Chapter 5

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

5-1. Introduction

In Chapter 3, we described on ^{35}Cl NQR application for detecting small changes in electric field gradient(efg) at ^{35}Cl nuclei made by hydrogen transfers in hydrogen bonds at a remote position from the resonant nuclei in a molecule.   We could find a marked ^{35}Cl NQR relaxation in solid p-chlorobenzoic acid having a dimer structure, in which the presence of double hydrogen transfer has been reported [1] and showed for the first time that the NQR relaxation can be a quite sensitive probe for detecting the hydrogen transfer in hydrogen bonded systems compared with the conventional ^1H NMR relaxation studies.

In Chapter 4, as an application of the NQR technique, we tried to find H-motions in a new three-molecular hydrogen bonded system, (chloranilic acid)-(1,4-diazine) 1:2 complex $[(C_6Cl_2O_2(OH)_2)-(C_4N_2H_4)_2]$ (abbreviated to 1,4-complex) [2], and succeeded to observe two kinds of modes of hydrogen transfer motions, one of which was a new kind of mode undetected by ^1H NMR method.   In the analysis of the hydrogen bonded structure in 1,4-complex, we predicted three kinds of hydrogen

transfer modes, namely, H-jumps between two equivalent monovalent chloranilate(1-) ions, between (1-) and (2-) ions, and between (1-) ions and neutral chloranilic acid(0) molecules. We could detect the first mode by both NQR and NMR relaxation measurements in the low-temperature range, but nothing in NMR and only a single relaxation increase in NQR at high-temperatures. This disagreement affords us an unsolved problem associated with the sensitivity of NQR and also the validity of our hydrogen transfer models.

In this Chapter, we intend to solve this problem and measure NQR and NMR in another three-molecular hydrogen bonded system, (chloranilic acid)-(1,2-diazine) 1:2 complex[$(C_6Cl_2O_2(OH)_2)$-$(C_4N_2H_4)_2$] (abbreviated to 1,2-complex) having an analogous structure to 1,4-complex as shown in Figure 5-1.

In crystals of 1,2-complex, two 1,2-diazine molecules form with chloranilic acid strong O—H⋯N hydrogen-bonds with the O⋯N distance of 2.582 Å [3], which are significantly shorter than the averaged hydrogen bonded N⋯O distance of 2.878 Å [4], implying the formation of strong N—H⋯O hydrogen bond in this complex. The X-ray diffraction result [3] that the H atoms in the two hydrogen bonds have large displacement parameters suggests that these protons are disordered in the hydrogen bond in solid 1,2-diazine complex, in which molecular planes are stacked in columns along a axis [3]. It is noted that only one site of two nitrogen atoms of 1,2-diazine is used for hydrogen bonding in solid, and the other N site is far from the neighboring chloranilic acid molecules. The interplanar angle between the rings in chloranilic acid and 1,2-diazine are 12.4° [2]. 1,2-Diazine complex has an inversion symmetry at the center of chloranilic acid [3].

A characteristic feature in 1,2-complex is a high pK_a of 2.24 of 1,2-diazine compared with 0.75 of 1,4-diazine in solution [5,6], illustrated in Figure 5-2, together with pK_{a1} = 0.76 and pK_{a2} = 2.72 of chloranilic acid in solution [7].

Since pK_a in 1,2-diazine is larger than that in 1,4-diazine, we can expect that the stability of chloranilic acid with high ionic charges increases in 1,2-complex compared with in 1,4-complex suggesting the more easy formation of chloranilate(1-) and (2-) ions.
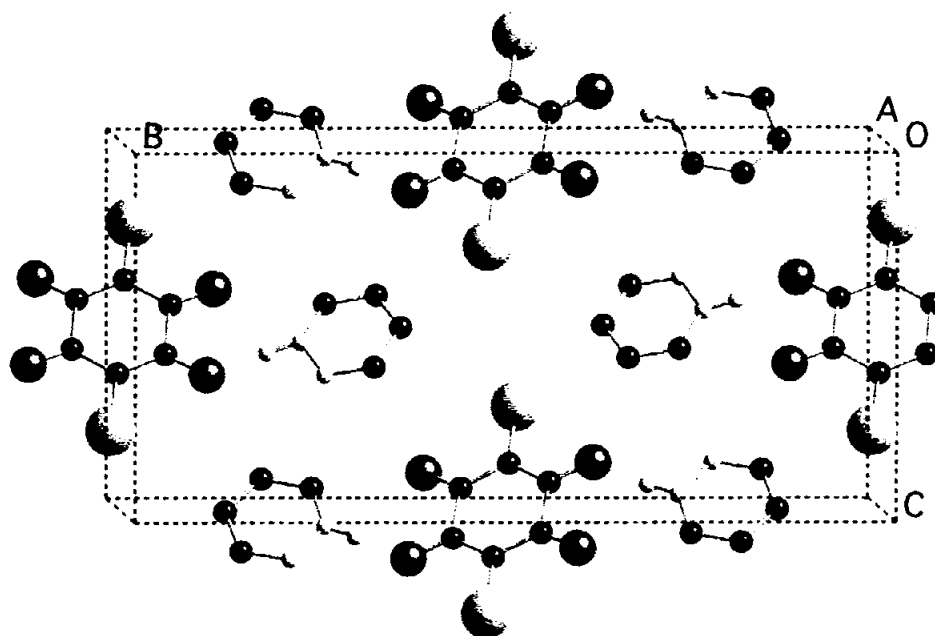
Space group	$P2_1/c$
Lattice parameters	$a = 3.799, b = 20.292, c = 9.675$ Å
	$\beta = 99.69°$
	$Z = 2$

Figure 5-1. The structure of $C_6O_2Cl_2(OH)_2\text{-}(1,2\text{-}C_4H_4N_2)_2$ determined by X-ray diffraction at room temperature [3].
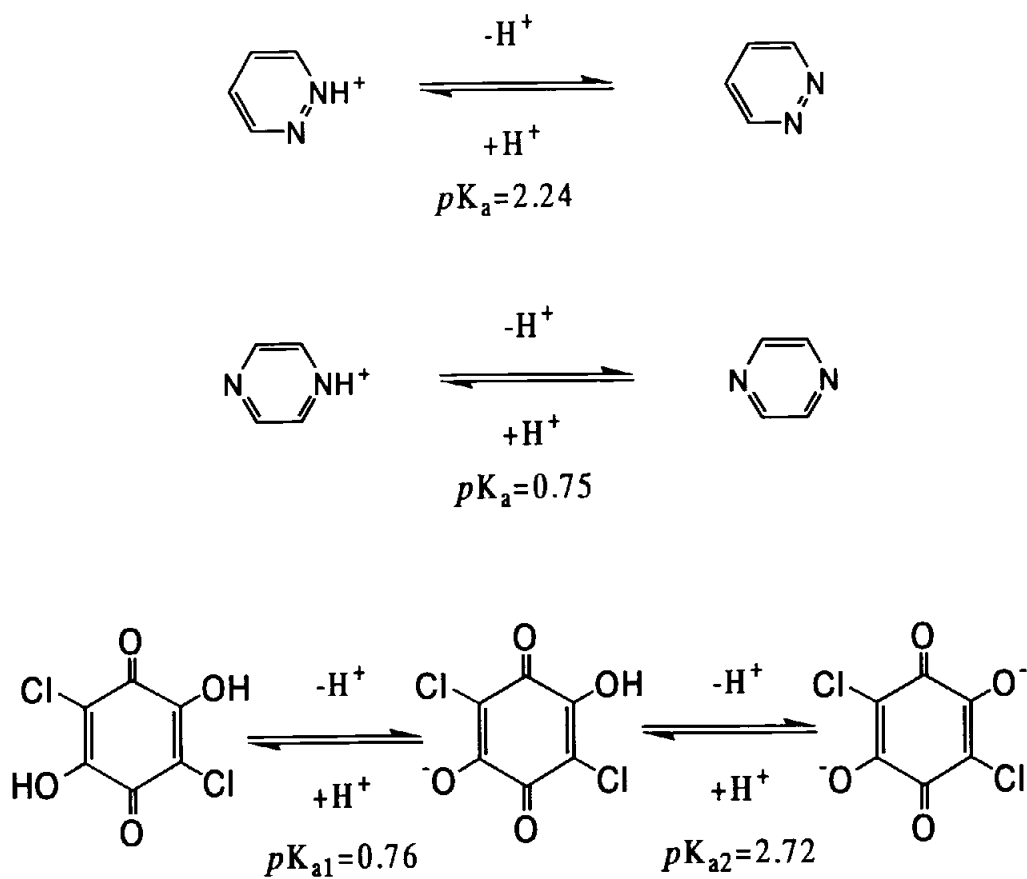
Figure 5-2. pK_a values of 1,2-diazine, 1,4-diazine and chloranilic acid in aqueous solution [5,6,7].

5-2. Experimental

A molecular complex of chloranilic acid($C_6O_2Cl_2(OH)_2$) with 1,2-diazine(1,2-$C_4H_4N_2$) with a ratio of 1:2 was prepared by mixing chloranilic acid dissolved in CH_3CN and liquid 1,2-diazine with a molor ratio of 1:2 [3], and obtained dark purple crystals were recrystallized from methanol.

^{35}Cl NQR frequencies were measured with a Dean-type external quenching superregenerative spectrometer with Zeeman modulation [8] 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 a temperature range from 77 K to room temperature

^1H NMR spin-lattice relaxation time (T_{1H}) in 1,4-complex 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.

5-3.   Results

5-3-1. ^{35}Cl NQR Frequencies

The temperature dependence of ^{35}Cl NQR frequencies observed in $(C_6O_2Cl_2(OH)_2)-(C_4N_2H_4)_2$ complex (abbreviated to 1,2-complex) is shown in Figure 5-3. A single resonance line was observed at 34.940 ± 0.001 MHz at 77 ± 1 K in agreement with the crystal structural data [3] reporting the equivalence of all chlorine atoms in crystals at room temperature.   Upon heating from 77 K, the frequency was gradually increased and showed a broad maximum at $ca.$ 170 K.   Upon further heating to room temperature, the resonance frequency was decreased and weakened, and then disappeared in the noise level at $ca.$ 300 K.

5-3-2. ^{35}Cl NQR Spin-Lattice Relaxation Time (T_{1Q})

A temperature dependence of ^{35}Cl NQR spin-lattice relaxation time (T_{1Q}) is shown in Figure 5-4. T_{1Q} of 2.5 s observed at 77 K was decreased upon heating, and showed two shoulders of $ca.$ 1.5 and 0.5 s around 100 and 170 K, respectively.   Upon further heating, T_{1Q} was decreased down to 200 ms at room temperature.   The rough temperature dependence of T_{1Q} observed in the whole temperature range studied is

analogous to that in 1,4-complex, but we could observe three minima in contrast to two

minima in 1,4-complex.

5-3-3. ^{1}H NMR Spin-Lattice Relaxation Time (T_{1H})

A temperature dependence of ^{1}H NMR spin-lattice relaxation time (T_{1H})

observed at 54.3 MHz is shown in Figure 5-5.   A single shallow minimum of 40 ±3 s

was observed at ca. 110 K.   The log T_{1H} vs T^{-1} plots was seen to be almost symmetric.

This temperature dependence is analogous to that in 1,4-complex in both of the depth of

the minimum and the slope of high- and low-temperature sides of the minimum, but the

minimum temperature is a little sifted toward the low temperature side compared with
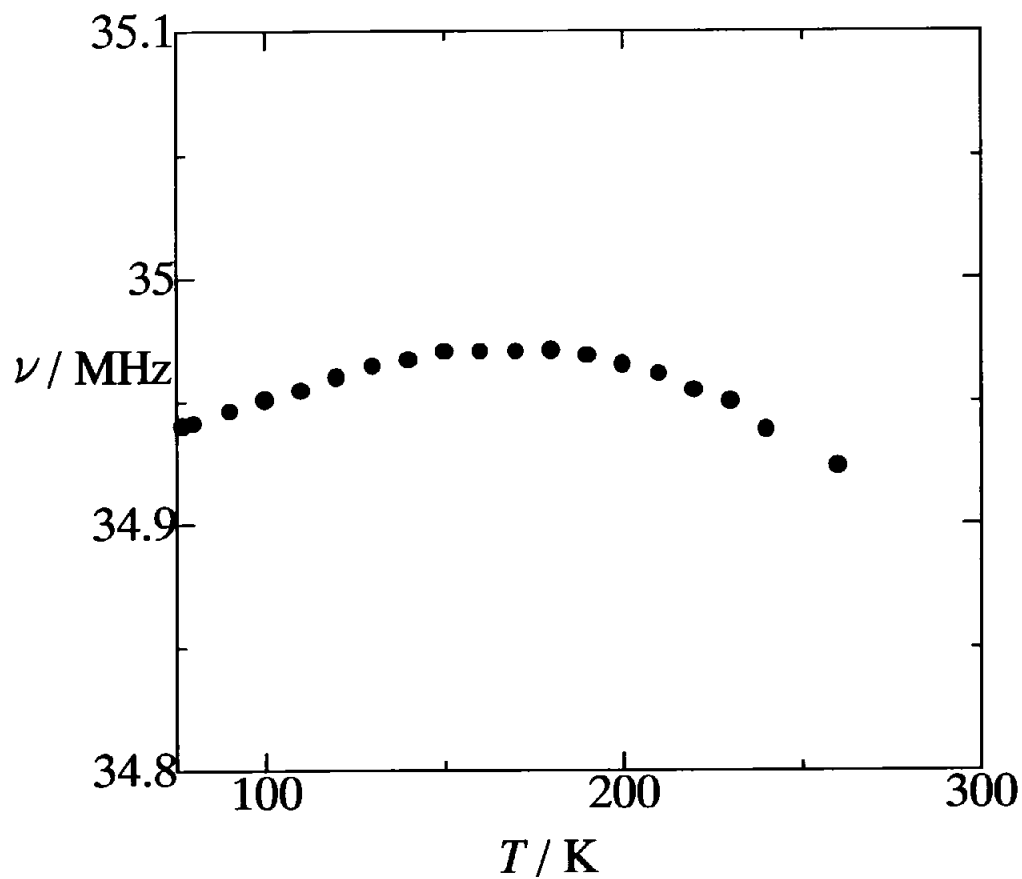
that in 1,4-complex.

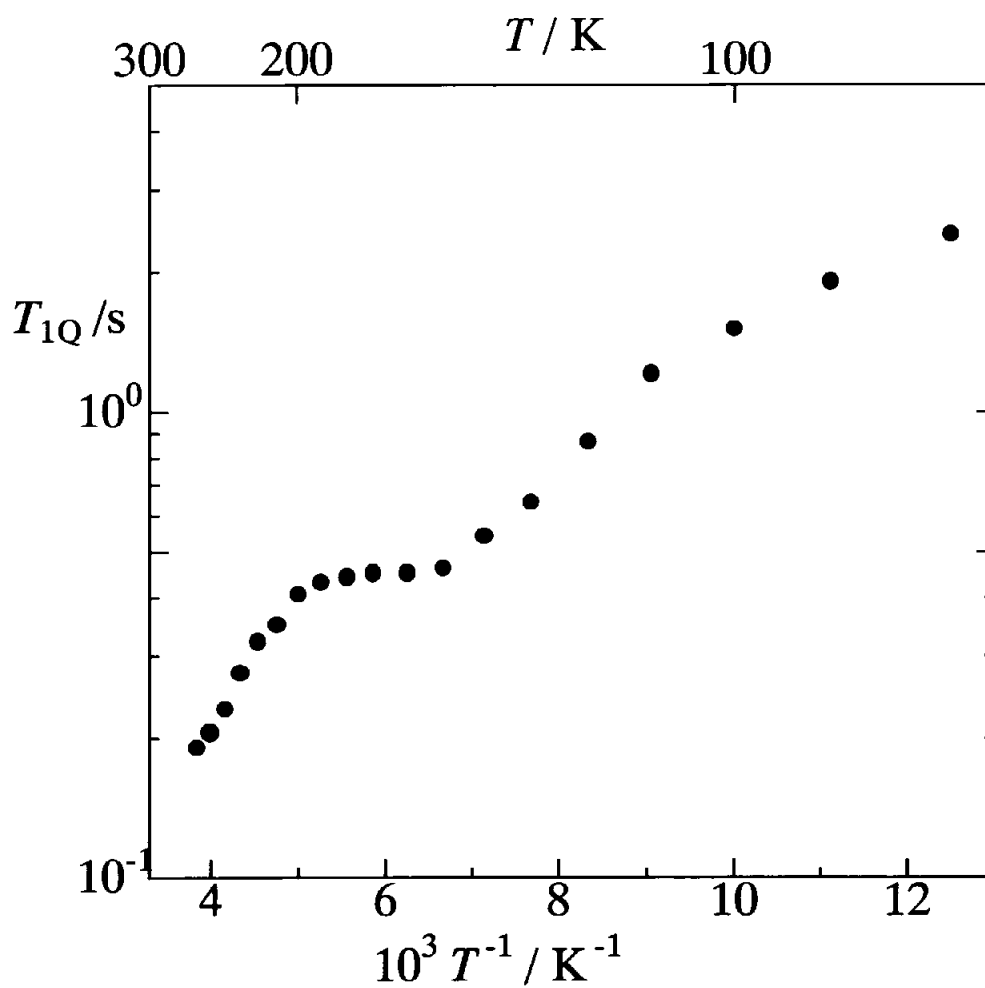Figure 5-3. A temperature dependence of ^{35}Cl NQR frequency (v) observed in $C_6O_2Cl_2(OH)_2$-$(1,2\text{-}C_4H_4N_2)_2$.

Figure 5-4.   A temperature dependence of the ^{35}Cl NQR spin-lattice relaxation time T_{1Q} observed in $C_6O_2Cl_2(OH)_2$-$(1,2-C_4H_4N_2)_2$.
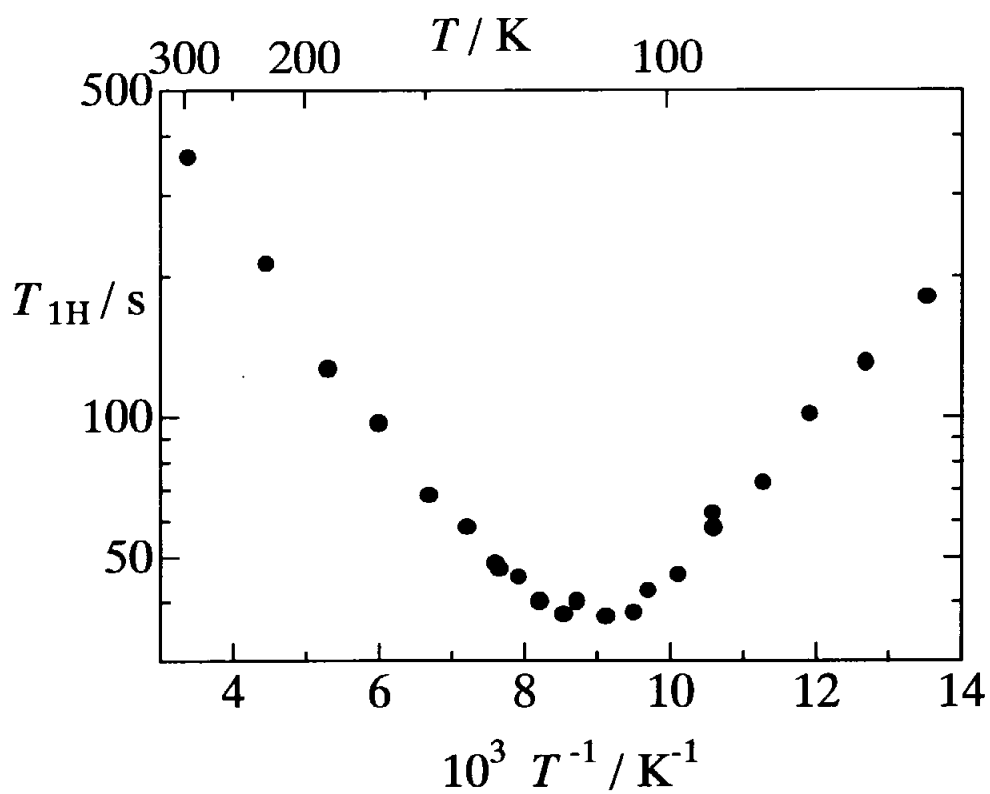
Figure 5-5.   A temperature dependence of the ^1H NMR spin-lattice relaxation time T_{1H} observed in $C_6O_2Cl_2(OH)_2$-$(1,2$-$C_4H_4N_2)_2$ at a Larmor frequency of 54.3 MHz.

5-4. Discussion

5-4-1. ^{35}Cl NQR Frequency

The temperature dependence of ^{35}Cl NQR frequency given in Fig. 5-3 showed an anomalous positive temperature coefficient in the low-temperature range77-160 K, which is unexplainable by the conventional Bayer theory [9] accounting for the influence from lattice and molecular vibrations described in Chapter 3. The origin of this unusual behavior is discussed in 5-4-4.

It should be noted that ^{35}Cl resonance frequency of 34.94 MHz observed at 77 K is much lower than 36.40 MHz obtained in the foregoing chrolanilic acid-1,4-diazine system (abbreviated to 1,4-complex) described in Chapter 4. This marked difference is unexplainable by only differences in electric field gradient (efg) made by surrounding crystal lattices described in Chapter 3, but attributable to differences in electronic structures in these two complexes. It has been reported that ^{35}Cl NQR frequency in crystalline chloranilic acid($C_6O_2Cl_2(OH)_2$) is 37.15 MHz at 77 K, while its divalent sodium salt containing $[C_6O_2Cl_2O_2]^{-2}$ ions gives an averaged frequency of ca. 35.20 MHz (an average of 35.538 and 33.853 MHz) at 77 K [10]. From these frequencies, we can expect that the present 1,2-complex contains chloranilic acid with a formal charge close to 2- in crystals at 77 K as can be expressed as
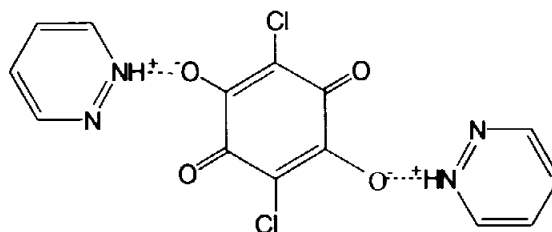
This contrasts with the result in the previous 1,4-complex in which the monovalent chloranilate(1-) was shown to be the most populated species at low temperatures from the observed ^{35}Cl frequency.   The present result in 1,2-complex can be supported by a larger pK_a value of 2.24 in 1.2-diazine [5] than that of 0.75 in 1,4-diazine [6], i.e., since 1,2-diazne is a stronger base than 1,4-dazne, 1,2-diazine can easily draw two hydrogen atoms from chloranilic acid.

5-4-2. ^1H NMR Spin-Lattice Relaxation Time (T_{1H})

The very long T_{1H} values observed in the whole temperature range studied and a single shallow minimum value of 45 s around 110 K shown in Fig.5-5 are quite analogous to those in 1,4-complex shown in Chapter 3.   Applying the same discussions described in Chapter 3, we can reasonably assigned this T_{1H} minimum observed in 1,2-complex to the fluctuations of the magnetic dipolar interactions caused by the hydrogen transfer between chloranilic acid and two 1,2-diazine molecules hydrogen bonded with each other.   As a hydrogen transfer model averaging H-H dipolar interactions, H-jumps between the divalent and monovalent chloranilate ions shown in the following figure can be accepted, because H-motions should be excited from the most populated chloranilate (2-) (Structure I), and, in this case, the next stable form is monovalent

chloranilate (1-) (Structure II and III). Here we assume that the structures II and III containing chloranilate (1-) ions have the same energy which have been supported by the crystal structure [3] requiring an inversion center on chloranilic acid molecules and also a single NQR frequency observed down to 77 K.
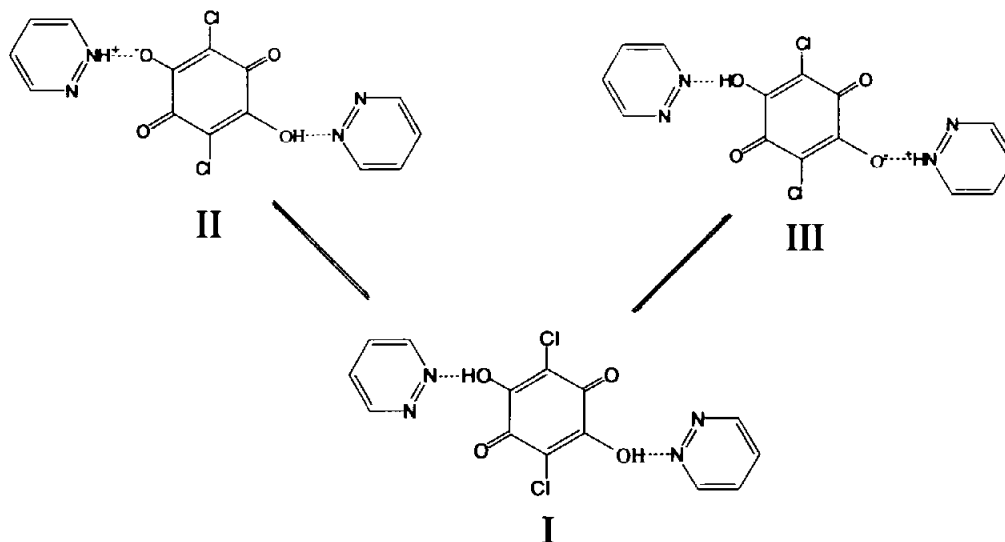
Upon heating the chloranilate(2-) ions stable at low temperatures, H-jumps, I↔II and I↔III shown above are expected to take place with the same rate and contribute to the ^1H relaxation at low temperatures.

The observed T_{1H} temperature dependence shown in Fig. 5-5 is explainable by the conventional BPP-type analysis [11] described in Chapter 3 and 4, but the T_{1H} slopes at the low and high temperature sides exhibited a little asymmetry. The evaluated activation energies (E_a) from the high- and low-temperature sides of the minimum as shown in Fig. 5-6 were 3.8 ± 0.5 kJ mol^{-1} and 3.2 ± 0.5 kJ mol^{-1}. An analogous asymmetry was also observed in 1,4-complex as described in Chapter 4. The deviation from the BPP equation is attributable to hydrogen transfer in the asymmetric potential wells for N—H···O H-bond and also the effect from the tunneling H-exchange.

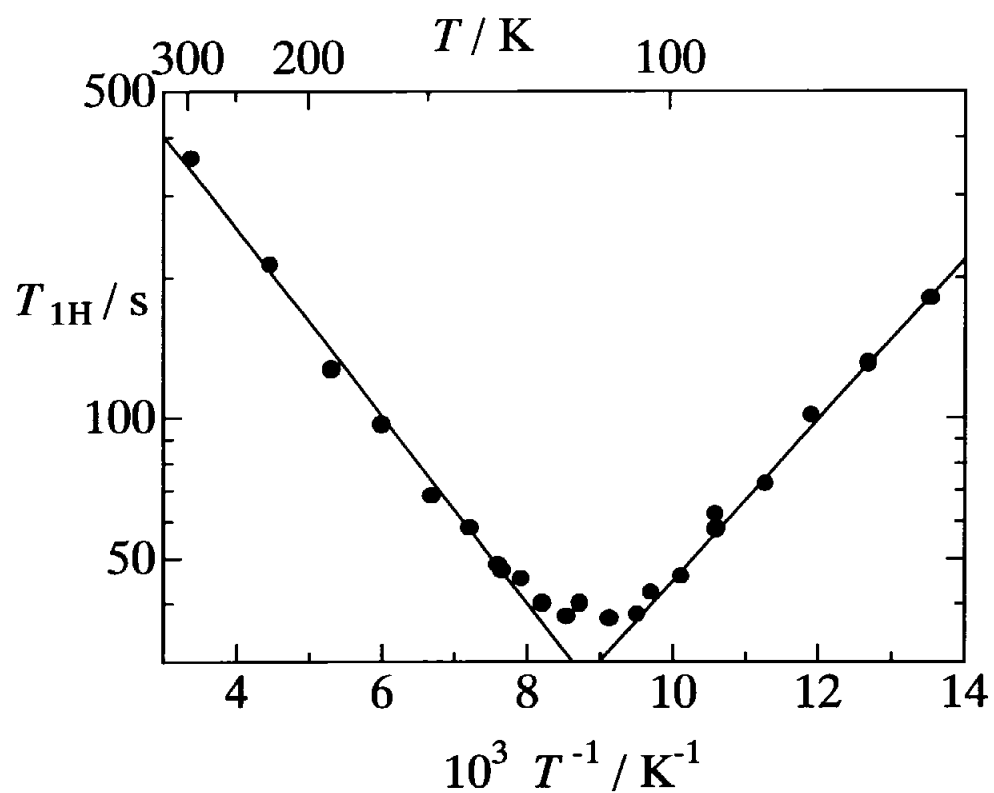Figure 5-6. A temperature dependence of the ^1H NMR spin-lattice relaxation time T_{1H} observed in $C_6O_2Cl_2(OH)_2$-$(1,2$-$C_4H_4N_2)_2$ at a Larmor frequency of 54.3 MHz. Solid lines are drawn to obtain activation energies.

5-4-3. ^{35}Cl NQR Spin-Lattice Relaxation Time (T_{1Q})

The observed T_{1Q} shown in Fig. 5-4 gave a complicated temperature dependence compared with that of T_{1H} and is explainable at least three T_{1Q} minima shown in Figure 5-7. By the same reasons described in the discussion on T_{1Q} in 1,4-complex in Chapter 4, all of these three relaxation processes can be assigned to hydrogen transfer motions associated with the two hydrogen bonds in a complex, shown in Figure 5-8. Here, we assume Debye type relaxation processes as observed in ^{1}H NMR and the Arrhenius-type activation equation used in the study of 1,4-complex in Chapter 4 [12]. We fitted superimposed three relaxation mechanisms and the best-fitted calculated values are shown in Figure 5-7. In the fitting for the lowest-temperature minimum, we used the activation energy (E_a) determined in the T_{1H} analysis and the minimum temperature after adjusting the frequency difference in the NQR and NMR measurements. The determined values of the best-fitted parameters are shown in Table 5-1.

In the discussion of 1,4-complex in Chapter 4, we observed a single hydrogen transfer motion from ^{1}H NMR while two motions from ^{35}Cl NQR, in which the disagreement was reasonably explained by considering two kinds of hydrogen transfer models. i.e., correlated and uncorrelated hydrogen transfers in 1,4-complex containing two hydrogen bonds. In the previous Chapter, we proposed the possibility of three kinds of H-motions in the three different valence states (2-, 1- and 0) of a chloranilic acid molecule in the present three molecular system. In the previous study of 1,4-complex, we could determine a hydrogen transfer mode between two kinds of chloranilate(1-) ions (II↔III) at low temperatures, but we could not assign the T_{1Q}

decrease observed at high temperatures to a definite motional mode because two kinds of modes, namely, between chloranilate(1-) and (2-) or between (1-) and (0) are possible.

In the present study of 1,2-complex, we could observe clearly divided three relaxation processes assignable to three kinds of hydrogen transfer modes that we predicted. The lowest-temperature relaxation was explained by the equivalent two modes I↔II and I↔III shown in Fig. 5-8 taking place with the same probability as derived from the above discussion of T_{1H}. As for the other two mechanisms expected in the high temperature range, one is the symmetric H-exchange keeping the chloranilate (1-) structure named the correlated motion in the study of 1,4-complex given by II↔III in Figure 5-8. The other should be the hydrogen transfer between chloranilate(1-) and (0) expressed by II↔IV and III↔IV in Figure 5-8. We can assign the former to the relaxation giving the minimum around 160 K, and the latter to that observed around room temperature. This indicates that the latter process has a higher barrier than the former, because, in the present 1,2-complex, the time averaged structure of chloranilic acid was shown to be close to 2– implying a high barrier for getting a neutral molecule. This can also be shown from the consideration of a marked difference in $pK_{a1}(=0.76)$ and $pK_{a2}(=2.72)$ [5,6] of chloranilic acid and also $pK_{a1}(=2.24)$ of 1,2-diazine in solution [7].
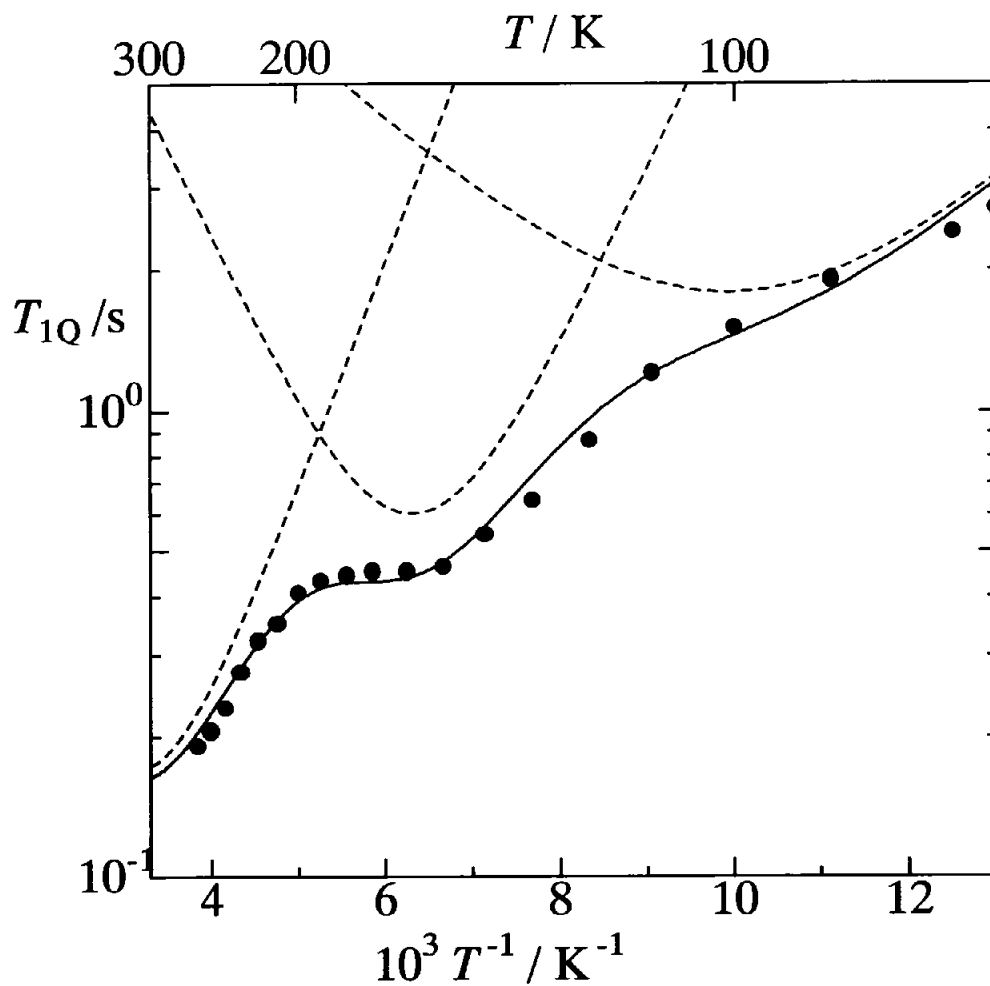
Figure 5-7.   A temperature dependence of the ^{35}Cl NQR spin-lattice relaxation time T_{1Q} observed in $C_6O_2Cl_2(OH)_2$-$(1,2$-$C_4H_4N_2)_2$. The solid curve is the best-fitted calculated values expressed by the superposition of three components (dashed curves).

Table 5-1.   Motional parameters in hydrogen transfers determined in $C_6O_2Cl_2(OH)_2$-$(1,2$-$C_4H_4N_2)_2$ derived ^{35}Cl NQR relaxation data.

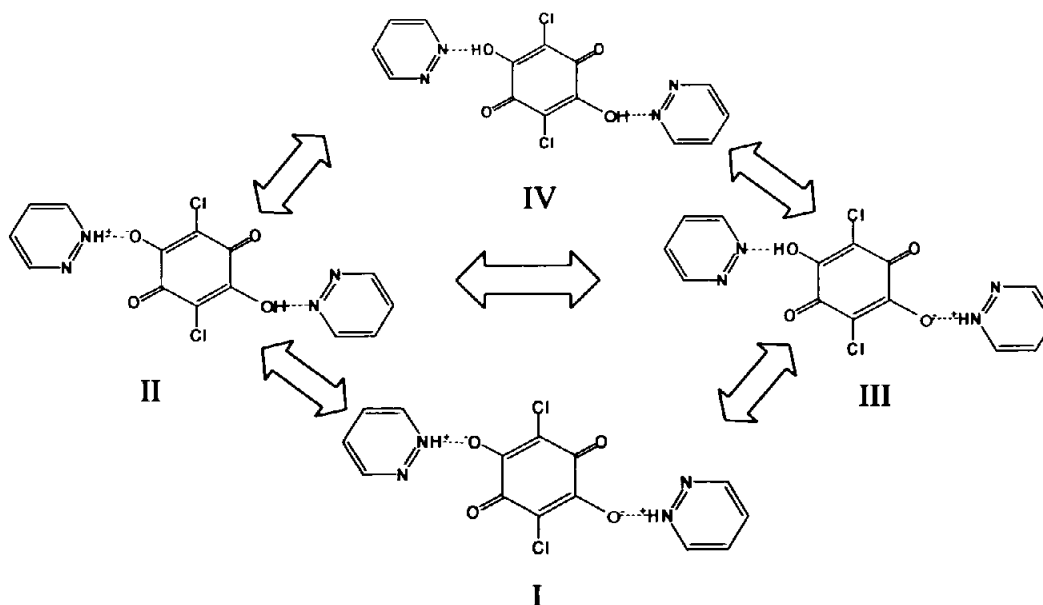|	low temp.	intermediate temp.	high temp.
C (s^{-2})	$2.45 \pm 0.1 \times 10^8$	$7.6 \pm 0.1 \times 10^8$	$\sim 2.7 \times 10^9$
τ_0 (s)	$1.0 \pm 0.1 \times 10^{-10}$	$1.6 \pm 0.1 \times 10^{-11}$	$\sim 1.4 \times 10^{-10}$
E_a $(kJ\ mol^{-1})$	3.2	7.4 ± 1.5	9.2 ± 1.5

Figure 5-8. Hydrogen transfer models. In the low-temperature range: I ⇔II (or III), where the hydrogen exchange causes an electric structural change between divalent- and monovalent ions. In the middle-temperature range II⇔III : (the correlated transfer model), where two hydrogen atoms jump simultaneously, causing no course electric structural change. In the high-temperature range: IV⇔III(or II), where the hydrogen exchange gives rise to an electric structural change between neutral- and monovalent ions.

5-4-4. The Effect of Hydrogen Transfer to NQR Frequency

An unusual temperature dependence of NQR frequency was measured in 1,2-diazine complex. This temperature dependence has a gentle maximum at 170 K shown in Figure 5-3. This result can not be explained by only the Bayer-law [9] predicting a monotonous frequency decrease upon heating. We can attribute this anomalous temperature dependence of frequency behavior to the H-exchange taking place in this system. Since the population of monovalent chloranlic acid is increase by the H-exchange upon heating from 77 K, the NQR frequency which is determined by the averaged efg of constituent molecular species is increased because chloranilate ion (1-) ions gives a higher resonance frequency than (2-) ions. Therefore, the temperature dependence of NQR frequency is expected to have a positive slope below 170 K. As described in Chapter 3, since the amplitude of lattice vibrations is small in the low temperature range, its effect to the negative temperature dependence due to Bayer-law [9] is small. Accordingly the observed temperature dependence of the NQR frequency is dominated by the H-motion in the law temperature range. Further heating, the effect from the Bayer-law becomes more important than the H-exchanges because of the increasing amplitude of lattice vibrations upon heating.

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