Chapter 4

Hydrogen Transfer in Crystalline
## Chloranilic Acid - 1,4-Diazine (1:2) Complex

4-1.   Introduction

In the previous Chapter, we reported for the first time that NQR can be used as a quite sensitive technique to detect the hydrogen transfer by applying this method to p-chlorobenzoic acid forming an hydrogen bonded dimer structure in crystals [1].   In that study, the NQR relaxation measurement of ^{35}Cl even at a position remote from hydrogen bonds could provides an effective probe much more sensitive than the familiar ^{1}H NMR technique.   This is because a marked fluctuation of electric field gradient (efg) at resonant nuclei far from the hydrogen atoms can be made through π-electrons by hydrogen transfer between molecules.   On the other hand, ^{1}H NMR relaxation due to the fluctuation of magnetic dipolar interactions caused by hydrogen transfers can provide only a small contribution to the total relaxation because of a small displacement of hydrogen atoms in jumping processes.

In this Chapter, we intend to detect new hydrogen transfer modes by applying the NQR method to an hydrogen bonded three molecular system, (chloranilic acid)-(1,4-diazine) 1:2 complex with the crystal structure shown in Figure 4-1 [2].   In crystal, two

1,4-diazine molecules form strong O—H$\cdots$N hydrogen-bonds with O$\cdots$N of 2.590Å with chloranilic acid, which is located on an inversion center in crystal, and the molecular planes are stacked in columns along a axis[2]. Only one site of two nitrogen atoms in a 1,4-diazine molecule is used for hydrogen bonding. Since the other N site is far from hydrogen bonding system, interactions are little between the second N and O of chloranilic acid The interplanar angle between the rings in chloranilic acid and 1,4-diazine are 52.4° [2]. In this system, we can expect three kinds of different ionic structures of chloranilic acid formed by hydrogen transfers in two hydrogen bonds in this molecular system, where we can expect more complicated H-motions compared with in the previous p-chlorobenzoic acid dimers.
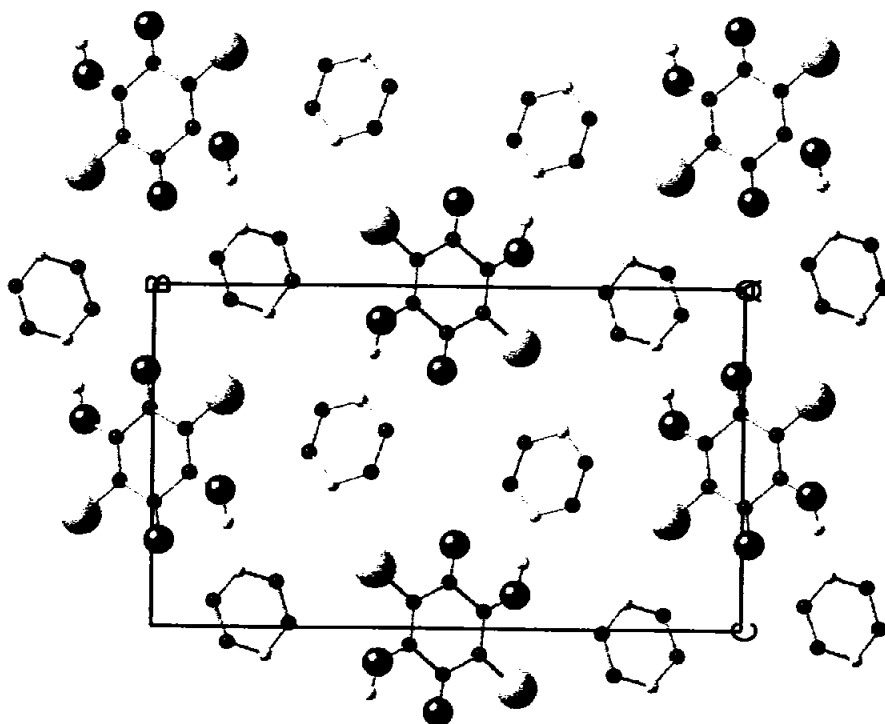
Space group $P2_1/n$

Lattice parameters $a = 3.828, b = 18.514, c = 10.795$ Å

$\beta = 94.484°$

$Z = 2$

Figure 4-1.   The crystal structure of $C_6O_2Cl_2(OH)_2$-$(1,4-C_4H_4N_2)_2$ determined by X-ray diffraction at room temperature [2].

4-2. Experimental

A molecular complex of chloranilic acid ($C_6O_2Cl_2(OH)_2$) with 1,4-diazine(1,4-$C_4H_4N_2$) with a ratio of 1:2 was prepared by mixing a CH_3CN solution of chloranilic acid and liquid 1,4-diazine with a molor ratio of 1:2 [2]. Obtained dark purple crystals were recrystallized from methanol. A partially deuterated analog $C_6O_2Cl_2(OD)_2$-(1,4-$C_4H_4N_2)_2$ was obtained by recrystallizations of the protonated compound from CH_3OD. To obtain pure duterated crystal, recrystallizations were repeated for three times from CH_3OD.

^{35}Cl NQR frequencies were measured with a Dean-type external quenching superregenerative spectrometer with Zeeman modulation[3] in a temperature range 77 K to room temperature. The ^{35}Cl NQR spin-lattice relaxation time (T_{1Q}) was measured with a home-made pulsed spectrometer described in Chapter 2 in temperature ranges from 77 K to room temperature for the protonated sample and 77-130 K for the deuterated analog.

^1H NMR spin-lattice relaxation time(T_{1H}) in the protonated sample was measured with a homemade pulsed spectrometer described in Chapter 2 at a Larmor frequency of 54.3 MHz in a temperature range 85-300 K.

4-2.   Result

4-2-1. ^{35}Cl NQR Frequency

Temperature dependences of ^{35}Cl NQR frequencies observed in $C_6O_2Cl_2(OH)_2$-$(1,4\text{-}C_4H_4N_2)_2$ and $C_6O_2Cl_2(OD)_2\text{-}(1,4\text{-}C_4H_4N_2)_2$ are shown in Figure 4-2. A single resonance line was observed at 36.3997 ± 0.0005 and 36.466 ± 0.001 MHz at 77 ± 1 K for the protonated and deuterated analogs, respectively. These results agree with the crystal structure of the protonated complex that all chlorine atoms in crystals are crystallographically equivalent at room temperature [2]. Upon heating, these resonance frequencies were gradually decreased and weakened, and disappeared in the noise level at ca. 300 and ca. 120 K in protonated and deuterated analogs, respectively.

4-2-2. ^{35}Cl NQR Spin-Lattice Relaxation Time (T_{1Q})

Temperature dependences of ^{35}Cl NQR spin-lattice relaxation time(T_{1Q}) observed in both analogs are shown in Figure 4-3. On heating the protonated complex from 77 K, T_{1Q} was decreased, and showed a shallow minimum of ca. 600 ms at ca. 120 K. Upon further heating to room temperature, T_{1Q} again monotonously decreased down to ca. 100 ms. On the other hand, the deuterated complex showed T_{1Q} longer than in the protonated complex in the temperature range studied, where it decreased on heating and gave almost temperature independent values of 1.9 s above ca. 110 K.
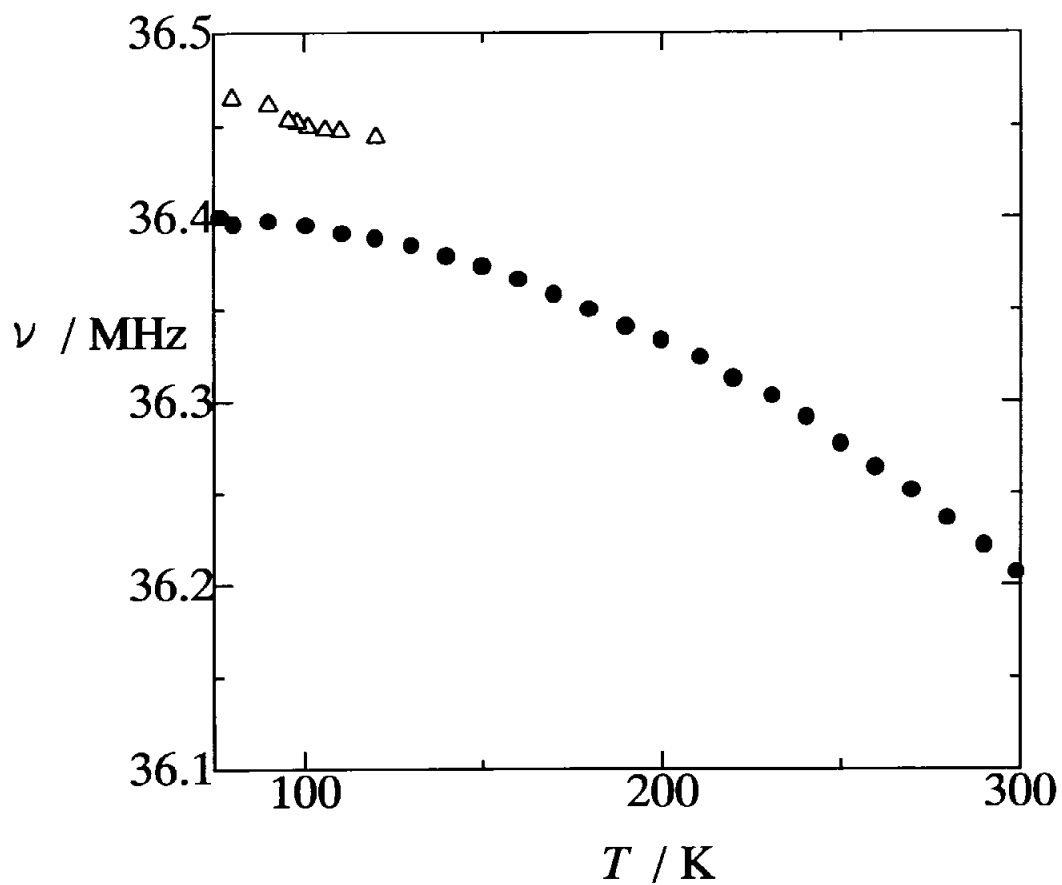
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Figure 4-2   Temperature dependences of ^{35}Cl NQR frequencies (v) observed in $C_6O_2Cl_2(OH)_2$-$(1,4\text{-}C_4H_4N_2)_2$ (●) and $C_6O_2Cl_2(OD)_2$-$(1,4\text{-}C_4H_4N_2)_2$ (△).
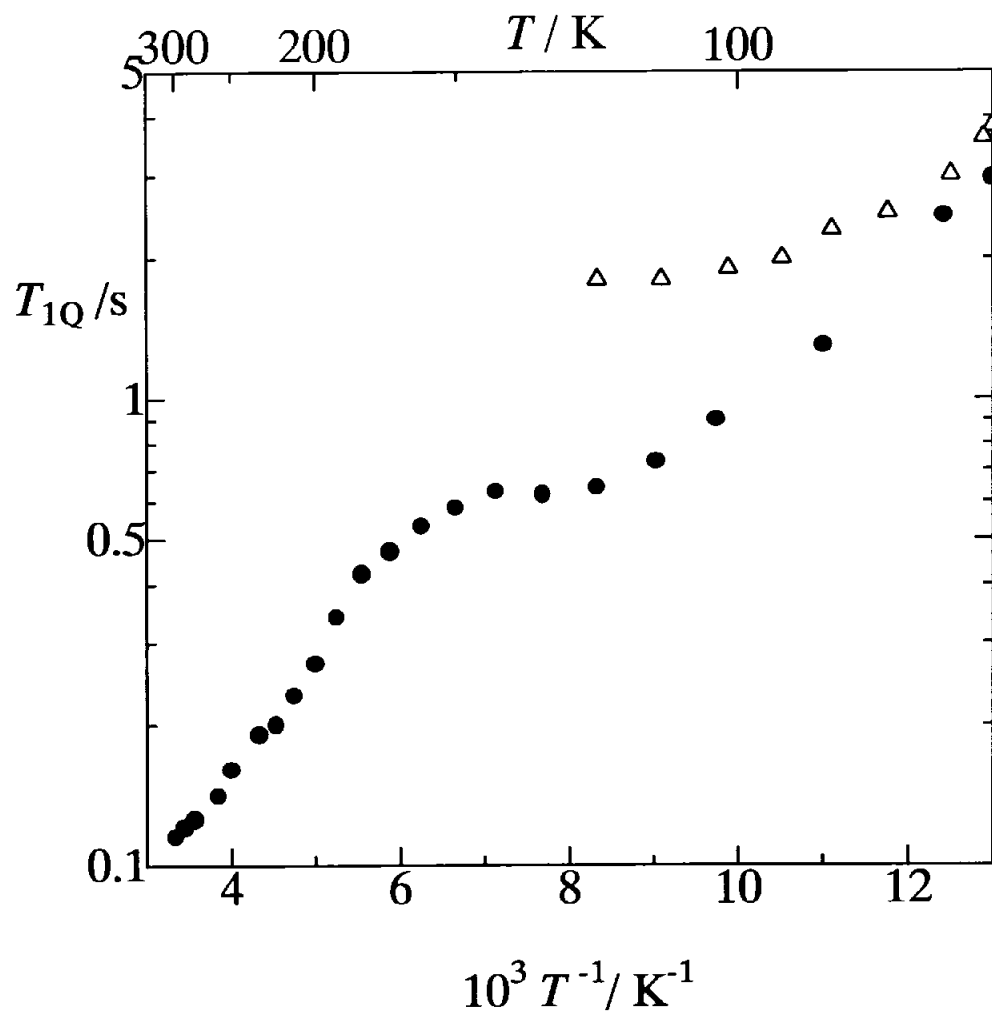
Figure 4-3.   Temperature dependences of the ^{35}Cl NQR spin-lattice relaxation times T_{1Q}observed in $C_6O_2Cl_2(OH)_2$-$(1,4$-$C_4H_4N_2)_2$ (●) and $C_6O_2Cl_2(OD)_2$-$(1,4$-$C_4H_4N_2)_2$ (△).

4-2-3. ^{1}H NMR Spin-Lattice Relaxation Time (T_{1H})

A temperature dependence of ^{1}H NMR spin-lattice relaxation time (T_{1H}) observed in the protonated complex at 54.3 MHz is shown in Figure 4-4. A single long T_{1H} minimum of ca. 45 s was observed at 135 K. This result indicates that no motion giving a marked fluctuation of magnetic dipolar filed at protons is present, such as the rotational motion or the two-site jump of 1,4-diazine about the N-N axis. The temperature dependence curve of ^{1}H NMR (T_{1H}) was seen to be almost symmetric, but slightly asymmetric.
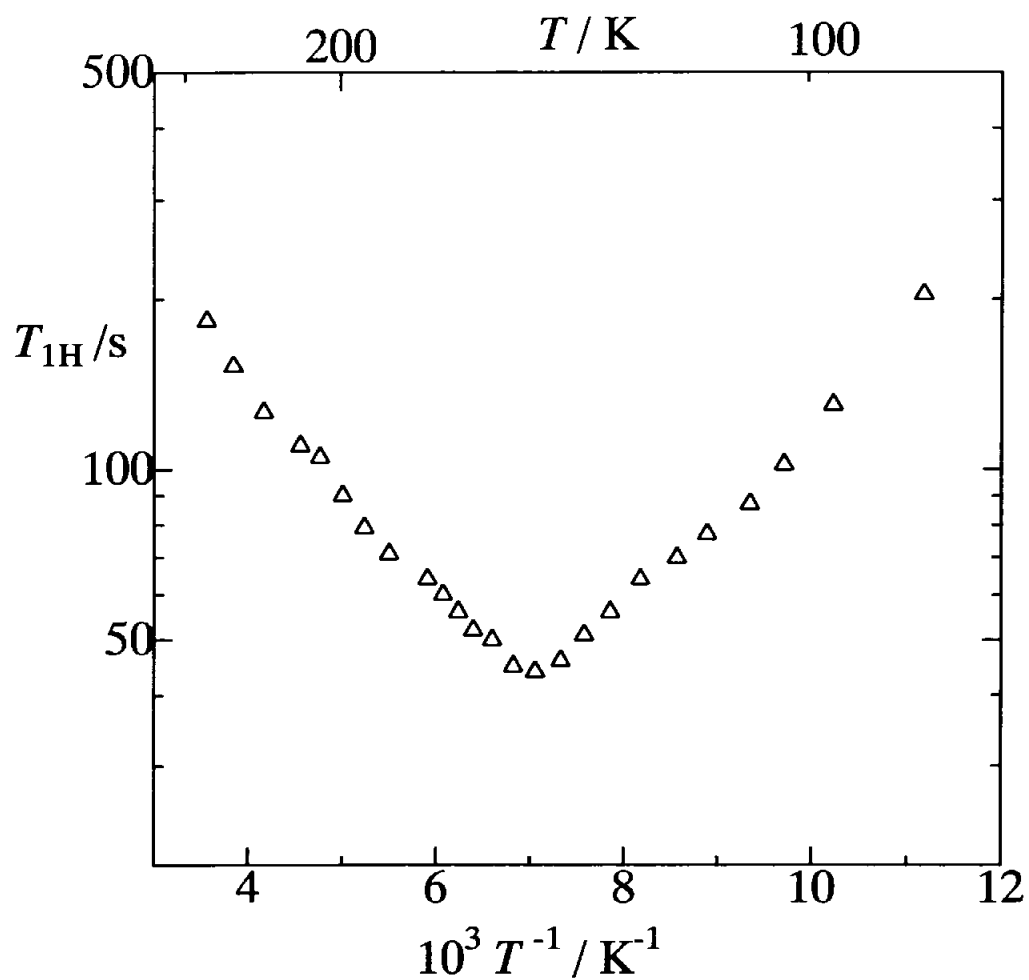
Figure 4-4.   A temperature dependence of the ^1H NMR spin-lattice relaxation time T_{1H} observed in $C_6O_2Cl_2(OH)_2$-$(1,4-C_4H_4N_2)_2$ at a Larmor frequency of 54.3 MHz.

4-4. Discussion

4-4-1. ^{35}Cl NQR Frequencies

NQR frequencies gradually decreased upon heating from 77 K in both complexes shown in Fig. 4-2 can be explained by the lattice vibrations [4] described in Chapter 3.

NQR frequencies in chloranilic acid $(C_6O_2Cl_2(OH)_2)$ and its sodium salt $(C_6O_2Cl_2(ONa)_2)$ observed at 77 K were reported to be 37.15 MHz, and 35.538 and 34.853 MHz [5], respectively. Generally, a shift of ^{35}Cl NQR frequency caused by the crystal field made by neighboring molecules is small being in the order of 10-100 kHz in most cases. For example, p-dichlorobenzene has three phases, around room temperature, α-, β- and γ-phases, and ^{35}Cl NQR frequencies in these phase are 34.269, 34.255 and 34.785 MHz, respectively [6,7,8]. In addition, o-dichlorobenzen shows four ^{35}Cl NQR frequency lines, 35.496, 35.424, 35.278 and 35.215 MHz at 196 K [9] which differences are made by crystal field. The observed difference of NQR frequencies in $C_6O_2Cl_2(OH)_2$ and $C_6O_2Cl_2(ONa)_2$ became almost about 2 MHz. This large difference can only be explained by the difference in the electronic population of chlorine atoms in these two systems. This difference can be attributed to the formal charges in $C_6O_2Cl_2(OH)_2$ and $C_6O_2Cl_2(ONa)_2$. If we assume the formal charge on chloranilic acid and its sodium salt to be zero and 2–, respectively, we can see that the frequency (36.4 MHz) observed in the present complex at 77 K comes to near by

intermediate (36.2 MHz) of the frequencies observed in the compounds with the two

extreme structures.   This result implies that chloranilic acid in the present complex is

partially ionized and its formal charge is close to 1-.   Since the presence of the

inversion symmetry on all chloranilic acid molecules in crystals was shown from the X-

ray diffraction at room temperature [2], we can expect that the equal contribution from

the following formulas I and II are the most probable time-averaged structures at low-

temperatures:

I   II
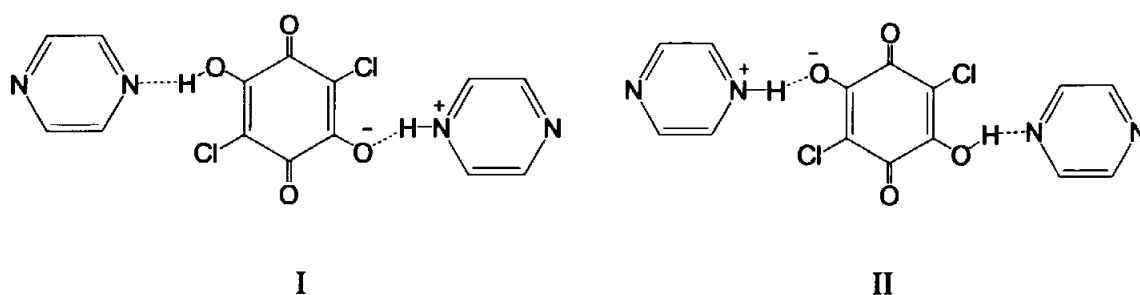
The formation of these ionic structures can be supported from the fact that chroranilic

acid and 1,4-diazine act as moderately strong acid and base with pK_{a1} values of 0.76 and

0.57, respectively, in an aqueous solution [10,11].

4-4-2. ^{1}H NMR Spin-Lattice Relaxation Time (T_{1H})

The long T_{1H} minimum of 45 s observed in the protonated complex at ca. 135

K was attributed to the averaging of magnetic dipolar interactions due to the hydrogen

transfer motion O-H---N ↔ O⁻---H-N⁺ by the following reasons:

First, ^{1}H NMR T_{1H} observed in the partially deuterated complex with two OD

groups in a chloranilic acid molecule around the T_{1H} minimum temperature range gave

T_{1H} values much longer than 500 s. This indicates that motions of protons in the

hydrogen bond contributes to this relaxation.

Second, in order to estimate the value of the minimum of T_{1H} due to hydrogen

transfer, we performed a rough calculation of the decrease in the second moment (ΔM_2)

of ^1H NMR by assuming the magnetic dipolar relaxation caused by molecular motions.

In this case, we can apply the BPP-type relaxation equation expressed as [12]

$$T_{1H}^{-1} = (2/3)\gamma^2 \Delta M_2 \ [\tau/(1+\omega_H^2\tau^2) + 4\tau/(1+4\omega_H^2\tau^2)] \ , \quad (4.1)$$

where γ, τ and ω_H are the ^1H magnetogyric ratio, the motional correlation time and the

Larmor frequency, respectively. ΔM_2, which is connected with the depth of T_{1H}

minimum, is given by [13]

$$\Delta M_2 = M_{2 \text{(rigid)}} - M_{2 \text{(motion)}}, \quad (4.2)$$

where $M_{2 \text{(rigid)}}$ denotes the second moment of the rigid molecule and is expressed as [13]

$$M_{2(\text{rigid})} = \frac{6}{5}I(I+1)\gamma^2\left(\frac{h}{2\pi}\right)^2 N^{-1}\sum_{j<k} r_{jk}^{-6} , \quad (4.3)$$

$M_{2 \text{(motion)}}$, which is the second moment in a reorienting molecule is occurred, is give by

[13]

$$M_{2(\text{motion})} = \frac{6}{5}I(I+1)\gamma^2\left(\frac{h}{2\pi}\right)^2 N^{-1}\sum_{j<k} r_{jk}^{-6}\left[\frac{1+3(\sin^2\theta_{jk}\cos^2\phi_0+\cos^2\theta_{jk})^2}{4}\right].(4.4)$$

I, N, r_{jk}, ϕ_0, and θ'_{jk} denote the nuclear spin quantum number (in this calculation, we used the nuclear spin of proton; 1/2), the number of protons in a molecule, the distance between ^1H_j and ^1H_k, the rotational angle, and the angle between the ^1H_j - ^1H_k vector and the rotational axis of the motion respectively. This model is illustrated in Figure 4-5. Here, we assumed the hydrogen transfer to be a reorientation by $\theta = 90°$, and estimated the intramolecular contributions to ΔM_2. Using the X-ray result [2] of the O-H distance(1.06 Å) and assuming the usually accepted N-H distance of 0.95 Å in aromatic N-H, we estimated the intramolecular contribution to ΔM_2 ($ca.$ 0.04 G^2) which gave a T_{1H} minimum of $ca.$ 20 s at the same Larmor frequency. This value is showed satisfactory agreement with the observed T_{1H} value of 45 s.

Third, quite analogous long T_{1H} minimum values were reported in same temperature range in crystalline benzoic acid and its derivatives [14] in which hydrogen transfer in the hydrogen bonded dimer structure in solid has been reported.

As the motional mode of the hydrogen transfer, we can expect the proton exchange between the two structures I and II shown above. This is because monovalent chloranilate ($C_6O_2Cl_2(OH)O^-$) is presumed to be the most populated structure from the foregoing NQR frequency analysis. The onset of this H-motion is consistent with the X-ray diffraction study [2] reporting large displacement parameters of hydrogen atoms attributable to disorder of hydrogen atoms in the hydrogen bonds. The observed T_{1H} shown in Fig. 4-4 exhibits a little asymmetric temperature dependence different from the theoretically expected BPP-type temperature dependence given by Eq. (4.1). This asymmetry is attributable to the contribution from the tunneling proton exchange in the low-temperature side of the minimum as already discussed in solid benzoic acid [14,15,16] and p-chlorobenzoic acid in Chapter 3. The evaluated activation energies (E_a) from the high- and low-temperature sides of the minimum as shown in Fig. 4-6

were 3.9 ± 0.5 and 3.2 ± 0.5 kJ mol^{-1}. The obtained E_a in the high-temperature side, which corresponds to the barrier for the classical jumping motion of protons between the two structures, is acceptable because it is comparable to 5.5 kJ mol^{-1} [14,15,16] obtained for the proton exchange in the hydrogen bonded benzoic acid dimer in solid. These results are consistent with O-H---X (X: O or N) distances reported to be 2.633 $\overset{\circ}{A}$(X:O) in benzoic acid [17,18,19] and 2.590 $\overset{\circ}{A}$(X:N)in the present system[2] being close to each other.
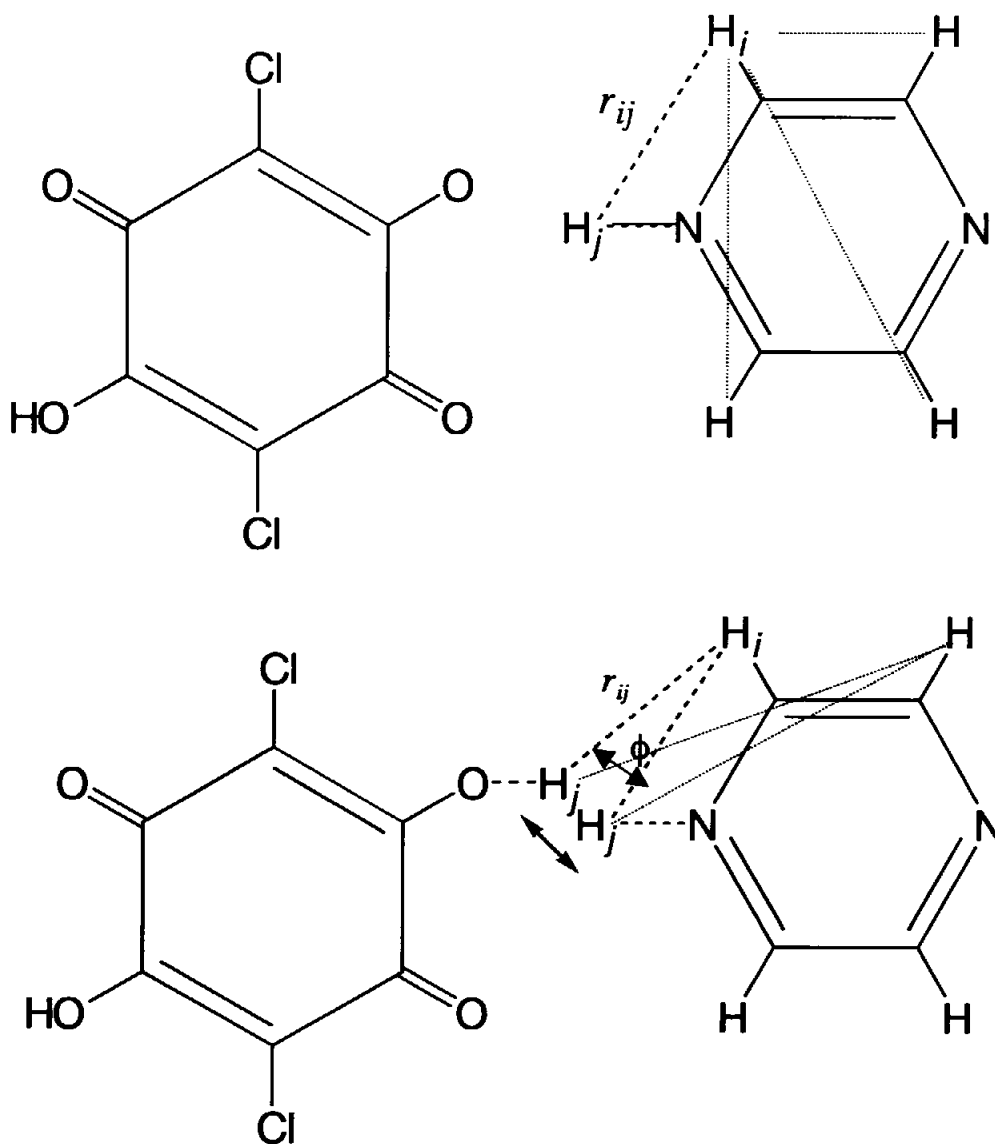
Figure 4-5.   Structure models for caluculation of second moments (M_2) of ^{1}H NMR line.   Using the upper model, the $M_{2(\text{rigid})}$ was calculated, where the interactions between hydrogen bonded H_i and the other three protons in a 1,4-diazine molecule were considered.   Using the lower model that assumed the hydrogen transfer to be a rotational motion with $\theta = 90°$ in Eq. (4.4), the $M_{2(\text{motion})}$ was calculated.   Using same model, the interaction with the other three protons were considered.   H positions were estimated by using results of X-ray diffraction [2].
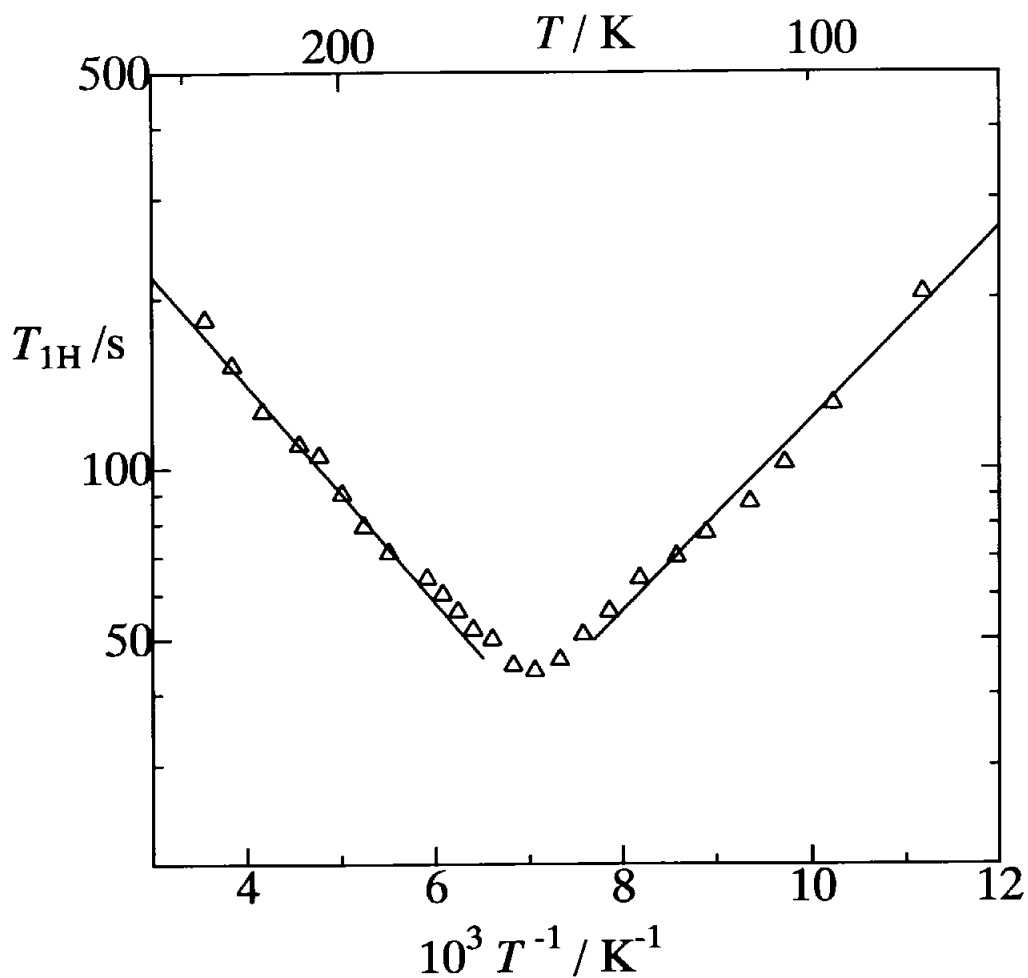
Figure 4-6. A temperature dependence of the ^1H NMR spin-lattice relaxation times T_{1H} observed in $C_6O_2Cl_2(OH)_2$-$(1,4$-$C_4H_4N_2)_2$ at a Larmor frequency of 54.3 MHz. Solid lines are drawn to obtain activation energies.

4-4-3. ^{35}Cl NQR Spin-Lattice Relaxation Time (T_{1Q})

The temperature dependency of T_{1Q} shown in Fig. 4-3 is assumed to be expressed by the superposition of the following Debye-type relaxation and the Arrhenius-type activation equations [20]:

$$T_{1Q}^{-1} = C \ [\tau_c/(1+\omega_Q^2\tau_c^2)] \qquad (4.5)$$

and

$$\tau_c = \tau_0\exp(E_a/RT), \qquad (4.6)$$

where C, τ_c, ω_Q, τ_0 and E_a denote the a parameter associated with efg averaged by molecular motions, the motional correlation time, the NQR angular frequency, the correlation time in the limit of infinite temperature and the activation energy, respectively.   The observed T_{1Q} data were fitted by superimposed two relaxation mechanisms given by Eqs. (4.5) and (4.6) and the best-fitted curve is shown in Figure 4-7. In this fitting calculation, we ignored the contribution from lattice vibrations which seems to be present in the background of the observed T_{1Q} temperature dependence. Since the T_{1Q} minimum observed around 120 K can be corresponded to the T_{1H} minimum at 135 K, by taking into account the difference in applied frequencies in these two measurements, we used the E_a determined in T_{1H} analysis as the fitting parameter for the low-temperature T_{1Q} minimum. The determined motional parameters are shown

in Table 4-1.   In accordance with T_{1H} analysis, the low-temperature minimum is attributed to the correlated hydrogen exchange between structures I and II.

Upon heating, the protons in two O-H groups in a chloranilic acid are expected to move independently between O and N sites. This motion enables the formation of divalent chroranilate ions ($C_6O_4Cl_2^{2-}$) and at the same time neutral chloranilic acid molecules. The structure changes in the correlated and uncorrelated hydrogen transfer models are given by Figure 4-8.   The uncorrelated hydrogen transfers of I (or II) ↔III, and I (or II) ↔ IV shown in the figure yield the structure changes between mono- and divalent ions, and also between monovalent ions and neutral molecules, respectively, indicating marked changes in the electronic structure which should result in the fluctuation of efg at resonant chlorine nuclei.
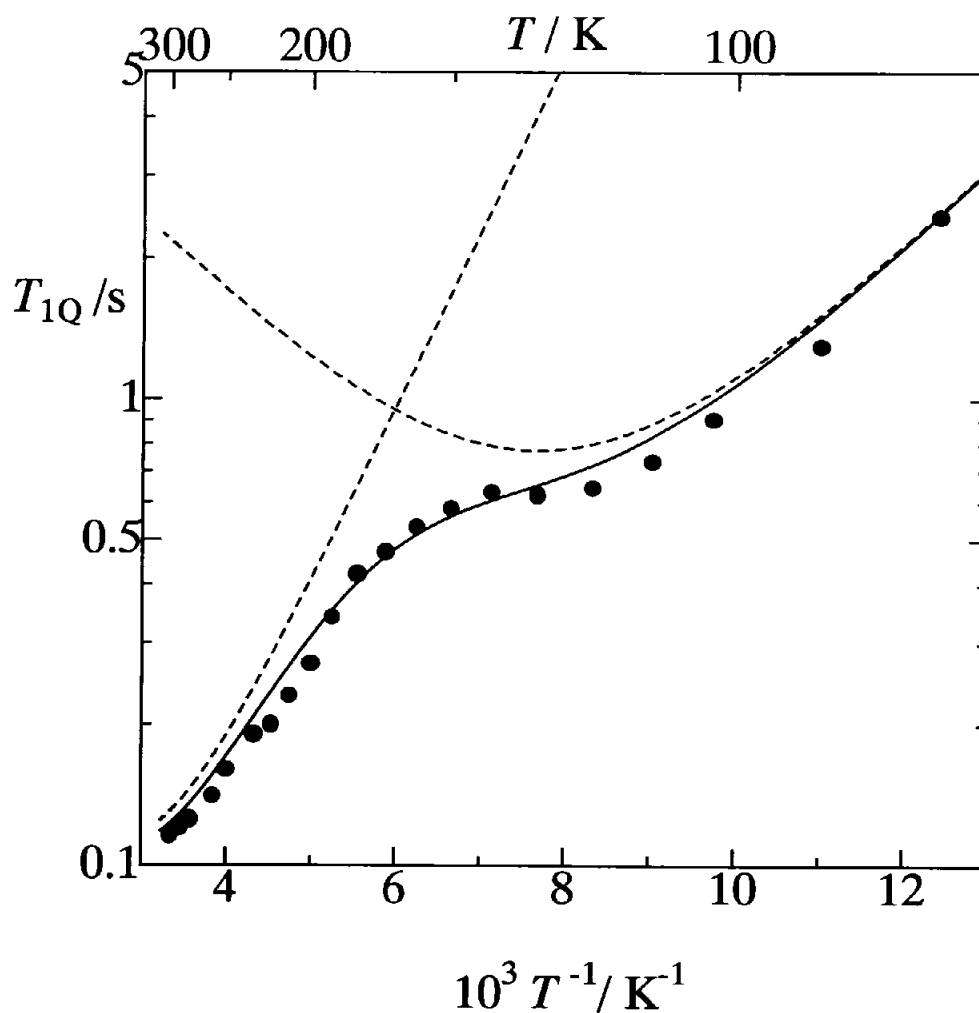
Figure 4-7.   A Temperature dependence of the ^{35}Cl NQR spin-lattice relaxation times T_{1Q}observed in $C_6O_2Cl_2(OH)_2$-$(1,4-C_4H_4N_2)_2$. The solid curve is the best-fitted, calculated values expressed by the superposition of two components (dashed curves).

Table 4-1. Motional parameters in hydrogen transfers determined in (chloranilic acid)-(1,4-diazine) 1:2 complex $C_6O_2Cl_2(OH)_2(C_4H_4N_2)_2$ derived from ^{35}Cl NQR relaxation data.

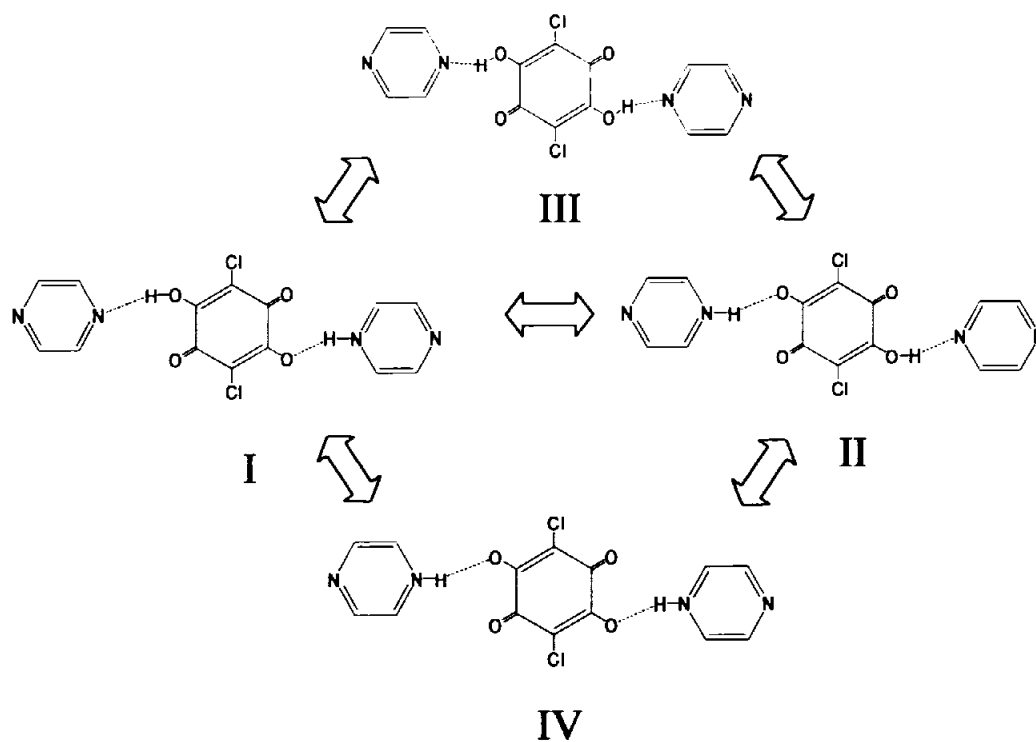|	correlated H-transfer	uncorrelated H-transfer
C (s^{-2})	$5.9 \pm 0.1 \times 10^8$	$\sim 4.0 \times 10^9$
τ_0 (s)	$2.2 \pm 0.1 \times 10^{-10}$	$\sim 4.1 \times 10^{-10}$
E_a (kJ mol^{-1})	3.2	7.2 ± 2.0

Figure 4-8. Hydrogen transfer models. The correlated transfer model I⇔II, where two hydrogen atoms jump simultaneously. The uncorrelated transfer model I (or II) ⇔ III and I (or II) ⇔ IV, where two hydrogen atoms move independently.

4-4-4. The Difference in Temperature Dependences of

^{1}H NMR T_{1H} and ^{35}Cl NQR T_{1Q}

The occurrence of correlated and uncorrelated hydrogen transfer can be supported from T_{1H} data which showed no marked relaxation processes in the range of the high-temperature T_{1Q} decrease. This can be explained by considering that, once the magnetic dipolar interactions are averaged by the simultaneous hydrogen exchange between the structures I and II, the further average by the uncorrelated motions of almost the same displacements of the same hydrogen atoms is quite small and should give much longer T_{1H} values than those from the correlated motion. We roughly evaluated the ΔM_2 value caused by the uncorrelated hydrogen transfers excited after the average by the correlated motions between I and II as schematically shown in Fig. 4-9 by assuming the same H-positions used the foregoing section. Since the ratio of the minimum of correlate and uncorrelate hydrogen transfers is depended on the fluctuation of r_1 and r_2 given in Fig. 4-9 contributing to the averaging of dipolar interactions by these two kinds of motional modes, we can roughly estimate this ratio from

$$\left(\frac{T_{1H(unc)}}{T_{1H(cor)}} \right) \approx \left(\frac{r_1}{r_2} \right)^6, \qquad (4.7)$$

where $T_{1H(nuc)}$, and $T_{1H(cor)}$ are T_{1H} values concerned with uncorrelated, and correlated hydrogen transfers, respectively. The distance r_1 between the hydrogen bonded proton and the other hydrogen bonded proton that almost determines the T_{1H} minimum caused

by the uncorrelated hydrogen transfer was calculated to be 6.912 Å from the structural data, and the distance r_2 between the hydrogen bonded proton and the neighboring proton that dominates the T_{1H} minimum due to the correlated hydrogen transfer was obtained to be 2.531 Å, which length was determined by using results of X-ray diffraction.   Using Eq. (4.7), we got a ratio of 387.   The T_{1H} evaluated from ΔM_2 by the uncorrelated hydrogen transfers became ca. 400 times longer than that from the correlated motion implying that T_{1H} from the uncorrelated motion is too long to be detected.   On the other hand, the uncorrelated motions gave finite probabilities of the formation of divalent and neutral structures in chloranilic acid which can markedly contribute to the NQR relaxation.   From the present T_{1Q} data showing only a monotonous decrease on heating without any minima at high temperatures, we cannot identify the contributed relaxation mechanism possible to be hydrogen exchanges I(and II) ↔III, I(and II) ↔ IV, or both shown in Figure 4-8.

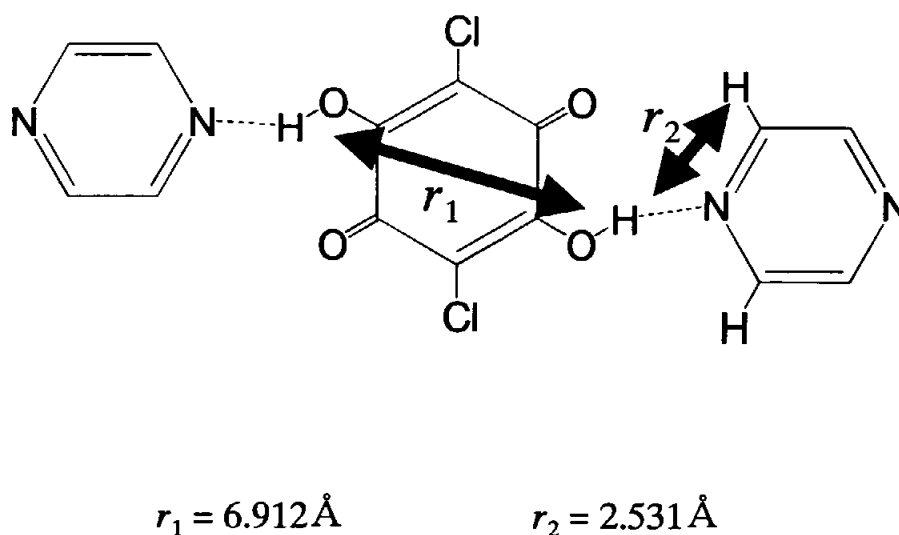$$r_1 = 6.912\,\text{Å} \qquad\qquad r_2 = 2.531\,\text{Å}$$

Figure 4-9.   A model for calculating ^{1}H NMR relaxations due to the correlated and uncorrelated hydrogen transfers.   The T_{1H} due to the correlated hydrogen transfer is almost determined by the fluctuation of the distance (r_2) between the hydrogen bonded proton and the neighboring protons.   On the other hand, the variation of the distance (r_1) between the hydrogen bonded proton and the other hydrogen bonded proton dominates the T_{1H} caused by the uncorrelated hydrogen transfer.

4-4-5. ^{35}Cl NQR Spin-Lattice Relaxation Time (T_{1Q}) in $C_6O_2Cl_2(OD)_2$-$(1,4$-$C_4H_4N_2)_2$

The deuterated complex gave T_{1Q} values with a gradual decrease on heating from 77 K and a flat value of *ca.* 1.9 s around 120 K where the T_{1Q} minimum in the protonated complex of *ca.* 800 ms was observed. The longer T_{1Q} in the deuterated complex indicates that the fluctuation of efg is decreased by the deuteration. This result is unexplainable by the general trend of the smaller tunneling in deuterated compounds as observed in *p*-chlorobenzoic acid described in Chapter 3.   In the present stage, this increase of T_{1Q} is attributable to the Ubbelohde effect [21,22,23,24] resulting in a longer O---N distance by deuteration of protons described in Chapter 3, *i.e.*, the increased crystalline unit cell caused by the deuteration.   This effect can be expected to decrease the fluctuation of efg from intermolecular origins and give the shallower T_{1Q} minimum.

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