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## Calorimetric and dielectric study of organic ferroelectrics, phenazine-chloranilic acid, and its bromo analog

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The heat capacities of single crystals of organic ferroelectric complexes phenazine-chloranilic acid (Phz-H<sub>2</sub>ca) and phenazine-bromanilic acid (Phz-H<sub>2</sub>ba) were measured. At temperatures below those of the reported ferroelectric phase transitions, heat capacity anomalies due to successive phase transitions were found in both complexes. Excess entropies involved in the low-temperature successive phase transitions are much larger than those due to the ferroelectric phase transitions. The temperature dependence of the complex dielectric constants showed the existence of multiple dielectric relaxation modes in both complexes and their deuterated analogs (Phz-D<sub>2</sub>ca and Phz-D<sub>2</sub>ba). We discuss the possibility of concerted hopping of neighboring protons within a hydrogen-bonded chain while taking into account the one-dimensional nature of the chain. © 2009 American Institute of Physics. [DOI: 10.1063/1.3058589]

### I. INTRODUCTION

The first report of ferroelectricity in phenazine-chloranilic acid (Phz-H<sub>2</sub>ca) and related complexes by Horiuchi *et al.*<sup>1</sup> renewed the interest in hydrogen-bonded (H-bonded) organic complexes. The ferroelectricity appears in the complexes consisting of two organic components, phenazine (C<sub>12</sub>H<sub>8</sub>N<sub>2</sub>, abbreviated to Phz) and chloranilic or bromanilic acid [C<sub>6</sub>H<sub>2</sub>O<sub>4</sub>Cl<sub>2</sub> (H<sub>2</sub>ca) or C<sub>6</sub>H<sub>2</sub>O<sub>4</sub>Br<sub>2</sub> (H<sub>2</sub>ba)], the molecules of which are centrosymmetric, i.e., nonpolar. The crystals of the two complexes are isomorphous with the space group  $P2_1/n$  at room temperature. With the appearance of ferroelectricity, the crystal loses the centrosymmetry to become  $P2_1$  below the ferroelectric phase transition at  $T_c=248$  K in the case of Phz-H<sub>2</sub>ca.

The Phz-H<sub>2</sub>ca crystal consists of segregated columns of planar molecules along the  $b$  axis as shown in Fig. 1. Electronic interaction within each column is expected owing to the close stacking of  $\pi$  electrons. Between the neighboring columns, strong H bonds are formed between a nitrogen atom of Phz and a hydroxy group of H<sub>2</sub>ca (or H<sub>2</sub>ba) along the diagonals of the  $ab$  plane ( $a-b$  at  $z=0$  and  $a+b$  at  $z=\frac{1}{2}$  in Fig. 1). This results in the formation of a one-dimensional chain of H bonds, the potential energy curve of which is the asymmetric double-well type. Crystallographically, the number of hydrogen atoms involved in the H bonds is one in the room-temperature phase and two in the low-temperature ferroelectric phase.

The electric dipole moments calculated quantum chemically for isolated Phz and H<sub>2</sub>ca molecules, the structures of which are obtained from the x-ray result at 160 K, were much smaller than those estimated from the saturated polar-

ization of the crystal.<sup>1</sup> On the other hand, the calculation on the crystal taking the periodicity into account yielded a result more consistent with the observation.<sup>2</sup> This is regarded as evidence of the important roles of the H-bond chain and  $\pi$  stacking.

The effects of deuteration were also reported by Horiuchi *et al.*<sup>3</sup> According to them, the deuteration of the hydrogen atoms of hydroxy groups in acid molecules markedly enhances the ferroelectric transition temperature, as shown in Fig. 2. Although the large deuteration effect in H-bonded ferroelectrics is well known,<sup>4-7</sup> the pressure also enhances the transition temperature in the present complexes<sup>3</sup> in contrast to the well-known tendency.

We previously reported the preliminary results of adiabatic calorimetry and dielectric measurements on a powder sample of Phz-H<sub>2</sub>ca.<sup>8</sup> The heat capacity anomalies due to successive phase transitions ( $T_1=146$  K and  $T_2=136$  K), unknown at that time, were reported as shown in Fig. 2. The existence of successive phase transitions at low temperatures was confirmed later by the nuclear quadrupole resonance

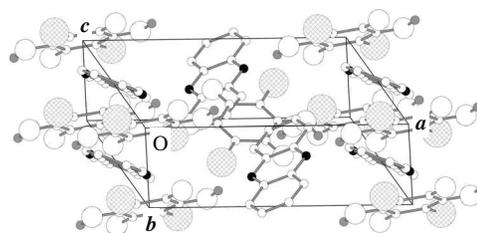


FIG. 1. Crystal structure of Phz-H<sub>2</sub>ca in the paraelectric phase at room temperature (Ref. 1). Small open circle, carbon atom; small filled circle, nitrogen atom; large open circle, oxygen atom; large shaded circle, chlorine atom; small gray circle, hydrogen atom involved in the H bond between Phz and H<sub>2</sub>ca molecules. Other hydrogen atoms not involved in the H bond are omitted for clarity.

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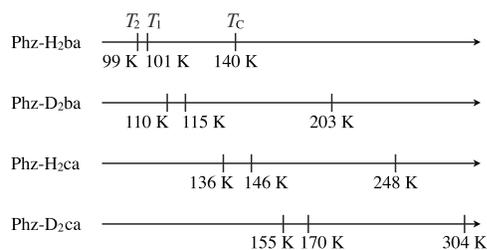


FIG. 2. Phase sequence of Phz-H<sub>2</sub>ca, Phz-H<sub>2</sub>ba, and their deuterated analogs determined by present calorimetric and dielectric measurements.  $T_c$  denotes the ferroelectric transition temperature.  $T_1$  and  $T_2$  are the transition temperatures of low-temperature successive phase transitions.

(NQR) of a <sup>35</sup>Cl nucleus.<sup>9</sup> The existence of successive phase transitions at low temperatures clearly demonstrates that the known ferroelectric phase is not the ground state of the crystal. The crystal below 136 K was reported to have essentially the same structure as that at 160 K,<sup>10,11</sup> which is between  $T_c$  and  $T_1$ , corresponding to the ferroelectric state. Asaji *et al.*<sup>9</sup> reported that the molecules are (partially) charged on average in the lowest-temperature phase below  $T_2$  because of the charge transfer between Phz and H<sub>2</sub>ca on the basis of their NQR results. It is noteworthy that there is a preliminary report denying the existence of the charge transfer by another group.<sup>12</sup> Regarding the dielectric relaxation of Phz-H<sub>2</sub>ca, the existence of multiple relaxation modes was revealed.<sup>8</sup>

It is natural to consider whether these characteristics found in Phz-H<sub>2</sub>ca are also the case in analogous ferroelectrics. We started the study along this line of enquiry. Here we report the results of our study utilizing precise calorimetry and dielectric measurements. Because the measurement on single crystals of Phz-H<sub>2</sub>ba yielded much sharper anomalies than those found previously for a powder sample of Phz-H<sub>2</sub>ca,<sup>8</sup> we decided to perform experiments on Phz-H<sub>2</sub>ca using single crystals. The results of these experiments are also reported in the present paper.

## II. EXPERIMENTAL

### A. Sample preparation

Single crystals of Phz-H<sub>2</sub>ca were grown by the so-called diffusion method using acetone ( $T_{\text{fus}}=178$  K) as a solvent in order to shift a possible thermal anomaly due to its fusion away from the expected ferroelectric transition temperature. Phz (Aldrich, 98%) and H<sub>2</sub>ca (TCI, >98%) were purified by fractional sublimation in vacuum prior to dissolving them in dehydrated acetone. The growth took about 1 month and yielded single crystals with typical dimensions of  $10 \times 1 \times 1$  mm<sup>3</sup>.

Single crystals of Phz-H<sub>2</sub>ba were prepared similarly using acetonitrile ( $T_{\text{fus}}=229$  K) as a solvent because of the different ferroelectric transition temperature. H<sub>2</sub>ba (>98%) was purchased from TCI. The typical dimensions of the crystals were  $20 \times 2 \times 1$  mm<sup>3</sup>.

For the deuterated complexes, the deuteration of the corresponding acid was performed by refluxing a CH<sub>3</sub>OD (Aldrich, >99%) solution of each acid for 20 h. A cycle of refluxing and drying was repeated three times. The resultant acids were used as the starting compounds in crystal growth.

The degree of deuteration was monitored by infrared absorption by the O–D stretching mode after crystal growth. The estimated degree of deuteration was 80% for both Phz-D<sub>2</sub>ca and Phz-D<sub>2</sub>ba.

### B. Adiabatic calorimetry

A number of single crystals were loaded into gold-plated copper calorimeter vessels (A and B), which were evacuated for about 1 h and sealed after introducing a small amount of helium gas ( $10^5$  Pa at room temperature) for promoting thermal equilibration within the vessel. The mass of the loaded samples was 1.502 87 g for Phz-H<sub>2</sub>ca using vessel A and 1.575 82 g for Phz-H<sub>2</sub>ba using vessel B after buoyancy correction.

The working thermometers mounted on the calorimeter vessels were platinum resistance thermometers (Minco, S1055 for vessel A and S1059 for B). Their temperature scales are based on ITS-90. The details of the adiabatic calorimeter used and its operation are described elsewhere.<sup>13</sup>

The thermal equilibrium inside the vessel was attained within the expected time (1–10 min depending on temperature) after the input of energy. The contributions of the sample to the total heat capacity including that of the vessel were 17% at 100 K, 19% at 200 K, and 26% at 300 K in the case of Phz-H<sub>2</sub>ca. The contribution was slightly smaller in the case of Phz-H<sub>2</sub>ba because of the larger mass of vessel B.

### C. Relaxation calorimetry

Because the measurement by adiabatic calorimetry was previously made on the powder sample,<sup>8</sup> the heat capacity below liquid N<sub>2</sub> temperature was measured using a commercially available relaxation calorimeter (QuantumDesign physical properties measurement system) for Phz-H<sub>2</sub>ca to shorten the experimental time. A small piece ( $3.5 \times 1.5 \times 1.0$  mm<sup>3</sup>, 6.567 mg) was cut from a single crystal. The piece was adhered to the sample stage using Apiezon N grease. The sample mass was precisely corrected by multiplying by a factor 0.9945 so that the heat capacities at 80 K match between adiabatic and relaxation calorimetries.

### D. Dielectric measurement

Complex dielectric constants were measured between 100 Hz and 1 MHz using a laboratory-made cryostat with a compressed pellet (10 mm in diameter and approximately 0.2 mm in thickness) made of crushed single crystals of each prepared complex. Although the reliability of the results diminishes at both ends of the measuring frequency, anomalies due to dielectric relaxation can still be identified. The rate of temperature increase was  $0.1$  K min<sup>-1</sup>.

## III. RESULTS AND DISCUSSION

### A. Heat capacity

The measured heat capacities of Phz-H<sub>2</sub>ca are shown in Fig. 3 together with those of Phz-H<sub>2</sub>ba,<sup>14</sup> which will be discussed later. The measurements from 80 K showed an anomaly at approximately 180 K due to the fusion of acetone remaining in the sample. The magnitude of the anomaly in-

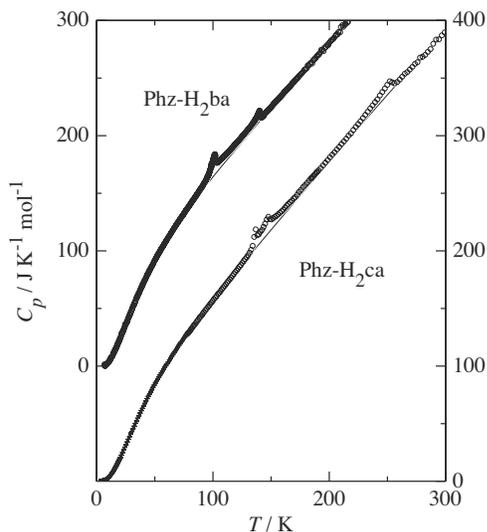


FIG. 3. Measured heat capacities of Phz-H<sub>2</sub>ca (right axis) and Phz-H<sub>2</sub>ba (left axis). Results for Phz-H<sub>2</sub>ca below approximately 80 K obtained from a commercially available relaxation calorimeter are shown by plus signs. Solid lines are baselines to separate excess heat capacities due to phase transitions. For details, see the text.

indicated that the amount of the acetone is 0.22 mass % of the loaded sample. The data around 180 K in Fig. 3 are obtained by starting the measurement from 175 K, the temperature to which acetone could be supercooled without crystallization.

It is emphasized that all anomalies are much sharper than those in the previous result<sup>8</sup> probably due to the improved sample quality realized by the use of single crystals. Figure 3 clearly shows the presence of three heat capacity anomalies at approximately 250, 147, and 136 K, in qualitative agreement with the previous result.<sup>8</sup> Close inspection revealed the absence of any anomaly below 80 K, also in agreement with the previous result obtained by adiabatic calorimetry.<sup>8</sup>

Similarly to that in the previous study,<sup>8</sup> supercooling was observed for the lowest anomaly at 136 K as shown in Fig. 4. The data plotted by crosses clearly show the supercooling. It is very interesting that the supercooled part increases with lowering temperature. As noted in the previous paper,<sup>8</sup> the overall shape of the heat capacity anomaly is similar to that of the well-known series of ferroelectrics  $A_2BX_4$ , which exhibit a normal-incommensurate-commensurate phase sequence upon cooling.<sup>15</sup> Also, the missed <sup>35</sup>Cl-NQR reso-

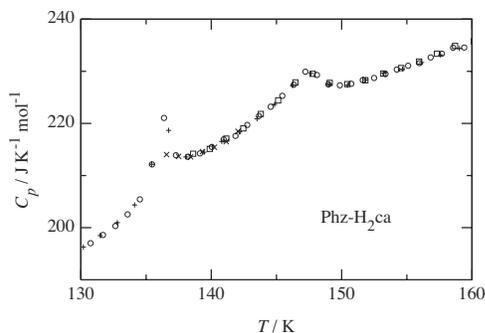


FIG. 4. Measured heat capacities of Phz-H<sub>2</sub>ca around the low-temperature successive phase transitions. Data obtained in separate runs are plotted by different symbols.

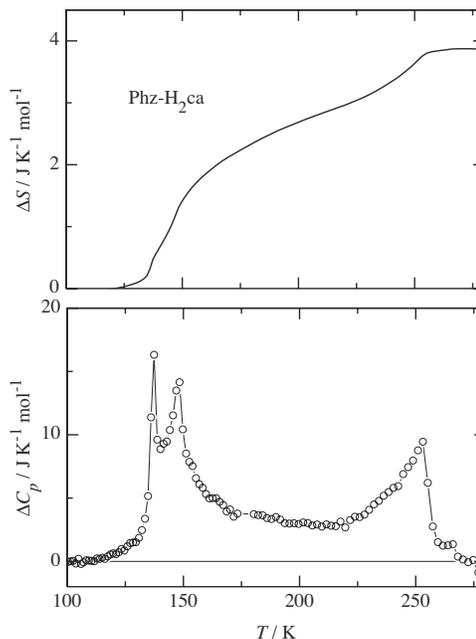


FIG. 5. Excess heat capacities (lower panel) and resultant excess entropy (upper panel) due to phase transitions of Phz-H<sub>2</sub>ca.

nance lines and shortened longitudinal relaxation time in <sup>1</sup>H-NMR between  $T_1$  and  $T_2$  reported by Asaji *et al.*<sup>9</sup> are naturally interpreted by assuming the incommensurate nature of the phase in this temperature range. If these successive transitions correspond to the normal-incommensurate-commensurate phase sequence widely observed in ferroelectrics,<sup>16</sup> the lowest transition should be the so-called lock-in transition. Most theories on the incommensurate transition predict a first-order lock-in transition.<sup>16</sup> Furthermore, some of them predict an increase in heat capacity due to the formation of “discommensuration” upon cooling.<sup>17,18</sup>

The separation of excess heat capacities from the measured ones is desirable for observing details of heat capacity anomalies due to the three phase transitions. The normal heat capacity was estimated by a least-squares fitting to the measured heat capacities at 2.3–110 and 260–300 K considering the Debye and Einstein models for “lattice” vibrations and the  $C_p - C_v$  correction. The available assignments of intramolecular vibrations<sup>19,20</sup> were taken into account. The resultant normal heat capacity is drawn by a solid line in Fig. 3. By subtracting this, excess heat capacities are obtained as exemplified in Fig. 5, where those of a single measurement run are plotted.

As clearly shown in Fig. 5, the contributions of the low-temperature successive phase transitions are much larger than that of the ferroelectric phase transition. Indeed, they amount to three quarters of the excess entropy, which was evaluated by numerical integration of the excess heat capacities. In turn, the contribution of the ferroelectric phase transition is small compared with  $R \ln 2 \approx 5.8 \text{ J K}^{-1} \text{ mol}^{-1}$ , a typical magnitude for an order-disorder transition. This is, at first glance, consistent with the proposed displacive nature of the ferroelectric phase transition.<sup>1</sup> On the other hand, the combined entropy amounts to approximately  $4 \text{ J K}^{-1} \text{ mol}^{-1}$  and is comparable to  $R \ln 2$ . Note that the expected entropy

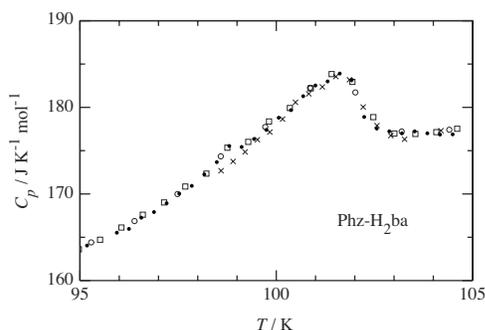


FIG. 6. Measured heat capacities of Phz-H<sub>2</sub>ba around the low-temperature successive phase transitions. Data obtained in separate runs are plotted by different symbols.

of transition is  $2R \ln 2$  for a simple order-disorder mechanism because there are two protons in the formula unit of the complex.

The measured heat capacities of Phz-H<sub>2</sub>ba are shown in Fig. 3. Two heat capacity anomalies can be identified in contrast to the three for Phz-H<sub>2</sub>ca. The location of the high-temperature anomaly at 140 K corresponds well to the reported ferroelectric phase transition temperature. The presence of the low-temperature anomaly again indicates that the known ferroelectric phase is not the ground state of Phz-H<sub>2</sub>ba.

Although the low-temperature anomaly appears to have a single peak in Fig. 3, this anomaly has a shoulder on the low-temperature side at 99 K as shown in Fig. 6. This shoulder indicates supercooling, suggesting that this shoulder is due to a first-order phase transition with small latent heat. Therefore, the phase sequence of Phz-H<sub>2</sub>ba is essentially the same as that of Phz-H<sub>2</sub>ca. The shape of the temperature dependence of excess heat capacity also shares characteristics with that of Phz-H<sub>2</sub>ca. There exists, however, a difference in transition temperatures. If all three phase transitions are seen as successive phase transitions driven by the same mechanism, the temperature ratio is expected to be of significance. The relative widths,  $(T_1 - T_2)/(T_c - T_2)$ , are about 0.1 in Phz-H<sub>2</sub>ca and 0.05 in Phz-H<sub>2</sub>ba.

The normal heat capacity was similarly estimated for Phz-H<sub>2</sub>ba. Since the complete assignment of intramolecular vibrations is unavailable for H<sub>2</sub>ba, a quantum chemical calculation was performed at the DFT/B3LYP/6-31G\* level.<sup>21</sup> The resultant excess heat capacities are shown in Fig. 7. Except for the smallness of the peak representing the lowest-temperature phase transition, the general trend in the temperature dependence of the excess heat capacity is very similar to that of Phz-H<sub>2</sub>ca. Total excess entropy is comparable to that of Phz-H<sub>2</sub>ca, although it is slightly smaller. This suggests that the mechanism that brings about the phase transition sequence is essentially the same in both complexes.

## B. Dielectric constants

Complex dielectric constants were measured using pellets made of crushed single crystals of each prepared complex. Although the apparent magnitude was of order 10 in all cases as shown in Fig. 8, in contrast to  $10^3$  reported for single crystals,<sup>1</sup> the resultant temperature dependence is

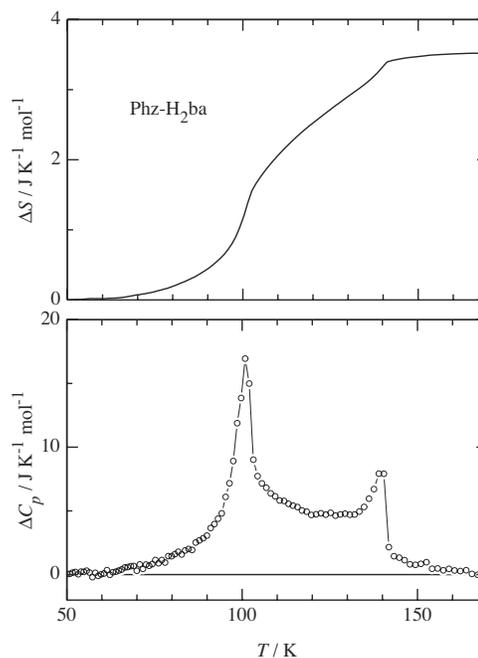


FIG. 7. Excess heat capacities (lower panel) and resultant excess entropy (upper panel) due to phase transitions of Phz-H<sub>2</sub>ba.

similar. The locations of the phase transitions can be identified for Phz-H<sub>2</sub>ca and Phz-H<sub>2</sub>ba by referring to the results of calorimetry. Similar anomalies can also easily be recognized in the results for deuterated complexes. The phase sequences thus established for all complexes are summarized in Fig. 2.

The present result of dielectric measurements on Phz-H<sub>2</sub>ca is essentially the same as that preliminarily reported by the present authors including the frequency dependence.<sup>8</sup> The results for its deuterated analog were similar with slight shifts of the peaks and shoulders in the imaginary part. Namely, at least the same number, 4 in reality, of

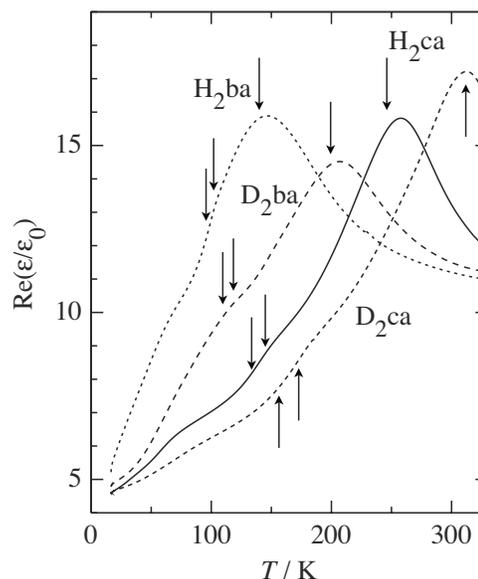


FIG. 8. Real parts of dielectric constants of Phz-H<sub>2</sub>ca (solid curve), Phz-H<sub>2</sub>ba (dotted curve), and their deuterated analogs (dashed and long-dashed curves) measured at 2 kHz. Arrows indicate assumed locations of phase transitions.

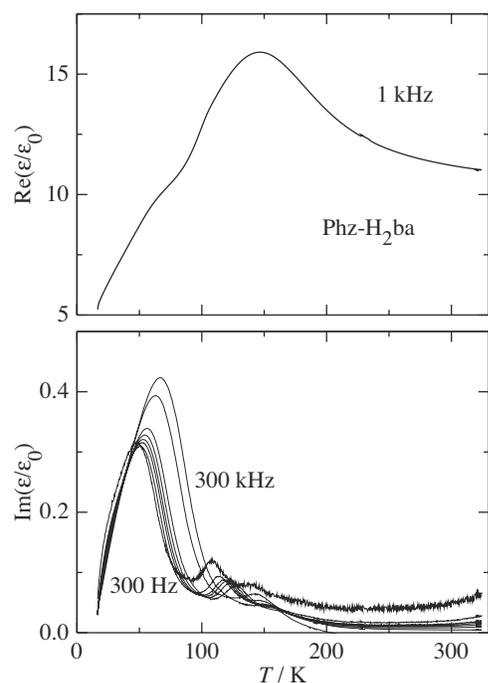


FIG. 9. Real (upper panel) and imaginary (lower panel) parts of dielectric constants of Phz-H<sub>2</sub>ba measured at various frequencies (300 Hz–300 kHz).

relaxation modes can be identified in addition to that located around the ferroelectric phase transition. The highest-temperature relaxation mode appears to be due to the critical relaxation.

The complex dielectric constants of Phz-H<sub>2</sub>ba are shown in Fig. 9. Multiple maxima can be recognized in the imaginary part, similarly in Phz-H<sub>2</sub>ca.<sup>8</sup> The results for the deuterated analog, i.e., Phz-D<sub>2</sub>ca, are similar with slight shifts of the peaks and shoulders in the imaginary part. There are multiple relaxation modes.

The distributions of the relaxation strength of the deuterated complexes are similar to those of the corresponding mother complexes (Phz-H<sub>2</sub>ca and Phz-H<sub>2</sub>ba). The distributions are, however, different between Phz-H<sub>2</sub>ca and Phz-H<sub>2</sub>ba. For example, the numbers of apparent peaks are 5 for Phz-H<sub>2</sub>ca and 3 for Phz-H<sub>2</sub>ba (including critical relaxation near  $T_c$ ), although slight windings possibly attributable to a shoulder due to another relaxation mode can be recognized, for example, around 25 K at 300 Hz for the latter. Also, while there are two relaxation peaks with comparative magnitude in Phz-H<sub>2</sub>ca (around 60 and 200 K at 1 kHz),<sup>8</sup> the peak around 50 K at 300 Hz in Fig. 9 is higher by a factor of 2–3 in Phz-H<sub>2</sub>ba.

The locations of the relaxation peaks were deduced by deconvoluting the temperature dependence of the imaginary part assuming a Lorentzian shape. The temperatures of relaxation peaks depend on the measuring frequency in accord with the so-called Arrhenius behavior shown in Fig. 10 for Phz-H<sub>2</sub>ca. From the slopes in the Arrhenius plot, the activation energy and attempt frequency at the high-temperature limit are redetermined because the measurements are newly performed on the sample with improved quality. The resultant parameters are, although slightly different, consistent

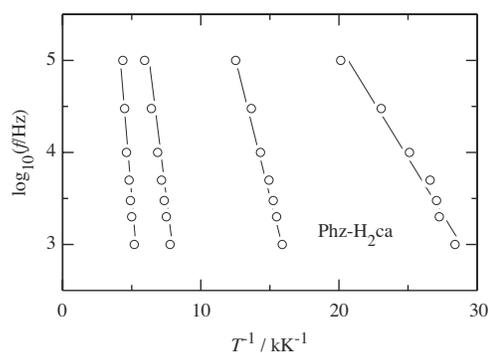


FIG. 10. Arrhenius plots of dielectric relaxation frequencies of Phz-H<sub>2</sub>ca.

with the previous result.<sup>8</sup> These quantities are similarly determined for all complexes and tabulated in Table I.

From the comparison of activation energies, it is considered that the two relaxation modes of Phz-H<sub>2</sub>ba correspond to the second and third modes of Phz-H<sub>2</sub>ca. A weak shoulder at the lowest temperature (approximately 25 K) appears to arise from the mode corresponding to the lowest mode of Phz-H<sub>2</sub>ca.

Asaji *et al.*<sup>22</sup> discovered the motional mode with an activation energy of 68 meV through their <sup>35</sup>Cl-NQR experiments (approximately 37 MHz resonance frequency) for Phz-H<sub>2</sub>ca and assigned it to the hopping motion of a proton within the H bond. Since the motional mode they discovered certainly contributes to dielectric relaxation and the mode detected at the lowest temperature has a similar activation energy, it seems reasonable to attribute this mode to the corresponding motional mode. Indeed, the extrapolation of the Arrhenius plot is consistent with this suggestion.

The upper limit of the attempt frequency is roughly estimated to be  $1 \times 10^{14}$  Hz on the basis of the frequency of the O–H stretching vibration in the case of H compounds. Table I shows that the attempt frequencies at infinite temperature are compatible with this limit. This means that the attempts are rarely successful. It is noteworthy that slow dynamics is expected in the magnetic relaxation in one-dimensional magnets.<sup>23–25</sup>

### C. H-bond chain and concerted hopping

The H-bond chain formed in the crystal can be schematically represented by an array of asymmetric double wells as

TABLE I. Summary of the dielectric relaxation modes in Phz-H<sub>2</sub>ca, Phz-H<sub>2</sub>ba, and their deuterated analogs.

	Phz-H <sub>2</sub> xa			Phz-D <sub>2</sub> xa		
	$E_a$ (meV)	$f_\infty$ (THz)	$n^a$	$E_a$ (meV)	$f_\infty$ (THz)	$n^a$
H <sub>2</sub> ca	49	0.011	1	67	0.0025	1
	110	3.5	2	100	0.033	2
	220	0.27	4	290	190	6
	480	0.022	8	370	0.040	8
H <sub>2</sub> ba	96	15	2	100	0.062	2
	220	3.4	4	290	49	6

<sup>a</sup>Number of involved hydrogens (deuterous), estimated from activation energy  $E_a$ .

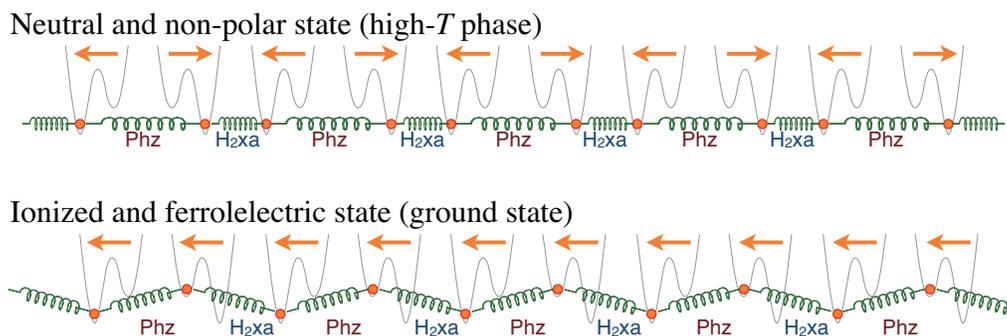


FIG. 11. (Color) Discrete Frenkel–Kontorowa model of Phz-H<sub>2</sub>xa (Phz-H<sub>2</sub>ca and analogs). Arrows indicate local polarization determined by the location of a proton (deuteron).

shown in Fig. 11. Here, the interaction between protons (deuterons) is phenomenologically introduced and represented by springs. The model in Fig. 11 is simply an asymmetric version of the discrete Frenkel–Kontorowa model,<sup>26</sup> which has been extensively studied in the field of incommensurate systems.<sup>27,28</sup> It is well known that the model shows incommensurate states as stable solutions. Although real systems are not purely one dimensional but three dimensional, it is widely accepted that the incommensurate phase is realized as a stable phase under some conditions. As discussed above, the temperature dependence of heat capacity anomalies suggests a close relation between the complexes under consideration and the phase sequence with the incommensurate phase.

We base the following discussion on the presence of multiple dielectric relaxation modes. Considering the motional mode of protons inside the H bond,<sup>9</sup> it seems natural to attribute the dielectric relaxation modes to different types of proton (deuteron) dynamics. Such an attribution was reported for a H-bonded organic complex of AB<sub>2</sub> type, in which two equivalent H bonds exist within an isolated trimer of the form B–A–B. Nihei *et al.*<sup>29</sup> found two motional modes of protons with activation energies that differed by a factor of 2. They attributed these modes to single-proton hopping (transfer) and the concerted transfer of two protons.

The present complexes consist of one-dimensional H-bond chains as shown in Fig. 11. The dielectric relaxation modes under consideration are found not in the paraelectric phase but in the ordered phase(s). If the location of the proton (deuteron) is expressed by a spin variable, the H-bond chain can be regarded as a one-dimensional spin chain. In such one-dimensional chains, there are two types of dynamics: domain wall (kink) diffusion and the formation of a kink pair. The domain wall here is equivalent to the discommensuration mentioned in relation to the normal-incommensurate-commensurate phase sequence above.

Upon the transfer of proton(s) with negative charge from one minimum to the other minimum within a double-well potential, the charge state of molecules may be one of three possibilities: neutral, singly, and doubly charged states. Considering the appearance of paraelectric and ferroelectric phases shown in Fig. 11, doubly charged states can be ignored. Consequently, only neutral and singly charged states are considered hereafter.

Starting from the ordered ferroelectric state, single-

proton transfer can create pairs of neutral molecules. Needless to say, the reverse process is possible. A combination of the normal and reverse processes is thus a possible candidate for the dielectric relaxation mode. This mode corresponds to the local excitation involving only one proton.

At nonzero temperatures below the ordering transition temperature, domain walls always exist between ordered domains. A shift of these walls requires the simultaneous hopping of even numbers of neighboring protons. This process certainly contributes to the dielectric relaxation. Also, the energy before and after the process is the same by virtue of the one-dimensional nature of the H-bond chain if the three dimensionality through  $\pi$  stacking is ignored. The process involves multiple protons, resulting in an activation energy larger than that of the single-proton hopping considered above. Assuming that the main factor determining the activation energy is the energy barrier separating the double-well potential of H bonds, the expected magnitude of the activation energy is roughly proportional to the number of protons involved in the process. The frequency of such concerted hopping may be low. However, the interaction brings about a rather strong correlation between the neighboring protons. The attempt frequency may remain within the range expected for the lattice vibration.

In Phz-H<sub>2</sub>ca and Phz-D<sub>2</sub>ca, the two dielectric relaxation modes observed at low temperatures have activation energies roughly satisfying  $2E_1 \approx E_2$ . In Phz-H<sub>2</sub>ba, there is a relaxation mode that is not separated at the lowest temperature. These observations are consistent with the two modes of proton hopping: single-proton hopping and the concerted hopping of two protons. Table I also indicates that the dielectric relaxation modes observed experimentally at higher temperatures have activation energies that are roughly even multiples of the smallest one. In the context of the above consideration, this implies that the motional dynamics of domain walls involving an even number of protons (deuterons) contributes to dielectric relaxation. This is, at first glance, very surprising. The fact that the combined excess entropy due to the successive phase transitions is smaller than  $2R \ln 2$  is, however, qualitatively consistent with such correlated dynamics.

Finally, we comment on the issue of whether the multiple dielectric relaxation modes are intrinsic to these complexes. As noted previously, the temperature dependence of the complex dielectric constants is similar between Phz-H<sub>2</sub>xa

and Phz-D<sub>2</sub>x<sub>a</sub> if  $x$  is common, resulting in the same number of relaxation modes in Table I. This suggests that the presence of multiple relaxation modes is intrinsic to each complex, at least in a broad sense. The domain wall dynamics discussed may be, for example, unusual in a single crystalline sample. The use of crushed crystals in the pellet preparation clearly produces lattice imperfections. The similar behavior for dielectric relaxation implies that at least the mechanism underlying the formation of such defects is similar in Phz-H<sub>2</sub>x<sub>a</sub> and Phz-D<sub>2</sub>x<sub>a</sub>. To determine whether multiple dielectric relaxation modes are equally active in single crystals, further studies are needed.

#### IV. CONCLUSION

The heat capacities of single crystals of Phz-H<sub>2</sub>ca and Phz-H<sub>2</sub>ba indicated the presence of successive phase transitions at temperatures below those of the reported ferroelectric phase transitions. Excess entropies involved in the low-temperature successive phase transitions are much larger than those due to the ferroelectric phase transitions. The temperature dependence of the complex dielectric constants showed the existence of multiple dielectric relaxation modes in both complexes and their deuterated analogs. On the basis of the one-dimensional Frenkel–Kontorowa model, the occurrence of the successive phase transitions and complicated dielectric relaxation behavior are discussed. The concerted hopping of protons (deuterons) is suggested as a possible origin of the multiple dielectric relaxation modes.

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