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Crystal Structures and Dielectric Properties of 2-Imidazoline Derivatives Having Intermolecular Hydrogen-bonded Networks

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A 2-imidazoline derivative and its monoprotonated iodide salt construct different types of intermolecular N–H···N hydrogen bonds in the crystalline state. The two crystals give completely different dielectric responses, and the difference is correlated to their different hydrogen-bonded networks.

Directional and relatively robust hydrogen bonds play an essential role in controlling crystal structures, physical properties, and chemical reactivities of molecular crystals.[1] It has been reported that hydrogen bonds in molecular crystals are also responsible for dielectric properties derived from intermolecular proton transfer.[2–4] Proton transfer in one-dimensional (1D) or two-dimensional (2D) molecular assemblies containing O–H···O, O–H···N, or N–H···N hydrogen bonds is induced by application of an external electric field, and its dynamic response is detected through the dielectric properties.[5–7] For example, in monosalts of diazabicyclo[2.2.2]octane (dabco), monoprotonated dabco ($\mathrm{dabcoH^+}$) molecules form straight 1D chains via N–H···N hydrogen bonds. Intermolecular proton transfer through the hydrogen bonds and consequent polarization reversal give rise to giant dielectric responses and ferroelectric properties.[7]

As a new candidate for hydrogen-bonding units capable of creating organic proton-transfer materials, we are exploring 2-imidazoline: a five-membered cyclic amidine containing proton-donating and proton-accepting nitrogen atoms, which has the ability of producing intermolecular N–H···N hydrogen bond. Unlike dabco, which is a simple saturated aliphatic diamine, various 2-imidazoline derivatives possessing functional substituents and π-conjugation backbones can be synthesized owing to the synthetic ease. A 2-imidazoline derivative that possesses a photochromic diarylethene unit exhibits a dielectric response derived from intermolecular proton transfer in the 1D N–H···N hydrogen-bonded imidazoline chains, and the photochromic reaction reversibly changes the dielectric properties.[8] This suggests the potential of 2-imidazoline to act as a building unit for novel organic proton-transfer dielectrics and ferroelectrics with plural functions and motivates us to explore related derivatives in order to examine the functionality of 2-imidazoline. Herein, we report on crystal structures and dielectric properties of a 2-imidazoline derivative, 1,4-bis(4,5-dihydro-1*H*-imidazol-2-yl)benzene (**1**), and its monoprotonated iodide **1HI** (Chart 1).

The compounds were synthesized according to a previously reported method,[9] and the details are described in Supporting Information (SI).[10] Terephthalaldehyde was reacted with ethylenediamine in THF/*t*-BuOH at room temperature, and the subsequent oxidation with molecular iodine under the presence of K_2CO_3 yielded the 2-imidazoline rings. Yellow precipitates in the reaction mixture were found to be the monoprotonated iodide **1HI**. Hydrogen iodide generated in the oxidation step reacted with the imidazoline ring.[9] The treatment of the yellow powders of **1HI** with triethylamine deprotonated the imidazoline ring to yield white powders of **1**. Both **1** and **1HI** were characterized by ^{1}H NMR, mass spectrometry, elemental analysis, and X-ray crystallography (see SI).[10]

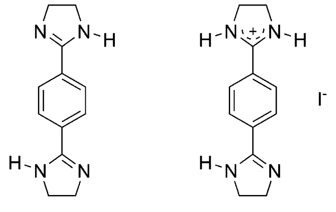

Chart 1. 2-Imidazoline derivatives **1** and **1HI**.

Colorless plate-like single crystals of **1** were prepared by vapor diffusion using methanol as a good solvent and ethyl acetate as a poor solvent. **1** has a triclinic crystal system with a space group of $P\bar{1}$ and $Z = 1$.[11] A half of a molecule of **1** is crystallographically independent, and an inversion center lies at the center of the benzene ring. Figure 1 shows the crystal structure of **1**. Each of the two imidazoline rings of **1** interacts with the rings of adjacent molecules via N–H···N hydrogen bonds to form a 1D ladder-like structure parallel to the *b* axis in which two imidazoline chains are bridged by phenylene spacers. The N–H hydrogen (H1 in Figure 1) observed in the difference Fourier map is located at one site between the nitrogen atoms. The orientation of the N–H hydrogens of the two imidazoline chains in the same ladder is antiparallel with each other. The intermolecular N···N distance in the hydrogen bond is 3.008 Å.

Vapor diffusion using methanol/ethyl acetate also gave yellow block-like single crystals of **1HI**. **1HI** has a monoclinic crystal system with $C2/c$ and $Z = 4$.[11] A crystallographically asymmetric unit contains halves of monoprotonated **1** ($\mathbf{1H^+}$) and iodide anion ($\mathbf{I^-}$). The crystal structure is composed of $\mathbf{1H^+}$ and $\mathbf{I^-}$ in a ratio of 1:1, as confirmed by elemental analysis. An inversion center lies at the center of the benzene ring. The $\mathbf{I^-}$ anion, with an occupancy factor of 0.5, is located at special sites of the $C2/c$ space group. Figure 2a shows the crystal structure of **1HI**. As in **1**, the imidazoline rings form N–H···N hydrogen bonds with adjacent molecules, but owing to the protonation of the imidazoline ring and the inclusion of the $\mathbf{I^-}$ anions, this compound gave a different hydrogen-bonding motif of 1D chains parallel to the *c* axis. The $\mathbf{I^-}$ anions are packed between

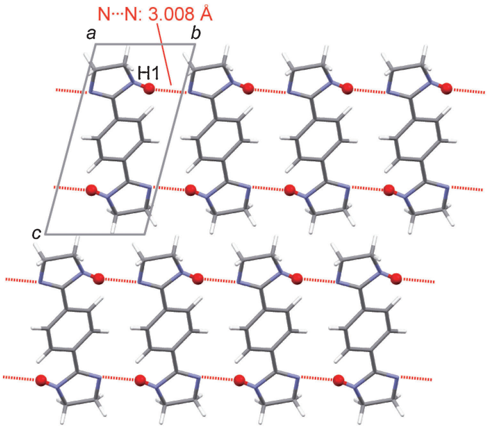

Figure 1. Crystal structure of **1** viewed along the *a* axis. Red dotted lines indicate intermolecular N–H···N hydrogen bonds. Red spheres are the N–H hydrogen atoms (H1) involved in the hydrogen bonds.

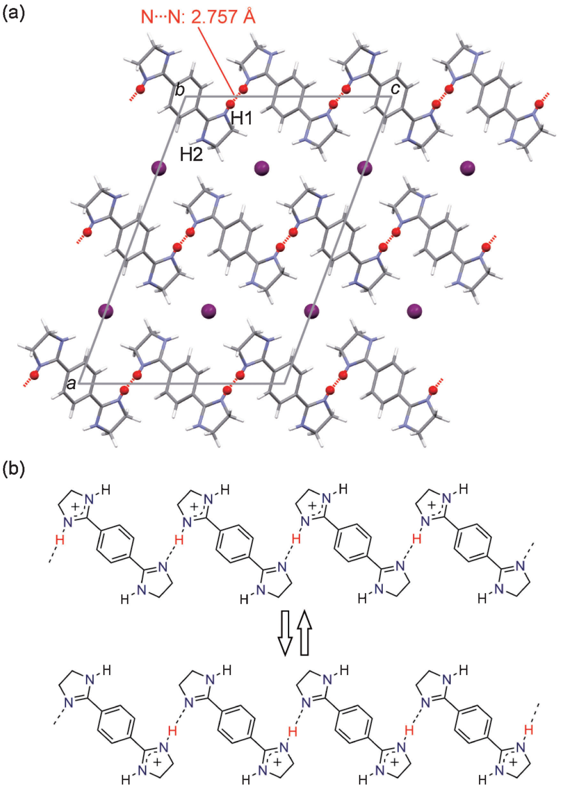

Figure 2. (a) Crystal structure of **1HI** viewed along the *b* axis. Red dotted lines indicate intermolecular N–H···N hydrogen bonds. Red and purple spheres are the N–H hydrogen atoms (H1) involved in the hydrogen bonds and the iodide anions, respectively. (b) Schematic illustration of the proton disordering observed in **1HI**.

the 1D chains. One nitrogen atom in each imidazoline ring is involved in a hydrogen bond with the neighboring molecule, while the other is not. The N–H hydrogen (H1 in Figure 2a) involved in the hydrogen bond is disordered into two sites between the nitrogen atoms with an occupancy ratio of 0.5:0.5. The N–H hydrogen (H2 in Figure 2a) not involved in the hydrogen bond has an occupancy factor of 1. This indicates that the crystal structure includes disordering of two equivalent structures of $\mathbf{1H^+}$ chains with opposite orientations of the N–H hydrogens and the positive charges in a ratio of 50:50, as shown in Figure 2b. Similar proton disordering is also observed in the 1D hydrogen-bonded chains of dabcoH$^+$ salts.[7d,7e] Weak correlations between the proton sites result in an almost random coexistence of short-range-ordered small domains with the opposite proton orientations and polarity rather than long-range ferroelectric or antiferroelectric orderings. Neutral molecules of **1** and diprotonated $\mathbf{H^+1H^+}$ dications can be formed as kink solutions at the domain boundaries within the chains. It is also noteworthy that the intermolecular N···N distance in the hydrogen bond is 2.757 Å, which is significantly shorter than the distance in **1** and comparative with that in dabcoH$^+$ salts that show giant dielectric responses.[7] This hydrogen bond strengthened by the protonation can be classified as a positive charge-assisted hydrogen bond.[2b]

The dielectric properties of these crystals were examined. Temperature and frequency dependence of the dielectric permittivity (real part, ε') was measured on single-crystal samples of **1** and **1HI** using an impedance analyzer. Gold-paste electrodes were attached to the single crystals along the direction of the 1D hydrogen-bonded networks (*b* axis for **1** and *c* axis for **1HI**). The properties were significantly different between the two compounds. The ε' value of **1** is almost constant (at around 10), and no dielectric anomaly is detected in the measuring frequency and temperature range (Figure S1 in SI).[10] In contrast, the ε' value of **1HI** shows a notable temperature and frequency dependence, as shown in Figure 3a. The value in the low-temperature region (150–260 K) is almost constant, at around 7. Above 260 K, a large dielectric response is observed in the low-frequency region, and ε' has a maximum at around 330 K ($\varepsilon' \approx 590$ at 0.1 Hz). The permittivity measured along the direction perpendicular to the 1D chain has smaller values, indicating that dielectric anisotropy derived from the 1D nature of the hydrogen-bonded assembly (Figure 3b).

The difference in the dielectric properties between the two compounds can be explained on the basis of the crystal structures, in particular the hydrogen-bond length and the symmetry. As shown in Figure 1, the intermolecular N···N distance in **1** is relatively long (3.008 Å), and there is no symmetry element between the nitrogen atoms involved in the hydrogen bonds (Figure S2a in SI).[10] An asymmetric potential curve of the proton coordinate between the nitrogen atoms has a large energy barrier and localizes the protons at one site. Therefore, the proton transfer does not take place even upon application of an electric field. On the other hand, the N···N distance in **1HI** is significantly short (2.757 Å, Figure 2a), and the $C2/c$ space group puts a twofold rotation axis parallel to the *b* axis at the midpoints between the nitrogen atoms involved in the hydrogen bonds (Figure S2b in SI).[10] This suggests that the stronger N–H···N hydrogen bond has a symmetric double-well potential energy curve for the proton coordinate, with a smaller energy barrier, which thus enables intermolecular proton transfer. In the low-temperature region below 260 K, the energy barrier cannot be overcome even upon application of an electric field, and the proton transfer is almost frozen. Above 260 K, the protons transfer to the corresponding adjacent nitrogen atoms

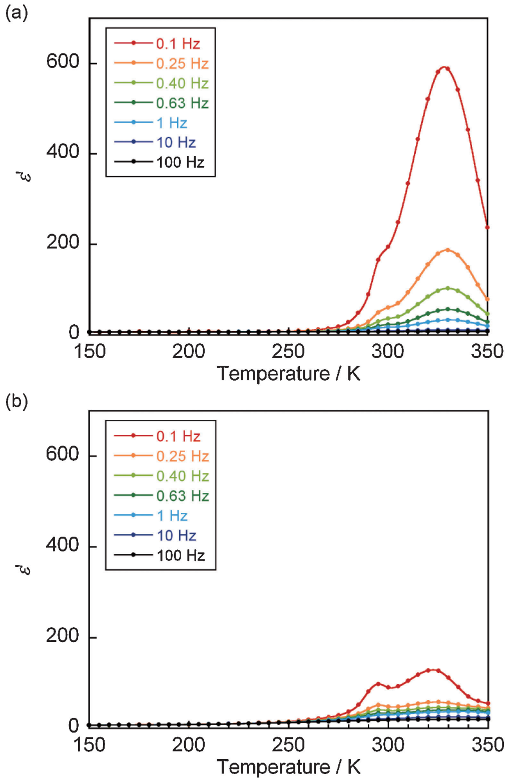

Figure 3. Temperature dependence of the dielectric permittivity (real part, ε') of single-crystal sample of **1HI** (a) measured along the *c* axis (parallel to the 1D chain) and (b) measured on the (100) face (perpendicular to the 1D chain).

with the assistance of thermal excitation, and the positions of the positive charges on the imidazolinium rings also transfer. The proton transfer leads to a migration of kink solitons and a fluctuation of the short-range-ordered small domains with opposite polarity. The consequent dynamic reversal of the polarity due to the proton transfer is detected in the dielectric response. The relatively large imaginary part of the permittivity (ε'') suggests the contribution of proton conduction due to the transport of charged solitons (Figure S3 in SI).[10] Differential scanning calorimetry gave no signs of a structural phase transition (Figure S4 in SI). Thus, the dielectric response of this compound can be associated with the weak and short-range order within the 1D chain rather than with a long-range one. The interchain interaction is also weak. This situation is similar to the dielectric response observed in 1D hydrogen-bonded chains of squaric acid derivatives[5b,5c] and dabcoH$^+$ salts.[7d,7e]

In conclusion, **1** and **1HI** exhibit completely different dielectric properties, arising from the differences in their crystal structures. The protonation of the imidazoline ring and the inclusion of the counter anions in **1HI** make the crystal structure suitable for intermolecular proton transfer. 2-Imidazoline derivatives, which possesses the hydrogen-bond and proton-transfer abilities and the structural and functional variety, has the potential to be a new building unit for the creation of molecule-based proton-transfer materials with plural functions.

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10 Supporting Information is available electronically on the CSJ-Journal Web site, http://www.csj.jp/journals/chem-lett/index.html.

11 Crystal data of **1**: $C_{12}H_{14}N_4$, $M_{\mathrm{r}_x} = 214.27$, $T = 93$ K, triclinic $P\bar{1}$, $a = 4.8835(7)$, $b = 5.1418(7)$, $c = 10.2239(15)$ Å, $\alpha = 104.433(2)$, $\beta = 93.893(2)$, $\gamma = 94.186(2)°$, $V = 246.97(6)$ Å^3, $Z = 1$, $D_{\mathrm{calcd}} = 1.441$ g cm^{-3}, 862 independent reflections ($R_{\mathrm{int}} = 0.0142$), R_1 ($I > 2\sigma(I)$) $= 0.0344$, wR_2 ($I > 2\sigma(I)$) $= 0.0926$, R_1 (all data) $= 0.0367$, wR_2 (all data) $= 0.0946$. Crystal data of **1HI**: $C_{12}H_{15}N_4I$, $M_{\mathrm{r}} = 342.18$, $T = 93$ K, monoclinic $C2/c$, $a = 19.994(2)$, $b = 4.7907(5)$, $c = 13.4753(14)$ Å, $\beta = 110.329(2)°$, $V = 1210.3(2)$ Å^3, $Z = 4$, $D_{\mathrm{calcd}} = 1.878$ g cm^{-3}, 1231 independent reflections ($R_{\mathrm{int}} = 0.0205$), R_1 ($I > 2\sigma(I)$) $= 0.0175$, wR_2 ($I > 2\sigma(I)$) $= 0.0473$, R_1 (all data) $= 0.0177$, wR_2 (all data) $= 0.0475$. Crystallographic data reported in this manuscript have been deposited with Cambridge Crystallographic Data Centre as supplementary publication Nos. CCDC-864131 (**1**) and -864132 (**1HI**). Copies of the data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge, CB2 1EZ, U.K.; fax: +44 1223 336033; or deposit@ccdc.cam.ac.uk).