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Communication

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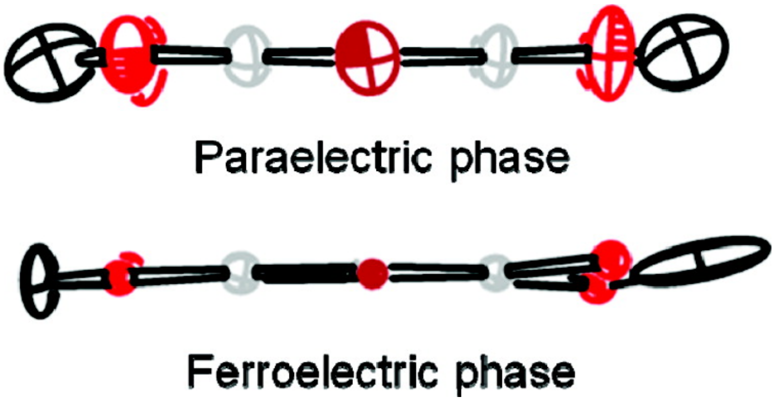

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COMMUNICATIONS

Structural Assignment of Polarization in Hydrogen-Bonded Supramolecular Ferroelectrics

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The studies on ferroelectrics have been motivated by interests not only in basic science but also in application to electronics.[1] Recently, Horiuchi et al. have developed new ferroelectric organic solids having supramolecular structure, the cocrystals of phenazine (Phz) with chloranilic acid (H_2ca) and bromanilic acid (H_2ba), in which nonpolar neutral molecules are connected by the intermolecular O−H···N hydrogen bonds (H-bonds).[2] The Phz-H_2ca crystal shows large dielectric constant around Curie temperature T_{c1} as high as 253 K (Figure 1a), and its deuterated analogue displays room-temperature ferroelectricity ($T_{c1} = 304$ K).[3] In the crystals of Phz-H_2xa (x = c, b), the observed polarization is much higher than the calculated value based on a molecular dipole model. Therefore, the H-bond and/or proton dynamics are anticipated to play an important role in the appearance of spontaneous polarization in this material. According to the previous crystal structural analysis of the Phz-H_2ca using a synchrotron X-ray, the molecules remain as the neutral species even in the ferroelectric phase.[2] However, the ordinary X-ray structural analysis on the electron-density distribution often suffers from poor accuracy to determine the hydrogen locations. In contrast, the neutron diffraction measures the nuclei distributions including anisotropic factors with sufficient accuracy. Furthermore, it provides also complementary information of the hydrogen since the electron cloud observed by the X-ray is more or less inclined toward the covalent bond from the nuclei position.[4] Therefore, the neutron diffraction studies are indispensable for investigation to elucidate the microscopic origin of ferroelectricity in such a H-bonded material. In this communication, we report the crystal structures for both the paraelectric and ferroelectric phases of the Phz-H_2xa obtained by the neutron diffraction and synchrotron X-ray diffraction to pursue the origin of polarization.

Single crystals ($1.0 \times 0.5 \times 7.0$ mm^3 for Phz-H_2ca and $6.5 \times 4.5 \times 1.1$ mm^3 for Phz-H_2ba) for neutron diffraction measurements were grown by the diffusion method in acetone solution. For X-ray diffraction measurements, the single crystal ($0.2 \times 0.2 \times 0.4$ mm^3) of Phz-H_2ca was grown in the methanol solution. Neutron diffraction experiments were performed at the T2-2 guide-hall of JRR-3 at the Japan Atomic Energy Agency, utilizing a four-circle diffractometer FONDER with 1.2453 Å neutron beam monochromatized by a Ge(311) monochromator.[5,6] The X-ray diffraction measurements were performed by using a monochromatized synchrotron X-ray (0.6875 Å) with an imaging plate system on BL-1A, PF in High Energy Accelerator Research Organization (KEK).[7]

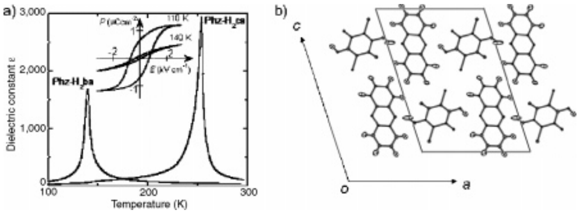

Figure 1. (a) Temperature dependence of the dielectric constant ϵ (f = 100 kHz, $E//b$) of the Phz-H_2xa. The inset shows the $P-E$ hysteresis loops of electric polarization of Phz-H_2ba (f = 1 Hz). (b) Crystal structure of Phz-H_2ba at ferroelectric (*FE* I) phase (110 K) obtained by the neutron diffraction, represented by thermal ellipsoids at the 50% probability level.

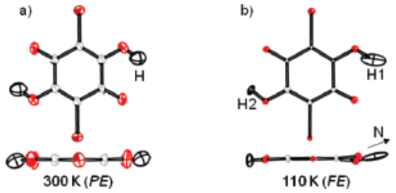

Figure 2. Molecular structure of H_2ba at (a) *PE* (T = 300 K) and (b) *FE* I (110 K) phases obtained by the neutron diffraction. Each structure is represented by thermal ellipsoids at the 50% probability level.

Figure 1b shows the crystal structure of ferroelectric (*FE* I) phase of Phz-H_2ba (T = 110 K) obtained by a neutron crystal structure analysis. For both the Phz-H_2xa cocrystals, lattice parameters, space group ($P2_1$), and atomic coordinates except for H atoms, agree with those obtained by the X-ray diffraction experiments. All the H-bonds appear to be O−H···N type even in the ferroelectric phase, confirming the neutral nature of the molecules, as supported also by the infrared spectral data collected at low temperatures (Figure S1). The paraelectric (*PE*) phase structure (Figure 2a) exhibits the symmetric (nonpolar) molecular structure of H_2ba without any hydrogen disorder. On the other hand, one can find the significantly elongated thermal ellipsoid of one H nuclei in the low-temperature *FE* I phase (Figure 2b), indicating an asymmetric structure with a broadly distributed H atom.[8] This broadly distributed H atom deviates from the π-skeleton plane of H_2ba and is displaced toward the nitrogen atom of the neighboring Phz molecule lying out of the H_2ba molecular plane. Very similar molecular structures are observed also for the Phz-H_2ca crystal.

Table 1 summarizes the H-bonding O−H, N···H, and N···O interatomic distances obtained by the neutron diffraction analysis for the *PE* and *FE* I phases of both the Phz-H_2xa crystals. As can be seen from the table, the phase transformation to the *FE* I yields two inequivalent H-bonding sites of the shortened and elongated N···O distances compared with the *PE* phase structure. The latter site shows a small change in the O−H and N···H distances upon

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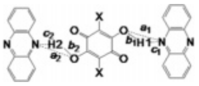
Table 1. Schematic Structure of the H-Bond Chain in Phz-H_2*x*a and Distances between the Atoms Related to the O−H···N H-Bond Obtained by the Neutron Diffraction Analysis



		X = Br		X = Cl	
		300 K	110 K	300 K	160 K
$d_{N\cdots O}$	a_1	2.740(6)	2.69(1)	2.714(7)	2.68(2)
	a_2		2.754(8)		2.75(2)
d_{O-H}	b_1	0.94(1)	1.17(3)	0.95(2)	1.32(4)
	b_2		0.97(1)		0.99(2)
$d_{N\cdots H}$	c_1	1.90(1)	1.62(4)	1.87(2)	1.41(5)
	c_2		1.91(1)		1.90(3)

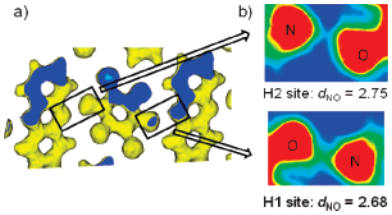


Figure 3. (a) Electron-density distribution map obtained by the maximum entropy method (MEM) analysis of the X-ray diffraction data of the Phz-H_2ca at 160 K. The equicontour level is at 0.7 eÅ^{-3}. (b) Contour map of the electron density near the H-bonding OH···N site extracted on the plane defined by two oxygen atoms and one nitrogen atom. The contour maps are drawn from 0 (blue) to 0.7 (red) eÅ^{-3}.

the transition. On the other site, the broadly distributed H nucleus approaches the center point in the strengthened O−H···N bond. This hydrogen displacement and simultaneous deformation of the H-bonds also imply incipient characters of the proton-transferred N−H$^+$···O$^-$ form and break the crystal inversion symmetry, generating the spontaneous polarization. The bond angle of CNC in Phz shows the different values, 119.5 (H1 site) and 117.9° (H2 site) in the Phz-H_2ca (160 K), reflecting the proton migration. The dipole moments, which are ordered along the H-bonded chain, are ferroelectrically coupled along the molecular stacking direction parallel to the 2_1-screw axis co-incident with the crystallographic *b*-axis, although the interaction along the *c*-axis appears to be antiferroelectric. The large dielectric constant ϵ observed along the *b*-axis[2] is consistent with this structural feature. The difference in Curie temperatures between Phz-H_2ca (253 K) and Phz-H_2ba (138 K) crystals may be ascribed to the different intrachain interaction between the H-bonded chains; their interchain distances are noticeably different, 9.060 Å for Phz-H_2ca and 9.222 Å for Phz-H_2ba at room temperature.[9] This is in accord with the effect of external static pressure that elevates the Curie temperature.[2]

In the X-ray analysis, it is generally difficult to specifically locate the electron density of the lightest element, H, using the conventional least-square refinement. In order to probe a small change, we calculated the electron-density distribution using the maximum entropy method (MEM).[10] Figure 3a shows the three-dimensional map of electron density obtained by the MEM analysis for the synchrotron radiation X-ray diffraction data of Phz-H_2ca at 160 K. From the electron-density contour plot of the OH···N site (Figure 3b), one can find two independent H-bonds. In the shorter N···O site (d_{NO} = 2.68 Å, lower panel of the Figure 3b), a more delocalized electron density can be observed than in the longer N···O site (d_{NO} = 2.75 Å, upper panel of the Figure 3b). Such delocalization and asymmetry of electron-density distribution in the two H-bonding sites correspond to the broadly distributed H nuclei which could be observed by the neutron diffraction analysis.

The above features seem to be akin to the situation reported for some cocrystals of acid and bases exhibiting a thermally induced displacement (migration) of hydrogen near the center of the strong H-bonds.[11] The phenomenon is emergent in the present case, where the proton affinity is comparable for the base and acid molecules. The dissociation constant between the neutral and monovalent species is actually very close to each other for the acids (pK_1 = 0.73, pK_2 = 3.08 for H_2ca, pK_1 = 0.80, pK_2 = 3.10 for H_2ba)[12] and the base Phz (pK_1 = 1.20, pK_2 = −4.3).[13] This is likely the origin of the spontaneous hydrogen deformation. The hydrogen disorder remaining in the phase *FE* I suggests some instability to additional structural transformation. Actually, Phz-H_2*x*a shows another phase transition below the transition temperature.[14]

The present diffraction study is the first example that unambiguously discloses the symmetry-breaking displacement of H atoms for emergence of ferroelectricity in the organic supramolecules. These structural changes are dissimilar to the collective proton ordering observed in the conventional H-bonded ferroelectrics like KH_2PO_4(KDP). Rather, the similar proton affinity of the acid and bases seemingly reduces the potential barrier for H to move toward the base, allowing the large displacing deformation. The resultant asymmetry of the H-bonds is the origin of the dipole moment. The structural study shows that the H-bond plays an essential role in producing the polarization in this system. Thus the development of H-bonded π-conjugated supramolecular systems is one of the most promising approaches to the organic ferroelectrics.

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Supporting Information Available: Neutron crystallography files (CIF) and the infrared spectral data of Phz-H_2ba. This material is available free of charge via the Internet at http://pubs.acs.org.

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