Antiferroelectric Phase Transition in a Proton-Transfer Salt of Squaric Acid and 2,3-Dimethylpyrazine

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Supporting Information

ABSTRACT: A proton-transfer reaction between squaric acid (H₂sq) and 2,3-dimethylpyrazine (2,3-Me₂pyz) results in crystallization of a new organic antiferroelectric (AFE), (2,3-Me₂pyzH⁺)(Hsq⁻)·H₂O (1), which possesses a layered structure. The structure of each layer can be described as partitioned into strips lined with methyl groups of the Me₂pyz⁺ cations and strips featuring extensive hydrogen bonding between the Hsq⁻ anions and water molecules. Variable-temperature dielectric measurements and crystal structures determined through a combination of single-crystal X-ray and neutron diffraction reveal an AFE ordering at 104 K. The phase transition is driven by ordering of protons within the hydrogen-bonded strips. Considering the extent of proton transfer, the paraelectric (PE) state can be formulated as (2,3-Me₄pyzH⁺)₂(Hsq⁻)·H₂O, whereas the AFE phase can be described as (2,3-Me₂pyzH⁺)(Hsq⁻)(H₂O). The structural transition caused by the localization of protons results in the change in color from yellow in the PE state to colorless in the AFE state. The occurrence and mechanism of the AFE phase transition have been also confirmed by heat capacity measurements and variable-temperature infrared and Raman spectroscopy. This work demonstrates a potentially promising approach to the design of new electrically ordered materials by engineering molecule-based crystal structures in which hydrogen-bonding interactions are intentionally partitioned into quasi-one-dimensional regions.

INTRODUCTION

Materials that exhibit electric ordering find important technological applications in ceramic capacitors, actuators, piezoelectric transducers, pyroelectric detectors, and sonars. They are also extensively investigated in the search for new types of functionality, for example, multiferroics. While this area of research has been heavily dominated by inorganic materials, especially transition metal oxides, organic ferroelectrics have become much more notable since the early 2000s, especially due to discoveries of several remarkable organic ferroelectric materials whose performance figures of merit are comparable to those of the state-of-the-art inorganic ferroelectrics.

Designing materials with electric ordering represents a nontrivial task. While phenomenologically analogous to ferro- and antiferroelectrics, magnetic materials only require sufficiently strong magnetic exchange coupling between moments on interacting magnetic sites to undergo magnetic ordering below the critical temperature. On the other hand, ferroelectric (FE) materials require symmetry breaking in the

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crystal structure, with the formation of a polar space group, to transition from the disordered paraelectric (PE) phase to the ordered FE phase. In contrast to magnetic ordering, electric ordering generally requires concerted atomic displacements to achieve the breaking of space-group symmetry. The current interest in organic FEs is justified by both the low density of these materials and the high synthetic tunability of the molecular components that comprise them. The design of FE or antiferroelectric (AFE) organic solids generally relies on three different mechanisms: charge ordering, polar group ordering, or proton transfer. The latter is especially appealing, because the possibility of proton transfer is predictable and can occur with a high degree of cooperativity, which in turn can trigger abrupt FE or AFE ordering. A classic example of this behavior among inorganic materials is the ferroelectric transition in KH2PO4. Among organic ferroelectrics, noteworthy cases are FE ordering in crociconic acid10 and AFE ordering in squaric acid.11 While these organic acids represent single-component FE and AFE materials, respectively, Horiuchi and co-workers also reported a fascinating example of two-component ferroelectrics obtained by cocrystallization of organic base phenazine and haloanilic acids.34 This work demonstrated the predictable formation of FE materials based on the analysis of pK values of individual components to ensure the feasibility of proton transfer in the solid state. Despite the potential for concerted proton displacements in cocrys-tals of organic acids and bases, the realm of organic FE and AFE materials remains relatively narrow, in large part due to the often unpredictable effects of crystal packing that lead to annihilation of local polarity induced by the acid–base proton transfer. Herein, we demonstrate the synthesis of a new organic AFE based on the combination of squaric acid (H2sq) and 2,3-dimethypyrazine (2,3-Me2pyz). A distinct feature of this AFE material is the partitioning of molecular layers in its crystal structure into regions that feature either van der Waals interactions between weakly polar methyl groups or extensive hydrogen bonding, due to the asymmetric nature of the 2,3-Me2pyz molecule with respect to its N–N axis. We use a combination of X-ray and neutron scattering, dielectric and heat capacity measurements, and vibrational spectroscopy to elucidate the behavior of this material and the nature of the electric phase transition observed at 104 K.

### EXPERIMENTAL SECTION

**Starting Materials.** Squaric acid, H2sq (98%, Oakwood Chemical), and 2,3-dimethypyrazine, 2,3-Me2pyz (99%, Alfa Aesar), were used as received. (2,3-Me2pyzH+)[(H2sq)2]H2O (1). H2sq (1.00 g, 8.77 mmol) was dissolved in 10 mL of deionized water at 50 °C and neat 2,3-Me2pyz (0.96 mL, 8.77 mmol) was added dropwise to this solution, resulting in the change of color from colorless to bright-yellow. The solution was cooled to room temperature, and yellow block-shaped crystals began to form within a few minutes. The solution was left undisturbed for 1 day, after which time the crystals were recovered by filtration and dried by suction. Yield = 0.86 g (43%). Anal. Calcd for C24H24N2O3 (1): C, 50.00; H, 5.04; N, 11.66. Found: C, 50.05; H, 4.98; N, 11.58.

**X-ray Crystallography.** Room-temperature powder X-ray diffractometry (PXRD) was performed on a Panalytical X’Pert Prof diffractometer with Cu Kα radiation (λ = 1.54178 Å). The PXRD patterns were collected over a 2θ range of 10–60° with a step of 0.03° and 0.50 s/step counting time. The data were processed with the CrystalSoffract software.

Single-crystal X-ray diffraction (SCXRD) experiments were performed on a Bruker APEX-II CCD X-ray diffractometer equipped with a graphite-monochromated Mo Kα radiation source (λ = 0.71073 Å). A single crystal of 1 was suspended in Paratone-N oil (Hampton Research) and cooled to the desired temperature in a N2 cold stream. The data sets were recorded as ω-scans at 0.4° step width and integrated with the Bruker SAINT software package. A multiscan empirical absorption correction was based on multiple equivalent measurements (SADABS).13 The space group determination was performed with XPREP.14 and the crystal structure solution and refinement were carried out using SHELX.15 The final refinement was performed with anisotropic atomic displacement parameters (ADPs) for all non-hydrogen atoms. The methyl and aromatic H atoms were placed in calculated positions and refined in the riding model, while the H atoms involved in hydrogen bonding were located from the difference Fourier electron density map and refined with isotropic ADPs, without restricting the N=H or O–H distances. A summary of pertinent information relating to data collection and crystal structure refinements is provided in Table 1.

**Neutron Diffraction.** Time-of-flight single-crystal neutron diffraction (SCND) was performed on the TOPAZ diffractometer at the Spallation Neutron Source (Oak Ridge National Laboratory). The crystal was mounted on a MiTeGen loop using a small amount of Super Glue. The data collection strategy was obtained with CrystalPlan.16 The data were collected for ~60 h at 90 K using 44 sample orientations with 8 C of proton charge at each of the beam power of 1 MW and for ~45 h at 230 K using 34 sample orientations with 6 C of proton charge at each of the same beam power. Peak integration and data reduction were performed in accordance with previously reported procedures.17 The positions of H atoms were located from the difference Fourier maps calculated using the neutron diffraction data. The crystal structures were refined anisotropically using SHELX15 and the ShelXle graphical interface.18 The details of data collection and crystal structure refinement are summarized in Table 1.

**Dielectric Measurements.** A single crystal of 1 with the size of 7 × 4 × 1.3 mm3 was selected for measuring the dielectric constant as a function of temperature and electric polarization as a function of applied electric field. To obtain a parallel capacitor geometry, Cr/Ag contacts were deposited on two opposite flat surfaces, corresponding to the [001] and [010] faces of the crystal (these faces are parallel to the layers observed in the crystal structure, as will be described below). The deposition had to be performed very carefully, due to the delicate nature of the crystal. First, the edges of the crystal were covered with a Kapton-tape mask, which also attached the crystal to an aluminum plate, for more efficient thermal contact with the cooling plate of the evaporator stage. The assembly was mounted in an evaporator chamber, which was subsequently evacuated for 10 s and then flushed with N2 gas, and this process was repeated five times to minimize the amount of moisture in the chamber. To avoid deterioration of the crystal under high vacuum, the sample stage was first cooled by liquid N2 to ~30 °C under 10–2 Torr, and then the pressure was decreased to 3 × 10–7 Torr as the sample stage temperature was lowered to ~110 °C. A 5 nm film of chromium followed by a 100 nm film of silver were deposited at the rate of 0.1 nm/s. The temperature of the sample stage increased to ~70 °C during the evaporation. After the deposition had been completed, the chamber was flushed with N2 gas for 20 min to warm the sample before opening the chamber. The crystal was flipped, and the deposition process was repeated on the other side. The crystal prepared in such a way had the active electrode area of ~11 mm2. After making electrical contacts, the assembly was covered with...
Apiezon-N grease to prevent degradation of the sample and to enhance thermal coupling to the sample platform. The capacitance was measured using a capacitance bridge (Andeen-Hagerling AH2700A) at AC electric field frequencies from 0.2 to 20 kHz. The dielectric constant was obtained from the capacitance by approximating an infinite parallel capacitor geometry. The temperature was varied at 1 K min⁻¹. The electric polarization was measured as a function of electric field at 2.5 and 200 K with the maximum applied voltages of 3 and 2 kV, respectively.

**Thermal Analysis.** Heat capacity measurements were performed on a 3.89 mg pellet of 1 in the temperature range from 300 to 2 K, using the Physical Property Measurement System (Quantum Design). Apiezon-N grease was used to thermally couple the sample to the platform of the calorimeter. The contribution of the platform, including the grease, was measured independently and subtracted from the total heat capacity data. Simultaneous differential scanning calorimetry and thermogravimetric analysis (SDT) were performed on a 7.52 mg powder sample of 1 contained in an alumina crucible. The measurement was carried out on a TA Instruments SDT 600Q analyzer under a 100 mL min⁻¹ flow of Ar gas, in the temperature range from 300 to 873 K and at a 5 K min⁻¹ heating rate.

**UV–Visible Spectroscopy.** The spectrum was collected on a microcrystalline sample of 1 at room temperature, using an Edinburgh FLS980 spectrometer with the integrating sphere accessory. Light output from a housed 450 W Xe lamp was passed through a single grating (1800 l/mm, 500 nm blaze) Czerny-Turner monochromator and then into the integrating sphere containing the powder sample or scattering reference (BaSO₄). The output from the integrating sphere was passed through a single grating (1800 L/mm, 500 nm blaze) Czerny-Turner and finally detected by a Peltier-cooled Hamamatsu R928 photomultiplier tube. Synchronous spectral scans were performed with both excitation and emission monochromators, with zero wavelength offset, stepping through the preset spectral range. Absorbance was then calculated using Edinburgh’s F900 software package.

**Infrared Spectroscopy.** A polycrystalline sample of 1 was mixed with KBr for transmittance Fourier transform infrared spectroscopy experiments. The measurements were performed on a Bruker Equinox 55 spectrometer equipped with a microscope and a low-profile cryostat (550–7500 cm⁻¹; 4.2–300 K). The middle infrared frequency range was examined to reveal hydrogen-bonding effects. Mode assignments were made using lattice dynamics calculations performed with Spartan, as well as by comparison with literature data. Traditional fitting techniques were employed as appropriate.

**Raman Spectroscopy.** Raman spectra were collected on a 1 mm thick, pelletized sample of 1, using an Acton SP2500 spectrometer with 1200 g mm⁻¹ grating and a 100 μm entrance slit, providing 3 cm⁻¹ resolution. The measurements were performed in the temperature range from 30 to 150 K. The sample was mounted on a copper coldfinger inside a continuous-flow He cryostat. Spectra were recorded from 90–3200 cm⁻¹ range in quasi-backscattering geometry with nonpolarized 532 nm light. A long-pass edge filter was used to attenuate elastically scattered light. A liquid nitrogen cooled Si CCD was used for detection. The power incident of the sample was around 2 mW.

## RESULTS AND DISCUSSION

**Synthesis and Stability Studies.** Compound 1 was obtained by a reaction between H₂Sᵥ and 2,3-Me₂pyz in water in a 1:1 molar ratio. Bright-yellow X-ray quality crystals (Figure S1) grew from the obtained yellow solution within 30 min at
room temperature. The typical crystals were elongated plates, with the long edge often exceeding 1 cm. The crystals are air- and moisture-stable and remain intact for prolonged periods if kept in a closed container. Upon exposure to air, 2,3-Me₂pyz and H₂O gradually sublime from the lattice over the course of several days, resulting in the formation of pure H₂sq. Heating a powdered sample of 1 to 50 °C under vacuum accelerates the decomposition process, producing pure H₂sq after 20 h, as confirmed by PXRD patterns recorded before and after the decomposition (Figure S2). Simultaneous differential scanning calorimetry and thermogravimetric analysis (SDTA) showed the loss of 2,3-Me₂pyz and H₂O beginning at room temperature and lasting until approximately 425 K, at which point 48.7% of the initial mass remained, in good agreement with the expected mass of 47.5% for the pure H₂sq residue. The remaining H₂sq is then stable until decomposition at 525 K (Figure S3).

On the basis of the observed behavior of 1, its crystals were stored in capped glass vials to prevent any degradation prior to their characterization with diffraction and other physical methods.

**Dielectric Properties.** The temperature-dependent capacitance measurements on a single crystal of 1 were performed to extract the complex dielectric constant, \( \varepsilon(\omega) = \varepsilon'(\omega) + i\varepsilon''(\omega) \). The data analysis revealed a sharp decrease in the real part \( \varepsilon' \) of the dielectric constant below \( \sim115 \) K (Figure 1), while the imaginary part \( \varepsilon'' \) remained near zero over the entire temperature range. The anomaly in the dielectric signal did not exhibit any notable frequency dependence (Figure S4). The pyroelectric current measured near the transition temperature was negligible, and no spontaneous electric polarization was observed. Furthermore, electric polarization measured at 2.5 K showed linear dependence on the applied electric field and the lack of hysteretic behavior (Figure S5). All of these observations suggest a possible AFE phase transition,\(^{19}\) which emerges from the spontaneous antiparallel ordering of electric dipoles and leads to the decrease in the macroscopic polarizability.\(^{20}\) The observation of this dielectric anomaly led us to investigate other temperature-dependent properties of this material, especially the possible changes in its crystal structure above and below the temperature of dielectric anomaly.

**Crystal Structure.** To elucidate the mechanism of the possible phase transition, the crystal structure of 1 was determined by a combination of SCXRD and SCND (for hydrogen atom detection) at 90 and 230 K, that is, below and above the observed decrease in the dielectric constant. At 230 K, the material crystallizes in the centrosymmetric triclinic space group \( P\bar{1} \) with \( Z = 2 \). Upon lowering the temperature to 90 K, a supercell with \( Z = 4 \) was detected, although the space group remained the same. (As will be shown below, the formation of the superstructure is due to the ordering of H atoms involved in hydrogen bonding.) The relationship between the two structures may also be expressed by considering the high-temperature structure in a nonstandard base-centered space group \( A\bar{1} \), obtained from the standard \( P\bar{1} \) lattice by means of a transformation matrix, \( \begin{bmatrix} 0 & 1 & 0 \\ -1 & 0 & 0 \\ 1 & 0 & 1 \end{bmatrix} \). This transformation results in a unit cell with \( Z = 4 \), with parameters and volume comparable to those of the low-temperature structure (Table 1). The structural transition leads to the loss of the \( A \)-centering, which is equivalent to the doubling of the primitive unit cell observed at 230 K.

The crystal structure of 1 is built of layers (Figure 2a), which are parallel to the (201) planes that correspond to the basal faces of the plate-like crystals. At 230 K, the distance between adjacent layers is 3.092 Å. In each layer, the base and acid components alternate in such a way that one can distinguish strips lined with methyl groups alternating with strips featuring extensive hydrogen bonding (Figure 2b). One proton from each squaric acid molecule is transferred to a neighboring 2,3-
Me₂pyz molecule, resulting in the formation of 2,3-Me₂pyzH⁺ ions. The protonated side of the 2,3-Me₂pyzH⁺ cations is oriented toward the region of hydrogen bonding, while the side with methyl substituents forms the methyl-lined strip. The protonated N atoms form asymmetric hydrogen bonds to the Hsq⁻ anions, with the N(1)−H(1)···O(1) distance of 2.640(3) Å at 230 K. Further, the region of extensive hydrogen bonding is composed of the Hsq⁻ anions and water molecules (Scheme 1 and Table 2). At 230 K, we observe a symmetric H-bonded dimer of the hydrosquarate anions, (Hsq₂)³⁻, with the bridging proton appearing on the inversion center and the O(3)−H(3)···O(3) distance of 2.485(5) Å. One of the hydrosquarate protons has been transferred from this dimer to the neighbor water molecules, resulting in a protonated dimer of water molecules, (H₅O₂)⁺. Thus, in the crystal-chemical formulation, the PE phase can be represented as (2,3-Me₂pyzH⁺)₂(Hsq₂)³⁻(H₅O₂)⁺. The proton H(5B), which participates in an asymmetric H-bond

**Scheme 1. Hydrogen Bonding between Molecular Components in the Crystal Structure of 1 at 230 K (a) and 90 K (b)**

The hydrogen bonds that become ordered at lower temperatures are highlighted with red color. The crystallographic numbering is indicated only for the most important atoms involved in hydrogen bonding. The full atom numbering scheme and atomic displacement ellipsoids are provided in Figure S6.

**Table 2. Distances between Atoms Involved in Hydrogen Bonding in the Structure of 1 from SCND**

<table>
<thead>
<tr>
<th>Hydrogen bond (B−H−A)</th>
<th>d(B−A), Å</th>
<th>d(B−H), Å</th>
<th>d(H−A), Å</th>
</tr>
</thead>
<tbody>
<tr>
<td>90 K</td>
<td>230 K</td>
<td>90 K</td>
<td>230 K</td>
</tr>
<tr>
<td>N(1)−H(1)−O(1)</td>
<td>2.625(3)</td>
<td>2.640(3)</td>
<td>1.080(5)</td>
</tr>
<tr>
<td>O(3)−H(3)−O(3)</td>
<td>2.512(6)</td>
<td>2.485(5)</td>
<td>1.056(8)</td>
</tr>
<tr>
<td>O(5)−H(2)−O(2)</td>
<td>2.445(4)</td>
<td>2.544(4)</td>
<td>1.339(8)</td>
</tr>
<tr>
<td>O(5)−H(5B)−O(5)</td>
<td>2.569(6)</td>
<td>2.552(7)</td>
<td>1.552(8)</td>
</tr>
<tr>
<td>O(5)−H(5A)−O(4)</td>
<td>2.651(6)</td>
<td>2.669(5)</td>
<td>0.982(9)</td>
</tr>
<tr>
<td>2.709(6)</td>
<td>2.766(9)</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

*The labels B and A indicate the N and/or O atoms involved in the hydrogen-bonding pairs.*
between water molecules with the O(5)–H(5B)...O(5)′ distance of 2.552(7) Å, is disordered over two equally occupied positions. This suggests that the protons H(2) and H(3), which are involved in H-bonding of the (Hsq)3− dimer, undergo dynamic shifts between the corresponding O atoms, so that when the H(3) proton is shifted closer to one of the hydroxsquarate anions, the proton is now observed to acquire an outer H(2) proton from the neighbor water molecule, while the Hsq− anion that acquired the H(3) proton transfers its outer H(2) proton to another water molecule. Accordingly, the H(5B) proton involved in H-bonding between the water molecules has become completely disordered, shifting the absorption bands of 2,3-Me2pyzH+ and the lowest unoccupied molecular orbitals, LUMO and LUMO+1, to correspond to πa-orbitals of Hsq−. Thus, the lowest-energy optical absorption bands correspond to charge transfer from the cation-based HOMO/HOMO−1 to the anion-based LUMO/LUMO+1. The involvement of the Hsq− anions in delocalized hydrogen bonding should lower the energy of LUMO and LUMO+1, while the loss of such delocalization will have an opposite effect, shifting the absorption bands completely to the UV region, which explains the loss of color by crystals of 1 in the AFE phase.

Thermodynamics of the Phase Transition. Heat capacity (Cp) measurements revealed a broad anomaly in the region of the structural phase transition (Figure 3).

Figure 3. Temperature dependence of C_p and C_p/T measured on a pelletized powder sample of 1. The black line in the inset shows the extrapolated baseline, while the vertical black lines mark the beginning and end points of the integrated region.

The ordering of protons within each layer also leads to “dimerization” of the layered structure, as shorter (∼2.80 Å) and longer (∼3.18 Å) interplanar separations alternate in the 90 K structure, in contrast to the uniform interplanar separation of ∼3.09 Å in the 230 K structure. The layers are oriented parallel to the (011) lattice plane in the 230 K structure, which is transformed to the (031) plane in the 90 K structure.

An examination of the crystal packing in the 90 K crystal structure reveals that the protons are shifted in a concerted fashion within the hydrogen-bonded region, producing a net in-plane dipole moment, while the protons of the next hydrogen-bonded region shift to produce a dipole moment in the opposite direction (Figure S7). Thus, because of the structural phase transition, net dipole moments formed in the adjacent hydrogen-bonded regions cancel each other, which explains the observed drop in the dielectric constant and suggests the occurrence of an AFE phase transition. The proton redistribution can also be described with the following reaction scheme:

\[
[2,3-\text{Me}_2\text{pyzH}^+\text{H}_2\text{O}]^+ + [2,3-\text{Me}_2\text{pyzH}^+\text{H}_2\text{O}]^+ \rightarrow \text{H}_2\text{O} → \text{H}^+ \rightarrow \text{H}_2\text{O}^+
\]

where the high-temperature PE state features delocalized protons in the hydrogen-bonded dimers, Hsq− and H2O2−, while the low-temperature AFE state contains only localized protons.

Such description of the PE → AFE phase transition also justifies the change in color from yellow in the PE state (Figures S1 and S8) to colorless in the AFE state. On the basis of the reported calculations of the electronic structure of squaric acid and pyrazine derivatives,21 we expect the highest occupied molecular orbitals, HOMO and HOMO−1, to be represented by π-orbitals of 2,3-Me2pyzH+ and the lowest unoccupied molecular orbitals, LUMO and LUMO+1, to correspond to πa-orbitals of Hsq−. Thus, the lowest-energy optical absorption bands correspond to charge transfer from the cation-based HOMO/HOMO−1 to the anion-based LUMO/LUMO+1. The involvement of the Hsq− anions in delocalized hydrogen bonding should lower the energy of LUMO and LUMO+1, while the loss of such delocalization will have an opposite effect, shifting the absorption bands completely to the UV region, which explains the loss of color by crystals of 1 in the AFE phase.

Thermodynamics of the Phase Transition. Heat capacity (C_p) measurements revealed a broad anomaly in the region of the structural phase transition (Figure 3). The change in entropy due to this phase transition,

\[
\Delta S_T = \int \frac{\Delta C_p}{T} dT,\nonumber
\]

was found by numerical integration of the C_p/T versus T curve after subtracting a baseline extrapolated from the regions above and below the C_p anomaly (Figure S5 inset). The procedure resulted in \(\Delta S_T = 0.55 \text{ J mol}^{-1} \text{ K}^{-1}\). On the basis of the Boltzmann–Planck formula, \(\Delta S_T = R \ln N\), where R is the ideal gas constant and N is the ratio of possible states in the high-temperature phase to those in the low-temperature phase, values of \(N = 2\) and \(\Delta S_T = 5.76 \text{ J mol}^{-1} \text{ K}^{-1}\) are expected for an ideal 2-fold order−disorder phase transition. The significantly smaller experimental value of \(\Delta S_T\)
suggests that the mechanism of this AFE phase transition cannot be thought of as the simple ordering of protons. Previous studies of the heat capacity anomaly around the AFE phase transition temperature in pure H$_2$Sq found $\Delta S = 0.228$ J mol$^{-1}$ K$^{-1}$, which similarly deviates from the value of 11.28 J mol$^{-1}$ K$^{-1}$ expected for two protons ordering per molecular unit.$^{22}$ On the basis of the investigation of isotope-dependent effects on the FE transition in KH$_2$PO$_4$, it was proposed that the suppression of the experimentally determined values $\Delta S$ might be due to tunneling terms unaccounted by the simple Boltzmann–Planck model.$^{23}$ The suppression of the $\Delta S$ value might also stem from glassy effects in the phase transition. In the present case, however, such effects are negligible, because the dielectric signal at the phase transition does not show any dissipation, as can be judged from the near-zero value of the out-of-phase dielectric constant (Figure 1a).

**Vibrational Spectroscopy.** Raman spectra collected over the 30–150 K temperature range (Figure 4a) resemble a combination of the spectra for pure H$_2$Sq$^{24}$ and 2,3-Me$_2$pyz$^{25}$, allowing straightforward assignment of the vibrational bands (Table S2). The positions of all observed peaks are essentially independent of temperature, suggesting the structural phase transition does not impact the strength of intramolecular bonds. Several peaks, however, exhibit a significant decrease in the full-width at half-maximum (fwhm) as the temperature is lowered (Figure 4b), indicating an increased ordering of atomic positions associated with these frequencies. In particular, the fwhm of the band assigned to the $\delta$(C′-O′) $A_1$ mode in squaric acid follows the phase transition seen in the dielectric measurements. The bands assigned to the 2,3-Me$_2$pyz moieties, in general, lack similar temperature dependence of the fwhm (Figure 4c), with the exception of the 1260 cm$^{-1}$ band, the intensity of which varied greatly due to the broad underlying absorption feature observed in the corresponding region at lower temperatures (Figure 4a).

The infrared response of 1 was also examined as a function of temperature. Similar to the Raman spectra, the vibrational modes derive from those of the H$_2$Sq$^{24}$ and 2,3-Me$_2$pyz$^{25}$ molecules. The room-temperature spectrum also shows a strong charge transfer band centered at 1400 cm$^{-1}$ (Figure 5a).
Evidence for assignment of the broad structure as a low-energy charge transfer band comes from the derivative-like (Fano) line shape of the superimposed vibrational modes.\textsuperscript{26} The charge transfer band gains oscillator strength with decreasing temperature. Examination of the contour plot (Figure 5b) reveals that the charge transfer band narrows across the PE $\rightarrow$ AFE phase transition temperature ($T_{\text{AFE}}$). These line width changes, on the order of 10\%, recover fully away from $T_{\text{AFE}}$. At the same time, the vibrational features sharpen with decreasing temperature. Vibrational line width trends are consistent with decreasing thermal fluctuations, as evidenced by the Raman scattering and the behavior of ADPs already discussed in the text, with a distinct narrowing near the 104 K AFE transition (Figure 5b).

We also should point out that several vibrational modes soften with decreasing temperature. This is a common signature of enhanced hydrogen bonding.\textsuperscript{27} As an example, we track two different vibrations associated with H$_2$Sq as a function of temperature. The A$_1$ symmetry $\delta$(O–H) mode softens with decreasing temperature (Figure 5c). The softening may also be connected to the symmetric $\leftrightarrow$ asymmetric positioning of the H atom in the O$\cdots$H$\cdots$O pathway. Three other vibrational modes, the B$_3$ symmetry $\pi$(O–H), B$_1$ symmetry $\delta$(O–H), and B$_2$ symmetry $\nu$(C$'$–O$'$) at 977, 1375, and 1822 cm\textsuperscript{–1}, respectively, follow the same trend, suggesting that they are also involved in hydrogen-bond driven proton transfer in I. In contrast, the upper panel of Figure 5 displays the position of the A$_1$ symmetry $\nu$(C$'$–C$'$) mode of H$_2$Sq as a function of temperature. The low-temperature hardening is a typical anharmonic response, and there is no sensitivity to $T_{\text{AFE}}$ within our resolution. The majority of H$_2$Sq\textsuperscript{24} and 2,3-Me$_2$pyz\textsuperscript{25} modes behave similarly, suggesting that they do not play a major role in the proton transfer in this system.

**CONCLUDING REMARKS**

The cocrysallization of 2,3-Me$_2$pyz and H$_2$Sq provides a remarkable example of an AFE ordered phase. The asymmetric nature of the 2,3-Me$_2$pyz molecule with respect to the N–N axis forces the partitioning of the resulting layered structure of (2,3-Me$_2$pyz$^+$)(Hsq$^-$)·H$_2$O (1) into regions lined with methyl groups and regions that feature extensive hydrogen-bonded interactions between deprotonated Hsq$^-$ anions and cocrysallized water molecules. The presence of these hydrogen-bonded regions eventually leads to the spontaneous AFE ordering at 104 K. The phase transition was conclusively confirmed by the combination of neutron and X-ray diffraction, dielectric and heat capacity measurements, and vibrational spectroscopy. The nature of the crystal structure of I and the mechanism of AFE ordering hint at a potentially promising approach to the design of new organic ferro- or antiferroelectrics. Other acid–base combinations can be explored, featuring components conducive to the separation of the structure into regions with distinctly different character of intermolecular interactions, whereas the size of the substituents on the molecular components can be systematically varied to arrive at different compositions and structural topologies. Efforts in this direction are currently underway in our laboratories.

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