Crystal polymorphism in 1-butyl-3-methylimidazolium halides: supporting ionic liquid formation by inhibition of crystallization†

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Crystallization of 1-butyl-3-methylimidazolium chloride from mixed ionic liquid or ionic liquid–aromatic solution, and from the melt yields different crystalline polymorphs, the first direct evidence for inhibition of crystallization in ionic liquids by polymorphism.

The potential to use ionic liquids (ILs) as non-volatile solvents for green chemistry and liquid electrolytes has led to extensive recent interest.[1,2] The utility of ILs arises from the combination of solvent/liquid properties exhibited, the principal feature being, *a priori*, a low melting point. We report here, the first observation of crystalline polymorphs of an IL material, demonstrating the importance of alkyl-substituent mobility in controlling the melting/solidification transition of IL salts.

The low melting points exhibited by ILs result from decreased lattice energies, frustration of crystallinity caused by reduced symmetry,[3] inhibition of crystallization through provision of a large number of similarly stabilized solid-state structures (polymorphism) which can also lead to plasticity and glass formation in the solid state,[4] and low energy melting transitions, *via* 'weaknesses' in the crystal lattice. However, the influences of hydrogen-bonding and other ion–ion interactions is not entirely simple, for example, 1,3-dimethylimidazolium methylsulfate[5] has strong, directional hydrogen-bonded ribbons in the solid state, but melts at 43 °C, whereas the corresponding hexafluorophosphate salt[6] contains no significant hydrogen-bonding, yet the melting point is higher. Similarly, increasing alkyl-substitution on the cation[7] leads to an initial reduction of melting points, followed by an increase in crystal stabilization.

The crystal structures of two polymorphs of 1-butyl-3-methylimidazolium chloride, [C4mim]Cl, and the crystal structure of one polymorph modification of the corresponding bromide, [C4mim]Br, have been determined.‡ An orthorhombic form (**I**) was isolated for both [C4mim]Cl and [C4mim]Br on cooling of the molten salt to room temperature. Whereas, on crystallization of [C4mim]Cl from mixtures of [C4mim]Cl with the room temperature ILs [C4mim][PF6] and [C4mim][BF4], or from [C4mim]Cl/benzene and [C4mim]Cl/toluene liquid clathrates,[6] a monoclinic form (**II**) was obtained.

Melting points were determined by DSC; the melting point of the orthorhombic form, **I**, was consistent with the reported melting point (66 °C), the monoclinic polymorph, form **II**, displayed a transition at 41 °C (determined by DSC) which displayed a broad peak characteristic of plastic crystal transitions. No crystal–crystal transformations were observed by DSC for **I**, **I**-Br, or **II**, on cooling from ambient temperature, which suggests that the orthorhombic structure is more thermodynamically stable, and that the monoclinic form **II** can

only be accessed *via* crystallization in the presence of a second solvent or solute species.

The identity of the two polymorphs was confirmed by single crystal X-ray diffraction at −100 °C. The absence of low temperature transitions in the DSC indicates that these structures correspond to the polymorphs **I** and **II** isolated at room temperature. The cation coordination environment for both **I** and **II** are shown in Fig. 1. For both polymorphs the asymmetric unit contains only one cation and one anion. The respective ion environments result from the competing influences of ion–ion and van der Waals attractive forces and the disruption of Coulombic packing by the uncharged hydrocarbon regions.

In all three structures, in common with other alkylimidazolium salts available in the CSD database, the β-carbon of the alkyl-group is twisted out of the plane of the imidazolium ring (95° for **I**, 100.1° for **I**-Br, and 88.6° for **II**). The conformational feature of the cation that differentiates **I** and **II** is the torsion angle around C(7)–C(8) in the butyl chain. An overlay of the cations in the two polymorphic modifications, and Fisher projections viewed along the C(7)–C(8) bond of the cations are shown in Fig. 2 and illustrate the differences.

A pronounced kink in the butyl-chain relative to the ring is displayed in **I**, this results from a twist in the all-*gauche* chain
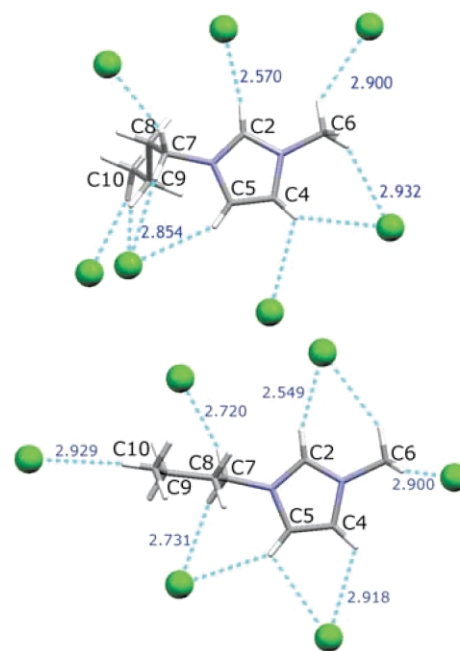

Fig. 1 The cation coordination environments in the orthorhombic (**I**, *top*) and monoclinic (**II**, *bottom*) polymorphs of [C4mim]Cl. In **I**, the cation has seven close anions, although only four provide close-contacts at, or below, the vdW distance, and in **II**, six (distances in Å).
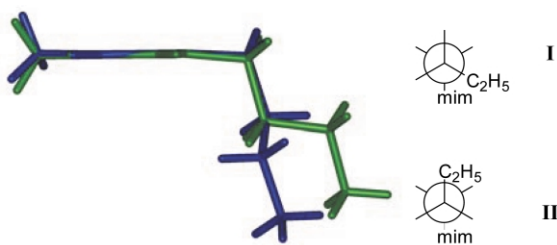
Fig. 2 Overlay of cations from the orthorhombic (**I**, *blue*) and monoclinic (**II**, *green*) polymorphs of [C₄mim][Cl] showing in Fisher projection, the conformation of the C(7)–C(8) bond of the butyl chain.

at the C(7)–C(8) bond (torsion angle, 67.96° for **I** and 66.21° for **I**-Br). In contrast, for the monoclinic polymorph **II**, all the C–C bonds of the alkyl-chain are in an *anti* configuration which projects the chain away from the imidazolium ring, with a torsion angle around C(7)–C(8) of 174.12°. Accommodating the kink in **I**, results in different hydrogen-bonding patterns between the imidazolium rings and halide anions.

In **I**, there are four short hydrogen-bond contacts between the cation and adjacent chloride ions. The shortest contact, to the C(2)–H hydrogen, results in an almost linear hydrogen bond (C–H⋯Cl, 2.57 Å, 161°). The remaining three contacts are with hydrogens H6B, H6C, and H7A of the *N*-methyl and methylene functions, respectively. Expanding the interaction limit to 0.2 Å beyond the van der Waals radii, reveals three further chloride anions within the local cation coordination environment, interacting with the two ring hydrogens H4A and H5A, and a further long contact to the methylene hydrogen H7B and terminal H10C. Thus, each ion has four counter-ion near-neighbours below the van der Waals contact limit, and a further three at slightly longer distance. In **I**-Br, the closest anion–cation interaction [C(2)–H⋯Br] is 2.59 Å.

For the monoclinic polymorph, **II**, distinguished by an *anti* conformation of the butyl-chain, each ion in the lattice has six neighbouring counter-ions in contact at the van der Waals distance. The shortest hydrogen-bond is again to the C(2)-hydrogen (C–H⋯Cl, 2.54 Å, 158°), the next closest interactions are with the hydrogens on the carbon in the alpha position of the alkyl chain, C(7). In contrast to **I**, the remaining ring-hydrogens (H4A, H5A) also display strong hydrogen-bonding interactions.

Interestingly, each ion in **I**, the more thermodynamically stable polymorph, has less Coulombic ion–ion interactions in the coordination sphere than **II**. This however, allows greater close packing of the methylene-groups and also an apparent terminal CH₃⋯π stacking contact, which help to stabilize the extended crystal lattice through combined Coulombic and van der Waals forces resulting in more efficient packing of the hydrocarbon-chains and a slightly higher crystal density. In **II**, the orientation of the butyl-chain away from the imidazolium ring produces cation pairs which form in a head-to-tail fashion, and have no other significant van der Waals contacts.

It is notable that in both polymorphs, a bifurcated hydrogen-bonding pattern from the C(4/5)-hydrogens to the anion, along the reflection axis of the imidazolium ring is observed. This differs from the packing observed in the crystal structures of [C₂mim]Br and **I**,[8] and [C₁mim]Cl in both the crystal[9] and liquid states.[10] A search of the CSD for [C₄mim]⁺ cations revealed only four structures,[11,12] three[11] show the butyl chain in the twisted conformation observed for **I**, whereas the fourth[12] shows two cations, one all-*gauche* and one all-*anti*.

The presence of two crystalline polymorphs, which differ only in the conformation of the alkyl chain, confirms that the potential energy surface for [C₄mim]Cl contains two, or more, local conformational energy minima, and provides direct evidence that the tendency for ILs to remain as super-cooled liquids which generally crystallize in a sluggish manner is a result of crystal-packing frustration caused by the introduction of the single, flexible alkyl-chain substituent into the imidazo-

lium cation. In addition, it could also be considered that since the two polymorphs have distinct, and non-mixing crystal lattices, then the formation of a eutectic liquid region below the melting points of both polymorphs might be anticipated from competition between the two crystalline forms.

Note added at proof: Hagamuchi and coworkers have just published two excellent, highly relevant papers.[13]

Notes and references

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