First example of interdigitated U-shape benzimidazolium ionic liquid crystals

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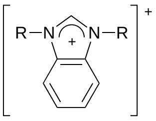
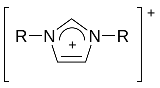
Self-assembly of U-shaped 1,3-dialkylbenzimidazolium salts through hydrogen bonds and interdigitation of alkyl chains produces a bilayer structure with lamellar α and β mesophases.

Self-assembly of molecules through hydrogen bonds and hydrophobic interactions to form supramolecular structures is currently an important chemical issue.[1,2] Hydrogen bonds are especially important in biological systems and in the design of new materials.[3] Specifically, hydrogen bonds have been used in the formation of liquid crystalline phases.[4] Here we report a new class of thermotropic ionic liquid crystals, 1,3-dialkyl-benzimidazolium [$(C_n)_2$-Bim] and -imidazolium [$(C_n)_2$-Im] salts. This model system is a good combination of liquid crystalline compounds having (1) extended $C–H\cdots X$ (X = halides) hydrogen bonds, (2) aromatic rigid cores and (3) hydrophobic interactions between alkyl chains.



$[(C_n)_2\text{-Bim}]^+$ ($R = C_nH_{2n+1}$)



$[(C_n)_2\text{-Im}]^+$ ($R = C_nH_{2n+1}$)

$(C_n)_2$-Bim chlorides and bromides (n = 12, 14, 16, 18) were obtained by the alkylation of 1-alkylbenzimidazoles as previously reported.[5,6] Crystals of $(C_{12})_2$-Bim chlorides and bromides suitable for X-ray single crystal diffraction were recrystallized from CH_2Cl_2.‡ PF_6 (n = 6, 12, 14, 16, 18) and iodide salts (n = 16) were prepared quantitatively *via* the simple displacement of anions. R_2-Im salts (n = 16, X = Cl, Br and PF_6) were prepared in a similar fashion. The purity of all compounds was confirmed by elementary analysis and ^{1}H NMR spectroscopy.

The molecular structure of $[(C_{12})_2\text{-Bim}]Cl$ is shown in Fig. 1(*a*). Two *N*-alkyl chains are approximately orthogonal to the Bim-aromatic plane (5° off the plane normal). The geometry looks like a two-leg stool. Each plane of Bim connects side by side to the neighbouring molecules through $C–H\cdots Cl$ hydrogen bonds, such that the aromatic rings line up in a row with all the legs pointing in the same direction. Each row further connects with the other through hydrogen bonds to form a plane, like a tiled roof and again with all the legs pointing in the same direction. Interdigitation of two such planes with interpenetrating alkyl chains generates a bilayer of 17.7 Å thickness. Each bilayer is further linked with anions through $C–H\cdots Cl$ and $C–H\cdots H_2O\cdots Cl$ hydrogen bonds to form a lamellar structure with a separation of 3.4 Å between the bilayers [Fig. 1(*b*)]. Hydrogen bonds play an important role in the formation of this structure and mesophase. Anions are not in the proximity of the positively charged N atoms, rather, each anion forms hydrogen bonds with four C–H groups [H(2), H″(5), H(10A) and H′(22A)] from three neighbouring Bim planes and two additional hydrogen bonds with H_2O molecules which bridge two H(22A) atoms [Fig. 1(*c*)]. The formation of hydrogen bonds between anions and positively charged H(2), H(10A) and H(22A) are known.[7,8] However, such interactions between anions and H″(5) was until now unknown. If one considers each alkyl chain as a rod, the rods exhibit hexagonal close-packing and the distances between the neighbouring rods are 4.1–4.6 Å.

$[(C_{12})_2\text{-Bim}]Br$ has a similar structure except that (1) the separation between neighbouring bilayers is 3.6 Å and (2) the alkyl chains tilt 20° from the plane normal. Therefore the bromide salt has a smaller bilayer thickness (16.8 Å) than that of the chloride (17.7 Å). To the best of our knowledge, this is the first ionic liquid crystal with lamellar structure formed from interdigitated U-shape molecular ions. Recently, imidazolium salts with liquid crystal behaviour were reported.[9] A rod-like structure with alkyl chains parallel to aromatic rings and perpendicular to the layer normal was proposed to produce the mesophase.

For $(C_n)_2$-Bim and $(C_n)_2$-Im salts, formation of mesomorphism depends on the type of anions and the length of the alkyl chains. $(C_n)_2$-Bim salts of chloride (n = 12, 14, 16, 18) and bromide (n = 14, 16, 18), show liquid crystal behaviour but not the iodide and PF_6 salts from n = 12 to 18. The ease of anions to form liquid crystals follows the order: Cl > Br > I, PF_6. This order is the same as the order of the strength of the $C–H\cdots X$ hydrogen bonds and is the reverse order of the anionic sizes and the separations between the bilayers. Table 1 gives the thermotropic properties of Bim and Im salts obtained from differential scanning calorimetry (DSC) spectra. Taking $[(C_{16})_2\text{-Bim}]Cl$ as an example, three crystal phases and two mesophases were observed. $[(C_{16})_2\text{-Bim}]Br$, however, only

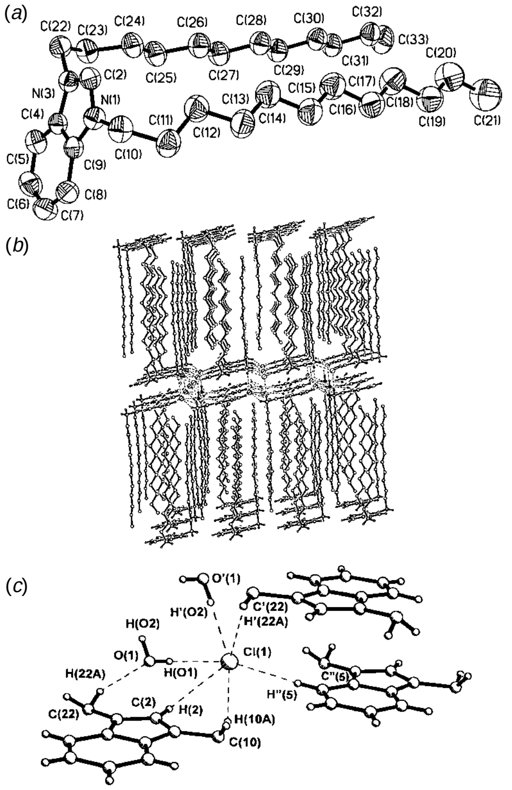


Fig. 1 (*a*) ORTEP drawing of the cation of $[(C_{12})_2\text{-Bim}]Cl$ (50% thermal ellipsolids) with atomic numbering, alkyl chain hydrogen atoms being omitted for clarity; (*b*) stacking of the bilayered structure *b*; (*c*) hydrogen bonds between the chloride anion and Bim cations, the tail end of alkyl chains being omitted for clarity

shows one crystal phase and one mesophase. Both chloride and bromide salts have similar K-S transition temperatures irrespective of their anion and carbon chain length differences. Chloride salts have a wider mesophase temperature range than that of the bromide salts of the same carbon chain lengths. The temperature range of mesophase increases upon increasing the carbon chain lengths. $(C_{16})_2$-Im salts have much lower melting points and wider mesophase temperature ranges than those of $(C_{16})_2$-Bim salts (Table 1).

The results of investigations of $[(C_{16})_2$-Bim]Cl using polarized optical microscopy (POM) and X-ray diffraction (XRD) are in close resemblance to those found for 1,2,ψ,ω-*n*-alkanetetraols, which form lamellar thermotropic liquid crystal phases.[10] The fan-like texture at 130 °C (Fig. 2) is characteristic for the lamellar α phase (L_α) as it is for that of tetraols. The XRD spectrum [Fig. 3(*a*)] indicates that the mesomorphic structure has a layer period of 28.4 Å and has no order in the lamellar planes. On cooling to 110 °C, the texture has hyperbolic lines across the fans (not shown) and is characteristic for the lamellar β phase (L_β), as was proposed for that of tetraols. The corresponding XRD spectrum [Fig. 3(*b*)] shows that the L_β has a layer period of 34.4 Å and has ordered layers. The layer period in L_β is 6 Å longer than the one at 25 °C [Fig. 3(*c*)]. In brief, from crystal to L_β, there is a sudden elongation of the layer period and there is an order in the layers; from L_β to L_α the layer period decreases and the order in the layers disappears. POM and XRD studies show that $[(C_{16})_2$-Bim]Br has a similar mesomorphism, although the DSC spectrum does not detect the L_β–L_α phase transition.

Table 1 Transition temperatures (°C) of compounds $[(C_n)_2$-Bim]Cl (**A**-*n*), $[(C_n)_2$-Bim]Br (**B**-*n*) and $[(C_{16})_2$-Im]X (C-X, X = Cl, Br, PF_6) (ΔH in kJ mol^{-1} in parentheses) determined by DSC at cooling rate of 10 °C min^{-1}

Cpd	K_1		K_2		L_β		L_α		I
A-18	●	78.9 (34.5)	●	105.5 (69.7)	●	111.8 (20.9)	●	150.4 (4.9)	●
A-16	●	76.1 (25.5)	●	102.1 (47.0)	●	110.9 (17.8)	●	147.8 (4.7)	●
A-14	●	79.7 (38.2)	●	102.0 (56.7)	●	109.0 (25.6)	●	140.5 (7.2)	●
A-12	●	79.9 (5.6)	●	98.1 (60.6)	●	112.7 (22.6)	●	127.1 (5.8)	●
B-18	●	80.4 (8.8)	●	103.9 (72.7)	●	110.3[a] (n.d.)	●	145.3 (4.3)	●
B-16	●			101.1 (85.0)	●	109.5[a] (n.d.)	●	132.2 (3.6)	●
B-14	●	76.7 (4.4)	●	103.6 (41.5)			●	129.5 (2.7)	●
C-Cl	●	31.1 (25.9)					●	151.5 (2.7)	●
C-Br	●	45.7 (31.2)					●	142.6 (2.2)	●
C-PF_6	●	61.3 (46.1)					●	103.3 (2.0)	●

K = crystal; L_α, L_β = lamellar mesophases; I = isotropic liquid; n.d. = not determined. [a] Determined by polarized optical microscopy.

Fig. 2 The fan-like texture of $[(C_{16})_2$-Bim]Cl at 130 °C

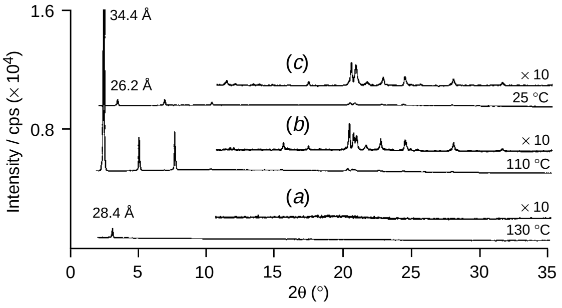


Fig. 3 Temperature dependence of XRD for $[(C_{16})_2$-Bim]Cl at (*a*) 130 °C; (*b*) 110 °C; (*c*) 25 °C

In summary, the self assembly of 1,3-dialkyl substituted Bim and Im salts forms bilayered lamellar supramolecules through extended hydrogen bonds. These ionic salts show liquid crystal behaviour of unprecedented mesomorphism compared to other known ionic liquid crystals. An extended mesophase range can be adjusted by altering the aromatic core, alkyl chain length and anion. This system presents an unusual ionic liquid solvent with lamellar structure. Ionic liquid solvents can modify the course of chemical reactions.[11] Lamellar liquid crystal solvents may even have profound effects on chemical reactions, especially when they contain intercalating metal ions, such as Pd^{2+}. They are therefore potentially useful ionic solvents and catalysts. This bilayer structure also mimics biological membranes.

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Footnotes

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‡ *Crystal data* for $[(C_{12})_2$-Bim]Cl. $C_{31}H_{57}N_2OCl$, M = 509.24, triclinic, space group $P\bar{1}$, a = 8.7589(10), b = 8.778(2), c = 21.218(2) Å, α = 82.695(14), β = 88.744(8), γ = 79.19(2)°, V = 1589.3(4) $Å^3$, Z = 2, $F(000)$ = 564, D_c = 1.064 mg m^{-3}, T = 296 K, crystal dimensions 0.6 × 0.5 × 0.5 mm; intensity data were collected on Siemens P4 diffractometer with graphite monochromatized MoKα radiation (λ = 0.71073 Å), 5606 non-zero (2σ) reflections out of 6012 collected with $2 < 2\theta < 50°$, solution SHELXS-86, refinement SHELXL-93 on F^2, R = 0.0403, wR_2 = 0.0953, C, N, O, Cl anisotropic, H isotropic. The final fourier difference map showed residual electron density of 0.170 e $Å^{-3}$. For $[(C_{12})_2$-Bim]Br. $C_{31}H_{57}N_2OBr$, M = 553.70, triclinic, space group $P\bar{1}$, a = 9.143(2), b = 9.1720(10), c = 20.340(3) Å, α = 90.344(12), β = 101.47(2), γ = 100.724(14)°, V = 1640.8(4) $Å^3$, Z = 2, $F(000)$ = 600, D_c = 1.121 mg m^{-3}, T = 296 K, Crystal dimensions 0.6 × 0.3 × 0.2 mm; 3997 non-zero (2σ) reflections out of 4302 collected with $3.5 < 2\theta < 45°$, solution SHELXS-86, refinement SHELXL-93 on F^2, R = 0.0520, wR_2 = 0.0693, C, N, O, Cl anisotropic, H isotropic. The final fourier difference map showed residual electron density of 0.187 e $Å^{-3}$. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Information for Authors, Issue No. 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 182/425.

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