# Short-Range Ferroelectric Order Induced by Proton Transfer-Mediated Ionicity

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Short-range ferroelectric order is postulated to explain unusual one-dimensional dielectric response in ferroelectric 1,4-diazabicyclo[2.2.2]octane. In this pure organic salt, the polar regions are created in the antiferroelectric matrix of hydrogen-bonded polycationic chains due to the random proton transfers in $NH^+\cdots N$ hydrogen bonds. This results in a local spontaneous polarization along the nonferroelectric direction of the crystal, inconsistently with its macroscopic symmetry. The phenomenon arising from a self-discrimination of the crystal ionic structure strongly resembles the behavior of ferroelectric relaxors induced by an artificial compositional disorder.

## Introduction

Hydrogen bonds are responsible for the structure and properties of a wide group of materials, from simple dielectrics to biological systems.[1] It is well known that the hydrogen bonds are also responsible for ferroelectric properties of numerous substances. The mechanisms of generation of ferroelectric spontaneous polarization in the hydrogen-bonded substances can be very different, as for example in potassium dihydrogen phosphate (KDP) and in triglicine sulfate (TGS). Recently, we have reported a new group of $NH^+\cdots N$ hydrogen-bonded ferroelectrics.[2,3] While continuing our studies on these materials, we have observed new, unprecedented dielectric properties of 1,4-diazabicyclo[2.2.2]octane tetrafluoroborate (denoted DabcoHBF₄), described in this report. We have associated these properties with the proton transfers in the homonuclear hydrogen bonds, leading to the formation of nanodomains with ferroelectric order. The existence of such polar regions submerged in the nonpolar crystal lattice is characteristic of ferroelectric relaxors, which belong to the most intensively studied electronic materials because of their extremely high dielectric constants, as well as their piezoelectric and electrooptic properties.[4,5] Relaxor behavior discovered in mixed perovskite crystals[6] was later found in simple ionic pyrochlores,[7] irradiated and doped poly(vinylidene fluoride-trifluoroethylene) copolymers,[8] and doped charge-transfer complexes.[9] In all of these materials, the relaxor properties derive from composition- or frustration-induced disorder,[4,6] resulting in correlated polar regions.

DabcoHBF₄ belongs to the recently discovered group of $NH^+\cdots N$ hydrogen-bonded ferroelectrics[2,3] of a general formula $[C_6H_{13}N_2]^+A^-$, where $A^-$ stands for tetrahedral anions $ClO_4^-$, $BF_4^-$, or $ReO_4^-$. In these crystals, the cations form linear aggregates and the anions are located close to the protons, as shown in Figure 1. The structural mechanism leading to ferroelectricity relies on the coupling of the proton site in the $NH^+\cdots N$ hydrogen bonds to the orientations and small shifts of the anions. DabcoHBF₄ undergoes two successive first-order phase transitions at 153 and 378 K. The latter temperature is a
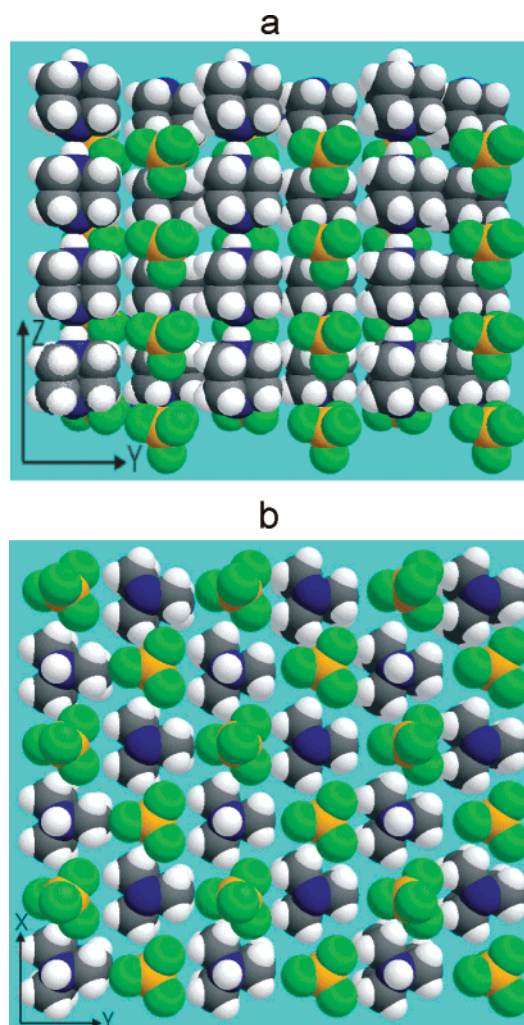
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**Figure 1.** Autostereogram[11] of the DabcoHBF₄ structure, in the ferroelectric phase II at 295 K, viewed: (a) down [100]; and (b) down [001]. Atoms are represented by the van der Waals spheres: carbon atoms, gray; hydrogens, white; nitrogens, navy blue; borons, orange; and fluorines, green.

ferroelectric Curie point between the ferroelectric structure, space group $Pm2_1n$, and the paraelectric phase, space group

*P*4/*mmm* (unit cell halved). Below 153 K, the crystal transforms to another ferroelectric orthorhombic phase, space group *Pb*2₁*a*.[10] The ferroelectric spontaneous polarization in Dabco-HBF₄ arises from ionic displacements along [010] of the orthorhombic unit cell. Below $T_C$, because of the positions of protons in the NH⁺···N bonds, the H-bonded polycationic chains are polarized in the opposite sense than their closest neighbors (see Figure 1). Thus, the ferroelectric ordering along [010], due to the ionic shifts, coexists with the antiferroelectric ordering of the chains, due to the polarization of the chains. In this pure (undoped, nonirradiated) organic salt, the relaxor-like dielectric properties, albeit much more subtle than in prototypical relaxors, have been detected exclusively in the direction of the hydrogen-bonded polycationic chains along [001]. The mechanism generating the regions with a local polarization along the nonferroelectric direction of the crystal originates from the capability of the compound to discriminate its own ionic structure by changing the proton site in a double-well potential describing the NH⁺···N hydrogen bond. The uniaxial character of the phenomenon can be understood in the terms of short-range ferroelectric and long-range antiferroelectric orders coexisting along the hydrogen-bonded chains.

## Experimental Section

For the dielectric measurements, the crystal plates of 0.2–0.5 mm thickness were cut perpendicular to [100], [010], and [001] of the DabcoHBF₄ crystals grown as described previously.[2] Complex dielectric permittivity was measured with a Hewlett-Packard 4192A impedance analyzer in the frequency range from 10 kHz to 10 MHz at the ac measuring field of 2–5 V/cm. The polarization of the crystal was derived from the pyroelectric charge measured as a function of temperature with a Keithley 6514 electrometer. A closed-cycle cooler CCC1204 (Oxford Instruments) was used for the low-temperature studies.

X-ray diffraction experiments were carried out using a KM-4 four-circle diffractometer with a CCD detector and a homemade temperature attachment applying a temperature-controlled air stream. Neutron-diffraction experiments were performed on the D9 four-circle diffractometer equipped with a furnace and a 2D-detector, at the ILL High-Flux Reactor in Grenoble.

## Results and Discussion

One of the characteristic signatures of relaxor properties is a broad peak in the temperature dependence of the real part, $\epsilon'$, of the complex dielectric constant $\epsilon = \epsilon' - i\epsilon''$, shifting to higher temperatures with increasing frequency. While in the classical relaxors it is an isotropic feature, in DabcoHBF₄ we have observed an exceptional uniaxial dielectric response. This is clearly seen in Figure 2, comparing the dielectric functions of the crystal along [001] to those along [010]. The dielectric response of the crystal along [100] is similar to that along [010], and hence has not been presented here. The two anomalies seen in Figure 2a and 2b correspond to the ferroelectric−ferroelectric phase transition at 153 K, and to the ferroelectric−paraelectric one at $T_C = 378$ K. When accounted for ionic conductivity at frequencies lower than 500 kHz, the dispersion in $\epsilon_x'$ along [100] or in $\epsilon_y'$ along [010] is negligible. The tangent of dielectric loss (tan δ), shown in the inset in Figure 2a, rises with frequency and temperature up to $T_C$, where it suddenly decreases and simultaneously its frequency dependence vanishes in the paraelectric phase. The contribution of the ferroelectric domain structure to the dielectric response of the crystal is small. While the dielectric properties along [010] and [100] are typical of a
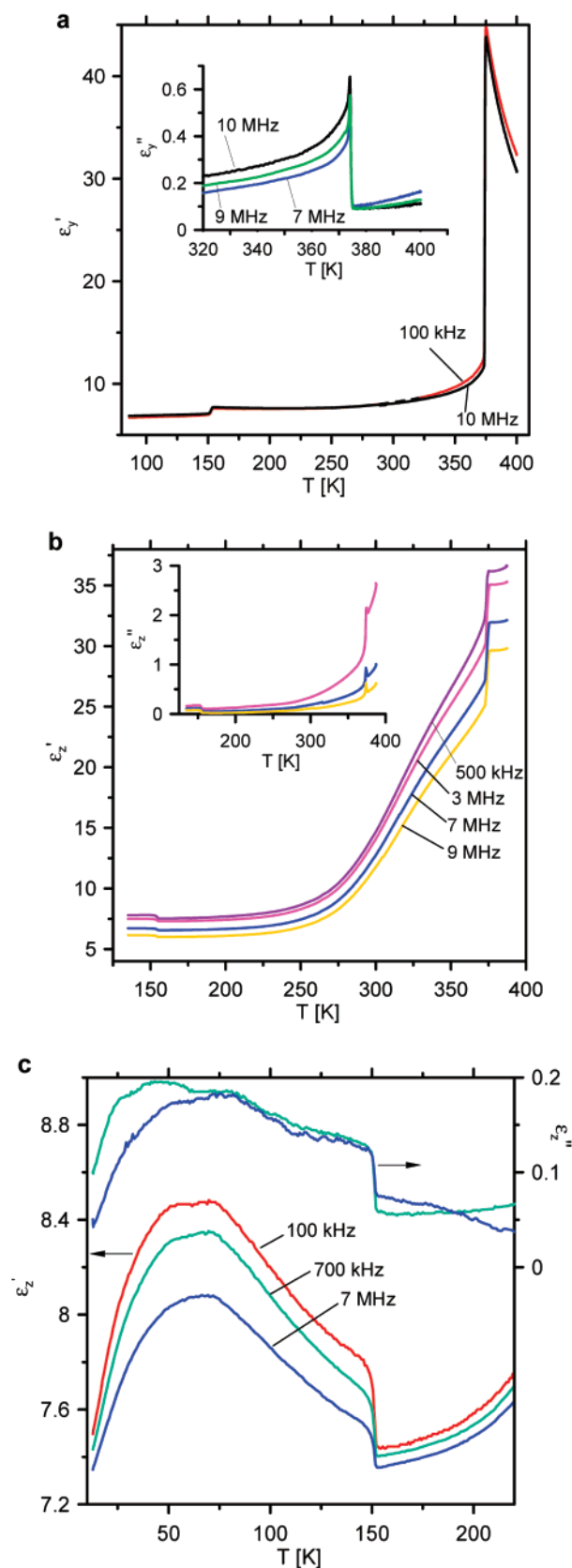


**Figure 2.** Temperature and frequency dependencies of $\epsilon'$ and tan δ for DabcoHBF₄ (a) along [010], and (b, c) along [001]. The dispersion in $\epsilon_y'(T)$ along [010] is negligible between 500 kHz and 10 MHz; therefore, only the 10 MHz curve has been plotted. At frequencies lower than 500 kHz, a weak dispersion in $\epsilon_y'(T)$ arises on approaching the paraelectric phase, as indicated by the 100 kHz curve in plot (a), which can be primarily attributed to the ionic conductivity of the crystal.

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ferroelectric crystal, these along the nonferroelectric [001] direction are surprising for several reasons. First of all, $\epsilon_z'$ rises strongly with temperature starting from about 200 K, and just below $T_C$ its magnitude exceeds almost 3-fold that of $\epsilon_y'$ (see Figure 2a and 2b). For comparison, at 370 K and at the electric field frequency of 100 kHz, the dielectric constant $\epsilon_y'$ is equal to 11.6, while $\epsilon_z' = 35.4$. At $T_C$, the magnitude of $\epsilon_z'$ increases to a relatively high value, at which it remains weakly temperature-dependent in the paraelectric phase. This behavior can be justified by the antiferroelectric−paraelectric character of the phase transition along [001]. The polycationic chains gradually lose their polarization and antiparallel arrangement, when the hopping of the anions and protons along the chains, parallel to [001], intensifies. These ionic motions cause fluctuations of the local dipole moments contributing to the dielectric response of the crystal in this direction. The increment of permittivity at $T_C$ can be attributed to a sudden increase of the frequency of the ionic stochastic motions. The temperature dependence of $\epsilon_z'$ testifies that the anionic and protonic hopping are triggered in the temperature range of the onset of the cationic reorientations[12] around 200 K.

Yet, most importantly, the frequency dispersion in both the real and the imaginary parts of the complex dielectric permittivity along [001] (Figure 2a and 2c) persists in the temperature range of both the ferroelectric phases and also in the paraelectric phase, which cannot be reconciled with the crystal symmetry. This effect, observed for all studied samples, cannot arise from the normal-state ferroelectric domains or their walls, as their polarizations are parallel to [010], and thus their components along [001] are equal zero. The likely explanation is the existence of fluctuating, polar regions, with two possible orientations of the spontaneous polarization enforced by the arrangement of the hydrogen-bonded chains. This short-range ferroelectric order exists along the [001] direction, which is perpendicular to the point group mirror- or glide-symmetry planes of the averaged structure of the bulk crystal. Thus, the dielectric response of the crystal is affected by an additional contribution, arising from the small polar regions submerged in the DabcoHBF$_4$ crystal matrix. This effect is clearly observed across all crystalline phases and down to the lowest temperatures, as shown in Figure 2b and 2c.

Indeed, in the paraelectric phase I, we have detected by single-crystal X-ray diffraction very weak intensities at the nodes of the extinguished reflections of the orthorhombic ferroelectric phase II. The presence of such superstructure reflections, significantly broadened when compared to the fundamental ones, has been also clearly evidenced by the neutron diffraction, much more susceptible to the positions of protons than X-rays. The preliminary analysis of these data indicates that the crystal is built of two constituent phases: the prevailing paraelectric tetragonal host matrix, and submerged polar domains with the unit cell commensurate with that of the ferroelectric phase. The $\theta$-widths of the additional reflections allowed the average size of the coherently diffracting regions to be estimated[13] as 50 nm. The dielectric evidence, that these domains acquire a polarization component along [001], locally breaking the mirror-/glide-plane symmetry of the crystal in all of the DabcoHBF$_4$ phases, justifies the assumption that the structure of nanodomains is analogous to that of ferroelectric DabcoHReO$_4$. Our X-ray and neutron studies of DabcoHReO$_4$ showed that this crystal is isostructural with DabcoHBF$_4$, with very similar unit-cell parameters and ionic positions in the crystal structure, but due to the sites of protons all of the NH$^+\cdots$N bonded chains are parallel.[3] Such a close resemblance of the structures implies that their mutual
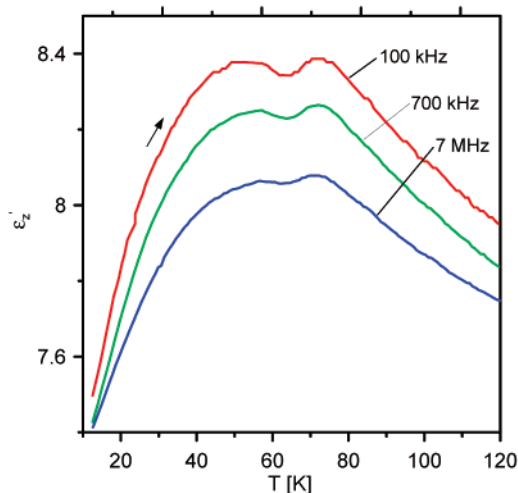


**Figure 3.** Temperature and frequency dependencies of the real part of electric permittivity measured along [001], on heating the Dabco-HBF$_4$ crystal.

interconversions are very likely. The protonic correlations analogous to those in the DabcoHReO$_4$ would result in the short-range ferroelectric order along [001], inconsistent with the macroscopic symmetry of the DabcoHBF$_4$ crystal. The temperature dependence of the intensities of the superstructure reflections above $T_C$ allowed the Burns temperature[14] to be roughly estimated as 470 K. The Burns temperature is interpreted as the temperature of the short-range polar order nucleation, usually several hundred degrees above the temperature of the ralaxor peak in $\epsilon'(T)$.

The dispersion in $\epsilon'$ and tan $\delta$ indicates a inhomogeneous distribution of the domain sizes and their dynamical fluctuations. The slowing down of the dynamic processes at low temperatures, manifested by the broad frequency-dependent peak in dielectric permittivity around 60 K, and frequency/temperature dependence of the dielectric loss, shown in Figure 2c, are characteristic of a relaxor/glasslike behavior.[4] It should be stressed that we have not observed any trace of this effect for the measuring electric field parallel to the [100] or [010] directions of the crystal. The relatively weak frequency dependence of the $\epsilon'(T)$ maximum may be a consequence of the 1-D character of the phenomenon and its complex nature. The complex character of the dielectric response of the crystal can be inferred from the temperature dependence of the dielectric losses observed below 150 K and from the shape of the $\epsilon'(T)$ maxima in Figure 2c. More clear evidence for this conclusion has been provided by the dielectric measurements performed while heating the samples. The temperature-history dependence of the dielectric permittivity is one of the characteristic features of the ferroelectric relaxors. As shown in Figure 3, in the heating run, the broad peaks in the $\epsilon'(T)$ dependences exhibit clearly two submaxima, which can arise from two different dielectric contributions. Because of the overlapping effect and possible different frequency/temperature behavior of these contributions, it was difficult to determine the temperature dependences of the relaxation times and their accordance with the Vogel−Fulcher law, one of the basic characteristics of the relaxors.[6] It is also noteworthly that we deal with a 1-D system, which in fact, in such a pure form, has never been studied before. Therefore, its certain properties can be manifested quite differently from those of their 3-D counterparts. On the other hand, even among the classical relaxors, a very weak frequency dependence of the $\epsilon'(T)$ maxima has been encountered, for example, in the highly ordered Pb(Sc$_{0.5}$Nb$_{0.5}$)$_3$.[15]
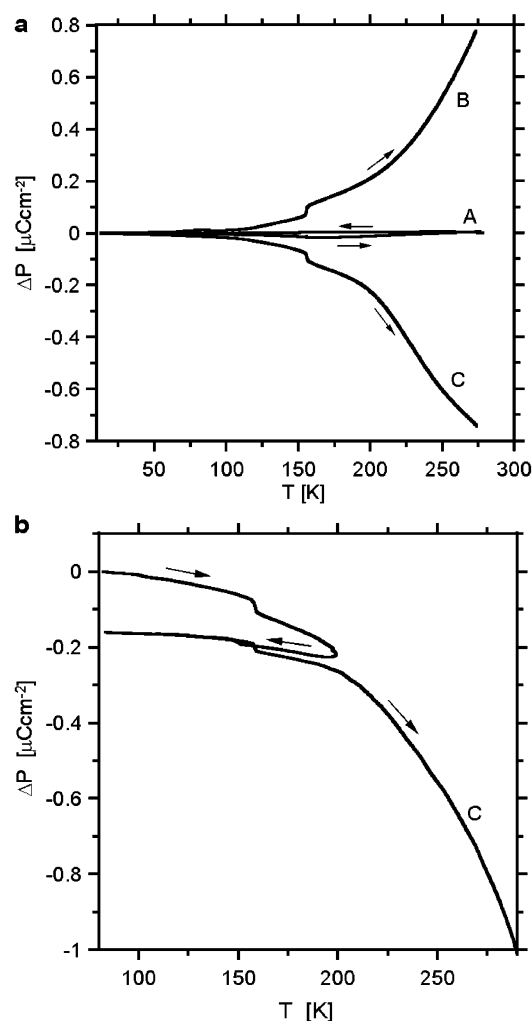
**Figure 4.** Temperature evolution of the polarization along [001] for various electrical (a) and thermal (b) histories, measured for the unpoled (curve A), and field-cooled crystals at the dc bias fields of +9.3 kV/cm (curve B) and −9.3 kV/cm (curve C). The polarization changes $\Delta P$ refer to the starting points at 12 K (a) and 80 K (b).



**Figure 5.** The four-member interval of the NH$^+\cdots$N hydrogen-bonded chain consisting of the two oppositely polarized monocations, one dication, and one neutral molecule.



**Figure 6.** A schematic diagram of the DabcoHBF$_4$ structure with the cations colored yellow, neutral molecules green, and dications red; the proton sites are indicated with plus signs. Different orientations of the triangles representing anions illustrate their coupling to the H$^+$-sites in their surroundings. This two-dimensional scheme approximately corresponds to the section along the (110) plane of the DabcoHBF$_4$ structure (cf. Figure 1a and 1b), which contains the antiferroelectrically ordered H-bonded chains. Two left chains are undisturbed, while four defects (two neutral molecules and two dications) enclose a polar nanoregion extending from the second chain to one chain behind the drawing to the right, marked by the solid line. The formation of this nanoregion would require only six H-transfers and in a real DabcoHBF$_4$ structure would have dimensions of about 4 × 4 × 1 nm$^3$.

Another important property of a relaxor system is a field-induced long-range ferroelectric order contributing to a macroscopic polarization.[16] The nanodomains can be aligned by subjecting the sample to the sufficiently high electric field, and then their arrangement can be frozen in low temperatures. The temperature behavior of polarization along [001] in DabcoHBF$_4$ depends on the electric-field history of the sample, as can be seen in Figure 4a. In the field-cooled cycles, the dc bias of ±9.3 kV/cm was applied to the sample at 320 K and then removed after cooling to 12 K. It is evident that the polarization reversible by dc electric field can be induced in DabcoHBF$_4$ along the polycationic hydrogen-bonded chains, which would be symmetry-forbidden for the nondefected, ideal crystal structure. The depolarization of the poled crystal proceeds progressively with increasing temperature, with the only discontinuity observed at 153 K due to the phase transition involving transformations of the hydrogen bonds.[10] After the sample was heated to ca. 200 K and cooled again (Figure 4b), the polarization did not return to its previous low-temperature value, as would be expected for a normal ferroelectric, but resembled the behavior of typical ferroelectric relaxors.[16] The crystal cooled to 12 K could not be poled by the application of the electric field because the system was frozen in a glasslike state. Thus, except for the local symmetry breaking and the local
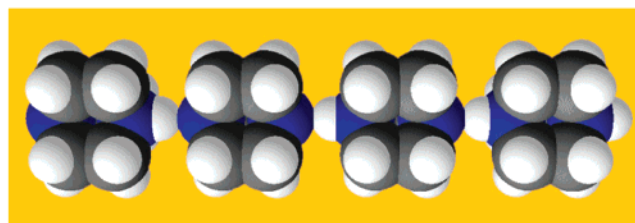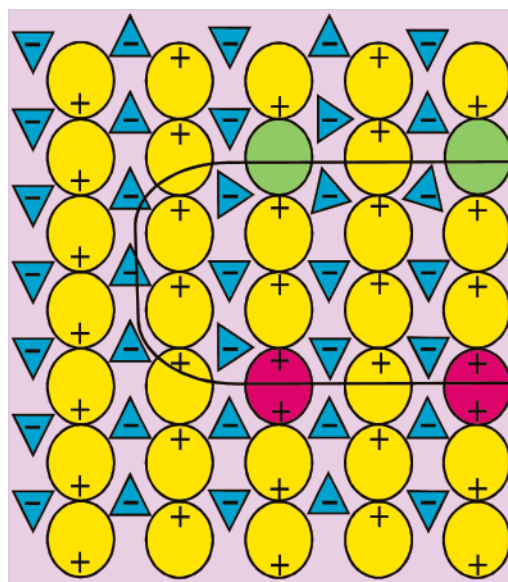
polarization inconsistent with the macroscopic symmetry of the crystal, also the temperature behavior of the polarization induced along [001] testifies to the relaxor properties of DabcoHBF$_4$.

The short-range ferroelectric order in DabcoHBF$_4$ can be explained by the structural and chemical features of the crystal:[17] (i) the DabcoH$^+$ cations can easily transform into neutral Dabco molecules or into dications $^+$HDabcoH$^+$, (ii) the NH$^+\cdots$N hydrogen bonds are relatively long and the proton transfer requires thermal longitudinal-type excitations along the chains; and (iii) the proton transfers are coupled by electrostatic interactions to the orientations of the near anions.[18] Thus, the events of the proton jumping coincide with the NH$^+\cdots$N hydrogen bond being squeezed and the surrounding anions reoriented. Because of similar energies of the neutral molecule, cation, and dication, and no direct coupling between the anionic sites along the chains, these different forms can coexist within one chain and in the crystal, as illustrated in Figure 5. The elevated temperatures intensify the rotations of the bulky tetrahedral anions and vibrations of the DabcoH$^+$ cations bumping against their neighbors in the chains. The proton transfer is likely to occur when the NH$^+\cdots$N hydrogen bond is

squeezed and the momentary orientation of the close anions favors the opposite site of $H^+$. Such events result in a conjunction of structural defects generating random fields, which in turn induce short-range ferroelectric ordering. Four different types of the proton transfers are possible in the Dabco monosalts: (i) the $H^+$ transfer between the monocations creates a new domain along the chain; (ii) the $H^+$ transfer from a monocation to a neutral molecule shifts the domain wall, in the opposite sense than the $H^+$ transfer; (iii) the $H^+$ transfer from a dication to a monocation moves the domain wall in the direction of the transfer; and (iv) the $H^+$ transfer from a dication to a neutral molecule annihilates the defects (Figure 6). Thus, the $H^+$ transfers may reverse the polarization of the chains in the manner of solitonic waves, typical of the hydrogen-bonded aggregates,[19] while the reorientations of the anions, coupled to the $H^+$ locations, propagate the domain walls along [100] or [010]. Thus, the fluctuations of the protons in the $NH^+\cdots N$ hydrogen bonds lead to the formation of the chain intervals polarized in the opposite direction than required by the crystal symmetry (see Figures 1 and 6). The formation of such a "reversed" chain interval results in a nanoregion, composed of the interval itself and its four closest neighboring chains, all polarized in the same sense along [001]. Thus, one H-transfer would form a polarized domain 5.3 Å long down [001] and 10 Å along [100] and [010], and the formation of the approximately $1.5 \times 1.5 \times 1.0$ nm$^3$ domain polarized along [001] would require two H-transfers only. A domain formed by six H-transfers has been schematically illustrated in Figure 6.

## Conclusions

The relaxor-like properties have been observed for a new type of organic ferroelectric crystals. DabcoHBF$_4$ is different from traditional relaxors, as it is a pure substance where the defects and nanodomains arise from structural self-discrimination induced by proton transfers. Thus, the chemical substitution and lattice defects, leading to the disorder and polar nanoregions in traditional relaxors, can be replaced with a thermochemical process of the valence and ionicity differentiation. It is plausible that the relaxor properties are much more common than has been assumed, and they may play an important role in systems where they have not been even remotely considered. For example, in the DabcoH$^+$:TCNQ$^{-\delta}$ and DabcoD$^+$:TCNQ$^{-\delta}$ complexes (TCNQ stands for 7,7,8,8-tetracyano-*p*-quinodimethane), anomalous dielectric properties, apparently at the absence of structural phase transition, were reported most recently.[20] Such anomalous dielectric behavior independent of phase transition may be an indication of possible short-range

polar order, although any definite conclusions require further detailed studies which would include the frequency dependences of the dielectric functions. We believe that analogous effects of self-discrimination are also induced by electron transfers, which along with the proton transfers are the most frequent chemical processes in nature. Indeed, recent results of low-temperature dielectric response of a charge-transfer complex, 2,6-dimethyltetrathiafulvalene-*p*-chloranil,[21] strongly suggest such a possibility. In light of our studies, the classical relaxors can be contemplated as extreme representatives of a broader group of functional materials, in which the short-range polar order leads to anomalous physical properties.

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