

Ferroelectricity in NH···N Hydrogen Bonded Crystals

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NH···N hydrogen bonded crystals of $[C_6H_7N_2]^+ \cdot ClO_4^-$ and $[C_6H_7N_2]^+ \cdot BF_4^-$ undergo ferroelectric phase transitions at 377.0(5) and 378.1(5) K, respectively. Owing to particularly simple structure, built of linear NH···N bonded aggregates, the spontaneous polarization of the crystals can be straightforwardly calculated from ionic displacements. The NH···N bonded structures have been compared with transformations of analogous bistable OH···O hydrogen bonds in H₂O ices and KH₂PO₄-type ferroelectrics. [S0031-9007(98)08248-9]

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Properties of many substances depend on specific features of hydrogen bonds. This applies equally to water [1] built of small H₂O molecules and to living tissues built of huge biopolymers [2]. The hydrogen bonds are directional, but much weaker than covalent bonds binding atoms into molecules. Therefore the hydrogen-bonded aggregates easily undergo transformations, induced by breaking and formation of alternative hydrogen bonds, proton transfers, or proton disordering. Such transformations change properties of crystals and enable the biopolymers to perform their living functions. The transformations of hydrogen bonds can be conveniently studied in crystals undergoing structural phase transitions, but of the crystals with biologically most common NH···O, OH···O, and NH···N hydrogen bonds, only those OH···O bonded are known to undergo phase transitions connected with proton disordering, for example, H₂O ices or KH₂PO₄ (KDP) ferroelectrics [3]. We demonstrate here that similar transformations also occur in the NH···N hydrogen-bonded monosalts of diazabicyclo[2.2.2]octane (dabco), C₆H₇N₂, which are ferroelectrics of potential technological importance. The N···HN hydrogen bonds are considerably weaker and longer than their O···HO counterparts, and they may shed new light on the mechanism of the phase transition in the H₂O ices and KDP-type ferroelectrics [4–8]. Transformations of OH···O hydrogen bonds in ices and alcohols are mainly attributed to rotations of the water molecules and OH groups, although H transfers are not ruled out [9–11]. Theoretically predicted ferroelectricity of alcohols or ices [12] still lacks convincing experimental evidence. From the topological point of view, the disadvantage of studying OH···O hydrogen bonds is that oxygen atoms form zigzaglike motives in hydrogen-bonded networks. The hydrogen bonds in such aggregates are usually inclined to the chemical bond of the oxygen atom, or to other hydrogen bonds by about 109° or 120°. Similar zigzag chains are formed in the hydrochloric acid crystals, where the ferroelectric phase transition induced by the onset of H ordering in the Cl···HCl bonds is due to freezing of the molecular rotations [13]. This does not apply to

the NH···N hydrogen bonds, which may lie exactly along the direction of the aggregates which they form. Nearly ideal linear NH···N hydrogen-bonded chains have been found in the crystals of dabco perchlorate [14]. Disordering of the proton, and even its centering between the nitrogen atoms, has already been observed in so called proton sponges [15], where intramolecular N···HN⁺ hydrogen bonds are squeezed due to strains in molecular skeletons. Recently the mechanism of concerted H transfers in NH···N bonded molecular dimers was investigated [16]. It was also established that the H site in the N···HN or N···HN⁺ hydrogen bonds is coupled to the molecular arrangements and to proton-anion distances [17]. This implies that the NH···N hydrogen-bonded crystals should also undergo phase transitions coupled with H disordering. Indeed, the phase transitions in dabco perchlorate (dabcoHClO₄) and tetrafluoroborate (dabcoHBF₄) crystals, fully confirm this supposition.

The dabcoHClO₄ and dabcoHBF₄ crystals are isostructural: they crystallize in the orthorhombic space group *Pm*2₁*n* and form colorless plates with the shortest dimension along [*y*] and the longest along [*z*]. The crystals contain chains of hydrogen-bonded dabcoH⁺ cations, as illustrated in Fig. 1. At room temperature the acidic hydrogen atoms are ordered in the N···HN⁺ hydrogen bonds. A high-temperature phase transition has been observed in dabcoHClO₄ at *T*_c = 377.0(5) K and in dabcoHBF₄ at *T*_c = 378.1(5) K (see Fig. 2). Also low-temperature phase transitions related to conformational properties of the dabcoH⁺ cations, and to triggering of hindered rotations of the cations and anions about their pseudo-three-fold axes along the hydrogen-bonded chains (Fig. 1), have been detected below 200 K. This type of molecular dynamics is consistent with the solid-state NMR results for the dabco salts [18]. The spontaneous polarization hysteresis loop and the anomalous increase in dielectric permittivity (Fig. 3) testify to the ferroelectric nature of the high-temperature phase transitions at *T*_c. Broad precursory effects evident from calorimetric measurements testify to the increasing dynamic

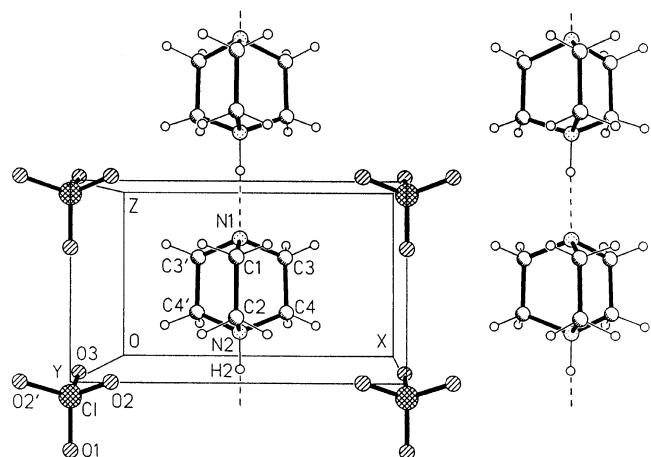


FIG. 1. Structure of the dabcoHClO₄ crystal viewed down axis [y]. The hydrogen bonds are indicated as dashed lines and the H atoms as small circles.

disorder of the ions starting from about (T_c -60) K. The transition enthalpy is of 5.6(4) kJ mol⁻¹ and entropy of 14.9(8) J mol⁻¹ K⁻¹ for dabcoHClO₄ and, respectively, 4.4(3) kJ mol⁻¹ and 11.6(7) J mol⁻¹ K⁻¹ for dabcoHBF₄. The first-order character of the transitions is apparent from the temperature hystereses of T_c of about 2 K, and from the discontinuities in dielectric permittivities (Fig. 3) or in thermal expansion of the crystals (Fig. 4).

Above T_c the crystals become tetragonal, as indicated by the temperature dependence of the unit-cell dimensions (Fig. 4), and they assume centrosymmetric space group $P4/mmm$. According to the symmetry change the crystals belong to $4/mmm Fmm2$ species [19,20] and they can be

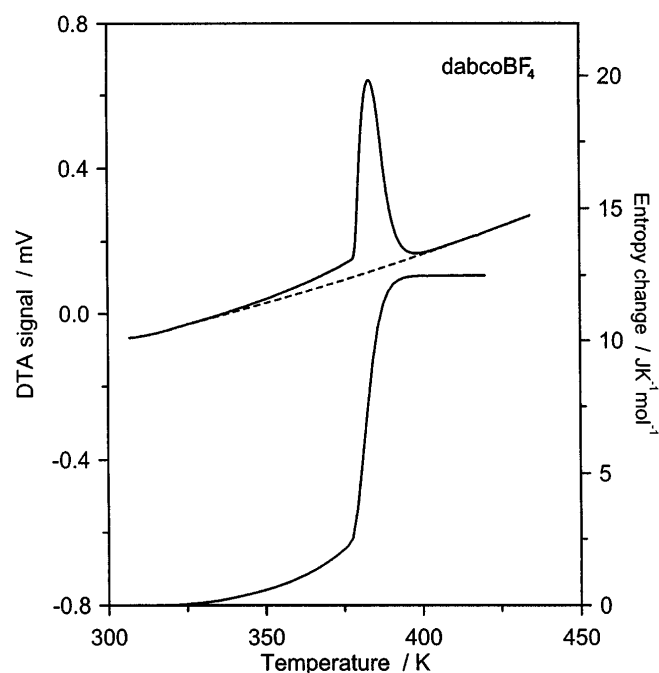


FIG. 2. Differential thermal analysis signal (the upper curve) and the transition entropy changes for dabcoHBF₄.

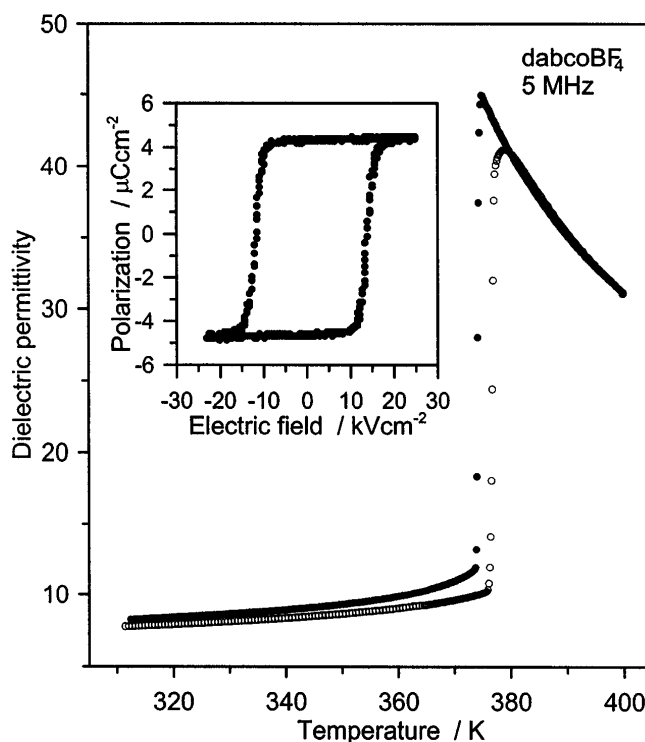


FIG. 3. Dielectric permittivity measured in the heated (o) and cooled (●) dabcoHBF₄ crystal along axis [y]. The inset shows the ferroelectric hysteresis loop for the same sample at room temperature.

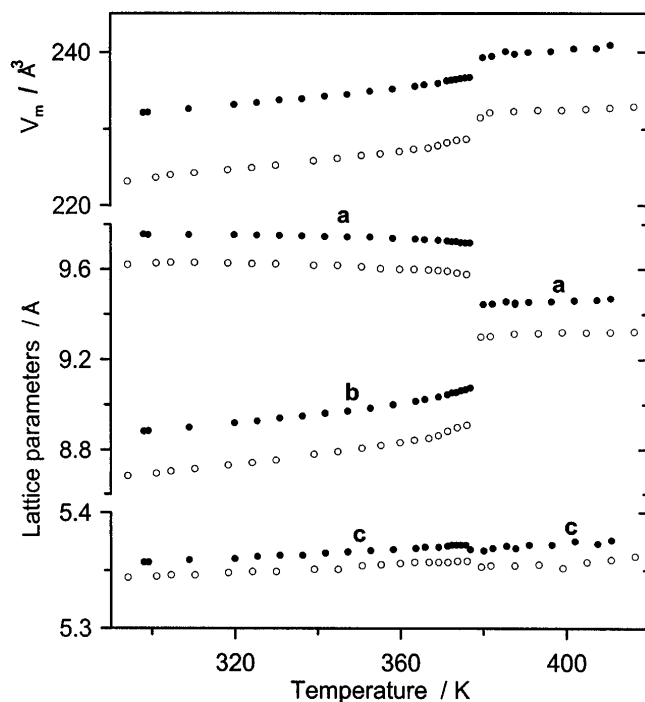


FIG. 4. Temperature dependence of the unit-cell dimensions and molecular volume of dabcoHClO₄ (●) and dabcoHBF₄ (○) crystals (the ordinate unit for *a* and *b* has been reduced compared to *c*, to contain the nearly 1 Å changes of *a* and *b* in one plot).

classified as proper ferroelectrics and improper ferroelastics [21], although the dielectric permittivity is relatively low in the vicinity of T_c both in the para- and ferroelectric phases. Thus two ferroelastic states [22] are formed with domain walls (110) and $(1\bar{1}0)$, referred to the prototypic phase shown in Fig. 5, and four ferroelectric domains [23] with two opposite senses of spontaneous polarization along direction [110], and two along $[1\bar{1}0]$ (directions [100] and [010], respectively, of the ferroelectric phase shown in Figs. 1 and 6). Considerable spontaneous strain ($a/b \cong 1.11$ at 293 K) favors the growth of single-domain crystals, which was confirmed by x-ray diffraction. However, cycling through T_c results in the multidomain structure. The change in ϵ_y of the ferroelectric phase after the as-grown sample is heated and cooled through T_c can be ascribed to the formation of the domains. In the paraelectric phase of dabcoHClO₄, the central Cl atom of the anion and the acidic H atoms have been located, each in two disordered sites, as illustrated in Fig. 5. Because of the disorder of protons and anions, the chains of hydrogen-bonded cations loose their polarization. This result is corroborated by the appearance of a sharp extra line in the solid state ¹H NMR spectrum of dabcoHClO₄ at 392 K, absent when the protons are exchanged by deuterons, which can be assigned to fast transformations of the N...HN⁺ hydrogen bonds [18]. In the paraelectric phase the ions are located on the fourfold

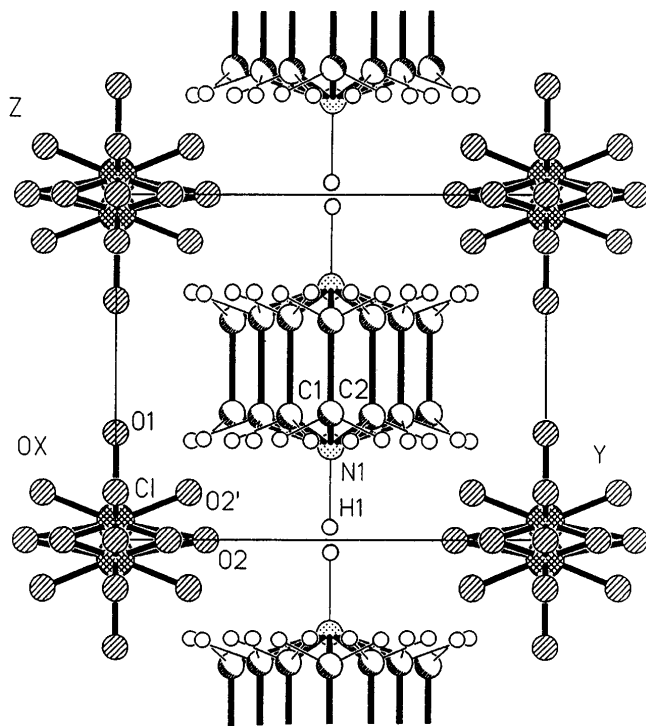


FIG. 5. Disordered structure of the dabcoHClO₄ crystal in the paraelectric phase at 380 K. Partially occupied sites of the C, H, O, and Cl atoms and fully occupied sites of the N atoms constitute the model obtained from x-ray diffraction. Axes [z] of the paraelectric and ferroelectric phases are colinear, while [x] and [y] lie at about 45° to their counterparts.

axes, inconsistent with their own symmetries. The crystal symmetry requirements are satisfied by the orientational disorders of the cations about the line passing through the N atoms, and of the anions about one of the bonds. Dynamical rotations are observed in dabco salts even below 200 K [18]. Owing to fluctuations of the potential barriers to the rotations, the sites of the atoms in rotating ions are smeared along the circles perpendicular to the fourfold axes. We have modeled this type of the structure dynamics with partially occupied atom sites closely located around the circles (Fig. 5). This model agrees perfectly with the x-ray diffraction data, gives low reliability factor $wR2$ of 0.033 for 148 observed symmetry-independent reflections, and allowed the hydrogen atoms at all the disordered sites of the carbon and nitrogen atoms to be located from difference Fourier maps and refined with isotropic thermal parameters. Disordering of the perchlorate anion is due to its rotations about the central Cl atom and to its hopping between two sites 0.543(10) Å apart (Fig. 5). A similar type of ClO₄⁻ disorder, but without rotations, was previously observed in another crystal [24]. The difference in the total transition entropy gain, close to $R \ln 6$ for dabcoHClO₄ and to $R \ln 4$ for dabcoHBF₄ (R is the gas constant), indicates that the BF₄⁻ anions may be disordered to a lesser extent. The displacements of the anions result in fluctuations of the negative charge along the direction of chains, which can activate the proton transfers through the barrier separating two potential-energy minima and become coupled with the proton hopping in the N...HN⁺ hydrogen bonds [17]. The proton hopping can be further facilitated by strong vibrations of the cations bumping against each other in the chains and so causing fluctuations in the height of the potential energy barrier

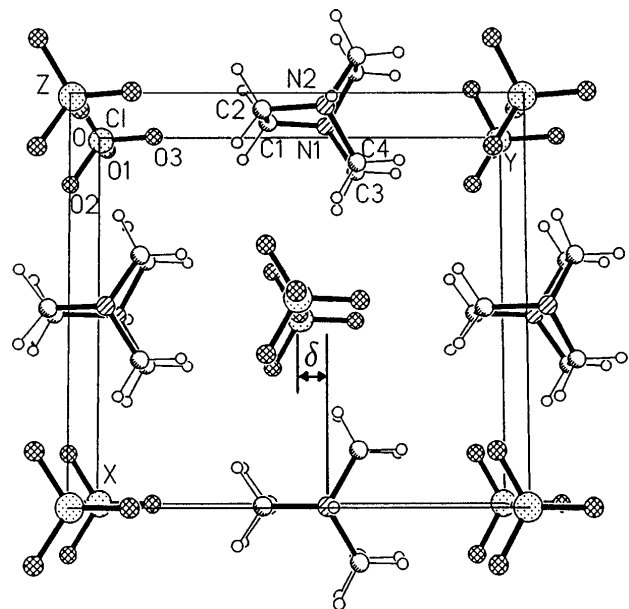


FIG. 6. View of the dabcoHClO₄ structure at 293 K along the hydrogen-bonded chains. All dabco⁺ cations are displaced along [y] by δ relative to the ClO₄⁻ anions.

separating the proton sites. On lowering the temperature of the dabco salts below T_c , the onset of ordering of the anions and protons along $[z]$ restores the close packing arrangement and the cations and anions displace from their equidistant sites in the tetragonal phase. This breaks the tetragonal symmetry of the paraphase and results in the spontaneous polarization.

The exceptionally simple structure of the ferroelectric dabco salts allows their spontaneous polarization to be easily calculated from the displacement of the ions. For example, the BF_4^- anions and dabcoH^+ cations are displaced by $0.626(1)$ Å along $[y]$ at room temperature, as illustrated in Fig. 6, which gives the spontaneous polarization of $4.34 \mu\text{C}/\text{cm}^2$, identical within error as the experimental result of $4.6(3) \mu\text{C}/\text{cm}^2$ (Fig. 3). The respective values for dabcoHClO_4 are $0.6067(7)$ Å and $4.19 \mu\text{C}/\text{cm}^2$. The direction of the spontaneous polarization in the ferroelectric phase of dabco salts is perpendicular to the chains and to the $\text{N}\cdots\text{HN}^+$ hydrogen bonds, analogically as in KDP and other KDP-type ferroelectrics, where spontaneous polarization occurs nearly perpendicular to the $\text{OH}\cdots\text{O}$ hydrogen bonds.

The mechanism leading to the ferroelectricity in the dabco salts pertains to most materials with bistable hydrogen bonds and provides new experimental results in these areas where our understanding of the transformations of hydrogen bonds is lacking. The long-standing controversy concerns the role of the proton disordering in hydrogen bonds [6] and of other structural transformations for the KDP-type ferroelectric phase transitions [25]. The ability of protons to become disordered in the KDP-type crystals has been connected to the $\text{O}\cdots\text{O}$ distance [26]. This distance is shorter than 2.6 Å in the KDP-type structures, while the $\text{N}\cdots\text{N}$ distance in the dabco homoconjugated polycations of dabcoHClO_4 is $2.841(5)$, and $2.839(7)$ Å in dabcoHBF_4^+ at 293 K. This may imply that the H disordering is a consequence of the dynamics, rotations, and hopping of the ions much heavier than the protons. Some contribution of the coupling between H sites and the dynamics of ions was postulated for the KDP-type ferroelectrics [5,7], but it mainly concerns the thermodynamical behavior of simple molecular crystals, like ices. To our knowledge the dabco salts are the only structures where the H dynamics in hydrogen bonds is clearly coupled to the disorder of the anions. This latter feature resembles the phase transitions in ionic crystals, like NaNO_2 , where the ferroelectricity is due to the disorder of the ions only. The considerable role of the ionic disordering in the ferroelectric phase transitions of the dabco salts manifests itself by a negligible negative isotope effect of D/H exchange on T_c . We have determined that the $\text{N}\cdots\text{DN}^+$ hydrogen bonds in dabcoHClO_4 and dabcoHBF_4 are longer by about 0.02 Å. The longer D bonds provide somewhat more space for disordering the ions, which counteracts the hindered dynam-

ics of deuterons compared to protons. Thus the elevated pressures are expected to increase T_c , differently than in KDP. The mixed transformations, involving disordering of the H atoms coupled with clear disordering and displacements of the other structural units, may be characteristic of longer hydrogen bonds, like the $\text{N}\cdots\text{HN}^+$ ones. Similar molecular-scale transformations are likely to assist the functions of biological systems.

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