Crystal Structure and Origin of Polarization of Hydrogen-Bonded Organic Ferroelectrics Composed of pi-Condugated Supramolecules

R. Kumai(A), Sachio Horiuchi(A), H. Sagayama(B), T. Arima(B,C), M. Watanabe(B), Y. Noda(B), and Y. Tokura(A,C)
(A)CERC, AIST, (B)IMRAM, Tohoku Univ., (C)ERATO-SSS, JST

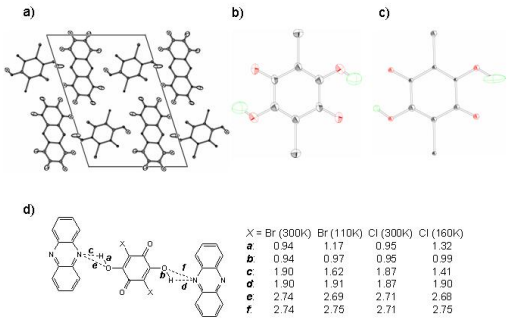
Ferroelectrics have been motivated not only by basic science but also by application because of those various utilizations for electronics. Recently we have developed new ferroelectrics by using a molecular solid with supramolecular structure, the cocrystal of phenazine (Phz, C12H8N2) with chloranilic acid (H2ca, C6H2O4Cl2) or bromanilic acid (H2ba, C6H2O4Cl2), in which nonpolar pi-conjugated molecules are connected by the intermolecular O-H...N hydrogen bonds. Here, we report the low-temperature crystal structure of Phz-H2ca and Phz-H2ba [1] obtained by the neutron diffraction in order to make clear for the origin of polarization.

Figure 1a shows the crystal structure of ferroelectric phase of Phz-H2ba at 110 K obtained by a neutron crystal structure analysis. Lattice parameters, space group (P21), and atomic coordinates except for hydrogen atoms, agree with those obtained by the X-ray diffraction experiments. The O-H bond in the hydrogen-bonded site is clearly observed, suggesting that both molecules (Phz and H2ca or H2ba) are neutral even in the ferroelectric phase, which is consistent with the infrared spectra. The molecular structure of H2ba at paraelectric phase (300 K) and ferroelectric phase (110K) are shown in Figs. 1b and 1c. One can find a highly elongated thermal ellipsoid of one hydrogen atom in the low-temperature structure, which implies disordering of the hydrogen atom position. A similar situation is observed in the ferroelectric phase of Phz-H2ca.

Figure 1d is summarized interatomic distances between O-H (a, b) and N...H (c, d) and N...O (e, f) related with the hydrogen bonding in the paraeletric and ferroelectric phases of the Phz-H2ca and Phz-H2ba crystals obtained by the present neutron study. As can be seen from the asymmetric OH bond, the two hydrogen-bonded sites are not equivalent in the ferroelectric phase. This asymmetry in the hydrogen-bond chain is the origin of the polarization in the Phz-H2xa (x=Cl, Br) system.

Appendix

Phz-H2ca 300K: C18H10Cl2N2O4, Z = 2, Monoclinic P21/n, a = 12.422(6) A, b = 3.849(6) A, c = 16.981(12) A, beta= 107.83(4) deg., V = 772.9(14) A3, R = 0.0531 for 725 independent reflections ($|Fo| > 4$ sigma). Phz-H2ca 160K: C18H10Cl2N2O4, Z = 2, Monoclinic P21, a = 12.423(4) A, b = 3.788(8) A, c = 16.914(6) A, beta = 107.89(3) deg., V = 757.5(17) A3, R = 0.0488 for 919 independent reflections ($|Fo| > 4$ sigma). Phz-H2ba 300K: C18H10Br2N2O4, Z = 2, Monoclinic P21/n, a = 12.386(5) A, b = 3.908(5) A, c = 17.433(7) A, beta = 107.86(3) deg., V = 803.1(12) A3, R = 0.0460 for 685 independent reflections ($|Fo| > 4$ sigma). Phz-H2ba 110K: C18H10Br2N2O4, Z = 2, Monoclinic P21, a = 12.371(4) A, b = 3.845(3) A, c = 17.342(5) A, beta = 107.74(2), V = 785.8(7) A3, R = 0.0387 for 1314 independent reflections ($|Fo| > 4$ sigma).



X = Br (300K)	Br (110K)	Cl (300K)	Cl (160K)
a: 0.94	1.17	0.95	1.32
b: 0.94	0.97	0.95	0.99
c: 1.90	1.62	1.87	1.41
d: 1.90	1.91	1.87	1.90
e: 2.74	2.69	2.71	2.68
f: 2.74	2.75	2.71	2.75

Fig. 1. a-c) Crystal structure of Phen-H2ba at ferroelectric (a,c) and paraelectric (b) phase. d) Schematic structure of hydrogen-bond chain in Phz-H2xa and related bond lengths.