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Room-temperature ferroelectricity in diisopropylammonium bromide[†]

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A room-temperature ferroelectric, diisopropylammonium bromide (**DPB**), with dielectric constant $\varepsilon \approx$ 12 000 and a clear hysteresis loop at T_c = 425 K is reported. At 417 K DPB undergoes the irreversible phase

transition from nonpolar orthorhombic $P2_12_12_1$ to the ferroelectric monoclinic phase ($P2_1$) and

subsequently, at 425 K, to the paraelectric prototype phase $(P2_1/m)$. The molecular mechanism of the

paraelectric-ferroelectric transition is ascribed to the 'order-disorder' behaviour of the diisopropylammo-

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It is widely known that ferroelectric crystals are important basic materials for technological applications in capacitors and in piezoelectric, pyroelectric, and electrooptical devices.¹ Their nonlinear characteristics were found to be very useful, for example, in optical second-harmonic generators and other nonlinear optical devices. Much of the attention in this field has been focused on developing ferroelectric inorganic compounds such as KH₂PO₄ (KDP),² perovskite-type compounds (BaTiO₃) and LiNbO₃.³ Over the past two decades one can observe a great deal of progress in the synthesis of acentric inorganic-organic hybrids which may be characterized by polar/ferroelectric packing arrangements.⁴ Recently, the molecule-based ferroelectric, simple alkylammonium organic salt diisopropylammonium chloride (abbreviated as DPC) has been synthesized and characterized.⁵ It undergoes a reversible phase transition (PT) from a high temperature paraelectric phase (2/m) to a low temperature ferroelectric phase (2) at *ca*. 440 K. DPC exhibits one of the largest values of spontaneous polarization, $P_s = 8.9 \ \mu C \ cm^{-2}$, within the molecule-based ferroelectrics, thus this group of compounds may be very promising from the point of view of practical applications. Initially, the closely related bromine analog, diisopropylammonium bromide (DPB), had seemed to be a good candidate to exhibit polar properties in the room temperature phase, however, further research indicated that the phase situation and a rich polymorphism of DPB appeared to be quite

nium cations.

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complicated. Two polymorphs of DPB are known at room temperature: monoclinic $P2_1^6$ and orthorhombic $P2_12_1^2$.⁷ The crystal structure of the latter polymorph (abbreviated in this paper as O) was presented as a private communications by G. J. Reiss.⁷ The monoclinic polymorph was obtained accidentally during the reaction of BrRe(CO)₅ and lithium diisopropylamide.⁶ It undergoes an irreversible PT below room temperature to the monoclinic phase $(P2_1/n)$.⁸ In turn, **O** presented in this paper was obtained during the reaction of HBr and diisopropylamine and did not disclose any PTs below room temperature. Our present studies has revealed that O undergoes a polymorphic irreversible structural PT to a polar monoclinic phase (M(II)) at 417 K that is associated with the substantial rearrangement of the crystal packing. This new phase is stable from 90 to 425 K and at 425 K transforms to paraelectric phase $P2_1/m$.

It should be emphasized that the high Curie temperature $(T_{\rm c})$ exceeding room temperature (RT) in ferroelectric materials is a very important parameter for ongoing design of all-organic electronics.

The fact that ionic organic compound DPB exhibits strong ferroelectricity suggests that other simple organic salts may have comparable ferroelectric properties to those encountered in inorganic ferroelectrics. Hence, this discovery is surely expected to encourage the development of ferroelectric organic materials.

The main purpose of the present study is to characterize the ferroelectric properties in DPB based on X-ray diffraction and dielectric measurements over a wide temperature range.

Colorless crystals of O were prepared by reaction of diisopropylamine with 48% aqueous HBr (molar ratio 1:1). After a few days, transparent solids were formed by a slow evaporation from the colorless solution. The obtained polycrystalline material was twice recrystallized in a mixture of methanol and ethanol (1:1) at decreased temperature (about 263 K). The single crystals of DPB were grown at the constant

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temperature of 263 K. Chemical analysis gave the following mass percentages (values in brackets are theoretical): C, 39.32 \pm 0.1 (39.57); N, 7.75 \pm 0.1 (7.69); H 8.61 \pm 0.05 (8.86). The calorimetric measurements (DSC) of **O** revealed a heat anomaly at *ca.* 417 K indicating an irreversible PT (O \rightarrow M(II)) occurring in this system (scan 1 in Fig. 1). Further heating of the sample disclosed sequential reversible PT at 425 K which is observable during successive heating and cooling scans (3, 4 in Fig. 1).

On the basis of the thermal characteristic (DSC) it is difficult to state unequivocally the character of the hightemperature PT (M(II) \leftrightarrow M(I)). The heat anomaly visible as a well-shaped peak may suggest a first order PT. Nevertheless, neither the temperature hysteresis nor the phase front close to T_c was seen during the observations under a polarizing microscope, thus the PT at 425 K seems to be close to the second order type. The compound remained stable up to 470 K (Fig. S1, ESI†) and above this temperature a continuous decomposition took place. Furthermore, the calorimetric measurements excluded the PT below room temperature (90– 300 K) which is mentioned by Haberecht *et al.*⁸ in the monoclinic polymorph $P2_1$.

The crystal structure of as-grown **DPB**^{\ddagger} is isomorphic to **DPC**.⁹ The counterions and the Br⁻ anion interact *via* two hydrogen bonds and form one-dimensional chains propagating in the *a*-axis.¹⁰

Above 417 K the crystal structure transforms to monoclinic M(II) during a non-reversible phase transition.¹⁰ The new polar phase is stabilized down to 90 K after cooling. The second polymorph is isomorphic to the crystal of **DPB** obtained as reported in ref. 6. The key difference between polymorph **O** and M(II) is the mutual orientation of the neighboring hydrogen bonded chains. The transformation between the polymorphs requires reconstruction of the cationic substruc-



Fig. 1 (a) DSC curves for the **DPB** compound upon cooling and heating runs (2 K min⁻¹, m = 11.6 mg); (b) phase identification based on X-ray diffraction measurements.

 \ddagger Crystal data, experimental details and structure refinement results for DPB are in the ESI.†

ture. In **O** the cations are arranged in such a way that dihedral angle between two neighbouring diisopropylammonium cations is equal to 85.7° , whereas after the transition similar cations are oriented parallel to each other.

The new arrangement is induced by reorientation of all the counterions along the internal long axis by approx. 90° and rotation along the [100] orthorhombic direction. Fig. 2(a) and (b) show the H-bonded chains in polymorph **O** and **M**(**I**), respectively. Phase transition changes the arrangement of H-bonded patterns.

Reorientation of counterions changes the packing of the chains and induces deformation of the anionic substructure. After the transition, the chains elongate and the distance between two Br⁻ ions in a chain increases from 5.42 Å to 5.52 Å. At the same time there is a contraction of the crystal in the direction perpendicular to the chains and mutual Brdistances decrease from 7.97 Å to 7.85 Å (see Fig. 3). Consequently, the crystal volume changes *ca.* $\sim 0.5\%$, however the total displacement of Br⁻ ions from initial positions that is given by the square root of the sum of the square of all atomic displacements is significant (0.17 Å). It is worth noting that both structures are described at the same room temperature, so the thermal expansion does not affect the distances. This rather complex rearrangement of the crystal structure has an insignificant impact on the hydrogen bonds which have similar strength and geometry in both polymorphs (see Table 1). It means that mainly steric effects are responsible for the transformation.

Polymorph M(II) experiences phase transition to the structurally disordered M(I) phase at 425 K.¹⁰ Disopropylammonium cations adopt two equivalent, oppositely directed positions. Such an arrangement introduces the symmetry centre and the polar properties vanish. A similar microscopic model of the high temperature transformation has been recently proposed for isomorphic DPC crystals,⁵ although the interpretation of the diffraction data has been intuitive rather than based on the results of calculations.



Fig. 2 H-bonded chains in (a) **O** and (b) **M(II)**, T = 295 K. Phase transition changes the orientation of H-bonded patterns whereas the geometry as well as the strength of H-bonds is similar in both forms. The dihedral angle between two neighbouring C–C–N–C–C planes in **O** is marked. In **M(II)** the same angle is equal to 0°. Hydrogen atoms not involved in H-bonds are omitted for clarity.



Fig. 3 Crystal packing of (a) **O** and (b) **M(II)** as seen along the H-bonded chains, T = 295 K. The planes on which the hydrogen bonds are located are parallel in **M(II)**, whereas in **O** they are rotated about 22° and 24° to each other. The unit cell of polymorph **O** may be transformed to **M(II)** using (0 0.5 -0.5, -1 0 0, 0 0.5 0.5) rotation matrix and (0.25 0 0.25) translation vector.

Model of disorder in **DPB** appears to be more complex than those proposed for the chlorine analog, but at least it does not change the conformation of the counterion and gives good reliability factors. Fig. 4(a) shows two equivalent orientations of diisopropylammonium counterions in paraelectric, M(i), phase. Both are 50% occupied and related to the mirror plane. It seems that a maximum of two carbon atoms lie on the mirror plane and the whole cation may rotate along its long axis.

Compared to the low temperature phase, the coordinates of the counterion change only slightly; the displacement of N atom from its initial position is very weak and equals to 0.02 Å with δy equal to -0.002 Å. In both phases the dihedral angle formed between the (010) plane and the plane on which C–C– N–C–C atoms are located equals to 44.5°. The symmetry centre that appears in the parent phase allows for the antiparallel arrangement of dipoles and the resultant dipole moment vanishes to zero. Fig. 4(b) presents the unit cells in both monoclinic phases.



Fig. 4 (a) Model for the disorder of the disopropylammonium counterions in the paraelectric P_{2_1}/m phase. The site occupation factors equal 0.5 for both available positions. The mirror plane introduces two equivalent positions, (b) position of the counterions in the non-polar **M(I)** and polar **M(II)** phases.

The transition to centrosymmetric **M**(I) phase has a low impact on positions of Br⁻ anions. Distortion amplitude for Br⁻ is equal to 0.055(1) Å when comparing atomic positions at 295 and 435 K. Additionally displacement of Br⁻ ions in the polar *b* direction equals only 0.006(1) Å.

The temperature dependence of the real part of the complex dielectric permittivity of the **DPB** was measured upon heating and cooling at frequencies ranging between 20 Hz and 2 MHz (Fig. 5(a)). The polymorphic irreversible PT at 417 K is accompanied by a significant increase in the dielectric constant (see inset of Fig. 5(a)), whereas the PT at 425 K manifests itself as a characteristically strong peak in the dielectric permittivity curve. The maximum value of the permittivity, $\varepsilon_{b(max)}$, reaches ~12 000 at the T_c .

The behavior of the electric permittivity as a function of the temperature suggests that this PT has a strong ferroelectric character. Our preliminary dielectric dispersion studies between 20 Hz and 1 MHz reveal that the fundamental relaxation process over the **M**(**I**) phase takes place in the kilohertz frequency region. The Curie–Weiss law ($\varepsilon = \varepsilon_0 + C_{+/-}$ / $(T - T_0)$ is well obeyed close to the T_c (see Fig. S5, ESI†). C_+ was estimated to be 5 × 10³ K, which is comparable with the values encountered in typical 'order–disorder' ferroelectrics (*e.g.*, for TGS $C_+ = 3.2 \times 10^3$ K) and the ratio $C_+/C_- = 6$ is characteristic of first-order ferroelectric transitions.

To check the existence of the spontaneous polarization, which could be reversible in an external electric field, we performed hysteresis loop measurements. The positive result of this measurement is a crucial evidence of the ferroelectric character of the M(II) phase (Fig. 5(b)).

Table 1 Hydrogen bonds in polymorphs O, M(II) and M(I) ^a					
Polymorph, T (K)	D-H···A	D-H (Å)	H···A (Å)	D…A (Å)	D–H···A (°)
O , 295	N1-H1A…Br1	0.90(3)	2.46(3)	3.353(2)	178(2)
0 [′]	N1–H1B…Br1 ⁱ	0.85(2)	2.49(3)	3.334(2)	172(2)
М(п), 295	N1-H1A····Br1	0.85(3)	2.51(4)	3.346(3)	168(3)
MÎ	N1-1B…Br1 ⁱⁱ	0.91(4)	2.43(4)	3.335(3)	173(3)
M (I), 435	N1-H1A····Br1	0.89	2.47	3.360(3)	177.2
M(I)	N1-1B…Br1 ⁱⁱ	0.89	2.51	3.393(3)	178.1

^{*a*} Symmetry code(s): $^{i} -x + 1$, -y + 1, -z + 1; $^{ii} -x + 1$, y + 1/2, -z + 1.



Fig. 5 (a) Temperature dependence of the real part of the complex electric permittivity measured along the *b*-direction (on cooling). The inset in (a) presents the results during first heating (irreversible PT at 417 K); (b) hysteresis loops observed at various temperatures close to T_c (sample thickness = 0.6 mm, f = 20 Hz).

The obtained value of the spontaneous polarization was found to be *ca.* 1.5×10^{-3} C m⁻² at 424 (1 K below T_c). Because of the strong increase of the coercive field ($E_c > 10$ kV cm⁻¹) we were not able to observe the electric hysteresis loop for ($T_c - T$) > 1.5 K. The value of P_s at 424 K is far from the expected saturated value of P_s , which in the case of the chlorine analog is close to $9 \times 10^{-2} \mu$ C cm⁻² (*ca.* 20 K below T_c). Taking into account the fact that dielectric constant in **DPB** is distinctly larger than that in **DPC** the saturated spontaneous polarization should be comparable in both crystals.

In general, the molecular mechanism of paraelectricferroelectric transition seems to be common for both diisopropylammonium analogs, DPC and DPB. The dynamics of the organic cations contribute mainly to the 'orderdisorder' mechanism of this transition. Nevertheless, a substantial difference in the disorder of the organic cations of both analogs should be emphasized. In the case of DPC, in the paraelectric phase four carbon atoms are placed on the mirror plane, whereas in DPB only two C atoms occupy this plane. The molecular mechanism of PT proposed in this paper seems to justify the fact that reorientational motion of diisopropylammonium cations should take place around its center of gravity. The thermodynamic properties of the ferroelectric transition in DPC and DPB only partially reflect the isomorphism of these crystals. The entropy transitions are comparable, being of the order of 1.14 (DPC) and 1.43 (DPB) J $mol^{-1} K^{-1}$, however they are significantly smaller than they are predicted theoretically for a simple two-site positions model ($\Delta S = R \ln 2 (= 5.76 \text{ J mol}^{-1} \text{ K}^{-1})$), which suggests that a 'displacive' contribution to the molecular mechanism of PT should be also considered. Nevertheless, the preliminary dielectric dispersion analysis, especially the presence of the relaxation process in the radio-frequency region, supports the 'order-disorder' type ferroelectric. Because the 'order disorder' contribution seems to be the main origin of the spontaneous polarization (P_s), thus the arrangement of two diisopropylammonium cations in the unit cell is crucial in the explanation of the ferroelectric properties and especially the P_s value, which is relatively large in this type of crystal.

In summary, the present work has successfully demonstrated that very simple (1:1) alkylammonium organic salt, diisopropylamine bromide (**DPB**), exhibits ferroelectric properties at room temperature and seems to be a very promising candidate for applications.

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- 10 (*a*) Crystal data for **DPB-O**: T = 298 K, $C_6H_{16}BrN$, $M_r = 182.11$, orthorhombic $P_{2_12_12_1}$, a = 8.0233(1) Å, b = 8.3080(2) Å, c = 13.5868(3) Å, Z = 4, V = 905.66(3) Å³, $D_{calc} = 1.336$ g cm⁻³, $\mu = 0.644$ mm⁻¹, 8913 reflections measured, 1711 unique ($R_{int} = 0.0206$), 85 parameters, 2 restraints. The final $R(F^2 > 2\sigma(F^2))$, $wR(F^2)$, *S* values were 0.0187, 0.0446 and 1.06, respectively. Asymmetric unit contains one diisopropylammonium counterion and Br⁻ ion. All atoms adopt general positions with C_1 site symmetry; (*b*) Crystal data for **DPB-M**(\mathbf{I}): T = 298 K, $C_6H_{16}BrN$, $M_r = 182.11$,

monoclinic *P*2₁, *a* = 7.8586(5) Å, *b* = 8.0818(5) Å, *c* = 7.8918(5) Å, β = 116.290(4), *Z* = 2, *V* = 449.38(5) Å³, *D*_{calc} = 1.346 g cm⁻³, μ = 4.944 mm⁻¹, 4536 reflections measured, 1533 unique (*R*_{int} = 0.0275), 84 parameters, 3 restraints. The final *R*(*F*² > 2 σ (*F*²)), *wR*(*F*²), *S* values were 0.0230, 0.0453 and 0.898, respectively. Asymmetric unit contains one diisopropylammonium counterion and Br⁻ ion. All atoms adopt general positions; (*c*) Crystal data for **DPB**-**M**(**i**): *T* = 435 K, C₆H₁₆BrN, *M*_r = 182.11, monoclinic *P*2₁/*m*, *a* = 7.9465(14) Å, *b* = 8.1567(14) Å, *c* = 7.9743(14) Å, β =

116.379(11), Z = 2, V = 463.05(14) Å³, $D_{\text{calc}} = 1.306$ g cm⁻³, $\mu = 2.634$ mm⁻¹, 4620 reflections measured, 944 unique ($R_{\text{int}} = 0.0429$), 59 parameters, 5 restraints. The final $R(F^2 > 2\sigma(F^2))$, $wR(F^2)$, S values were 0.0444, 0.1459 and 1.124, respectively. Asymmetric unit contains one diisopropylammonium counterion and Br⁻ ion. Bromine atoms as well as two carbons from the counterion lie on the mirror plane (C_s site symmetry), whereas remaining atoms adopt general positions.