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Crystal structure, phase transition and conductivity study of two new organic – inorganic hybrids: $[(CH_2)_7(NH_3)_2]X_2$, X = Cl/Br



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ABSTRACT

Two hybrids 1,7-heptanediammonium di-halide, $[(C_7H_{20}N_2]X_2, X = Cl/Br crystallize in monoclinic P2_1/c, Z = 4. [(C_7H_{20}N_2]Cl_2: a = 4.7838 (2) Å, b = 16.9879 (8) Å, c = 13.9476 (8) Å, \beta = 97.773 (2)°, V = 1203.58(10) Å^3, D = 1.137 g/cm^3, \lambda = 0.71073 Å, R = 0.052 for 1055 reflections with I > 2\sigma(I), T = 298(2) K. [(C_7H_{20}N_2]Br_2: a = 4.7952 (10) Å, b = 16.9740 (5) Å, c = 13.9281 (5) Å, \beta = 97.793 (2)°, V = 1203.83(6) Å^3, D = 1.612 g/cm^3, \lambda = 0.71073 Å, R = 0.03 for 1959 reflections with I > 2\sigma(I) T = 298(2) K. Asymmetric unit cell of [(C_7H_{20}N_2]X_2,X = Cl/Br, each consist of one heptane-1,7-diammonium cation and two halide anions. The organic hydrocarbon layers pack in a stacked herringbone manner, hydrogen bonded to the halide ions. Lattice potential energy is 1568.59 kJ/mol and 1560.78 kJ/mol, and cation molar volumes are 0.295 nm³ and 0.300 nm³ for chloride and bromide respectively. DTA confirmed chain melting transitions for both hybrids below T ~ 340 K. Dielectric and ac conductivity measurements (290 < T K < 410; 0.080 < f kHz<100) indicated higher conductivity and activation energy of bromide for T > 340 K. Cross over from Jonscher's universal dielectric response at low temperatures T < 340 K to super-linear power law for T > 340 K is observed. At high temperatures halide ion hopping in accordance with the jump relaxation model prevails.$

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1. Introduction

Recently, organic-Inorganic hybrid (OI) materials have attracted much attention due to their interesting structure, optical and electrical properties [1]. The class of hybrid materials is very large showing different structures and properties that promise wide applications in different fields. Alkylene-diammonium dihalide hybrids, $[(CH_2)_n(NH_3)_2]X_2$; n = 2, ...6 and X = Cl/Br show several interesting structural phase transitions, they mimic lipid bilayer, being solids they provide an excellent model for the study of transport in cell membranes [2]. Besides these hybrids are precursor ligands in transition metal complexes [3] and have structure-directing properties in the synthesis of a number of nanoparticles [4,5]. Room temperature crystal structure determination of the chlorides and bromides where n = 2, 3, 4, 5 and 6 [6–16] crystallize in monoclinic system with space group $P2_1/c$ except for bromide with n = 2 (space group C2/m), at 100 K [8] and the chloride where n = 5 which is orthorhombic with space group

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Pbam [12]. To the best of our knowledge, no structure analysis or physical properties concerning n = 7 hybrids were reported. This is most likely due to difficulty in growing single crystal of anhydrous 1,7 -heptanediammonium hybrids. It is worth noting that for n = 8and 10 only hydrated hybrids were obtained [17]. In this article we report synthesis, characterization, single crystal structure analysis, phase transitions and conductivity study of chloride and bromide hybrids where n = 7. Differential thermal scanning (290 K < T < 580 K) and impedance spectroscopy (290 K < T < 410 K) in the frequency range 100 Hz - 100 kHz were used to study the phase transitions and electric transport properties of the two samples 1,7-heptane-diammonium crystals [(CH₂)₇(NH₃)₂]X₂, X = Cl/Br, henceforth C7C and C7B.

2. Experimental

Samples were synthesized by adding slight excess 30% HCl/HBr to 1,7- diaminoheptane. The resulting solution is heated to 70 °C for 1 h. Slow cooling to room temperature yields colorless solids. The solids were washed with a 1:1 solution of ethanol and methylene chloride. Samples were re-dissolved in ethanol and re-crystallized twice. Colorless prismatic and needle crystals were grown from

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ethanol solution kept in vacuum desiccator for 6 months, for chloride and bromide hybrids respectively. Chemical analysis and ir absorption spectrum (in the range 400 cm⁻¹–4000 cm⁻¹) were carried out at the micro analysis center at university of Cairo.

The elemental analysis showed the percent of carbon = 39.50% (40.46%), 29.30% (28.78%) and hydrogen = 10.12% (9.701%), 6.50% (6.902%) for C7Cl and C7Br respectively; theoretical values are given in brackets.

The IR spectrum was obtained using FTIR 1650 Perkin Elmer spectrometer. The IR and the chemical analysis results confirmed formation of the two samples with chemical formula $[(CH_2)_7(NH_3)_2] X_2, X = Cl/Br.$

Differential thermal scanning (DSC) measurements were carried out on a Shimadzu thermal scanner model DSC-50 at 10 °C/min. Powdered crystals weighing 2.5 mg were used. Measurements were performed in a flow of dry nitrogen gas at a rate of 50 ml/min. The data were calibrated with the melting transition of Indium at 157 °C.

X-ray crystallographic data were collected on Enraf-Nonius 590 Kappa CCD single crystal diffractometer with graphite monochromator using MoK α ($\lambda = 0.71073$ Å). The intensities were collected at room temperature using φ - ω -scan mode. The cell refinement and data reduction were carried out using Denzo and Scalepak programs [18]. The crystal structure was solved by the direct method using SIR92 program [19] which revealed the positions of all non-hydrogen atoms and refined by the full matrix least square refinement based on F² using maXus package [20]. The temperature factors of all non-hydrogen atoms were introduced as a riding model with C–H = 0.96 and refined isotropically. Molecular graphics were prepared using ORTEP Program [21].

Ac conductivity is measured using computer controlled SR-830 lock-In amplifier. A home built cryostat was used. Temperature was measured using a copper constantan thermocouple. Well ground crystallites were pressed in the form of a disc 1.0 cm in diameter and 1.2 mm thickness under a pressure of 2.4 kPa. The surfaces were coated with Ag paste to ensure good electrical contacts. The sample chamber was evacuated for 12 h prior to measurements to ensure moisture free atmosphere. Several virgin samples were measured to ensure reproducibility of results.

3. Results and discussion

3.1. Crystal structure

The two isomorphous hybrids crystallize in monoclinic $P_{2_1/c}$ with 4 molecules/unit cell each. Lattice spacing are a = 4.7838 (2) Å, 4.79520 (10) Å, b = 16.9879 (8) Å, 16.9740 (5) Å, c = 13.9476 (8) Å, 13.9281 (5) Å, β = 97.773 (2)°, 97.793(2)°, V = 1203.58 (10) Å³, 1203.83 (10) Å³ for chloride and bromide respectively as listed in Table 1 along with data collection parameters and refinement. Table 2 lists the fractional atomic coordinates and equivalent isotropic thermal parameters. Table 3 lists the anisotropic displacement parameters (Å²). The selected bond length and bond angles and dihedral angles are listed in Table 4. Table 5 lists the hydrogen bonds geometry of the two samples.

As can be seen from Table 4, for C7C the chains deviate slightly from planarity. It is expected that as the temperature increases conformation changes will take place, which would lead to phase transitions.

Fig. 1a is an ORTEP view of the atoms where X = CI/Br and Fig. 1b shows ORTEP view of molecular arrangement in the unit cell of C7B. The cation exists in an ideal fully extended conformation in layers and lies on a mirror plane. The chains extend in a zigzag structure of seven carbon atoms with two NH₃ cations attached at chain ends

X-ray data collection parameters and refinement, of C7C and C7B at 298 K.

	a. (C7C)	b. (C7B)
Formula	C7H20N2Cl2	$C_7H_{20}N_2Br_2$
M _r	207.784	292.059
Space group	Monoclinic $P2_1/c$	Monoclinic $P2_1/c$
a	4.7838 (2)Å	4.79520 (10)Å
В	16.9879 (8)Å	16.9740 (5)Å
С	14.9476 (8)Å	14.9281 (5)Å
β	97.773 (2)°	97.793 (2)°
V	1203.58 (10)Å ³	1203.83 (6)Å ³
Z	4	4
D _x	1.147 Mg m ⁻³	1.612 Mg m^{-3}
λ	0.71073	0.71073
θ_{max}	27.48°	27.48°
μ	0.70 mm^{-1}	6.69 mm^{-1}
Measured reflections	2756	5182
Independent reflections	3088	2993
Observed reflections	1055	1959
Criterion	I > 3.00 sigma(I)	I > 3.00 sigma(I)
R _{int}	0.052	0.030
Н	$-6 \rightarrow 6$	$-6 \rightarrow 6$
К	$0 \rightarrow 21$	$0 \rightarrow 21$
L	$-19 \rightarrow 19$	$-19 \rightarrow 19$
R(all)	0.185	0.072
R(gt)	0.093	0.041
wR(ref)	0.266	0.080
wR(all)	0.276	0.086
S(ref)	2.278	1.613
Δ/σ_{max}	0.037	0.016
Δho_{max}	0.98eÅ ³	0.96eÅ ³
Δho_{min}	–1.32eÅ ³	–0.81eÅ ³
wR(gt)	0.266	0.080

which are hydrogen bonded to the halide anion. Each two parallel chains are connected to each other forming a couple via halide ion Cl(2)/Br(2). The nearly perpendicular couples are connected via Cl(1)/Br(1). Fig. 1c depicts molecular arrangement and hydrogen bond net-work of C7Cl along a-axis. It reveals the occurrence of four short N–Cl non-bonded contacts, three of these contacts may be ascribed to charge-assisted hydrogen-bond formation and the fourth is a short contact directed approximately along the extension of the C–N bond. Three, H3A, H3B, and H3C, have values within the range of the hydrogen bond distance 2.393 Å, 2.254 Å and 2.289 Å respectively.

It is worth mentioning that hydrogen bond length of H–Cl1 is shorter than H–Br1 while the opposite is true where the H–Br2 is slightly longer than the hydrogen bond attached to H–Cl2 as listed in Table 5. The average bond length N–C = 1.511 (Å), C–C = 1.51 (Å), C–H = 0.960 (Å) are in the acceptable range with previously reported similar hybrids [6–16].

3.2. Lattice potential energy, molecular and cation volume

Estimation of lattice potential energy U (pot) for the general type of the hybrids of M_pX_q can be obtained using Eq. (1) below [22]:

$$U(\text{pot}) = \sum n_i z^2 \left[\alpha / V^{1/3} + \beta \right]$$
(1)

where α and β are appropriate fitting coefficients chosen according to the stoichiometry of the hybrid, n_i is the number of ions with a charge z_i in the formula unit, V_m is the molecular volume.

For MX_2 (1:2) hybrids, the lattice potential energy is given by Ref. [22]:

$$U(pot) = \left| Z^{+} \right| \left| Z^{-} \right| v \left[\alpha / V^{1/3} + \beta \right]$$
(2)

Table 2 Fractional atomic coordinates and equivalent isotropic thermal parameters ($Å^2$): $U_{eq} = 1/3 \Sigma_i \Sigma_j U_{ij} ai \times aj^* a_i a_j$ of: (a) C7C and (b) C7B.

	Х	Y	Z	U _{eq}
a. C7C				
Cl1	0.1100 (5)	0.39416 (13)	0.44708 (17)	0.0411 (13)
Cl2	0.9822 (5)	0.22301 (17)	0.21276 (18)	0.0512 (14)
N3	0.358 (3)	0.5791 (9)	0.3931 (11)	0.140 (13)
N4	0.529 (3)	0.2302 (11)	-0.1499 (14)	0.153 (14)
C5	0.571 (4)	0.3835 (12)	0.0459 (13)	0.122 (14)
C6	0.380 (4)	0.4180 (11)	0.1036 (16)	0.129 (15)
C7	0.431 (4)	0.3297 (15)	-0.0206 (15)	0.145 (17)
C8	0.538 (4)	0.4646 (13)	0.1800 (14)	0.126 (15)
C9	0.356 (4)	0.5023 (14)	0.2447 (12)	0.128 (15)
C10	0.524 (4)	0.5443 (12)	0.3229 (14)	0.128 (14)
C11	0.642 (4)	0.2870 (14)	-0.0769 (16)	0.150 (18)
H5A	0.633750	0.426830	0.012540	0.122894
H5B	0.729751	0.360710	0.083230	0.122894
H6A	0.236098	0.447901	0.067616	0.125190
H6B	0.295888	0.373801	0.129766	0.125190
H7A	0.367134	0.287075	0.013565	0.135445
H7B	0.272794	0.353125	-0.057365	0.135445
H8A	0.676000	0.432048	0.215253	0.130145
H8B	0.632610	0.504888	0.150473	0.130145
H9A	0.240596	0.541826	0.211957	0.127421
H9B	0.237076	0.462996	0.266317	0.127421
b. C7B				
Br1	0.89132 (10)	0.10604 (3)	0.05259 (3)	0.0446 (2)
Br2	0.01542 (12)	0.27716 (4)	0.28703 (3)	0.0567 (3)
N3	0.6526 (8)	-0.0734 (2)	0.1088 (2)	0.040 (2)
N4	0.4626 (8)	0.2704 (2)	0.6448 (3)	0.044 (2)
C5	0.6520 (10)	-0.0032 (3)	0.2549 (3)	0.041 (2)
C6	0.6189 (10)	0.0833 (3)	0.3927 (3)	0.043 (2)
C7	0.4649 (10)	0.0322 (3)	0.3182 (3)	0.044 (3)
C8	0.4269 (11)	0.1185 (3)	0.4556 (3)	0.046 (3)
C9	0.3460 (11)	0.2109 (3)	0.5768 (4)	0.052 (3)
C10	0.4772 (10)	-0.0420 (3)	0.1756 (3)	0.044 (2)
C11	0.5610 (9)	0.1771 (3)	0.5233 (3)	0.041 (2)
H5A	0.768344	-0.042840	0.287047	0.046964
H5B	0.768993	0.036760	0.233807	0.046964
H6A	0.711798	0.125789	0.366413	0.047343
H6B	0.756078	0.051449	0.429043	0.047343
H7A	0.370261	-0.008611	0.346840	0.047806
H7B	0.328201	0.065589	0.283930	0.047806
H8A	0.353249	0.077369	0.489741	0.048644
H8B	0.274329	0.145539	0.420061	0.048644
H9A	0.260914	0.169391	0.607469	0.056149
H9B	0.203944	0.237431	0.536339	0.056149

where Z^+ and Z^- are the respective charges on the cation and anion of the compound, v is the number of ions per molecule and equals to (p + q). For the case of hybrids of formula MX₂ with charge ratio (2:1) $Z^+ = 2$, $Z^- = 1$, p = 1, q = 2, v = 3, $\alpha = 133.5$ kJ mol⁻¹ nm, $\beta = 60.9$ kJ mol⁻¹, and V_m (nm³) is given by Ref. [23]:

$$Vm(nm^3) = Mm/(\rho NA) = 1.66045 \times 10^{-3} M_m/\rho$$
 (3)

where N_A is Avogadro's number, ρ (g cm⁻³) is the density and M_m (g/mol) is the molar mass as obtained from reported crystal structure data [6–16]. Values of (V_m) as calculated from Eq. (3) are V_m (C7C) = 0.294 nm³ and V_m (C7B) = 0.301 nm³. This yields lattice energy U (pot) = 1568.59 kJ/mol and 1560.78 kJ/mol for C7C and C7B respectively. Fig. 2a shows the lattice potential energy U_{pot} as a function of number of carbon atoms in the chain, along with U_{pot} for n = 2, 3, ...6 as obtained from reported X-ray results (see Table 6) [6–16]. It indicates nearly linear decrease of lattice potential energy with chain length for C7C and C7B such that U_{pot} of the chlorides is always higher than that of the bromides. It is to be noted that U_{pot} of C7B is presented on a secondary axis with different scale from that of C7C for clear data presentation. It is to be

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pointed out that for n = 3 and 5 the lattice potential energy U_{pot} deviates slightly from the observed linear relation. This could be associated with the difference in crystal symmetry, where dichloride of n = 3 and 5 are orthorhombic, while all the other hybrids are monoclinic. The difference $\Delta U_{pot} = [U_{pot}(C7C)-U_{pot}(C7B)]$ decreases with increasing the chain length, reaching a minimum for n = 5 as depicted in insert (i). It is to be noted that the observed minimum is most likely associated with symmetry differences of n = 5 hybrid.

Fig. 2b shows the molecular volume (V_m) as a function of number of carbon atoms/chain. As expected nearly linear increase of (V_m) as chain length increases.

In addition, since for a hybrid of M_pX_q [24]:

$$V_m = pV^+ + qV^- \tag{4}$$

where V^+ and V^- are the volumes of the cation and anion, p = 1 and q = 2 for MX₂ (1:2) and V(Cl⁻) = 0.0298 nm³ and V(Br⁻) = 0.0363 [24]. The volume of the cations (V^+) C7H20N2 of C7C and C7B as well as (V^+) for n = 2, 6 are also calculated. Fig. 2c shows variation of the cations volume (V^+) as a function of number of C atom/chain (n). The cation volume increases with increasing chain length. Slight deviation of (V^+) vs. chain length from linearity for n = 5 is also observed. It is to be noted that difference between bromide and chloride molecular volumes [$\Delta V_m = V_m$ (C7B)– V_m (C7C)] and cation volumes [$\Delta V^+ = V^+$ (C7B)– V^+ (C7C)] show minima for n = 5 hybrid which corresponding to that found for [ΔU_{pot}], see in (insert (i) of Fig. 2a.

3.3. Thermal behavior

Fig. 3 shows the DSC scans of the two hybrids C7C and C7B. Near room temperatures, asymmetric endothermic peaks $T_{C7C} = 334.1 \pm 2 \text{ K} (\Delta S = 13.07 \text{ J/mol.K}) \text{ and } T_{C7B} = 336.1 \pm 1 \text{ K}$ $(\Delta S = 13.65 \text{ J/mol.K})$ were observed for C7C and C7B respectively. At high temperatures endothermic peak located at $T_{C7C} = 440.4$ K $(\Delta S = 27.12 \text{ J/mol.K})$ can be associated with change of crystal morphology while exothermic peak at $T_{C7C}\,=\,546$ K reflects dissociation. Two consecutive endothermic peaks at $T_{\text{C7B}} = 529.6\ \text{K}$ $(\Delta S = 25.13 \text{ J/mol.K})$ and $T_{C7B} = 541.6 \text{ K} (\Delta S = 28.13 \text{ J/mol.K})$ are attributed to pre-melting and melting of C7B respectively. Due to the non-linear behavior of heat flux with increasing temperature in the range 295 K-330 K and to the small differences in transition temperatures of T_{C7C} and T_{C7B} , DTA measurements at a heating rate of 5 °C/min. were performed and presented in inserts (i) and (ii) of Fig. 3. The results showed several peaks near room temperature. Starting from the high temperature side, C7C showed broad endothermic peak at $T_{0(C7C)} = 432 \pm 3$ K, a prominent transition at $T_{1(C7C)}=330.5\pm1$ K having a shoulder at $T_{2(C7C)}=321.6\pm3$ K and an inconspicuous small peak at $T_{3(C7C)} = 307.9$ K. The bromide hybrid, C7B, showed two consecutive peaks corresponding to phase transformations located at $T_{1(C7B)} = 333.8 \pm 2$ K and $T_{2(C7B)} = 302.2 \pm 1$ K. Previous studies of phospholipids, alkylammonium and alkylene-diammonium hybrids have attributed consecutive thermodynamic transitions near ambient to be associated with chain melting transitions where major and minor transitions near ambient have been reported [25-30]. Minor transition is associated with dynamic two-fold rotational disorder of the chain and the major transition is attributed to the "melting" of the chain. At the chain melting transition the rapid diffusion of one or more gauche bonds up and down the hydrocarbon chain takes place, leading to decrease of the chain length [26].

Table 3	
Anisotropic displacement parameters (Å ²) of: a) C7C and b) C7B	•

U ₁₁		U ₁₂	U ₁₃	U ₂₂	U ₂₃	U ₃₃
a. C7C						
Cl1	0.0406 (13)	0.0007 (11)	0.0049 (10)	0.0388 (14)	-0.0038 (12)	0.0431 (15)
Cl2	0.0472 (15)	-0.0041 (12)	0.0057 (12)	0.0562 (18)	-0.0108 (13)	0.0492 (16)
N3	0.157 (14)	0.028 (11)	0.070 (12)	0.136 (14)	0.012 (11)	0.133 (13)
N4	0.156 (16)	-0.022 (11)	0.035 (13)	0.129 (14)	-0.057 (13)	0.175 (18)
C5	0.107 (14)	-0.021 (12)	0.011 (12)	0.139 (17)	-0.036 (13)	0.119 (16)
C6	0.111 (15)	-0.033 (12)	0.025 (13)	0.128 (16)	-0.018 (14)	0.146 (18)
C7	0.105 (14)	0.011 (14)	0.026 (13)	0.18 (2)	0.008 (17)	0.145 (19)
C8	0.116 (14)	-0.019 (12)	0.014 (12)	0.141 (18)	0.007 (13)	0.119 (15)
C9	0.106 (13)	-0.002 (14)	0.006 (11)	0.17 (2)	-0.015 (14)	0.100 (14)
C10	0.104 (14)	-0.021 (12)	-0.003 (11)	0.148 (19)	-0.007 (14)	0.127 (16)
C11	0.137 (17)	-0.011 (15)	0.053 (15)	0.17 (2)	0.004 (16)	0.149 (19)
b. C7B						
Br1	0.0441 (3)	0.0006 (2)	0.0059 (2)	0.0394 (3)	-0.0031 (2)	0.0493 (3)
Br2	0.0529 (4)	-0.0047 (3)	0.0060 (3)	0.0588 (4)	-0.0120 (3)	0.0572 (4)
N3	0.041 (2)	-0.0003 (18)	-0.0044(17)	0.040 (2)	-0.0016 (18)	0.037 (2)
N4	0.038 (2)	-0.0061 (18)	0.0055 (17)	0.045 (2)	-0.0064 (19)	0.047 (2)
C5	0.033 (2)	-0.006 (2)	0.004 (2)	0.044 (3)	0.000 (2)	0.046 (3)
C6	0.038 (3)	-0.013 (2)	0.003 (2)	0.043 (3)	0.002 (2)	0.046 (3)
C7	0.037 (3)	-0.008 (2)	0.004 (2)	0.047 (3)	-0.003 (2)	0.048 (3)
C8	0.038 (3)	-0.005 (2)	0.006 (2)	0.046 (3)	-0.001 (2)	0.054 (3)
C9	0.042 (3)	-0.004(2)	0.005 (2)	0.053 (3)	-0.008 (3)	0.061 (3)
C10	0.038 (2)	-0.004 (2)	0.003 (2)	0.043 (3)	0.000 (2)	0.050 (3)
C11	0.032 (2)	-0.007 (2)	0.003 (2)	0.043 (3)	-0.003 (2)	0.048 (3)

Table 4

Select	ed interatomi	c distances	(Å) and	l bond	angles (°)	with	e.s.d's in	parenthese	es
and di	hedral angles	of: a) C7C a	nd b) (C7B.					

Organic chain	Bond distance (Å)		Bond distance (Å)
	a) C7C		b) C7B
N3-C10	1.52 (2)	N3-C10	1.487 (4)
N4-C11	1.50 (2)	N4-C9	1.486 (4)
C5–C6	1.46 (2)	C5–C7	1.512 (5)
C5–C7	1.45 (2)	C5-C10	1.507 (5)
C6–C8	1.51 (2)	C6–C7	1.521 (5)
C7-C11	1.58 (3)	C6–C8	1.523 (5)
C8–C9	1.53 (2)	C8-C11	1.500 (5)
C9-C10	1.51 (2)	C9-C11	1.501 (5)
C10–H3A	2.08 (2)	C10–H3A	2.026 (4)
C10–H3B	2.06 (2)	C10–H3B	2.011 (3)
C10–H3C	2.05 (2)	C10-H3C	2.025 (4)
	Bond angles (°)		Bond angles (°)
C6-C5-C7	113.0 (14)	C7-C5-C10	110.5 (3)
C5-C6-C8	111.6 (14)	C7-C6-C8	113.6 (3)
C5-C7-C11	112.8 (15)	C5-C7-C6	114.4 (3)
C6-C8-C9	115.3 (14)	C6-C8-C9	150.5 (2)
C8-C9-C10	113.4 (14)	C6-C8-C11	115.9 (3)
N3-C10-C9	116.4 (13)	C8-C9-C11	34.8 (2)
N4-C11-C7	119 (2)	N4-C9-C8	148.4 (3)
N4-C11-C7-C5	-179 (3)	N4-C9-C11-C8	-179.2 (6)
N3-C10-C9-C8	-176 (2)	N3-C10-C5-C7	176.6 (6)
C6-C5-C7-C11	-175 (3)	C10-C5-C7-C6	-171.2 (6)
C5-C6-C8-C9	-179 (2)	C7-C6-C8-C11	-172.9 (6)
C6-C8-C9-C10	177 (2)	C5-C7-C6-C8	179.9 (6)
C7-C5-C6-C8	172 (2)	C8-C6-C7-C5	179.8 (6)

3.4. Dielectric constant

3.4.1. Temperature dependence of the dielectric constant

Fig. 4a shows the real part of the dielectric constant (ε') of C7C between room temperature and 440 K at selected frequencies, on heating. Variation of (ε') with temperature reflects anomalous changes at T₃(C7C)<u>~</u>310 K, T₂(C7C)<u>~</u>321.5 K, T₁(C7C) = 335.8 K and T₀(C7C)<u>~</u>432 K. which are in reasonable agreement with endothermic peaks observed in DTA and DSC thermographs. Fig. 4b depicts (ε') -T of C7C on cooling. It shows a large decrease of (ε')

Table 5Hydrogen bond geometry and symmetry code of C7C and C7B.

(D-H-A)	d (D-H) (Å)	D (H-A) (Å)	(D-H-A) (°)	d(D-A) (Å)
a) N4-H4C-Cl1	0.960 (2)	2.477(2)	105. (2)	3.37 (2)
b) N4–H4B–Cl2	0.960 (2)	2.254(2)	167.28	3.20 (2)
c) N4–H4A–Cl2	0.960 (15)	2.516 (2)	107.03	3.28 (2)
d) N3–H3A–Cl1	0.960 (2)	2.393 (2)	153.27	3.516 (12)
e) N3–H3C–Cl2	0.960 (13)	2.289 (2)	166.18	3.230 (13)
f) N3-H3A-Br1	0.960 (3)	2.4615(3)	153.5 (2)	3.511 (3)
g) N3-H3B-Br1	0.960 (3)	2.4795 (3)	160.2 (2)	3.511 (3)
h) N3–H3C–Br2	0.960 (3)	2.3413 (4)	163.7 (2)	3.274 (3)
i) N4–H4A–Br2	0.960 (3)	2.596	131.88	3.315 (3)
j) N4–H4B–Br2	0.960 (3)	2.3335 (4)	163.4(2)	3.265 (3)
k) N4-H4C-Br1	0.960 (3)	2.4408 (3)	160.2 (2)	3.360 (3)

Symmetry code: a) x,1/2–y,1/2 + z, b) 1 + x,1/2-y,1/2 + z, c) x,1/2-y,1/2 + z, d) 1-x,1-y,1-z, e) 1-x,y-1/2,1/2-z, f) 1-x,-y,-z, g) 2-x,-y,-z, h) 1-x,1/2 + y,1/2-z, i) x,1/2-y,z-1/2, j) x-1,1/2-y,z-1/2, k) x,1/2-y,z-1/2.

values with anomalies at $T'_{0(C7C)} \simeq 422 \text{ K } T'_{1(C7C)} \simeq 319.7 \text{ K}$, such a shift of $\Delta T \sim 10 \text{ K}$ and $\Delta T \simeq 16 \text{ K}$ of $T_{0(C7C)}$ and $T_{1(C7C)}$ respectively confirms the first order nature of both transitions. Insert of Fig. 4a depicts a heating/cooling cycle of $(\epsilon') - T$ at 0.81 kHz. It shows that ϵ' follows a different path on cooling, where the large drop in (ϵ') values and it temperature dependence clearly indicates an irreversible phase transition.

Fig. 4c and d shows variation of imaginary part of the dielectric constant (ε'') vs. temperature on heating and cooling respectively. Results reflect anomalies observed in [ln (ε'')] vs. T, on heating and cooling, albeit higher (ε'') magnitude.

Similar behavior is observed for C7B, however (ϵ') values are of much lower magnitude at low temperature T < T_(1C7B) and shows large scattering at low frequency. It undergoes thermal hysteresis of about 4 K at T_(1C7B) on cooling, whereas transition at T_(2C7B) could not be seen as it must have shifted to lower temperatures. The two hybrids show decreasing dielectric constant as frequency increases.

3.4.2. Frequency dependence of the dielectric constant

The variation of (ε') as a function of angular frequency $[\ln(\omega)]$ of C7C. on heating, is shown in Fig. 5a, similar results are observed on



Fig. 1. a: ORTEP view of $[(CH_2)_7(NH_3)_2]X_2$, X = CI/Br atoms. b: Arrangements of atoms in the unit cell of $[(CH_2)_7(NH_3)_2]Br_2$. c: Organic moieties arrangement along a-axis and the hydrogen bond net-work of $[(CH_2)_7(NH_3)_2]Cl_2$.



Fig. 2. a: Lattice potential energy Upot (kJ/mol) vs. number of carbon atoms/chain (n) of C7C and C7B. Insert (i): Δ Upot (kJ/mol) vs. number of carbon atoms/chain (n). b: Molecular volume (V_m (nm³)) vs. number of carbon atoms/chain (n) of C7C and C7B. c: Cation volume (V⁺ nm³) vs. number of carbon atoms/chain of C7C and C7B.

cooling and will not be shown. Fig. 5b and c depict variations of slope (m) = d[ln($\epsilon')$]/d[ln(ω)] with temperature on heating and cooling respectively. It demonstrates quite clearly the slope changes taking place at the transitions $T_{3(C7C)} = 310$ K, $T_{2(C7C)} = 321$ K, and $T_{1(C7C)} = 335$ K and $T_{0(C7C)} = 432$ K on heating and at $T_{3(C7C)} = 308$ K, $T'_{2(C7C)} = 318.5$ K, $T'_{1(C7C)} = 329$ K and $T'_{0(C7C)} = 421$ K on cooling.

The imaginary part (ε'') of the dielectric constant as a function of angular frequency $[\ln(\omega)]$, of C7C, is shown in Fig. 5d and e, for heating and cooling respectively. The graphs show increasing $[\ln(\varepsilon'')]$ with temperature and decreasing with frequency according to $\varepsilon'' \alpha \omega^{-n}$. They also show high values of ε'' at high temperatures and low frequencies, which can be attributed to the motion of the charge carriers within the sample [31]. Similar characteristics of $[\ln(\varepsilon'')]$ vs. $[\ln(\omega)]$ are observed for C7B on heating and cooling. Fig. 5f. shows typical behavior of $[\ln(\varepsilon'')]$ vs. d $[\ln(\omega)]$ of C7B at two temperatures indicating higher values (ε'') on cooling which is typical for both samples. The general features of $[\ln(\varepsilon'')]$ vs. d $[\ln(\omega)]$ graphs are characterized by a shallow minimum that shifts to higher frequencies with increasing temperature, except for C7C in the temperature range 295 K-335 K, where no shallow minimum is noted. The shallow minimum of $[\ln (\varepsilon'')]$ vs. $[\ln(\omega)]$ observed for C7C and C7B at T > $T_{(1C7C)}$ is similar to results of super-cooled liquids, plastic crystals where the molecules are disordered with respect to their orientation degrees of freedom as well as of ionically conducting crystals and electronic semiconductors [32]. It demonstrates the change from the universal dielectric response (UDR) [33] to the superliner power law (SLPL) as suggested by Lunkenheimer and Loidl [32,34]. The graph also shows a relaxation peak at high frequency in the temperature range 345-385 K centered at $[\ln (\omega)] \sim 12.65$ (f = 50 kHz). The latter is somewhat similar to the "Boson peak" that characterizes glassy samples which is typical of vibration excitations [34].

3.5. Conductivity results

3.5.1. Temperature dependent conductivity

The variation of the ac conductivity $[\ln (\sigma_{ac})]$ as a function of the reciprocal temperature [1000/T (K)] at selected frequencies of C7C, on heating and cooling, is shown in Fig. 6a and b respectively. Thermally activated behavior following Arrhenius relation as given by Eq. (5) is observed.

$$\sigma_{ac}(T) = A(T)\exp(-\Delta E/kT)$$
(5)

where the pre-exponential term A(T) is temperature dependent. Anomalous changes in the variation of [ln (σ_{ac})] – [1000/T(K)] are detected at the transitions $T_{1(C7C)} = 335.8$ K and $T_{2(C7C)} = 319$ K on heating and at T'_{1(C7C)} = 325 K on cooling. Fig. 6c depicts heating/ cooling cycle at f = 2 kHz. It shows that cooling run follows the same trajectory as the heating run with slightly higher (σ_{ac}) values, up to T = 340 K. Activation energy of C7C and its fit to Eq. (6) below are shown in Fig. 6d.

Table 6

Number of carbon atom/chain (n), lattice potential energy (U_{pot} kJ/mol), molecular volume (V_m nm³) and cation volume (V^+ nm³) of [(CH_2)_n(NH_3)₂] X₂, X = Cl/Br, n = 2, 3, 4, 5, 6 and 7. Calculation were carried out from structure data measured at room temperature except for [$C_2H_{10}N_2$]Br₂ and [$C_5H_{16}N_2$]Br₂ which were measured at 100 K and 150 K respectively.

Sample	Sp. Gr.	n	(U _{pot}) kJ/mol	$V_m (nm^3)$	$V^{+}(nm^{3})$	Ref.
C ₂ H ₁₀ N ₂ Cl ₂	$P2_1/c$	2	1868.7	0.151	0.092	[6]
$C_2H_{10}N_2Br_2$	$P2_1/c$	2	1800.7	0.174	0.101	[7]
C ₂ H ₁₀ N ₂ Br ₂ (100 K)	C2/m	2	1811.0	0.170	0.170	[8]
$C_3H_{12}N_2Cl_2$	$Pna2_1$	3	1762.6	0.188	0.129	[9]
$C_4H_{14}N_2Cl_2$	$P2_1/c$	4	1725.6	0.204	0.145	[10]
$C_4H_{14}N_2Br_2$	$P2_1/c$	4	1680.9	0.226	0.153	[11]
$C_5H_{16}N_2Cl_2$	Pbam	5	1649.5	0.243	0.183	[15]
C ₅ H ₁₆ N ₂ Br ₂ (150 K)	$P2_1/c$	5	1645.4	0.245	0.172	[16]
$C_6H_{18}N_2Cl_2$	$P2_1/c$	6	1628.4	0.255	0.195	[12]
$C_6H_{18}N_2Br_2$	$P2_1/c$	6	1594.3	0.277	0.204	[13]
$C_6H_{18}N_2Cl_2$	$P2_1/c$	6	1623.3	0.258	0.199	[14]
$C_6H_{18}N_2Br_2$	$P2_1/c$	6	1592.5	0.278	0.206	[14]
$C_7H_{20}N_2Cl_2$	$P2_1/c$	7	1560.8	0.301	0.228	This work
$C_7 H_{20} N_2 B r_2$	$P2_1/c$	7	1569.9	0.294	0.234	This work



Fig. 3. DSC thermograph of C7C and C7B. Inserts (i): DTA measurements at a rate of 5 °C/min. of C7C. Inserts (ii): DTA measurements at a rate of 5 °C/min. of C7B.

$$\Delta E = \Delta E_0 [1 - \exp(-f_0/f)]^{\alpha}$$
(6)

where ΔE_0 is the activation energy in limit $f \rightarrow 0$ and α is a constant with values between $0 < \alpha < 1.0$. It can be seen that in the high temperature, phase (I), $\Delta E_{cool} > \Delta E_{heat}$ with activation energy ΔE_0 in the range of ionic hopping.

Fig. 7a and b depicts $[\ln (\sigma_{ac})]$ vs. [1000/T(K)] of C7B at selected frequencies, on heating and cooling respectively. results below T₁ and T'₁, (σ_{ac}) are nearly temperature independent but strongly frequency dependent suggesting extrinsic type conduction, with activation energy ΔE (C7B) ≥ 0.013 eV on heating. Anomalous changes of conductivity are observed at T_{1(C7B)} = 338 K on heating and at T' (_{C7B)} = 334 K on cooling. Fig. 7c shows $[\ln (\sigma_{ac})]$ vs. [1000/T(K)] at f = 6 kHz for C7C and C7B on heating in the temperature range above T_{1(C7C)}. It indicates higher conductivity of C7B. Similar behavior is observed for the cooling cycle, see Fig. 7d. The two samples show a gradual increase of conductivity as temperature increases, Figs. 6 and 7(a, b), such that the curves tend to merge at high temperatures which implies frequency dependent mobility.

Fig. 7c and d depicts frequency dependence of ΔE and its fit to Eq. (6) in the temperature range T > T₁ of C7C and C7B on heating and cooling respectively. Table 7 lists fit parameters for high temperature phase (I) and low temperature phase (II) of the two samples on heating and cooling. Due to the limited number of data points above T_{0(C7C)}, no calculations of ΔE were performed.

The activation energy values in phase (I) lie in the range of vacancy conduction indicating that hopping of halide ions among vacant sites are responsible for conduction [35]. At low temperatures (T < $T_{2(C7C)}$) activation energy of C7C (on heating) is ΔE ~0.4 eV which could be associated with proton conduction [36].

Fig. 7c and d shows higher conductivity values for C7B compared to C7C. This can be attributed to differences in the ionic size of the halide ions and their different electro-negativity which affects both the hydrogen bonding and the coulomb interactions. For the larger size halide ion (Br^-) the hydrogen bond strength is lower than that of the smaller (Cl^-) ion. The decrease of the hydrogen bond strength may be looked at as a decrease of the interaction of the charge carrier with its environment and thus to

an increase in molecular mobility and conductivity. Besides, for the larger ion the charge is more spread over the larger ionic surface, hence reduces the charge surface density. This leads to decrease of Coulomb interaction hence decreasing inter-ionic interactions which results in an increase of mobility and conductivity.

3.6. Frequency dependence

Fig. 8a and b shows frequency dependence of conductivity at different temperatures as $[\ln (\sigma_T)]$ vs. $[\ln (\omega)]$ at selected temperatures of C7C on heating and cooling respectively. Inserts (i) and (ii) show $[\ln (\sigma_T)]$ vs. $[\ln (\omega)]$ at selected temperatures of C7B on heating and cooling respectively. At low temperatures, and low frequencies few data points are scattered and have been omitted from the plots. The graphs display typical properties of experimental conductivity of most ionic conductors as well as glassy materials [33,37,38].

The dispersive behavior of the conductivity is generally expressed by Jonscher's universal dispersive response (UDR) as given by Eq. (7) [33].

$$\sigma_T = \sigma_{dc} + \sigma_{ac} = \sigma_{dc} + A(T)\omega^{s(T)}$$
(7)

where σ_{dc} and σ_{ac} are the DC conductivity due to band conduction and AC conductivity is related to hopping conduction respectively, and the pre-exponential factor A (T) is a temperature-dependent constant and the exponent s(T) measures the degree of correlation, It usually has values between 0 in case of random hopping and tends to 1.0 for correlated hopping [37,38]. At higher frequencies, conductivity increases and eventually starts to attain a highfrequency plateau. Such plateaus are known to exist in fast ionic conductors such as RbAgI₅ and Na- β -alumina [39]. First attempts to fit the data of Fig 8a to Eq. (7) were successful in temperature region below T~340 K, but failed at higher temperatures where good fits were obtained using the superlinear power law Eq. (8) [36]:

$$\sigma_{\mathrm{T}}(\omega) = \sigma_{\mathrm{dc}} + A_1 \omega(\mathrm{T})^{\mathrm{S1(T)}} + A_2(\mathrm{T})\omega^{\mathrm{S2(T)}}$$
(8)



Fig. 4. a: Real part of dielectric constant (ε') vs. T (K) of C7C on heating. b: (ε') vs. T (K) of C7C on cooling. c: Imaginary part of the dielectric constant ($\log(\varepsilon'')$) vs. temperature of C7C on heating. d: Imaginary part of the dielectric constant ($\log(\varepsilon'')$) vs. temperature of C7C cooling.

Good fits were also obtained using Eq. (8) for C7C over the whole temperature range on cooling as well as for C7B data on heating and cooling. Above 340 K the graphs are characterized by four regions: (i) an almost temperature-independent plateau region at the lowest frequency in which $\sigma = cf^0$; (ii) Jonscher (UDR) regime where $\sigma = cf^{s1}$, (0 < s < 1); (iii) a region of high-frequency dispersion, where $\sigma = cf^{s2}$ and (iv) a plateau region. Fig. 9a and b shows fits of $[\ln (\sigma_T)]$ vs. $[\ln(\omega)]$ of C7C, on heating and cooling, at selected temperatures in regions below and above 340 K according to Eqs. (7) and (8) respectively. Fig. 10a depicts variation of fit parameter (σ_0 (T< 340 K)) vs. temperature, as $[\ln(\sigma_0$ (T< 340)] vs. 1000/T. The calculated activation energy values are $\Delta E_a = 0.32$ eV for 299 < T(K) < 310 K and $\Delta E_a = 0.49$ eV for 310 < T(K) < 327. It suggests that proton conduction is responsible for conduction in the low temperature range [36]. It also reveals change in activation energy which can be associated with phase transition due to conformation and reorientation of the chain in that temperature range.

Parameters s and [lnA] vs. temperature are shown in Fig. 10b. Below T = 310 K parameter s is nearly temperature independent and maintains a value 0.83 \pm 0.01, whereas it maintains a value of 0.77 \pm 0.01 above it. According to [37,38] conductivity by tunneling is function of frequency and independent on temperature, the frequency dependence arises from term ωR^4 where R is the distance. The parameter s is given by Refs. [37,38]:



Fig. 5. a: $[ln(\varepsilon')]$ as function of angular frequency $[ln(\omega)]$ of C7C on heating. b: slope $(m) = d[ln(\varepsilon')]/d[ln(\omega)]$ vs. temperature of C7C on heating. c: slope $(m) = d[ln(\varepsilon')]/d[ln(\omega)]$ vs. temperature of C7C on cooling. d: $[ln(\varepsilon'')]$ as a function of angular frequency $[ln(\omega)]$ of C7C on heating. e: $[ln(\varepsilon'')]$ as a function of angular frequency $[ln(\omega)]$ of C7C on cooling. f. Typical behavior of $[ln(\varepsilon'')]$ vs. $d[ln(\omega)]$ of C7B for heating/cooling cycle.

 $s = 1 + 4/\ln[\omega T_0] \tag{9}$

tunneling mechanism and that their different values is a result of the phase transition, where the R_{ω} and potential deformation change due to conformation and orientation of the chain. [InA] shows also changes from $(-25.42 \pm 0.07(\Omega.cm)^{-1})$ for T < 309 K to $(-24.35 \pm 0.4(\Omega.cm)^{-1})$ above.

which shows that s is independent of T. Considering τ_0 to be of the order of an inverse of the optical phonon frequency ($\sim 10^{-13}$ s) and for typical audio frequency ($\omega \sim 10^4 \ s^{-1}$) an s value of ~0.8 is obtained. The exact value depends on the magnitude of the deformation potential for the localized states and on R_{ω} [38]. Hence, one can suggest that the obtained s values of 0.83 ± 0.01 (T < 310 K) and 0.77 \pm 0.01 (T > 310 K) are within the range observed for proton

Fig. 10c depicts $\sigma_{0(T>T1)}$ as function of reciprocal temperature, the calculated activation energy $\Delta E = 0.78$ eV is a reasonable agreement with results listed in Table 7 as obtained from $[\ln(\sigma_T)]$ vs. 1000/T plot.

The fit parameters s_1 , $[ln(A_1)]$ and s_2 , $[ln(A_2)]$ of C7C are shown



Fig. 6. a: Ac conductivity $[\ln (\sigma_T)]$ vs. [1000/T (K)] at selected frequencies of C7C on heating. b: Ac conductivity $[\ln (\sigma_T)]$ vs. [1000/T(K)] at selected frequencies of C7C, on cooling. c: Ac conductivity $[\ln (\sigma_T)]$ vs. [1000/T(K)] for a heating/cooling cycle of C7C at f = 2 kHz d: Activation energy ($\Delta E(eV)$) of C7C and its fit to Eq. (6).

in Fig. 10d and e respectively. General gradual decrease of s_1 and s_2 , an increase of $[\ln (A_1)]$ and $[\ln (A_2)]$ are observed as temperature increases with values $0.3 < s_1 < 0.45$ and $1.48 < s_2 < 1.6$. One can summarize the variation of $\ln (\sigma_T)$ with frequency at selected temperatures as follows:

(i) At high temperatures, in the low-frequency range, (dc conductivity) prevails. The dependence of the "universal" exponent s on temperature and frequency is related to the conduction mechanism [33,37,38]. The variation of the exponent s reflects the changes in the conduction mechanism throughout the temperature range investigated, and the phase change is expected to be manifested in the variation of s with temperature. In the case of quantum tunneling model the exponent s has values ~0.8 and is temperature independent [37,38], as was found in the temperature range T < 308 K. For small polarons conduction, there is an increase</p> of the exponent s with temperature [37] which can be ruled out as possible mechanism of conduction of the presently investigated samples. Overlapping large polarons (OLPs) show linearly decreasing s up to a certain temperature, followed by an increase in s at higher temperatures [37] thus, the observed variation of the exponent s cannot be associated with OLPs. Correlated barrier hopping model [36,37] predicts an increase in the exponent s towards unity as temperature tends to 0 K which rules out this mechanism as well.

In the context of the jump relaxation model [40], strong connections can be made between the frequency response and the temperature dependence of the conductivity as analyzed using the Arrhenius approach.

(i) The frequency response is entirely due to translational and localized hopping. Translational hopping gives the long



Fig. 7. a: $[\ln (\sigma_T)]$ vs. [1000/T(K)] of C7B at selected frequencies, on heating. b: $[\ln (\sigma_T)]$ vs. [1000/T(K)] of C7B at selected frequencies, on cooling. c: $[\ln (\sigma_T)]$ vs. [1000/T(K)] at f = 6 kHz of C7C and C7B on heating. d: $[\ln (\sigma_T)]$ vs. [1000/T(K)] at f = 6 kHz for C7C and C7B on cooling. e: Activation energy $\Delta E(eV)$ vs. $[\ln(f(Hz))]$ and its fit to Eq. (6) of C7C and C7B. f: Activation energy (ΔE) vs. $[\ln(f(Hz))]$ and its fit of C7C and C7B on cooling.

 Table 7

 Activation energy fit parameters of C7C and C7B according to Eq. (6).

Sample	Phase		$\Delta E_0 \left(eV \right)$	F(Hz)	α
C7C 1 C7C 1 C7C 1 C7C 1 C7C 1 C7B 1 C7B 1 C7B 1 C7B 1 C7B 1 C7B 1	I (424-388 K) II (325-309 K) I' (424-348 K) II'(344-325 K) I (424-388 K) II T < 336 K) I' (375-424 K) I' T < 226	Heat Heat Cool Cool Heat Heat Cool	$\begin{array}{c} 0.79 \pm 0.02 \\ 0.461 \pm 0.006 \\ 0.81 \pm 0.01 \\ 0.47 \pm 0.016 \\ 0.91 \pm 0.02 \\ 0.014 \ \text{frequency} \\ 0.98 \pm 0.07 \\ 0.912 \ \text{frequency} \end{array}$	2813 ± 603 98.2 ± 13.0 906 ± 134 396 ± 119 2474 ± 421 <i>i</i> independent 2684 ± 294	$\begin{array}{c} 0.67 \pm 0.09 \\ 0.715 \pm 0.004 \\ 0.52 \pm 0.03 \\ 0.78 \pm 0.13 \\ 0.87 \pm 0.10 \\ \end{array}$

range electrical transport in the limit of very long times, that is when the frequency tends to zero.

(ii) The dispersive behavior of the conductivity against frequency, which commences at the high-frequency end of the dc plateau, is associated with the activation energy, ΔE , determined from the Arrhenius plots of the temperature dependence of conductivity. In this frequency range, the

observation time is too short for all jumps to be successful; the neighborhood cannot completely relax to the new position of the ion after its jump. As a result, the activation energy involved in this translational or rotational hopping is smaller than that involved in the long-range diffusive conduction.

(iii) Finally, the very low activation energy is observed which is attributed to reorientation and/or liberation motion of the organic cation, impurities or space charges.

Thus, it seems that the results of the conductivity can be explained in terms of the jump relaxation model.

The study of the two hybrids indicates that replacement of chloride by bromide does not change conductivity mechanism. This would be expected since the differences in the structure characteristics, bond angles and bond lengths are minimal. It slightly affects conductivity values and activation energy which is related to differences of halide ion size and their electronegativity.



Fig. 8. a: $\ln[\sigma_T(\omega)]$ vs. $\ln[\omega(s^{-1})]$ of C7C at selected temperatures on heating. Insert (i): $\ln[\sigma_T(\omega)]$ vs. $\ln[\omega(s^{-1})]$ of C7B at selected temperatures on heating. b: $\ln[\sigma_T(\omega)]$ vs. $\ln[\omega(s^{-1})]$ of C7C at selected temperatures on cooling. Insert (ii): $\ln[\sigma_T(\omega)]$ vs. $\ln[\omega(s^{-1})]$ of C7B at selected temperatures on cooling.

4. Conclusion

X-ray analysis of the room temperature phase of $[(CH_2)_7(NH_3)_2]$ X₂, X = Cl/Br shows a monoclinic $P2_1/c$ unit cell with dimension: a = 4.7838 (2) Å, b = 16.9879 (8) Å, c = 13.9476 (8) Å, β = 97.773 (2)° and a = 4.7952 (10) Å, b = 16.9740 (5) Å, c = 13.9281 (5) Å, β = 97.793 (2)° for the chloride and bromide hybrids respectively. The calculated lattice potential energy of chloride is higher than that of the bromide and both hybrids have the lowest U_{pot} in comparison to lattice potential of [C_nH_2nN_2H_6X_2]; n= 2,3, ...6 and X=Cl/Br.

Calorimetric studies showed two transitions at $T_1 = 333.8$ K and $T_2 = 302.2$ K for the bromide hybrid ascribed to chain melting. The chloride hybrid undergoes thermotropic transitions at $T_0 = 434$ K. Near ambient, it showed three transitions at $T_1 = 330$ K, $T_2 = 319$ K and $T_3 = 308$ K. These transitions are associated with order-disorder change of 1, 7-diammonium chain. Dielectric constant results confirmed the phase transitions. Conductivity of the two



Fig. 9. a: $\ln[\sigma_T(\omega)]$ vs. $\ln[\omega(s^{-1})]$ fit to Eq. (8) of C7C at selected temperatures on heating. Symbols are data points and lines are the fits. b: $\ln[\sigma_T(\omega)]$ vs. $\ln[\omega(s^{-1})]$ fit to Eq. (8) of C7C at selected temperatures on cooling. Symbols are data points and lines are the fits. c: $\ln[\sigma_T(\omega)]$ vs. $\ln[\omega(s^{-1})]$ fit to Eq. (8) of C7C at selected temperatures on cooling. Symbols are data points and lines are the fits. c: $\ln[\sigma_T(\omega)]$ vs. $\ln[\omega(s^{-1})]$ of C7C and C7B fit to Eq. (8) at T < T₁ on heating. Symbols are data points and lines are the fits.

hybrids is thermally activated, where that of bromide is higher than chloride. At high temperatures, activation energy values are in the range ionic hopping (Cl/Br) among vacant sites for both samples. On heating, proton tunneling prevails in the temperature range T < 309 K while proton hopping following UDR prevails in the temperature range 319 < T (K) < 330, indicating change of conduction mechanism with structure phase change for C7C. Impurity conduction is effective for C7B at T < 330 K. Activation energy obtained on heating is always of higher values than that obtained on cooling for both hybrids. A cross over from Jonscher's universal dielectric relaxation (UDR) in the temperature range T < 325 K to superlinear power law (SLPL) for T > 340 K according to the jump relaxation model is observed, for C7C hybrid on heating. Conduction follows SLPL on cooling for C7C and on heating and cooling for C7B.



Fig. 10. a: Fit parameter $[\ln(\sigma_0)]$ vs. 1000/T (K) on heating at T < T₁. b: Fit parameters (s) and $[\ln(A)]$ vs. temperature on heating. c: Fit parameter $[\ln(\sigma_0)]$ vs. 1000/T (K) on heating at T < T₁. $T > T_1$. d: Fit parameters (s_1) and [ln(A_1)] vs. temperature on heating at $T > T_1$. e: Fit parameters (s_2) and [ln(A_2)] vs. temperature on heating at $T > T_1$.

Supplementary material

CCDC 806007 contains the supplementary crystallographic data for sample of chemical formula $C_7H_{20}Cl_2N_2$ and CCDC 805298 for sample of chemical formula: C7H20Br2N2. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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