

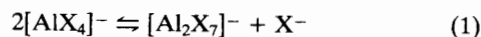
## Upon the Structure of Room Temperature Halogenoaluminate Ionic Liquids

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The X-ray structure of a monoclinic crystal of 1-methyl-3-ethylimidazolium iodide, [MeEtim]I, reveals the presence of discrete hydrogen-bonded ion-pairs [ $r\{C(2)H \cdots I^{-}\} = 0.293$  nm]: the structural implications of the presence of hydrogen-bonding in ionic liquids based upon [MeEtim]X–AlX<sub>3</sub> (X = Cl or Br) mixtures are discussed.

The field of room temperature chloroaluminate melts<sup>1</sup> gained tremendous momentum with the discovery, in 1982,<sup>2</sup> of a system based upon mixtures of 1-methyl-3-ethylimidazolium chloride, [MeEtim]Cl, and aluminium chloride: a system which is liquid at 20 °C over a wide range of compositions and, at certain acidic† compositions, is liquid at temperatures as low as –95 °C.<sup>3</sup> The analogous bromide system was reported earlier this year.<sup>4</sup> Like the related ionic liquids based upon mixtures of 1-butylpyridinium chloride, [Bupy]Cl, and aluminium chloride, the majority of the studies have centred upon the anionic equilibrium (1), and a recent structural analysis has confirmed the presence of both [AlCl<sub>4</sub>]<sup>–</sup> and [Al<sub>2</sub>Cl<sub>7</sub>]<sup>–</sup>.<sup>5</sup> The role of the cation, however, is poorly understood. Tait and Osteryoung<sup>6</sup> have proposed (upon i.r. evidence) that specific two-species ion-pair interactions occur in basic ionic liquids, possibly involving distortion of the imidazolium ring with concomitant loss of aromatic character and/or a hydrogen-bond between the hydrogen on the C(2) carbon atom of the ring and a chloride ion. In contrast, Wilkes and coworkers<sup>7</sup> have proposed a model in which the liquid consists of oligomeric chains held together by ion–ion interactions, each cation being associated with two anions (in the case of strongly basic liquids, two chloride ions), one above and one below the plane of the imidazolium ring: they explicitly state that no hydrogen-bonding is possible in this system. We present here structural evidence that 1-methyl-3-ethylimidazolium iodide forms crystals consisting of discrete hydrogen-bonded ion-pairs, and discuss the implication that this observation has for the structure of these ionic liquids.



† An acidic ionic liquid contains an excess of aluminium halide over [MeEtim]X, a basic ionic liquid contains an excess of [MeEtim]Cl over aluminium halide.<sup>1</sup>

[MeEtim]I (formed from the reaction between 1-methylimidazole and iodoethane) forms monoclinic crystals,‡ and the crystal structure reveals the presence of discrete ion-pairs. Furthermore, the structure of an ion-pair (Figure 1) reveals the unambiguous presence of a hydrogen-bond between the

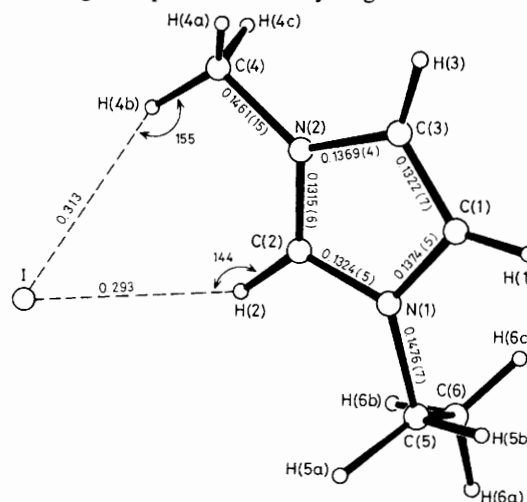


Figure 1. The structure of the [MeEtim]<sup>+</sup> ··· I<sup>–</sup> ion-pair showing bond distances (nm) and bond angles (°).

‡ Crystal data: C<sub>6</sub>H<sub>11</sub>IN<sub>2</sub>, *M* = 238.07, monoclinic, space group *P*2<sub>1</sub>/*c*, *a* = 0.8789(3), *b* = 0.8130(3), *c* = 1.3364(3) nm, β = 107.33(2)°, *U* = 0.911 71 nm<sup>3</sup>, *Z* = 4, *D<sub>c</sub>* = 1.734 g cm<sup>–3</sup>, μ(Mo-*K*<sub>α</sub>) = 34.05 cm<sup>–1</sup>, crystal dimensions = 0.25 × 0.20 × 0.15 mm. The data were measured on an Enraf–Nonius CAD4 diffractometer. 1089 Reflections were used in the refinement, which converged at *R* = 0.023, *R*' = 0.028.

Atomic co-ordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1, 1986.

hydrogen atom on the C(2) atom of the imidazolium ring and the iodide ion [0.293(3) nm, *cf.* van der Waals separation *ca.* 0.33 nm]. Moreover, the iodide ion is not situated above the imidazolium ring, which is itself planar and conventionally aromatic (*vide supra*). The pure 1-methyl-3-ethylimidazolium halide represents the limit of the condition for a basic ionic liquid, and it is reasonable to assume that this is also the situation which pertains in the liquid state, thus explaining the dramatic effect that Cl<sup>-</sup> concentration has upon  $\delta[\text{H}(2)]$  in <sup>1</sup>H n.m.r. spectra of basic ionic liquids.<sup>7</sup> Further evidence for the presence of strong hydrogen-bonding in the liquid state is obtained from i.r. spectroscopy. Tait and Osteryoung<sup>6</sup> assigned a band at *ca.* 3050 cm<sup>-1</sup> in a basic 71.4% [MeEtim]Cl–28.6% AlCl<sub>3</sub> ionic liquid to either N–H/O–H association or C–H ··· Cl<sup>-</sup> hydrogen-bonding. We find that a similar band is present at *ca.* 3080 cm<sup>-1</sup> in the i.r. spectra of all the salts [MeEtim]X (X = Cl, Br, or I), but absent from the i.r. spectra of the salts [MeEtim]<sub>2</sub>[UCl<sub>6</sub>] and [MeEtim]<sub>2</sub>[UO<sub>2</sub>Cl<sub>4</sub>], which show no crystallographic evidence for the presence of any hydrogen-bonding between the anion and the cations.<sup>8</sup> The presence of this band, both in the liquid and solid state, may thus be regarded as diagnostic of the presence of a strong, discrete C(2)–H ··· X<sup>-</sup> hydrogen-bond, and adds significant weight to the arguments of Tait and Osteryoung<sup>6</sup> for discrete ion-pairing in the liquid state.

Finally, the mass spectra of the salts [MeEtim]X (X = Cl, Br, or I) were obtained by positive ion fast atom bombardment mass spectrometry (matrix, glycerol; xenon atom beam;

gun voltage, 8 kV; ion source accelerating potential, 4 kV). As well as the observation of the expected ion associated with [MeEtim]<sup>+</sup> at *m/z* 111, strong peaks were observed corresponding to [(MeEtim)<sub>2</sub>X]<sup>+</sup>, pointing to the possibility that, in the gas phase, the hydrogen-bonding is not restricted to the simple ion-pairs found in the solid and liquid states.

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