Proton Migration in –N···H···O– Hydrogen-bonded Complex of (Chloranilic Acid)(1,2-Diazine)$_2$ Studied by Dielectric Response and Infrared Absorption Spectra

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A dielectric response by an intermolecular –N···H···O– proton transfer was observed around 120 K for (Chloranilic acid)(1,2-Diazine)$_2$ [CA(1,2-DA)$_2$]. This response, observed on the way of the migration from N–H···O at 300 K to O–H···N below 90 K, was demonstrated by infrared absorption spectra and the temperature dependence of lattice constants.

In biological systems, hydrogen bonds play an important role in constructing charge- and energy-transfer network, as well as in building up electrostatic interaction network.[1] In molecular crystals, the dynamics of hydrogen bonds also have attracted keen interests with respect to ferro and antiferro-electrics,[2] proton dipolar glass,[3] protonic solitons,[4] and elsewhere. The proton dynamics have been usually investigated in the symmetric O···H···O and N···H···N hydrogen bonds. However, it is of importance to explore new functions with dynamic hydrogen O···H···N bonds, where intermolecular proton dynamics between different molecules are coupled with π-electron bonds and degree of freedom in lattice.

Recently, Nihei et al. have proposed the intermolecular proton dynamics in O···H···N bonds for (CA)(DA)$_2$ [DA = 1,2-DA, 1,3-DA, and 1,4-DA] by ^{35}Cl NQR and ^{1}H NMR measurements.[5] As for (CA)(1,2-DA)$_2$, the ^{35}Cl NQR relaxation process suggests proton dynamic modes (1) and (2) as shown in Figure 1, but it has not been verified yet. In order to clarify the mode and mechanism of proton dynamics, dielectric constants, infrared absorption spectra, and lattice constants have been measured.

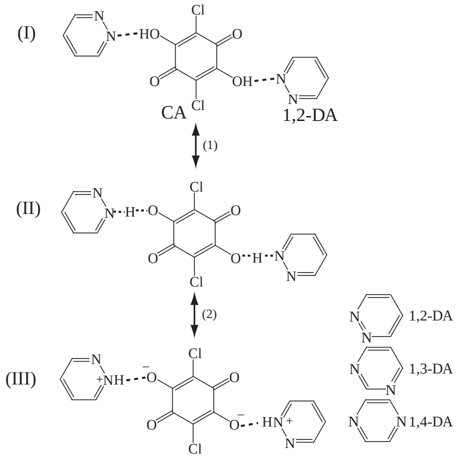

Figure 1. Proton dynamic modes in (Chloranilic acid)(1,2-Diazine)$_2$.

In this letter, we report the dielectric response of (CA)(1,2-DA)$_2$ around 120 K, and show that it is related to the proton migration from N–H···O at 300 K to O–H···N below 90 K, as observed by IR spectra.

Black plate crystals of (CA)(DA)$_2$ [DA = 1,2-DA, 1,3-DA, and 1,4-DA] were prepared by the direct or the diffusion method in methanol. All of them have a (CA)(DA)$_2$ unit, in which the short intermolecular hydrogen bonds (O···N = 2.582–2.615 Å)[6] exist. Owing to a decrease of pK_a from 2.3 of 1,2-DA, 1.3 of 1,3-DA, to 0.7 of 1,4-DA[6] with 0.58 of CA,[7] the hydrogen bond changes from the N–H···O to the O–H···N type. The CA and DA form segregated columns with stacking regularly along the shortest crystallographic *a* axis.[6]

Figure 2 depicts the temperature dependence of the dielectric constant ε for the most air-stable (CA)(1,2-DA)$_2$ along the hydrogen-bonded direction, namely the crystallographic *b*-axis. The measurement was carried out by the use of an impedance analyzer (Agilent Techologies 4294A) at 1 MHz from 300 to 2 K. The dielectric constant at 300 K is 9–13. It increases gradually to a broad maximum as the temperature lowers to around 120 K and then decreases as the temperature declines to 2 K. No structural transition was observed around 120 K by the temperature dependence of lattice constants, as shown in Figure 3. Since this material is an insulator, a small dielectric loss, $D < 0.003$, at 300 K is observed.

In order to clarify the proton-transfer mode around 120 K, the infrared absorption spectra (Nihon bunko, FT/IR620, MICRO-20) for a thin single crystal of (CA)(1,2-DA)$_2$ and KBr pellet of CA, (CA)(1,3-DA)$_2$, and (CA)(1,4-DA)$_2$ were measured. The absorption around 3200 cm^{-1} owing to the

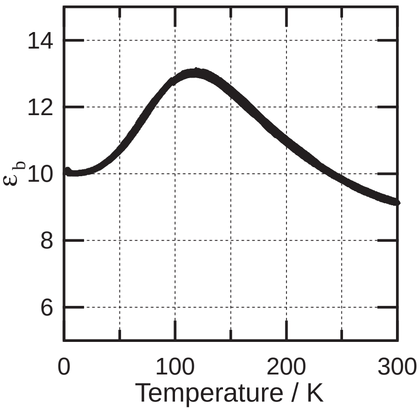

Figure 2. Temperature dependence of dielectric responses of (Chloranilic acid)(1,2-Diazine)$_2$ at 1 MHz.

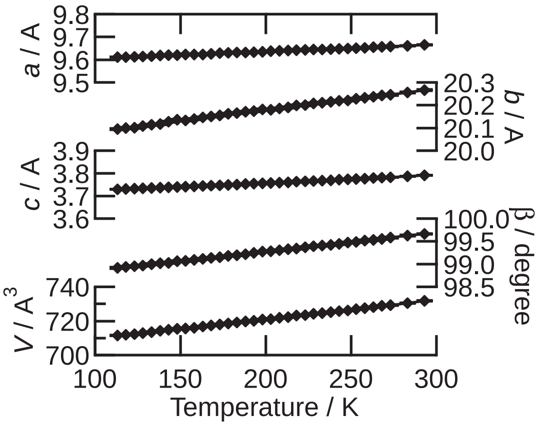

Figure 3. Temperature dependence of lattice constants for (Chloranilic acid)(1,2-Diazine)$_2$.

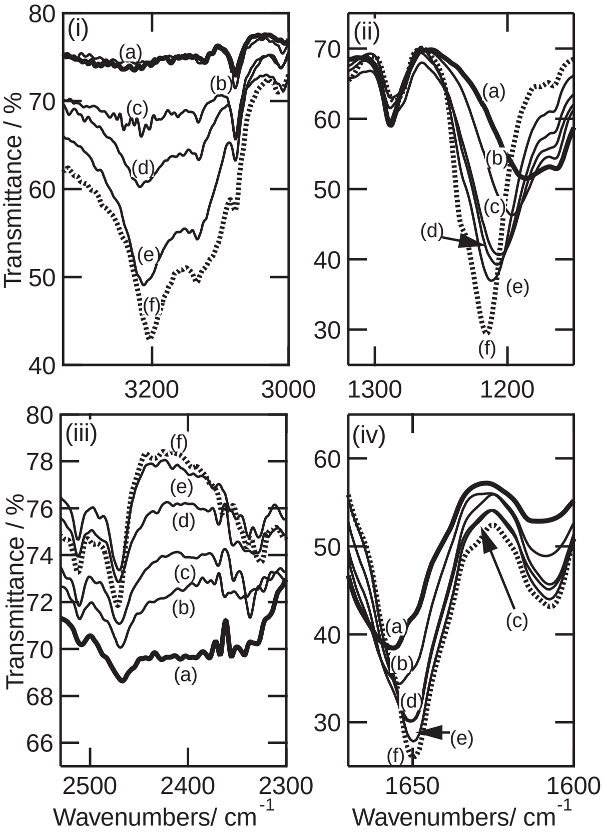

Figure 4. Infrared absorption spectra of (Chloranilic acid)(1,2-Diazine)$_2$ in (i) 3000–3330, (ii) 1150–1320, (iii) 2300–2530, (iv) 1600–1670 cm^{-1} at (a) 300 K, (b) 200 K, (c) 130 K, (d) 115 K, (e) 90 K, and (f) 30 K.

O–H stretching vibration is distinctly observed for CA;[8] it decreases in the order from CA, (CA)(1,4-DA)$_2$ to (CA)(1,3-DA)$_2$, and is absent for (CA)(1,2-DA)$_2$ with an increase of pK_a of DA at room temperature. The reason why the O–H stretching vibration varies is that the hydrogen bond changes from the O–H···N type to the N–H···O type, a change which is in good agreement with bond lengths.[6] With lowering temperatures, the absorption around 3200 cm^{-1} for (CA)(1,2-DA)$_2$ increases from 115 K, and is very strong below 90 K (Figure 4i). The deformation vibration of the O–H bond around 1200 cm^{-1} also increases with a small blue shift by temperatures being lowered from 300 to 30 K (Figure 4ii). On the other hand, the broad absorption band of the N–H bond around 2400 cm^{-1} is observed at 300 K and decrease gradually with lowering temperatures (Figure 4iii). The C=O stretching mode is observed around 1610 and 1660 cm^{-1} from 300 to 30 K (Figure 4vi). These results indicate a proton migration from the N atom side N–H···O at 300 K to O–H···N below 90 K for (CA)(1,2-DA)$_2$. The structure (II) in Figure 1 seems to be responsible for the broad maximum at 120 K in dielectric response, which is closely related to the proton migration.

In summary, the dielectric response was observed around 120 K for (CA)(1,2-DA)$_2$. The IR absorption spectra and temperature dependence of lattice constants demonstrate that this dielectric response appears on the way of the migration from N–H···O at 300 K to O–H···N below 90 K. The proton dynamics in the asymmetric hydrogen bond –N···H···O– is of great importance in developing a functional hydrogen-bonded system such as proton switching in charge-transfer salts.

This work was supported by a Grant-in-Aid for Scientific Research (Grant No. 17540315) by JSPS (Japan Society for Promotion of Science) and CREST (Core Research for Evolutional Science and Technology) of JST (Japan Science and Technology Corp.).

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Published on the web (Advance View) February 10, 2007; doi:10.1246/cl.2007.402