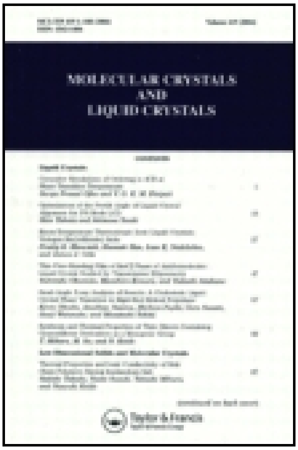

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NMR Study of Proton Dynamics in the Hydrogen Bonds in the Thermochromic Crystals of N-salicylideneaniline derivatives

Sadamu Takeda [a], Hideaki Chihara [a], Tamotsu Inabe [b], Tadaoki Mitani [b] & Yusei Maruyama [b]

[a] Department of Chemistry, Faculty of Science, Osaka University, Toyonaka, Osaka, 560, Japan

[b] Institute for Molecular Science, Myodaiji, Okazaki, 444, Japan

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NMR STUDY OF PROTON DYNAMICS IN THE HYDROGEN BONDS IN THE THERMOCHROMIC CRYSTALS OF *N*-SALICYLIDENEANILINE DERIVATIVES

SADAMU TAKEDA* AND HIDEAKI CHIHARA
Department of Chemistry, Faculty of Science, Osaka University, Toyonaka, Osaka 560, Japan

TAMOTSU INABE, TADAOKI MITANI AND YUSEI MARUYAMA
Institute for Molecular Science, Myodaiji, Okazaki 444, Japan

Abstract The crystals of several derivatives of *N*-salicylideneaniline which contain NHO hydrogen bonds in the molecule show thermochromism. To investigate the relation between the thermochromism and the proton transfer in the hydrogen bond, the proton dynamics of remarkably thermochromic crystal of BSP was precisely studied by solid state NMR method. The behavior of proton dynamics is good consistent with the temperature dependence of visible absorption spectra of this crystal. This result indicates that the thermochromism of this material is a prototype of "proton-electron cooperation". The transfer rate of proton in the NHO hydrogen bond was strongly affected by some chemical modifications, *e.g.* the fast tunneling in one case.

INTRODUCTION

In a molecular system, in which hydrogen bonds form a part of an electronically quasi-conjugated network, the switch of proton in a hydrogen bond is accompanied with a modulation of electronic state of bonds involved. Particularly in the case of the molecule which contains chemically asymmetric hydrogen bond, *e.g.* NHO hydrogen bond, the switch of proton position may induce a remarkable change in the electronic states related with OH and NH forms of the hydrogen bond. The coupling between proton and electron in this system is a key to create a new function and new phenomena in the molecular systems. Proton-electron coupling might be possible to control the proton motion, *i.e.* proton tunneling. Taking into construction of the intermolecular interaction for proton-electron coupled system, the motion of the protons may become collective and cooperate closely with electron system via quantum mechanical interaction.

A class of *N*-salicylideneaniline derivatives with NHO hydrogen bonds shows thermochromism and is believed as an starting material of proton-electron cooperation system. Precise investigation of nuclear magnetic resonance of proton of BSP (*N*,*N'*-bis(salicylidene) -*p*-phenylenediamine) and DNP (*N*,*N'*-di(2-hydroxy-1-naphthylidene)-*p*-phenylenediamine) is expected to provide detailed information of proton dynamics in the hydrogen bond in the crystalline state. In this paper, we mainly report the relation between proton dynamics and thermochromism of BSP and we briefly discuss the NMR result of DNP to elucidate the effect of chemical modifications on the proton dynamics in the NHO hydrogen bond.

RESULTS AND DISCUSSION

The spin-lattice relaxation rate T_1^{-1} of proton was determined by 90^0-train-τ-90^0 pulse sequence. The magnetization recovery curve was described by a single exponential function for all temperatures. Thus the spin temperature is established between the proton in the hydrogen bond and other protons present in the crystal and the dynamics of proton in the hydrogen bond can be directly estimated from the observed T_1^{-1} curve. The temperature dependence of T_1^{-1} of proton of BSP at 9.2 (○) and 37.5 (●) MHz is shown in Fig. 1, in which two maxima appeared near 70 K and 170 K. Both maxima were assigned to the switching motion of protons in the NHO hydrogen bonds, which will be discussed later.

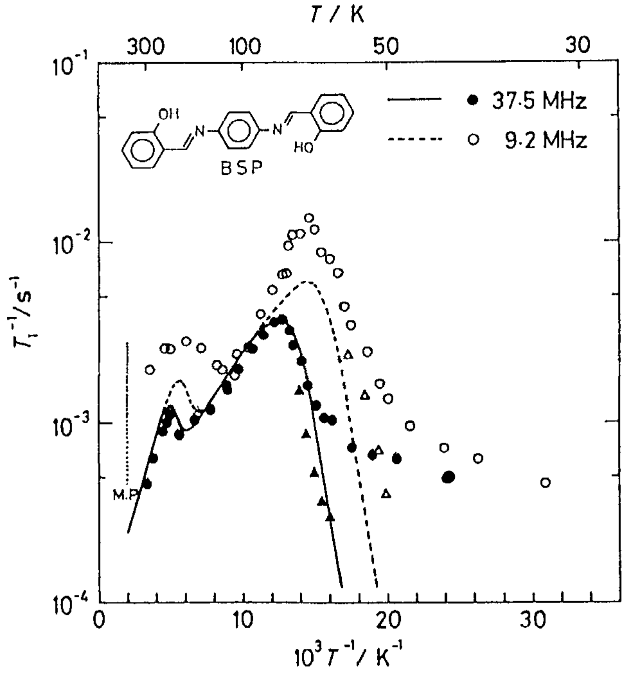

FIGURE 1 The temperature dependence of spin-lattice relaxation rate of proton of BSP at 9.2 and 37.5 MHz and m.p. indicates the melting point (485.5 K).

The slope of T_1^{-1} below 50 K is very small. If the Arrhenius relation is applied in this temperature region, the activation energy is determined to be 0.5 kJ/mol (40 cm^{-1}). The origin of this spin-lattice relaxation is not clear. Possibly some paramagnetic centers might contribute to the spin-lattice relaxation in such low temperature region, which is not taken into present discussion. The contribution of the low temperature relaxation was subtracted as a straight line from the observed values in Fig. 1 and full and open triangles (▲ for 37.5 MHz and △ for 9.2 MHz) were obtained.

The combination of two possible forms, OH and NH forms, of two hydrogen bonds in a BSP molecule may lead to four tautomeric forms, *i.e.* [OH,OH], [NH,OH], [NH,NH] and [OH,NH] forms which are numbered by 1 through 4 in order as shown in Fig. 2. Two of four tautomers, [OH,NH] and [NH,OH], are probably the same or very closely located in energy even in the crystalline state, because crystallographical inversion symmetry exists at a center of the molecule[1,2].

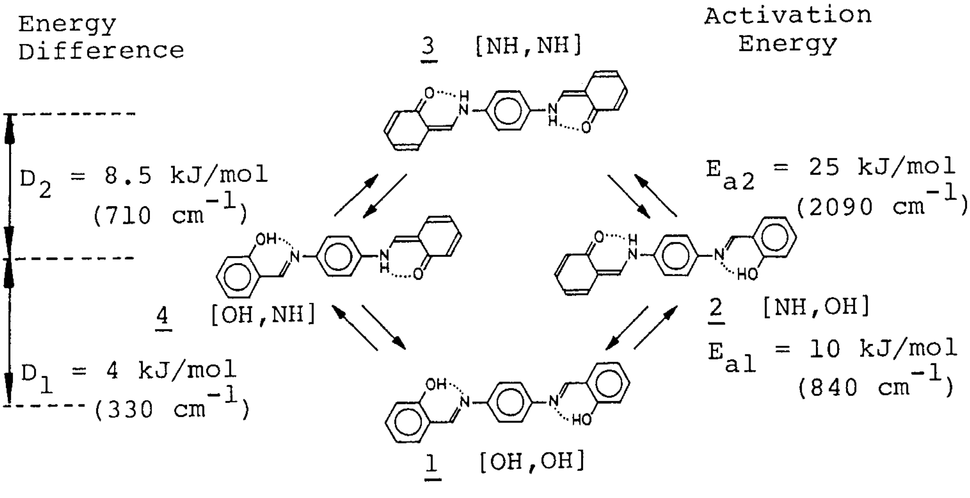

FIGURE 2 Schematic view of the proton dynamics of BSP and the energy values obtained by NMR.

According to the experimental results[1,2], OH form is more populated as temperature decreased from room temperature to 108 K and the OH form assumes more stable state than the NH form. A model of proton dynamics shown in Fig. 2 is, therefore, employed. The random switching of two protons leads to the transitions between four tautomers. In this model, the two tautomers, [OH,NH] and [NH,OH], are assumed to be degenerate in energy and thus there are three energetically different states. The probability of completely concerted switching of two protons, *i.e.* [OH,OH]←→[NH,NH] and [OH,NH]←→[NH,OH], is also assumed to be negligibly small compared with the independent switching shown in Fig. 2. The dependence of T_1^{-1} of BSP on temperature and on Larmor frequency shows no evidence of tunneling of proton in the vibrational ground state. Supposing the classical Arrhenius process for each proton switching, the dynamics of protons is described by two energy differences, D_1 and D_2, and two activation energies, Ea_1 and Ea_2; the transition rates of the elementary processes taken into account are described by

$$W_{12} = W_{14} = W_{01} \exp(-Ea_1/RT),$$

$$W_{21}/W_{12} = W_{41}/W_{14} = \exp(D_1/RT), \qquad (1)$$

$$W_{23} = W_{43} = W_{02} \exp(-Ea_2/RT)$$

and

$$W_{32}/W_{23} = W_{34}/W_{43} = \exp(D_2/RT).$$

The spin-lattice relaxation of proton in the hydrogen bond is dominated by the dipole interaction between proton and ^{14}N nucleus, because a distance between H and N in the hydrogen bond is very short compared with distances between a proton in the hydrogen bond and other protons present in the crystal. The spin-lattice relaxation formula related to proton dynamics was derived from the general expression of spin relaxation[4]. The detailed formula of the T_1^{-1} is not presented in this paper and only the result of calculation is presented.

By a calculation of the T_1^{-1} with using the crystal structural data[1,2], the solid and the broken curves were obtained for 37.5 and 9.2 MHz respectively. In this calculation the quadrupole splitting of ^{14}N nucleus is ignored. The quadrupole splitting might be negligibly small compared with 37.5 MHz of proton frequency[6], while for 9.2 MHz it induces a visible difference between the calculated broken curve and the observed values (○,△). It was concluded that the maximum of T_1^{-1} near 70 K is mainly induced by the transitions between [OH,OH] and [OH,NH] ([NH,OH]) tautomers, while the maximum of T_1^{-1} near 170 K is induced by the transitions between [OH,NH] ([NH,OH]) and [NH,NH] tautomers. Two activation energies, Ea_1 = 10 kJ/mol (840 cm^{-1}) and Ea_2 = 25 kJ/mol (2090 cm^{-1}), and two energy differences, D_1 = 4 kJ/mol (330 cm^{-1}) and D_2 = 8.5 kJ/mol (710 cm^{-1}), were derived from the slopes of T_1^{-1} in both high and low temperature sides of the maxima of T_1^{-1} and from maximum values of T_1^{-1} measured at 37.5 MHz. The pre-exponential factors were determined as that $W_{01} = W_{02} = 4.5\times10^{12}$ s^{-1}. The energy values associated with the proton dynamics are summarized in Fig. 2.

The temperature dependence of visible absorption spectra is believed to provide an information of a change of electronic state which is accompanied with the proton switching discussed above. The spectra of BSP at several temperatures are shown in fig. 3. At 4.2 K an absorption edge is observed rising sharply around 2.8 eV (22600 cm-1) which is assigned to a transition in the most stable tautomer, [OH,OH]. As the temperature increased above 150 K, the absorption band at 2.4 eV (19400 cm-1) remarkably grew up, which is related to increase of the population of metastable tautomers, [OH,NH], [NH,OH] and [NH,NH]. From the evolution of the spectra with temperature an energy difference between the tautomers was estimated to be 9 kJ/mol (800 cm^{-1})[1], which is larger than D_1 but smaller than D_1+D_2. This indicates that the temperature dependence of the absorption spectra is induced by overlapping two processes, D_1 and D_2, which are clearly distinguished by the NMR experiment.

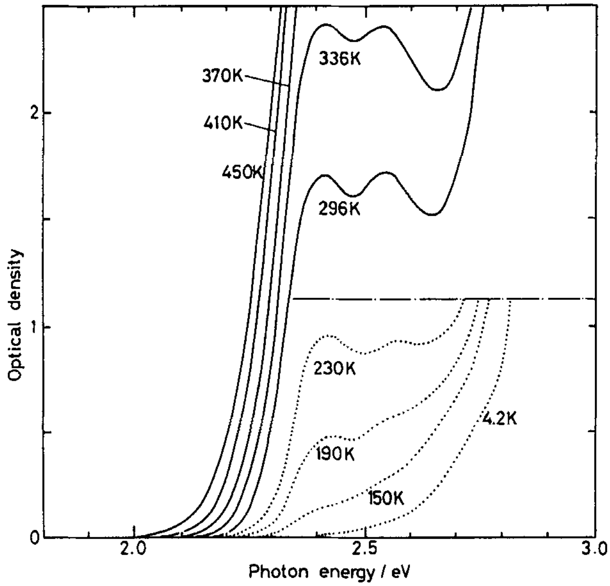

FIGURE 3 Temperature dependence of absorption spectra of single crystal of BSP.

The activation energies of two processes, Ea_1 and Ea_2, are remarkably different as shown in Fig. 2. In the first process shown in lower part of Fig. 2, the proton switching occurs from OH to NH form in a hydrogen bond, keeping another hydrogen bond to be "OH form". The value of Ea_1 is 10 kJ/mol. The second process shown in upper part of Fig. 2 is a proton switching under the "NH form" of the other hydrogen bond. The activation energy Ea_2 is 25 kJ/mol which is more than twice of Ea_1. This result suggests the presence of the interaction between two hydrogen bonds in a molecule through rearrangement of the configuration of π-electrons which is seen by absorption spectra. This type of proton-electron interaction may be an origin of proton-electron cooperation and can be controlled by chemical modifications.

One of examples of derivatives of BSP is DNP which has two 2-hydroxy-1-naphthylidene groups on the head and the tail of the molecule instead of two salicylidene groups of BSP. The scheme of proton dynamics of DNP is similar to Fig. 2 but includes tunneling effect. D_1, D_2, Ea_1 and Ea_2 of DNP are much smaller than those of BSP, which was confirmed by the measurement of T_1^{-1} of proton. Ea_2 is five times larger than Ea_1 for DNP. This result suggests that the proton moves much more easily by tunneling effect and the proton-electron coupling becomes relatively more dominant for the proton dynamics in DNP than in BSP. Systematic studies of this system using the effect of chemical modification including the construction of an intermolecular interaction on the proton dynamics will provide us with informations on approaching new phenomena of proton-electron cooperation.

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