Chapter 1

General Introduction

Hydrogen bonding is one of strong interactions operative between molecules in liquid and solid states, and we can see hydrogen bonding in many kinds of compounds that form molecular aggregates such as dimers, trimers, or infinite array molecules of 1,2 and 3-dimensional networks. These intermolecular hydrogen bondings play an important role in forming anisotropic interactions in condensed systems in which the hydrogen transfer through hydrogen bonds between molecules enabling charge and energy transfers in solid and biological systems has been intensively studied in connection with ferro- and antiferro-electrics [1], dipolar glasses [2], molecular solitons [3] and *etc*.

For hydrogen motion through hydrogen bonds, the length of A···B forming hydrogen bonding A—H···B works as an important parameter. In case of a short A··· B length implying a strong hydrogen bonding, hydrogen atoms can not move but stay at the center of hydrogen bond as shown in Figure1-1. This can be seen, for example, in KHF_2 and $NaHF_2$ having a point symmetry on the hydrogen atom[4]. On the other hand, in case of a long A···B length, *i.e.* week hydrogen bonding, hydrogen atoms also can not easily move from the site A to B except at high temperatures, because the thermal energy is not enough to overcome the potential barrier as shown in Figure 1-2. Examples of various kinds hydrogen bonds and their lengths are shown in Table 1-1

studied by neutron diffraction studies [4]. From these results we can expect that hydrogen transfer motions can be observed in case the A···B has intermediate distances between the above two extreme cases as shown in Figure 1-3, for example, compounds which have O···O distance with 2.5 ~ 2.7 Å have been reported to show disordered hydrogen positions in hydrogen bonding as given in Table 1-1.

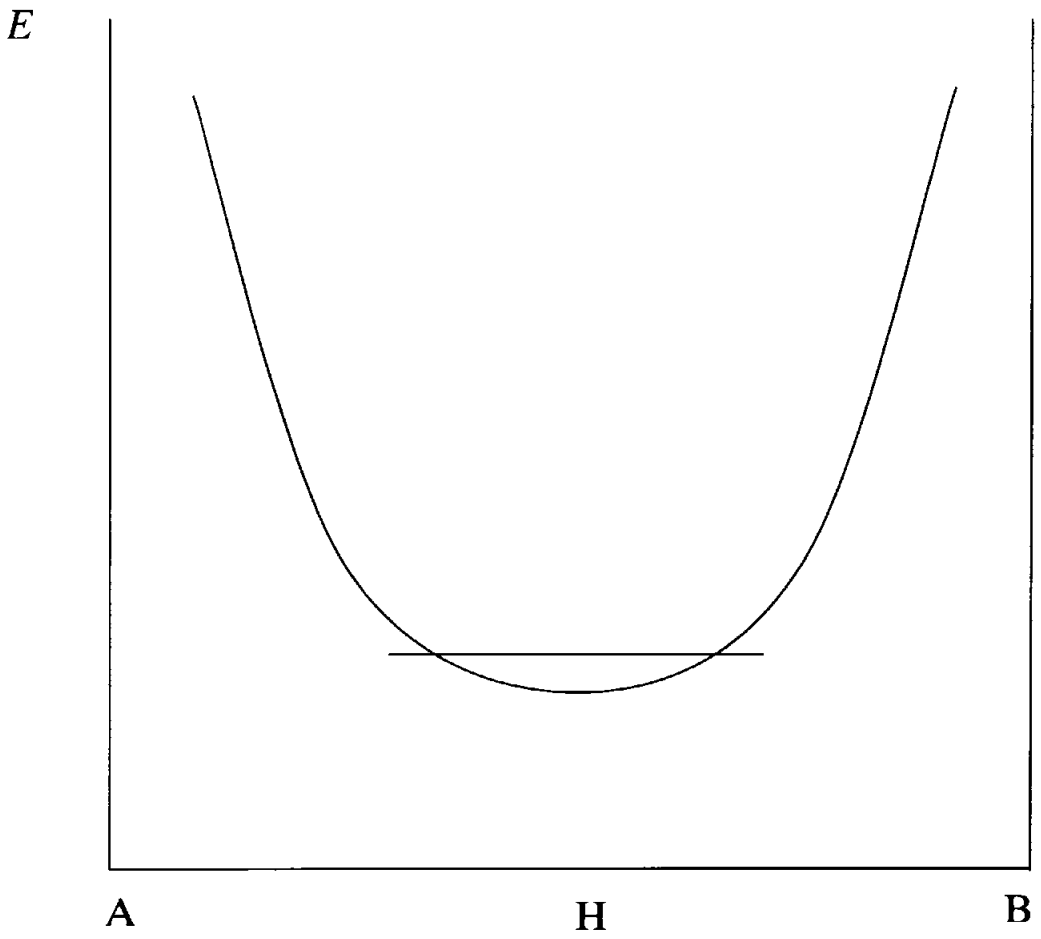


Figure 1-1. A potential curve in a hydrogen bond with a short A···B length. The hydrogen atom stays at the center of hydrogen bond and cannot move.

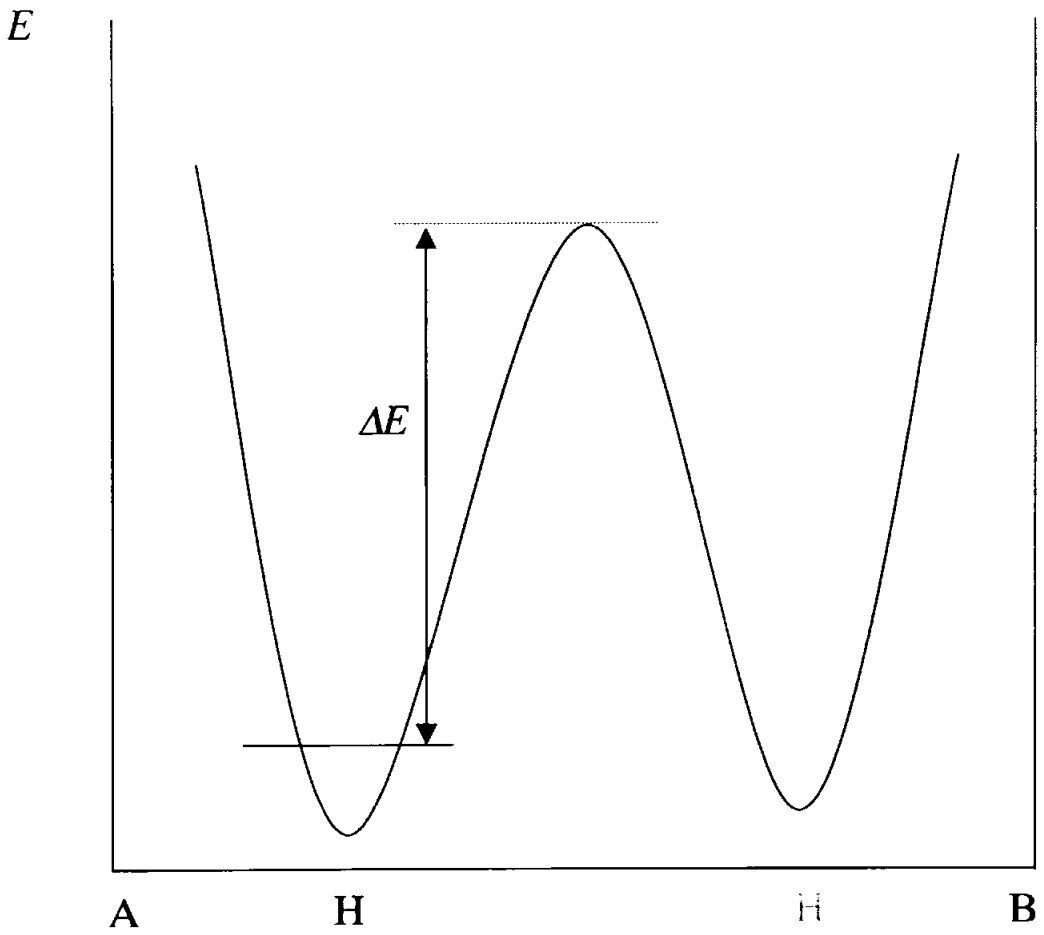


Figure 1-2. A potential curve in a hydrogen bond with a long A···B length. The hydrogen atom cannot move easily from site A to B, because of a high potential barrier ($\Delta E >> kT$).

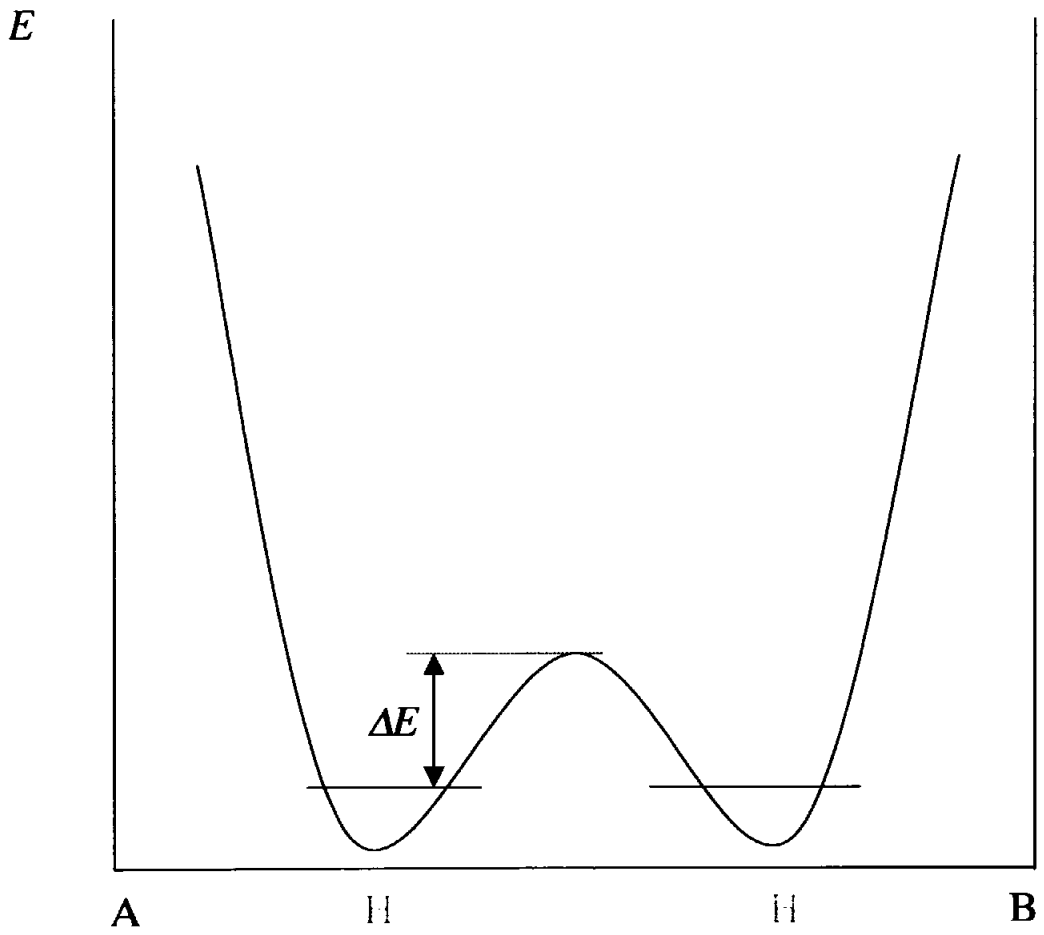


Figure 1-3. A potential curve model enabling disordered hydrogen positions in the hydrogen bonding. The hydrogen can move between two sites overcoming the low potential barrier ($\Delta E \leq kT$).

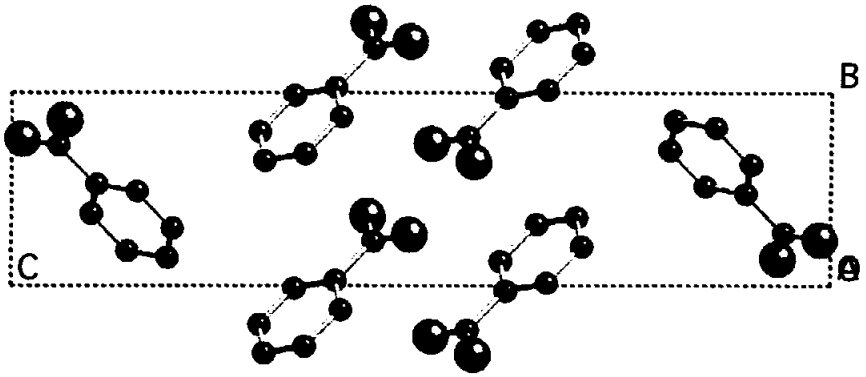
Table 1-1. Hydrogen bonded systems studies by neutron diffraction [4]

Compound	Bond type A···H···B	A···B (Å)	X···H (Å)	H···Y (Å)	Structure
KHF_2	F···H···F	2.26	1.13	1.13	Symmetric
$NaHF_2$	F···H···F	2.26	1.13	1.13	Symmetric
Acetamide · 1/2HCl	O···H···O	2.42	1.21	1.21	Symmetric
$HCrO_2$	O···H···O	2.49	1.245	1.245	Symmetric
$DCrO_2$	O···D···O	2.55	0.96	1.59	Disordered 1/2H
KH_2PO_4	O—H···O	2.49	1.09	1.40	Disordered 1/2H
KH_2AsO_4	O—H···O	2.52	1.06	1.46	Disordered 1/2H
KD_2AsO_4	O—D···O	2.52	1.03	1.49	Disordered 1/2H
$NH_4H_2PO_4$	O—H···O	2.48	1.07	1.41	Disordered 1/2H
	N—H···O	2.91	1.00	1.96	
D_2O(123 K)	O—D···O	2.76	1.01	1.75	Disordered 1/2H
		2.75	1.01	1.74	
Urea	N—H···O	3.03	0.99	2.06	
		2.99	1.00	2.08	
ND_3	N—D···N	3.35	1.01	2.37	
$(NH_4)SiF_6$	N—H···F	3.00	1.06	2.08	Disordered
PH_4I	P—H···I^-	4.24	1.39	2.87	

As an example, the hydrogen exchange in dimerized benzoic acid [5,6] in solid, which is shown in Figure1-4, has been extensively studied by ^{1}H nuclear magnetic resonance (NMR) [7,8], IR spectroscopy [7], X-ray diffraction [5], and neutron diffraction [6]. The temperature dependence of ^{1}H NMR spin-lattice relaxation time (T_{1H}) was measured, and analyzed in solid benzoic acid (BA) and ring-deutero benzoic acid (BA-d_5) [7,8]. An asymmetric temperature dependence of ^{1}H NMR spin-lattice relaxation time (T_{1H}) was observed in both BA and BA-d_5, as shown in Figure1-5. This result was explained by a two-state jump model (Fig. 1-6) for the classical random hydrogen jumping double proton transfer and the quantum mechanical proton tunneling coupled to crystalline phonons [7,8]. In the high temperature range above the temperature of the minimum, the observed relaxation was explained by the BPP type relaxation [7] due to the classical random hydrogen jump. On the other hand, the relaxation on the low-temperature side was attributed to the proton tunneling.

NMR measurement, however, seems to be rather insensitive for this purpose because of a small displacement of hydrogen positions (the order of 10^{-1}-10^{-2} Å) in the hydrogen exchanging process that usually requires the measurement of the relaxation time in the order of 10^2-10^3 s [7].

Nuclear quadruple resonance (NQR) is one of magnetic resonance spectroscopies of which can be detected in systems including nuclei with spins $I \geq 1$. For example, nuclei ^{35}Cl with I = 3/2 have the energy levels split by the interaction of the nuclear quadruple moment with the electron field gradient (efg) without the external magnetic field as shown in Figure1-7.



Space group	$P2_1/c$
Lattice parameters	$a = 5.510$ $b = 5.151$ $c = 21.973$ Å
	$\beta = 97.41^\circ$
	$Z = 4$

Figure 1-4. The structure of benzoic acid determined by X-ray diffraction at room temperature [5,6].

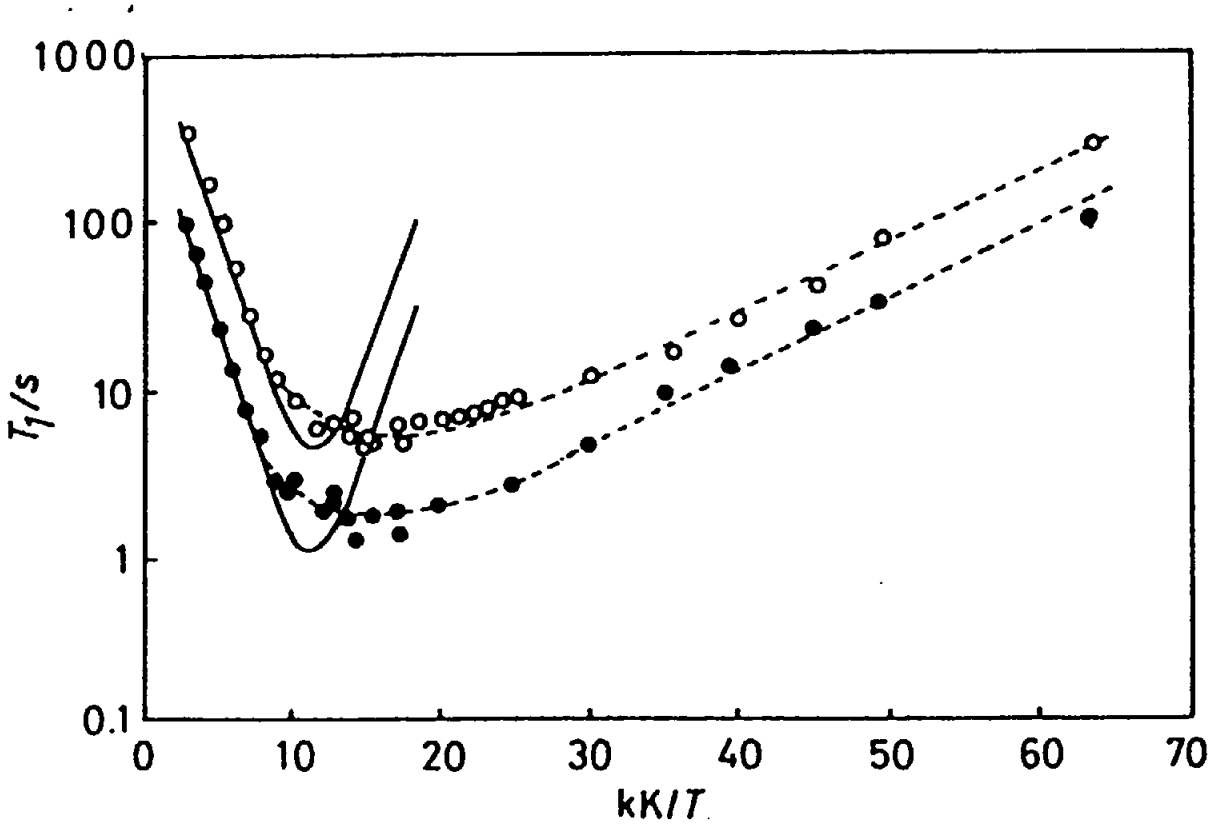


Figure 1-5. Temperature dependences of ^{1}H NMR spin-lattice relaxation time T_1 observed in benzoic acid (○) and benzoic acid-d_5 (●)at 59.53 MHz[7].

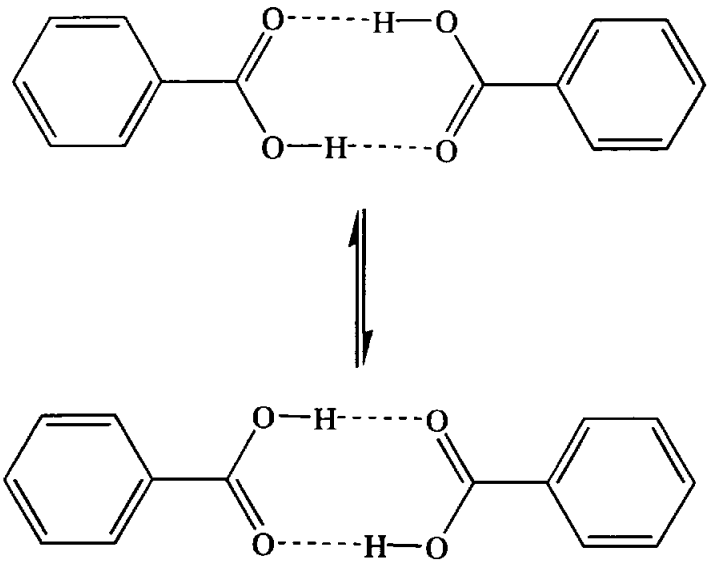
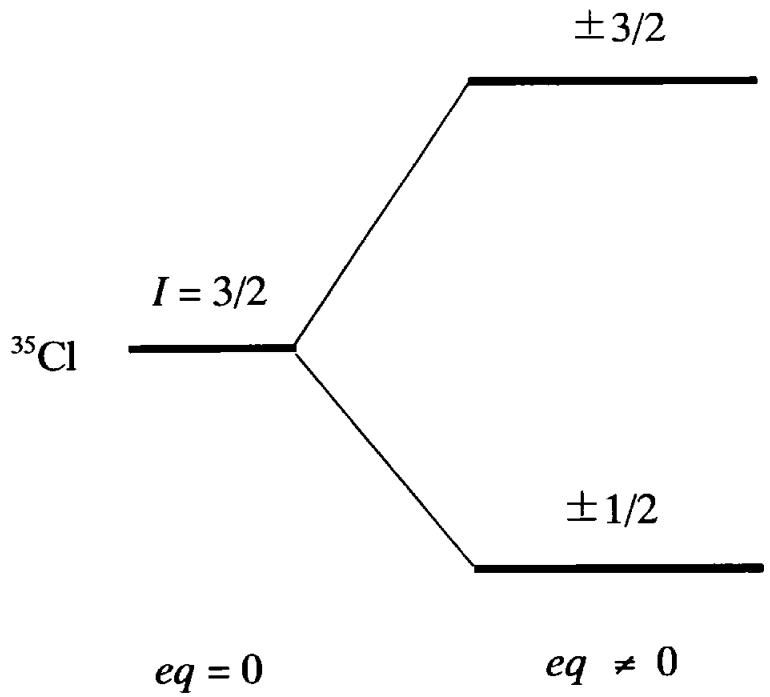


Figure 1-6. The double hydrogen transfer model in benzoic acid. Two hydrogen atoms in the calboxylic acid dimer jump at the same time.



eq : Electric Field Gradient

Figure 1-7. The nuclear energy diagram in ^{35}Cl with I = 3/2. The energy level is split by the interaction of the nuclear quadruple moment (eQ) with the electric field gradient (efg) with no external magnetic field.

In the present study, we intend to detect hydrogen motion by the NQR measurement of chlorine located in a remote position from the hydrogen bond in a molecule. We expect that this method is useful because a subtle fluctuation of efg in a remote position can be expected to be detected by the NQR technique more sensitively than the NMR technique. Such a long-range propagation of efg can be realized by employing a conjugated system like phenyl rings as illustrated in Figure 1-8.

p-Chlorobenzoic acid containing a chlorine atom on a phenyl ring has been reported to form a dimer structure [9], and the onset of the hydrogen transfer in hydrogen bond is suggested from the study of the ^{1}H NMR measurement [7] which has already shown this motion in benzoic acid In Chapter 3, we describe the hydrogen transfer detected by the NQR technique in *p*-chlorobenzoic acid.

In Chapter 4 and Chapter 5, we report the results of our application of the NQR technique to new hydrogen bonded systems and detection of new hydrogen motions in hydrogen bonded three molecule systems such as (chloranilic acid)-(1,4-diazine) 1:2 complex shown in Figure 1-9 having hydrogen transfer modes more complex than in *p*-chlorobenzoic acid and benzoic acid with a dimer structure.

In the present study, we used the home made puled NMR and NQR spectrometers which are described in Chapter 2.

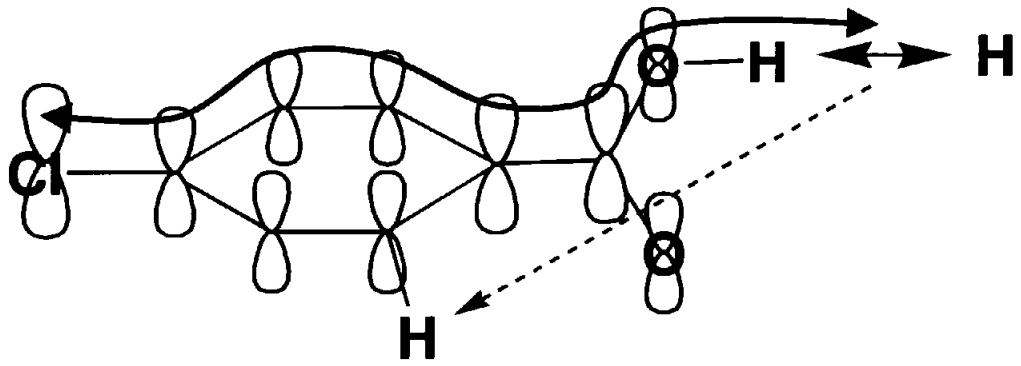


Figure 1-8. Comparison of ^{1}H NMR and ^{35}Cl NQR relaxation mechanisms in a diamagnetic hydrogen-bonded system. ^{1}H NMR relaxation due to the magnetic dipolar interaction expressed by the dotted line gives a very long T_{1H}, because of a small displacement of hydrogen position expressed by ◀⟷▶. NQR T_{1Q} is sensitively changed by this motion, because fluctuation of electric field gradient made by H-motion is conducted through the π-electron system to the chlorine atom shown by sold arrow.

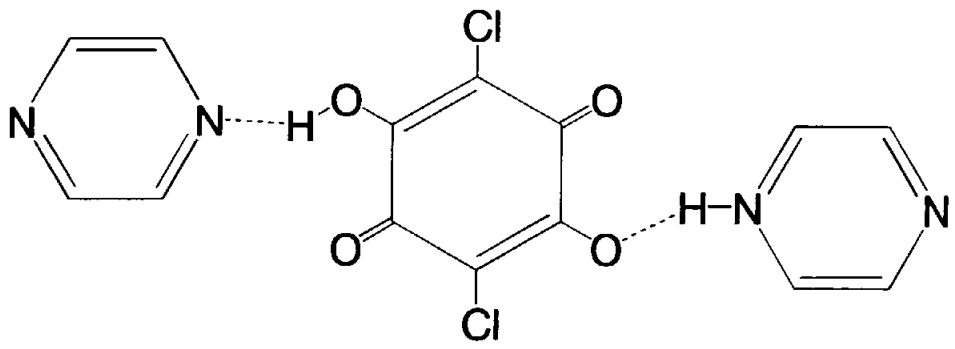


Figure 1-9. A three-molecular hydrogen bonded system, (chloranilic acid)-(1,2-diazine) 1:2 complex. Hydrogen bonded two hydrogen atoms can perform correlated and uncorrelated jumps between two sites.

References

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