9. Temperature dependence of the $^{19}$F NMR second moment $M_2$ of 4-ClC$_6$H$_4$NHCOCF$_3$.

hindered rotation of the CCl$_3$ group about the C–C axis [1, 5]. The contribution from this mechanism is supported by the observation that the three chlorines in the CCl$_3$ group showed the same $T_{1Q}$ values at high temperatures.

Assuming three equivalent potential wells for the reorientation, we can derive the following equations for the quadrupolar relaxation, which consists of the lattice vibrational and reorientational mechanisms [21]:

$$T_{1Q}^{-1} = (T_{1Q}^{-1})_{vib} + (T_{1Q}^{-1})_{reorn},$$  \hspace{1cm} (1)
\[ (T_{1Q}^{-1})_{\text{vib}} = a T^n, \]  
\[ (T_{1Q}^{-1})_{\text{reorn}} = \frac{(8/3)}{W_n}, \]  
\[ W = K \exp\left(-\frac{E_a}{RT}\right). \]

Here, \( W \) denotes the transition probability rate between the wells, and \( E_a \) is the activation energy for the reorientation. The index \( n \approx 2 \) is usually expected for the vibrational contribution [22, 23].

The observed \( T_{1Q} \) of \( v_1 \), \( v_2 \), and \( v_3 \) of the \( \text{CCl}_3 \) group was well fitted by (1) (see Figure 4). The determined parameters are listed in Table 3. The same activation energies of \( E_a = 27 \text{kJ mol}^{-1} \) were determined for \( v_1 \), \( v_2 \), and \( v_3 \) in accordance with the uniaxial-reorientation model about the \( \text{C}-\text{C} \) axis. \( n = 2.6, 2.4, \) and \( 2.1 \) were obtained for \( v_1 \), \( v_2 \), and \( v_3 \), respectively.

The temperature dependence of \( T_{1Q} \) of the ring-chlorine was explained by the lattice vibration alone with \( n = 2.2 \) in the whole temperature range studied (see Fig. 4 and Table 3). This result indicates that the phenyl ring performs no reorientational motion in this temperature range where the \( \text{CCl}_3 \) group can reorient.

### 4-ClC\(_6\)H\(_4\)NHCOCF\(_3\): For the mixed trihalogenomethyl group, an unsymmetric potential can be expected for the reorientation about the \( \text{C}-\text{C} \) axis. The quadrupole spin-lattice relaxation due to the reorientation between inequivalent wells has been discussed by Ainbinder et al. [21]. Their most important conclusion is that the spin-lattice relaxation process is described by two exponential decay curves with a long and a short relaxation time. It can be shown, however, that the relaxation process is practically determined by a single relaxation time, which only depends on the higher potential barrier (not on the lower one as described in [21]), in case the potential-energy difference of wells is much larger than the thermal energy.

The fact that recovery of the chlorine magnetization of the \( \text{CF}_2\text{Cl} \) group could be explained by a single exponential law means that the situation corresponds to one of the two extremes, namely, the potential is approximately symmetric or highly unsymmetric. Here, we tentatively assume the former case for simplicity to consistently interpret both the \( ^{35}\text{Cl} \) NQR and \( ^{19}\text{F} \) NMR data.

Using (1), the temperature dependence of \( \text{CF}_2\text{Cl} \) \( T_{1Q} \) was well explained, as shown in Figure 5. The best fit was obtained when \( a = 4 \times 10^{-4} \text{s}^{-1} \) and \( K = 0.7 \times 10^6 \text{s}^{-1} \) (see Table 3).

The slope of log \( T_{1F} \) vs. \( T^{-1} \) plots observed for the \( ^{19}\text{F} \) nuclei (Fig. 7) gives the same activation energy (13 kJ mol\(^{-1}\)) as that derived from \( T_{1Q} \). This implies that both \( T_{1F} \) and \( T_{1Q} \) are assignable to the same motional mode of the \( \text{CF}_2\text{Cl} \) group.

Assuming the slow motion limit, \( (\omega_F - \omega_H) \tau \gg 1 \), where \( \omega_F \) and \( \tau \) denote the angular Larmor frequency of \( ^{19}\text{F}(^1\text{H}) \) and the correlation time of the motion, respectively, the \( ^{19}\text{F} \) spin-lattice relaxation rate \( T_{1F}^{-1} \) of 4-ClC\(_6\)H\(_4\)NHCOCF\(_3\) can be expressed as [24].

\[ T_{1F}^{-1} = \frac{(9/20)\gamma_F^2 h^2}{C/(\omega_F - \omega_H)^2} \tau^6 (1/\omega_F^2 \tau) + (1/20)\gamma_F^2 \gamma_H^2 h^2 \]  
\[ = \frac{C}{(\omega_F - \omega_H)^2} \tau^6 (1/\omega_F^2 \tau). \]

Here, the gyromagnetic ratios of \( ^{19}\text{F} \) and \( ^1\text{H} \), and the \( ^{19}\text{F} - ^{19}\text{F} \) distance in the \( \text{CF}_2\text{Cl} \) group, are denoted by \( \gamma_F \) and \( \gamma_H \), and \( r \), respectively. \( C \) is a geometrical factor depending on the \( ^1\text{H}-^{19}\text{F} \) internuclear vectors [25]. In (5), the dipolar interaction with the NH protons was taken into account because \( (\omega_F - \omega_H)^2 \ll \omega_F^2 \), while

### Table 3. The optimized parameters for the three kinds of contributions to the spin-lattice relaxation of \( ^{35}\text{Cl} \) NQR in trihalogenomethyl derivatives of 4-chloroanilide (see text).

<table>
<thead>
<tr>
<th>Compounds</th>
<th>Libration</th>
<th>Reorientation of trihalogenomethyl group</th>
<th>Modulation due to trihalogenomethyl group reorientation</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>( a/s^{-1} ), ( K/s^{-1} ), ( E_a/kJ \text{mol}^{-1} )</td>
<td>( q'/q ), ( E_a/kJ \text{mol}^{-1} )</td>
<td></td>
</tr>
<tr>
<td>4-ClC(_6)H(_4)NHCOCCl(_3)</td>
<td>( v_1 )</td>
<td>( 5 \times 10^{-5} ), ( 2.6 \pm 0.3 )</td>
<td>( 3 \times 10^{13} ), ( 27 \pm 1 )</td>
</tr>
<tr>
<td></td>
<td>( v_2 )</td>
<td>( 3 \times 10^{-4} ), ( 2.4 \pm 0.3 )</td>
<td>( 3 \times 10^{13} ), ( 27 \pm 1 )</td>
</tr>
<tr>
<td></td>
<td>( v_3 )</td>
<td>( 9 \times 10^{-4} ), ( 2.1 \pm 0.2 )</td>
<td>( 3 \times 10^{13} ), ( 27 \pm 1 )</td>
</tr>
<tr>
<td></td>
<td>ring-Cl</td>
<td>( 1.5 \times 10^{-4} ), ( 2.24 \pm 0.07 )</td>
<td>( 0.7 \times 10^6 ), ( 13 \pm 1 )</td>
</tr>
<tr>
<td>4-ClC(_6)H(_4)NHCOCF(_2)Cl</td>
<td>CF(_2)Cl</td>
<td>( 4 \times 10^{-4} ), ( 2.3 \pm 0.2 )</td>
<td>( 0.17^* ), ( 13 \pm 1 )</td>
</tr>
<tr>
<td></td>
<td>ring-Cl</td>
<td>( 3 \times 10^{-4} ), ( 2.0 \pm 0.2 )</td>
<td>( - )</td>
</tr>
<tr>
<td>4-ClC(_6)H(_4)NHCOCF(_3)</td>
<td>( 7 \times 10^{-2} ), ( 1.11 \pm 0.07 )</td>
<td>( - )</td>
<td></td>
</tr>
</tbody>
</table>

* Calculated by assuming \( K = 0.7 \times 10^6 \text{s}^{-1} \) for the \( \text{CF}_2\text{Cl} \) reorientation.
that with chlorine was neglected because of its small gyromagnetic ratio as compared with that of $^{1}$H or $^{19}$F. The correlation time $\tau$ is related to the transition probability rate $W$ defined by (4) as follows [25]:

$$\tau^{-1} = 3W = 3K \exp(-E_a/R T).$$  \hspace{1cm}(6)

$T_{1F}$ was calculated to be $70 \pm 40$ s at ca. 330 K for the Larmor frequency of 19 MHz, using the motional parameters $K = 0.7 \times 10^9$ s$^{-1}$ and $E_a = 13$ kJ mol$^{-1}$ obtained from the $T_{1Q}$ data analysis and the molecular structure estimated from the crystal data of related compounds [26–29]. Since this theoretical $T_{1F}$ is close to the observed value of $45 \pm 10$ s at 330 K, $T_{1F}$ is explainable by the CF$_2$Cl reorientation between equivalent potential wells, although the possibility of the reorientation in an unsymmetric potential cannot be completely ruled out. Finally, it should be noticed that the observed $T_{1F}$ value cannot be ascribed to the $^{19}$F–$^{19}$F dipolar interaction alone, because this mechanism gives rise to $T_{1F}$ of ca. 400 s at ca. 330 K.

The $T_{1Q}$ of the ring-chlorine of 4-$\text{ClC}_2$H$_4$NHCOCF$_3$Cl shows a rather anomalous decrease above ca. 150 K, which cannot be attributed to the onset of a phenyl-ring reorientation. This is because it is unrealistic to expect reorientation of the whole molecule at such low temperatures. Indeed, the $T_{1Q}$ of the ring-chlorine of the other two compounds studied can be essentially described by the lattice vibrational mechanism. We will show in the following that this anomaly is ascribable to the modulation effect caused by the CF$_2$Cl reorientation.

When a mixed trihalogenomethyl group like CF$_3$Cl performs reorientation, the electric field gradient (EFG) at the ring-chlorine in neighboring molecules may be affected because there are different electrostatic interactions between Cl···Cl and Cl···F. This EFG fluctuation provides an effective relaxation mechanism which can be written as [21]

$$T_{1Q}^{-1}_{\text{mod}} = (2/3)\omega_0^2(q'/q)^2\tau/(1 + \omega_0^2 \tau^2).$$  \hspace{1cm}(7)

Here, $\omega_0$, $(q'/q)$, and $\tau$ denote the $^{35}$Cl quadrupole angular resonance frequency, the fluctuation fraction of the EFG, and the reorientational correlation time of the CF$_2$Cl group given by (6), respectively. In the slow motion limit, $\omega_0 \gg 1$, (7) becomes

$$T_{1Q}^{-1}_{\text{mod}} = (2/3)(q'/q)^2\tau^{-1}.$$  \hspace{1cm}(8)

Taking this modulation mechanism into account, the observed $T_{1Q}$ can be written as

$$T_{1Q}^{-1} = (T_{1Q}^{-1})_{\text{ib}} + (T_{1Q}^{-1})_{\text{mod}}.$$  \hspace{1cm}(9)

By the use of (9) with (2) and (8), the observed temperature dependence of $T_{1Q}$ of the ring-chlorine is well explained as shown in Figure 5. The determined parameters are listed in Table 3; $a = 3 \times 10^{-4}$ s$^{-1}$ K$^{-n}$, $n = 2.0$, $E_a = 13$ kJ mol$^{-1}$, and $3K(q'/q)^2 = 6 \times 10^4$ s$^{-1}$. The fact that $E_a$ agrees precisely with that obtained from the $T_{1Q}$ fitting of the CF$_2$Cl group strongly supports the presence of the modulation mechanism. The fluctuation fraction $(q'/q)$ of the EFG was derived to be 0.17 using the determined $K$ value $(0.7 \times 10^6$ s$^{-1}$) for the CF$_2$Cl group. This large fluctuation suggests a strong electrostatic interaction between the CF$_2$Cl and the ring-chlorine in the neighboring molecule in the crystal.

4-$\text{ClC}_2$H$_4$NHCOCF$_3$: The almost constant $^{19}$F $M_2$ (2.4 G$^2$) above ca. 100 K (Fig. 9) indicates the onset of rapid $C_3$ reorientation of the CF$_3$ group as low as 100 K [20]. The temperature dependence of $T_{1F}$ below ca. 180 K can be described by the magnetic dipolar relaxation in the limit of the fast motion, $\omega_F \tau \ll 1$, where $\omega_F$ is the angular Larmor frequency and $\tau$ is the reorientational correlation time. On the other hand, the $T_{1F}$ decrease at high temperatures is attributable to spin-rotational relaxation [30], because a frequency independent $T_{1F}$ decrease was observed with increasing temperature (Figure 8).

If we assume that the spin-lattice relaxation process involves only dipolar and spin-rotational interactions, the observed $T_{1F}$ can be expressed as

$$T_{1F}^{-1} = T_{1D}^{-1} + T_{1SR}^{-1}. \hspace{1cm}(10)$$

Here, $T_{1D}$ and $T_{1SR}$ are the dipolar and the spin-rotational relaxation times, respectively. $T_{1SR}$ can be written as

$$T_{1SR}^{-1} = \alpha \tau^{-1},$$  \hspace{1cm}(11)

where $\alpha$ is a constant connected with the spin-rotation constant [30]. $T_{1D}$ is given, if $\omega_F \tau \ll 1$, by

$$T_{1D}^{-1} = (10/3)\gamma_F^2 \Delta M_2 \tau,$$  \hspace{1cm}(12)

where $\Delta M_2$ is the second moment difference between the rigid lattice and the motionally narrowed state [31].

When only the dipolar interaction within the CF$_3$ group contributes to $M_2$, $\Delta M_2$ is related to the motionally narrowed value, $\langle M_2 \rangle$, as

$$\Delta M_2 = 3\langle M_2 \rangle.$$  \hspace{1cm}(13)

Substituting the observed $M_2$ value into $\langle M_2 \rangle$ in the above equation, we have estimated $\Delta M_2 = 7.2$ G$^2$. By
applying the usual Arrhenius relationship
\[ \tau = \tau_0 \exp \left( \frac{E_a}{RT} \right), \]  
(14) 
the activation energy, \( E_a \), the correlation time at infinite temperature, \( \tau_0 \), for reorientation of the \( CF_3 \) group, and the proportionality constant, \( \alpha \), were determined by the fitting calculation using
\[ \left( 10 \right) - \left( 12 \right): E_a = 4.3 \, \text{kJ mol}^{-1}, \quad \tau_0 = 2.0 \times 10^{-13} \, \text{s}, \quad \alpha = 2.2 \times 10^{-13}. \]

The theoretical curve with these parameters could exactly reproduce the observed \( T_{1F} \) values (Figure 8). 

The temperature dependence of \( ^{35}\text{Cl} \) \( T_{1Q} \) of \( 4\text{-ClC}_6\text{H}_4\text{NHCOCF}_3 \) could be expressed by (2). However, the index \( n = 1.1 \) appreciably deviates from the theoretically predicted value \( n \approx 2 \) [22, 23]. EFG modulation caused by \( CF_3 \) motion may be a possible explanation for this relaxation anomaly, although the details of the motion are not clear at present.

Remarks on the Motional Parameters: The activation energy for the \( CF_3 \) group reorientation was shown to be very small compared with those for the \( CF_2\text{Cl} \) and \( CC_1 \) groups. The motional parameters for these groups are summarized in Table 4. \( E_a \) increases in the order of \( CF_3 < CF_2\text{Cl} < CC_1 \), suggesting a correlation between the potential barrier to the reorientation and the volume of the reorienting trihalogenomethyl group. For the \( CF_2\text{Cl} \) group we obtained \( \tau_0 = 5 \times 10^{-7} \, \text{s} \) from the \( T_{1Q} \) analysis by assuming reorientation among three equal potential wells. This value may seem to be extraordinarily long compared with those \( \left( 10^{-13} - 10^{-14} \right) \) obtained for the \( CF_3 \) and \( CC_1 \) groups. A similar problem was reported for the reorientation of \( \text{sym-C}_6\text{Cl}_3\text{F}_3 \) molecules in crystals and was solved by assuming molecular jumps between the equilibrium and the metastable orientations [32]. Even assuming the An-derson-type unequal potential wells, \( \tau_0 \) of the same order of magnitude is expected for the present case [21, 33]. In order to obtain more realistic \( \tau_0 \) values, more complicated potential wells seem to have to be introduced: for example, the potential having a metastable position between equilibrium positions separated by 120° rotation. We can say, of course, that the observed data can be better explained by applying complicated potential models having more parameters to be fitted than the above simple model. In this study, satisfactory explanation was obtained by the symmetric potential model, indicating that the extent of asymmetry is not so marked in the present compounds. We have tried no further calculation including complicated shapes of potential curves.

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Table 4. Activation energies, \( E_a \), and correlation times at infinite temperature, \( \tau_0 \), for the reorientational motion of the trihalogenomethyl group \( CX_3 \) in \( 4\text{-ClC}_6\text{H}_4\text{NHCOCX}_3 \).

<table>
<thead>
<tr>
<th>( CX_3 ) group</th>
<th>( E_a/\text{kJ mol}^{-1} )</th>
<th>( \tau_0/\text{s} )</th>
<th>Method</th>
</tr>
</thead>
<tbody>
<tr>
<td>( CF_3 )</td>
<td>( 4.3 \pm 0.1 )</td>
<td>( 2.0 \times 10^{-13} )</td>
<td>NMR</td>
</tr>
<tr>
<td>( CF_2\text{Cl} )</td>
<td>( 13 \pm 1 )</td>
<td>( 5 \times 10^{-7} * )</td>
<td>NQR and NMR</td>
</tr>
<tr>
<td>( CC_1 )</td>
<td>( 27 \pm 1 )</td>
<td>( 1 \times 10^{-14} * )</td>
<td>NQR</td>
</tr>
</tbody>
</table>

* Calculated by \( \tau_0 = (3 \, \text{K})^{-1} \) from the value of \( K \) given in Table 3.

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