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Molecular Motion in Some Hydrogen-Bonded Complexes of Trichloroacetic Acid as Studied by ^{35}Cl-NQR

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The paper presents the results of ^{35}Cl-NQR frequency and spin-lattice relaxation time measurements as a function of the temperature in some solid hydrogen-bonded complexes: Trichloroacetic acid (TCA)-3-cyanopyridine, TCA-4-methylpyridine and $[CCl_3COO\cdots H\cdots OOCCCl_3]^-[K]^+$. The activation energies, E_a, for hindered rotation of CCl_3 group of the TCA molecule were determined. Employing the available E_a data for the other complexes of this type a linear dependence between the activation energy and ^{35}Cl-NQR frequency shift was obtained. This dependence allowed us to find $E_a=f(\Delta pK_a)$ as well as $E_a=f'(P)$ where P is the proton transfer degree. The influence of hydrogen bond on the potential barrier of the rotating CCl_3 groups of TCA in the complexes studied is also discussed.

A series of solid complexes formed by trichloroacetic acid (TCA) with different organic bases ranging from very weak to very strong, was investigated in Refs. 1—5. The purpose of these works was to analyze the proton transfer process in the series investigated via its effect on the chlorine NQR parameters. In the systems studied the hydrogen bond was found to change from the covalent form $A\text{-}H\cdots B$ through the symmetric hydrogen bond $A^{\delta-}\cdots H\cdots B^{\delta+}$ to the totally polar form $A^-\cdots H\text{-}B^+$. The more polar the hydrogen bond the lower is the mean NQR frequency of the TCA ^{35}Cl nuclei. The three ^{35}Cl-NQR lines observed for most of the complexes are the indication of crystallographic nonequivalence of the three chlorine atoms of the CCl_3 group in TCA complexed with a base. When the sample temperature is increased the CCl_3 groups would perform hindered rotations across potential barriers the heights of which are likely to depend on the polarity of the hydrogen bonding in the complexes considered. Temperature investigations of ^{35}Cl-NQR spin-lattice relaxation times T_1 allow determination of the activation energies for these hindered rotations. These, in turn should provide helpful data to distinguish between intra- and intermolecular effects in hydrogen-bonded complexes.

In a previous unpublished work, we had measured the ν_Q and T_1 temperature dependences of the ^{35}Cl-NQR in two TCA-B complexes (B=3-cyanopyridine and 4-methylpyridine) both being strongly hydrogen bonded. Moreover we had measured $\nu_Q(T)$ and $T_1(T)$ for complex $[CCl_3COO\cdots H\cdots OOCCCl_3]^-[K]^+$ which has a symmetric hydrogen bond.[6] Later, Fichtner et al.[3] provided further results on TCA complexes including weaker ones and they correlated the ^{35}Cl-NQR frequency shift and the ^{35}Cl-NQR line fading-out temperature for each complex. These facts led us to search for similar correlation between the activation energies and the frequency shifts, the frequency shifts and the $\Delta pK_a=pK_a(\text{base})-pK_a(\text{TCA})$ and consequently the activation energies and the ΔpK_a. In this paper we present the results of this investigation.

Experimental

The complexes with trichloroacetic acid were obtained in a crystalline form by dissolving the anhydrous bases in a small volume of a mixture of chloroform and carbon tetrachloride (1 : 3) and adding the acid.[5] The resulting precipitates were recrystallized from the chloroform–carbon tetrachloride mixture (1 : 3), and analysis results were satisfactory. Melting points were determined with a hot stage microscope and were presented in Ref. 5.

Measurements of ^{35}Cl-NQR frequency, ν_Q, and spin-lattice relaxation time, T_1, were performed on a laboratory built pulse spectrometer. The $\pi/2\text{-}\tau\text{-}\pi$ sequence was used, with typical pulse widths of 15 and 30 μs respectively. The output RF power of the transmitter was of the order of 1 kW. In order to improve the signal to noise ratio and permit signal recording, a two-channel boxcar integrator with a digital memory was used. High stability of the pulse duration, pulse intervals and sequence repetition period was ensured by a programmed digital generator enabling automatization of the measurements. The ^{35}Cl-NQR frequency was measured with an accuracy of ±1 kHz.

The sample was contained in a copper cell in a temperature-controlled cryostat which provided a temperature stability better than 0.1 K and an absolute accuracy of 0.2 K.

Selection of TCA Complexes for Molecular Motion Studies

In Ref. 5 66 complexes are reported among which three were investigated during the end of the experimental period so that they were not taken into account in the calculations we present in this paper. Consequently, only 63 complexes appear in Fig. 1. ^{35}Cl-NQR spectra of all complexes reveal different but always negative shift of the mean ^{35}Cl-NQR frequency with respect to the mean frequency for pure TCA, i.e. $\Delta\bar{\nu}_Q=\bar{\nu}_Q-\bar{\nu}_{TCA}<0$. The relation between $\Delta\bar{\nu}_Q$ and ΔpK_a allows us to draw the curve presented in Fig.1 which illustrates the proton transfer process in the hydrogen bond. The solid line in Fig. 1 has been drawn according to the equation:[5]

$$\Delta\bar{\nu}_Q=\frac{(\bar{\nu}_{HB}-\bar{\nu}_{TCA})+(\bar{\nu}_{PT}-\bar{\nu}_{TCA})\times10^{\xi\Delta pK_a+C'}}{1+10^{\xi\Delta pK_a+C'}} \qquad (1)$$

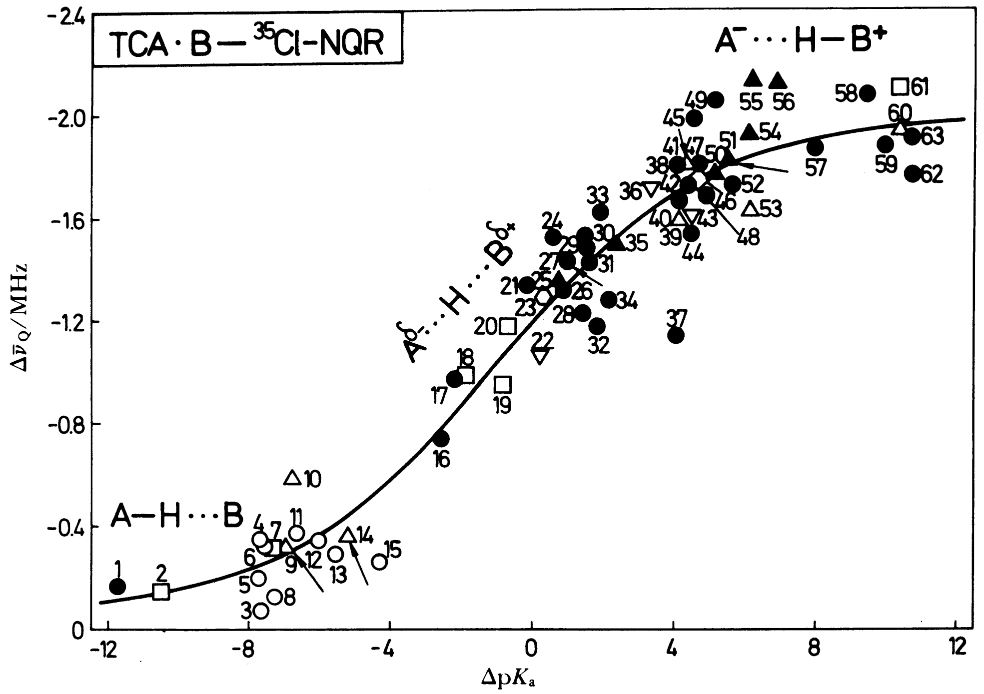

Fig. 1. Shift in mean ^{35}Cl-NQR frequency of the TCA-B complexes versus ΔpK_a. The complexes are labelled according to their base as follows; 1: nitrobenzene, 2: acetonitrile, 3: 2-methylbenzoic acid, 4: acetone, 5: benzoic acid, 6: benzaldehyde, 7: cyclohexanone, 8: phenol, 9: 2-methylbenzaldehyde, 10: 4-methylbenzaldehyde, 11: acetophenone, 12: *p*-anisaldehyde, 13: ethyl acetate, 14: 2,4,6-trimethylbenzaldehyde, 15: *t*-butyl alcohol, 16: triphenylphosphine oxide, 17: 4-nitropyridine *N*-oxide, 18: acetamide, 19: 2-pyrrolidone, 20: *N*,*N*-dimethylacetamide, 21: 4-chloropyridine *N*-oxide, 22: 2-bromopyridine, 23: pyridine *N*-oxide, 24: 3-methylpyridine *N*-oxide, 25: 4-methylpyridine *N*-oxide, 26: 2,6-dimethylpyridine *N*-oxide, 27: 3-cyanopyridine, 28: 4-cyanopyridine, 29: 2,4,6-trimethylpyridine *N*-oxide, 30: 4-benzyloxypyridine *N*-oxide, 31: 4-methoxypyridine *N*-oxide, 32: 4-hydroxypyridine *N*-oxide, 33: 4-methoxy-2-methylpyridine *N*-oxide, 34: 4-phenoxypyridine *N*-oxide, 35: 3-bromopyridine, 36: benzo[*h*]quinoline, 37: cytosine, 38: 8-methylquinoline, 39: aniline, 40: trimethylamine oxide, 41: *N*-methylaniline, 42: 8-quinolinol, 43: quinoline, 44: *N*,*N*-dimethyldodecylamine oxide, 45: 7-methylquinoline, 46: pyridine, 47: 6-methylquinoline, 48: isoquinoline, 49: 3-methylisoquinoline, 50: 4-methylquinoline, 51: 4-methylpyridine, 52: 3,5-dimethylpyridine, 53: *N*,*N*-diethylaniline, 54: 2,4-dimethylpyridine, 55: 2,6-dimethylpyridine, 56: 2,4,6-trimethylpyridine, 57: morpholine, 58: tributylamine, 59: *N*-ethylpiperidine, 60: triethylamine, 61: triethylamine, 62: piperidine, 63: dibutylamine.
Solid line represents the fit with Eq. 1. The complexes studied in this work are denoted by arrows. References: ○;7) ◇;8) ;9) □;10) ▲;1) △;3) ▽;4) ●.5)

where (for group of 63 complexes) $\bar{\nu}_{HB}$= 40.066 MHz, $\bar{\nu}_{PT}$=38.123 MHz, $\bar{\nu}_{TCA}$=40.124 MHz, ξ=0.145 and C'= 0.146.

As it has been already mentioned in the introduction the aim of the paper is to find the correlation between the character of the hydrogen bond and the height of the potential barrier for hindered rotation of CCl_3 groups. The investigation was performed on complexes of different degree of proton transfer corresponding to different points on the curve $\Delta\bar{\nu}_Q = f(\Delta pK_a)$ (Fig. 1). The complexes chosen for this investigation are shown by arrows in Fig. 1. They are also listed in Table 1 which gives the ^{35}Cl-NQR frequencies (ν_Q), mean frequencies ($\bar{\nu}_Q$) and corresponding frequency shifts with respect to pure TCA, and the pK_a of the bases. Moreover, Table 1 gives values of proton transfer degree, *P*, in the hydrogen bond of the complexes TCA-B, determined from the relation used by Chihara and Nakamura in Ref. 8:

$$\bar{\nu}_Q = \bar{\nu}_{HB} + P(\bar{\nu}_{PT} - \bar{\nu}_{HB}). \qquad (2)$$

The analysis was performed for the complexes with a weak hydrogen bond (*P*=0.12; 0.14) as well as for the complexes with almost total proton transfer (*P*=0.88; 0.90). This table also gives the data for $[A\cdots H\cdots A]^-$-$[Me]^+$ type complexes in which the hydrogen bond remains unchanged while the cation changes. Investigation of this group of compounds will be only used to verify our considerations related to the TCA-B type

Table 1. ^{35}Cl-NQR Frequencies (ν_Q) of Pure TCA and a Series of Complexes of Type TCA-B and
$[A\cdots H\cdots A]^-[Me]^+$ (at 77 K) Together with Mean Frequencies ($\bar{\nu}_Q$), Frequency Shifts with
Respect to Pure TCA ($\Delta\bar{\nu}_Q$), pK_a Values of the Bases, Values of the Proton
Transfer Degree (P) and Calculated Activation Energies
for the CCl_3 Group Hindered Rotation (E_a)
^{35}Cl-NQR Frequencies and pK_a Values Were Taken from Refs. 1—3, 5, 6 and This Work

No.	Complex	ν_Q/MHz	$\bar{\nu}_Q$/MHz	$\Delta\bar{\nu}_Q$/MHz	pK_a of base	P	E_a/kJ mol^{-1}
	Trichloroacetic acid (≡TCA)	39.969 40.162 40.242	40.124	0	0.51	—	18.0[a)]
1	TCA-2-methylbenzaldehyde	39.651 39.651 40.121	39.808	−0.316	−6.50	0.12	8.3[c)]
2	TCA-2,4,6-trimethylbenzaldehyde	39.491 39.624 40.176	39.764	−0.360	−4.70	0.14	10.7[c)]
3	TCA-3-cyanopyridine	38.111 38.969 39.023	38.701	−1.423	+1.45	0.69	22.2[b)]
4	TCA-*N*-methylaniline	38.086 38.179 38.729	38.331	−1.793	+4.85	0.88	21.9[c)]
5	TCA-4-methylpyridine	37.867 38.035 39.002	38.301	−1.823	+6.02	0.90	27.8[b)]
6	$(CCl_3COO)_2HRb$	39.121 39.226 40.187	39.511	−0.613	—	—	23.8[c)]
7	$(CCl_3COO)_2HK$	39.114 39.146 39.749	39.336	−0.788	—	—	36.7[b)]
8	$(CCl_3COO)_2HTl$	39.044 39.099 39.824	39.322	−0.802	—	—	41.6[c)]

a) Calculated from $T_1(T)$ dependence (Ref. 13). b) Calculated from $T_1(T)$ dependence (this work). c) Calculated from $\delta\nu_Q$ (T)dependence (Ref. 3).

complexes.

Results of ^{35}Cl-NQR Frequency and Spin-Lattice Relaxation Study and Their Discussion

For compounds **3**, **5**, and **7** presented in Table 1 the temperature measurements of ^{35}Cl-NQR frequencies and spin-lattice relaxation times, were performed. The results of these measurements are shown in Figs. 2—6. For other complexes we employed the data available from Ref. 3. The ^{35}Cl-NQR spectra of all the complexes analyzed (Table 1) are composed of three lines which, in the case of TCA-B complexes, proves crystallographic nonequivalence of the sites of the three Cl atoms of CCl_3 group in TCA molecule. Moreover, only three lines in ^{35}Cl-NQR spectrum of $[A\cdots H\cdots A]^-[Me]^+$ complexes proves that the hydrogen bond in the dimer ion $[CCl_3COO\cdots H\cdots OOCCCl_3]^-$ is symmetrical. Each of the chlorine atoms of CCl_3 group performs torsional vibrations (librations), even at very low temperature. The amplitude of the librations increases with increasing temperature which results in still greater averaging of the electric field gradient evidenced as a decrease in ^{35}Cl-NQR frequency. At higher temperatures the energy of thermal excitations of CCl_3 group is sufficient to overcome the potential barrier separating the equilibrium sites of Cl atoms in the crystal.

The rate of hindered rotation of CCl_3 groups shows an exponential increase with temperature. Introducing the correlation time τ_c, which is a measure of the time a given CCl_3 group spends in the equilibrium position, we can consider the situation where $\tau_c > (2\pi\bar{\nu}_Q)^{-1} \approx 4\times10^{-9}$ s. In such a case the jumps of Cl atoms are not very frequent and the quadrupole transitions

Table 2. Parameters of the Fit of Experimental $\nu_Q(T)$ Values with Bayer Formula —Eq. 3 and Fade-Out Temperatures of the Resonance Lines

Complex	^{35}Cl-NQR line	a/MHz	b/MHz	c/K	$T_{\text{fade-out}}$/K
TCA-3-cyanopyridine	ν_1	38.200	1.912	240.06	145
	ν_2	39.030	3.708	313.05	
	ν_3	39.099	3.170	289.47	
TCA-4-methylpyridine	ν_1	38.031	1.402	173.08	145
	ν_2	38.170	1.270	179.88	
	ν_3	39.099	1.061	189.91	
$(CCl_3COO)_2HK$	ν_1	39.163	1.654	263.04	240
	ν_2	39.179	1.079	266.21	
	ν_3	39.862	1.040	183.75	

can occur if the CCl_3 group is in the stable equilibrium. That is why the slow hindered rotation does not influence the ^{35}Cl-NQR frequency. Thus, librations are mainly responsible for a decrease in NQR frequency with increasing temperature. This was the assumption taken by Bayer[11] who moreover treated a molecule as a quantum harmonic oscillator and obtained the following expression for the temperature dependence of NQR frequency:

$$\nu_Q(T) = a - \frac{b}{\exp(c/T)-1}, \tag{3}$$

$$a = \nu_Q(0);\; b = \frac{6\hbar\nu_Q(0)}{4I\omega_i - 3\hbar};\; c = \frac{\hbar\omega_i}{k}, \tag{4,5,6}$$

$\nu_Q(0)$ is the NQR frequency at 0 K, I is the relevant moment of inertia, ω_i is the librational frequency of the atomic group (here CCl_3). The experimental data of $\nu_Q(T)$ were fit with Eq. 3 (see Figs. 2—4). The appropriate fit parameters are given in Table 2. The data were also fit with other dependences that took into account the unharmonic character of vibrations but using the harmonic approximation of Eq. 3 is quite sufficient in the range of temperature studied which extend from 77 K to the fade-out temperature. At this temperature the lines became so broad and their intensity so small that they reach the sensitivity limit of the spectrometer. This happens when the frequency of the molecular reorientations is of the order of magnitude of the NQR line width. If the temperature is still increased the lines become unobservable. The highest fade-out temperature in this series is 240 K obtained for $(CCl_3COO)_2HK$ (Table 2; Figs. 2—4).

Let us consider now the influence of librations and hindered rotation discussed above on the NQR spin-lattice relaxation. According to Bayer[11] the fluctuations of the electric field gradient caused by librational motions lead to the following relation between T_1 and T:

$$T_1^{-1} = aT^n, \tag{7}$$

where a is a constant, n is usually close to 2. Abrupt changes in electric field gradient due to hindered rotation of molecular groups containing quadrupole nuclei lead to the exponential temperature dependence of relaxation time:[12]

$$T_1^{-1} = b\exp(-E_a/RT), \tag{8}$$

where b is a constant, R the gas constant, and E_a the activation energy of the hindered rotation.

As follows from the dependences $T_1^{-1}(T)$ obtained (Figs. 5—7), both mechanisms of quadrupole spin-lattice relaxation discussed above take place in the complexes studied. Their contribution to the relaxation process add up and this may be expressed as:

$$T_1^{-1} = aT^n + b\exp(-E_a/RT). \tag{9}$$

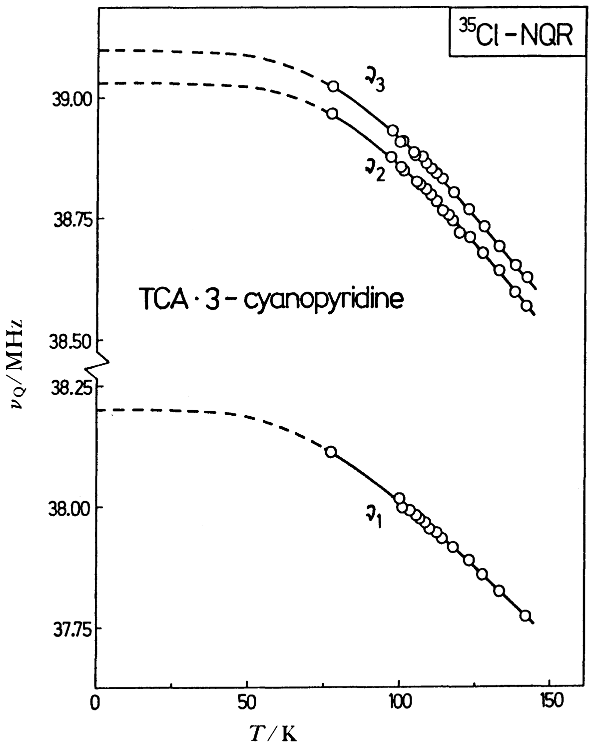

Fig. 2. Temperature dependence of the ^{35}Cl-NQR frequency in TCA-3-cyanopyridine complex. Solid and partly broken line represents the fit with Eq. 3; fitting parameters are given in Table 2.

The appropriate fit parameters between the experimental data of $T_1^{-1}(T)$ and Eq. 9 are given in Table 3. For us, most important are the values of the activation energy for hindered rotation of CCl_3 groups (E_a) in the complexes studied. As follows from Figs. 5—7 the relaxation process may be described at low temperatures by the first term of Eq. 9 only. This term characterizes the influence of librations on the relaxation. For higher temperatures, in the case of TCA-B complexes studied above 110—120 K while for $(CCl_3COO)_2HK$ complex above 170 K, the mechanism of hindered rotation becomes dominating. In these temperature ranges the dependence $T_1^{-1}(T)$ is described by the exponential part of Eq. 9. For the sake of comparison the results of $T_1^{-1}(T)$ for TCA[13] are presented (Table 3). However, this acid cannot be regarded as belonging neither to the TCA-B group nor to the group of $[A\cdots H\cdots A]^-$ $[Me]^+$ complexes. Trichloroacetic acid is a dimer in which two hydrogen bonds of $O\text{-}H\cdots O$ type occur. It can only be used as a reference standard in investigations of the mean ^{35}Cl-NQR frequency shift in the analyzed complexes. A comparison between $T_1^{-1}(T)$ dependences obtained for the complexes analyzed and the dependence for TCA, taking

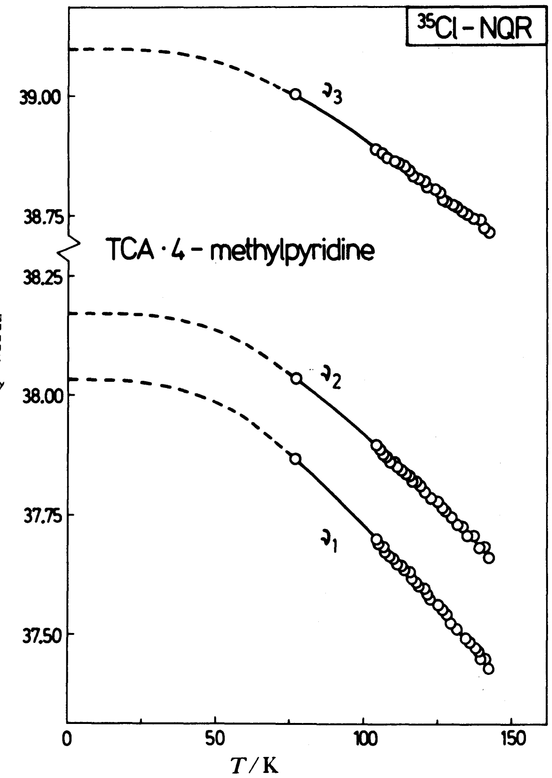

Fig. 3. Temperature dependence of the ^{35}Cl-NQR frequency in TCA-4-methylpyridine complex. Solid and partly broken line represents the fit with Eq. 3; fitting parameters are given in Table 2.

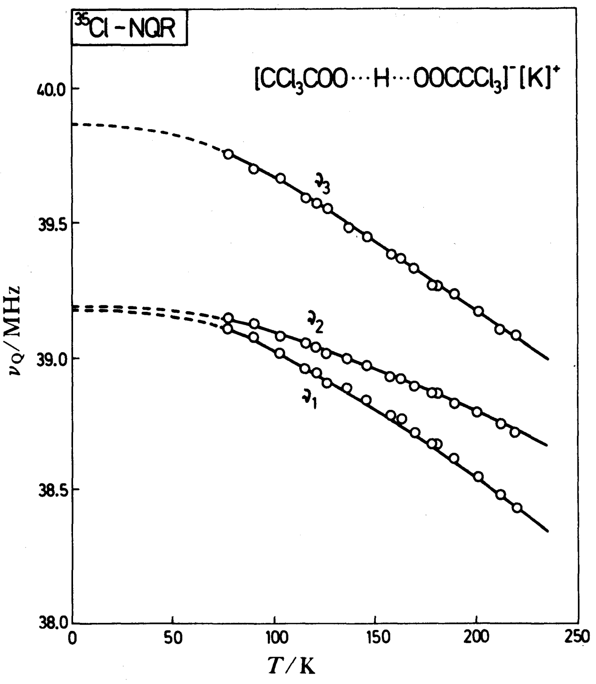

Fig. 4. Temperature dependence of the ^{35}Cl-NQR frequency in $(CCl_3COO)_2HK$. Solid and partly broken line represents the fit with Eq. 3; fitting parameters are given in Table 2.

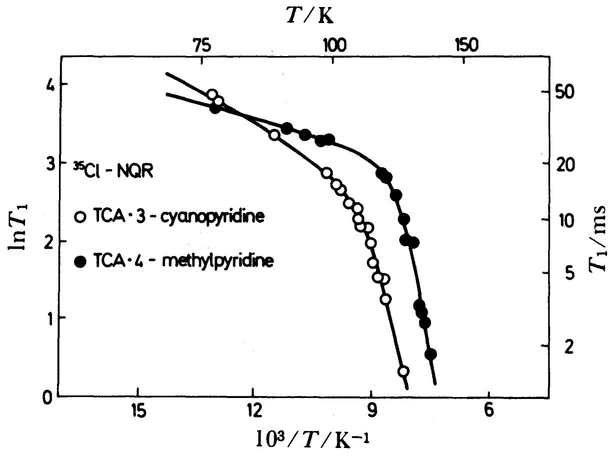

Fig. 5. Temperature dependence of ^{35}Cl-NQR spin-lattice relaxation time in complexes: TCA-3-cyanopyridine and TCA-4-methylpyridine. Solid line is the fit with Eq. 9; fitting parameters are given in Table 3.

Table 3. Parameters of the Fit of Experimental $T_1(T)$ Values with Eq. 9

Complex	$a/s^{-1}K^{-n}$	n	b/s^{-1}	$E_a/kJ\,mol^{-1}$
TCA[a]	6.88×10^{-3}	2	5.2×10^{10}	18.00
TCA-3-cyanopyridine	2.991×10^{-6}	3.64	1.914×10^{12}	22.22
TCA-4-methylpyridine	1.298×10^{-8}	1.74	4.167×10^{13}	27.82
$(CCl_3COO)_2HK$	7.012×10^{-3}	1.90	1.644×10^{13}	36.66

a) Ref. 13.

into account the $T_{\mathrm{fade\text{-}out}}$, is given in Fig. 7.

As it has been already mentioned the main aim of the investigation of dynamics of hydrogen-bonded complexes is the determination of the activation energy for the rotation of the CCl_3 group and an attempt to correlate the E_a values with the nature of the hydrogen bond. Table 1 gives the values of E_a for all the complexes analyzed in this paper. An attempt has been made to relate these values with the shift of the mean ^{35}Cl-NQR frequency for TCA-B type complexes (Fig. 8). As a result we have found that with increasing $|\Delta\bar{\nu}_Q|$ i.e. with the hydrogen bond getting more polar the activation energy for CCl_3 group rotation increases. This relation can be described by the following linear expression:

$$E_a = a\Delta\bar{\nu}_Q + b, \qquad (10)$$

where $a = -10.7$ kJ mol^{-1} MHz^{-1} and $b = 6.0$ kJ mol^{-1}. This kind of correlation has been supported by the linear dependence between E_a and $\Delta\bar{\nu}_Q$ for the complexes of the type $[CCl_3COO \cdots H \cdots OOCCCl_3]^- [Me]^+$ (Fig. 9). This linear dependence can also be expressed by Eq. 10 but with $a = -85.5$ kJ mol^{-1} MHz^{-1}, $b = -28.8$ kJ mol^{-1}. Despite the fact that for both groups of complexes studied the dependence $E_a(\Delta\bar{\nu}_Q)$ has a linear character we cannot expect an agreement as to the numerical values of E_a, a, and b for the two groups. They are essentially different. In the group of TCA-B complexes the changing nature of hydrogen bond results in an increase in the potential barrier for the rotating CCl_3 groups. In the group of $[CCl_3COO \cdots H \cdots OOCCCl_3]^- [Me]^+$ complexes the hydrogen-bond

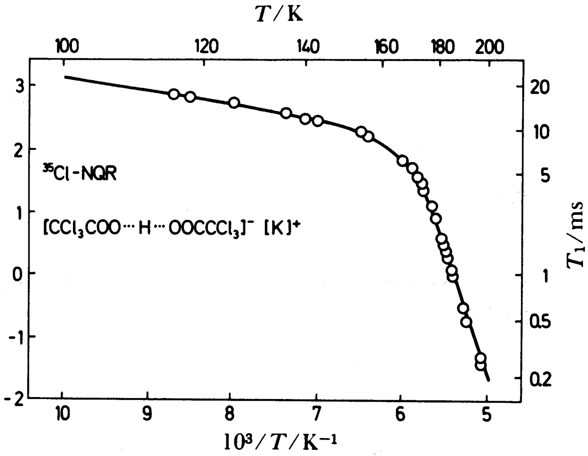

Fig. 6. Temperature dependence of ^{35}Cl-NQR spin-lattice relaxation time in $(CCl_3COO)_2HK$. Solid line is the fit with Eq. 9; fitting parameters are given in Table 3.

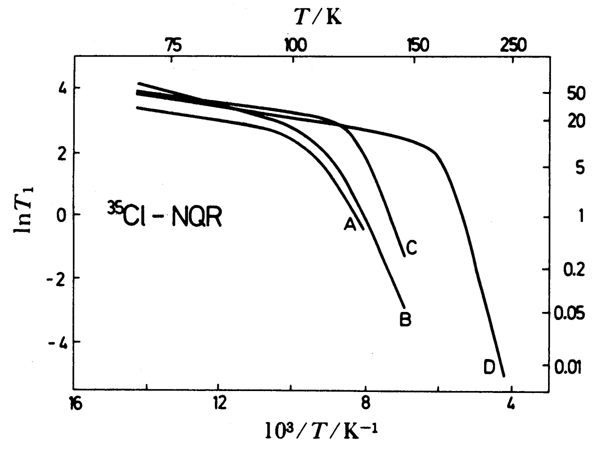

Fig. 7. A comparison of the temperature dependences of ^{35}Cl-NQR spin-lattice relaxation time in; (A): TCA, (B): TCA-3-cyanopyridine, (C): TCA-4-methylpyridine, (D): $(CCl_3COO)_2HK$. The lines were drawn according to Eq. 9 and the appropriate parameters given in Table 3 with $T_{\mathrm{fade\text{-}out}}$ taken into account.

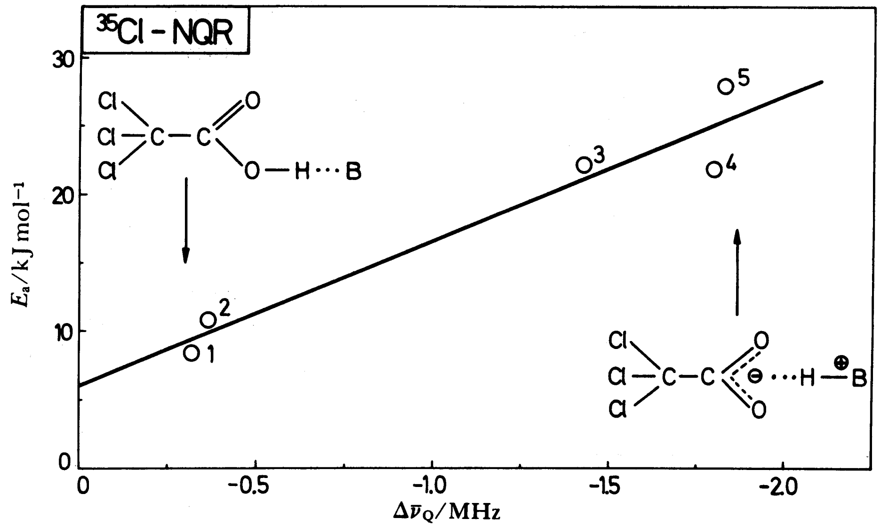

Fig. 8. Activation energy for hindered rotation of CCl_3 group in TCA versus the shift in mean ^{35}Cl-NQR frequency for TCA-B type complexes. Solid line drawn according to Eq. 10; for fitting parameters see text; for notation see Table 1.

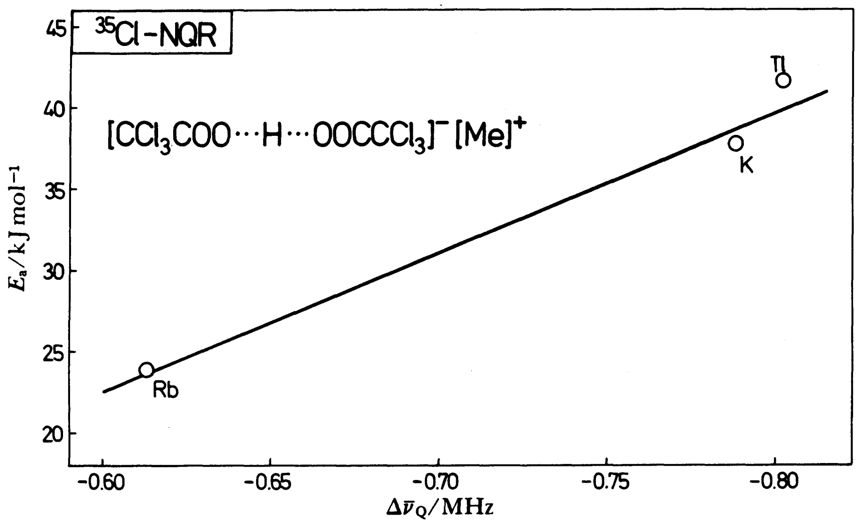

Fig. 9. Activation energy for hindered rotation of CCl_3 group in TCA versus the shift in mean ^{35}Cl-NQR frequency for $[A\cdots H\cdots A]^-[Me]^+$ type complexes. Solid line drawn according to Eq. 10; for fitting parameters see text.

remains the same (symmetrical bond) and the shift in the mean ^{35}Cl-NQR frequency is determined by the influence of $[Me]^+$ cation and in particular by its size as discussed in Refs. 14 and 15.

It is possible to relate the activation energy, E_a, for the rotation of the CCl_3 group in a complex of the series studied, to the parameter, pK_a, describing the strength of the base and acid forming the complex and obtain an expression $E_a=f(\Delta pK_a)$.

Using Eqs. 1 and 10 leads to:

$$E_a = \frac{E_a^{HB}+E_a^{PT}\times 10^{\xi\Delta pK_a+C'}}{1+10^{\xi\Delta pK_a+C'}}, \qquad (11)$$

where E_a^{HB}=6.6 kJ mol^{-1} is a constant equal to the activation energy for the rotation of CCl_3 group in a limit-case complex with a purely covalent structure, and E_a^{PT}=27.3 kJ mol^{-1} is a similar constant corresponding to the opposite limit case of a completely polar structure of the hydrogen bond. Figure 10 represents the curve corresponding to Eq. 11 for ΔpK_a ranging from −12 to +12. As follows from the above considerations the increase in the energy barrier for CCl_3 group rotation in TCA-B complexes is a direct result of the changing character of the hydrogen bond. The degree of proton transfer, P, being a significant parameter to describe the hydrogen bond, it is possible, using Eqs. 2 and 10, to express the activation energy, E_a, in term of this parameter:

$$E_a=20.7\,P+6.6, \qquad (12)$$

with $0\leqslant P\leqslant 1$.

Similarly, considering the series of complexes $[CCl_3COO\cdots H\cdots OOCCCl_3]^-[Me]^+$ it is possible to relate the ^{35}Cl-NQR frequency shift to the ionic radius of the cation (R). Using data available in Ref. 15 for the compounds studied here (Me=Rb, K, Tl) and also for Me=Na and NH_4 one gets the relation:

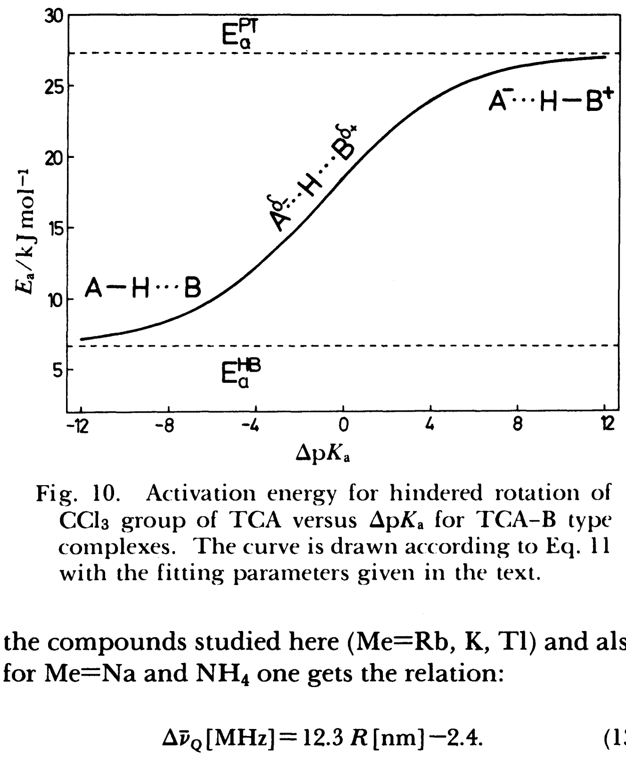

Fig. 10. Activation energy for hindered rotation of CCl_3 group of TCA versus ΔpK_a for TCA-B type complexes. The curve is drawn according to Eq. 11 with the fitting parameters given in the text.

$$\Delta\bar{\nu}_Q[\mathrm{MHz}]=12.3\,R[\mathrm{nm}]-2.4. \qquad (13)$$

Then using Eqs. 10 and 13, the corresponding activation energy for the rotation of the CCl_3 group can be written as:

$$E_a=-1054.3\,R+179.9 \qquad (14)$$

However, this relation cannot be applied in a wide range of R values. Both Eqs. 13 and 10 have been derived for a very narrow range of R values: In the case of Eq. 13 R changed between 0.098 nm (Na^+) to 0.149 nm (NH_4) while in the case of Eq. 10 this range was even narrower. Moreover, Eq. 13 cannot be linear as this is in contradiction to the dependence of the electric field gradient on r^{-3} where r is the distance between the nucleus considered and the charge producing the gradient in question. Despite the above limitations Eq. 14 applied for the appropriately narrow range of R values allows to obtain reasonable values of E_a.

On the other hand Eqs. 11 and 12 derived for TCA–B complexes can be applied on a wider scale. Eq. 1 was derived from the analysis of 63 complexes of ΔpK_a changing in a relatively wide range of values extending from −11.77 to +11.25. The relation between E_a and $\Delta\bar{\nu}_Q$ (Eq. 10) was also obtained for a wide range of ΔpK_a values (from −7.01 to +5.51). It should be however pointed out that the small number of experimental values of E_a which is a consequence of the time-consuming character of $T_1(T)$ measurements may also be a reason for the not very accurate E_a values obtained from Eqs. 11 and 12. In particular $E_a^{HB}=6.6\ \mathrm{kJ\ mol^{-1}}$ seems to be too low for a relatively big and heavy CCl_3 group, in spite of the fact that the CCl_3 group in question is in an almost free TCA molecule without any interactions with the base. Nevertheless the relations obtained in this paper and expressed as mathematical formulae allow direct determination of the activation energy for rotation of CCl_3 group of TCA in its different complexes from the values of $\Delta\bar{\nu}_Q$ or from the tabulated pK_a or R values.

Moreover, it was found beyond doubt that the influence of hydrogen bond in TCA–B complexes on the height of the potential barrier of CCl_3 group of TCA forming that complex, is decisive. The hydrogen bond in TCA–B complexes is the main source of the changes in electric field gradient at the Cl nuclei. These changes affect the nuclei studied through induction and polarization effects. The weakening of the O–H covalent bond produced by hydrogen bond formation originates: (1) A charge rearrangement that is relayed to the Cl–C bond through the bonds of the TCA molecule and (2) through two polarization mechanisms consisting of (a) direct effect acting on the Cl atom and (b) an indirect polarization effect acting on the Cl–C bond. As shown in Ref. 14 an increase in the electron density on the nearest O atom in TCA will produce a direct contribution that will increase the Cl frequency while the indirect effect will produce an opposite shift. We can also consider the polarization influence of electric dipole of hydrogen bond which leads only to negative shifts in ^{35}Cl-NQR frequency.[1] In the complexes studied only the negative shifts of NQR frequency were observed. However, without data on the crystal structure of the complexes studied it is difficult to calculate and determine accurately the contribution of individual mechanisms in the eventual shift of ^{35}Cl-NQR frequency. Nevertheless all the mechanisms considered result in a gradual increase in intermolecular interactions with a growing proton transfer degree. This in turn implies an increase in potential barriers for rotating CCl_3 groups. In the case of $[CCl_3COO\cdots H\cdots OOCCCl_3]^-\ [Me]^+$ type complexes it is also difficult to separate the influence of the cation radius resulting in weakening of intermolecular interactions from the effect of electrostatic interaction of the cation on the electric potential distribution in a dimer ion. However both effects directly influence intermolecular interactions strength and thus, the height of the potential barrier for rotation of CCl_3 groups in these complexes.

Investigation of quadrupole spin-lattice relaxation times T_1 versus temperature performed for a considerable group of complexes should give a more precise correlation between the values of E_a and $\Delta\bar{\nu}_Q$. On the other hand crystallographic studies of the complexes with a hydrogen bond would provide the possibility of more detail analysis of inter- and intramolecular interactions in them.

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