

## Crystallographic view of fluidic structures for room-temperature ionic liquids: 1-butyl-3-methylimidazolium hexafluorophosphate

Sergey M. Dibrov and Jay K. Kochi\*

Department of Chemistry, University of Houston, 4800 Calhoun Drive, Houston, TX 77204, USA

Correspondence e-mail: jkochi@uh.edu

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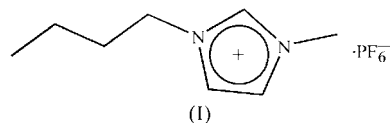
Shock-induced crystallization of the supercooled ionic liquid 1-butyl-3-methylimidazolium hexafluorophosphate,  $C_8H_{15}N_2^+PF_6^-$ , allows for the first time precise X-ray diffraction analysis directly pertinent to the fluid state. This intermediate-chain-length structure shows features of both short- and long-chain analogs. Two types of interplanar distances between imidazolium rings are observed. The anions are located in channels formed by the imidazolium rings and alkyl chains.

### Comment

Room-temperature ionic liquids are attracting significant interest owing to their chemical characteristics and potentially useful solvent properties (Rogers & Seddon, 2002, 2003; Wasserscheid & Welton, 2002). Since ionic liquids from the widely used imidazolium salts can retain some definite local 'structure' despite their homogeneous appearance, they potentially offer a unique opportunity to obtain direct and quantitative structural information about the fluid state (Bowron *et al.*, 2003).

Although crystalline halide salts of 1-butyl-3-methylimidazolium ( $BMIM^+$ ) have been characterized (Holbrey, Reichert, Nieuwenhuysen, Johnston *et al.*, 2003; Saha *et al.*, 2003), they are structurally compromised for the direct comparison of the liquid and solid structures by the presence of substantial hydrogen-bonding forces. By contrast, imidazolium salts of the weakly coordinating hexafluorophosphate ( $PF_6^-$ ) anion are less prone to participate in such extra hydrogen-bonding interactions and are thus more likely to lead to local interionic interactions that resemble those in liquid-state structures. Indeed, recent small-angle X-ray scattering (SAXS) studies of  $BMIM^+PF_6^-$ , (I), have provided an interesting semi-quantitative view of the structural inhomogeneity that can persist in ionic liquids (Billard *et al.*, 2003). Two peaks corresponding to an interplanar imidazolium distance of 4.4 Å and a centroid-to-centroid distance of 6.3 Å

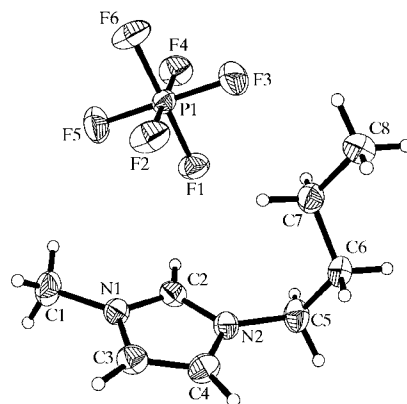
were observed, and the coherence distance of 15 Å was attributed to the extent of local order in the fluid state; beyond this limited resolution, no definitive structural information could be gleaned. Furthermore, the surface-layering effect has also been studied by X-ray reflectivity, and several possible structures of the  $BMIM^+PF_6^-$  surface have been proposed (Solutskin *et al.*, 2005).



We now report the successful crystallization of (I) for a definitive X-ray crystallographic structure analysis; a liquid sample of (I) was initially supercooled at 243 K and crystalline material was obtained by shock-induced crystallization. Many alternative attempts at the crystallization of this highly hygroscopic and low-melting salt have been unsuccessful because its melting point of 284 K is severely depressed by the trace presence of water and by other organic solvents. The entire bulk of the sample crystallizes spontaneously. Given this fact, we assume that the structure of such a crystalline material is very much akin to the structure of this ionic liquid in its fluid state.

The structure of (I) is shown in Fig. 1. The planar imidazolium ring is highly delocalized, as evidenced by the C–N and C–C bond distances; the N1–C2 and N2–C2 bonds [1.3226 (18) and 1.3259 (18) Å, respectively] are shorter than the N1–C3 and N2–C4 bonds [1.3751 (17) and 1.3781 (17) Å, respectively], and the C3–C4 bond length is 1.346 (2) Å. Atoms C1 and C5 lie in the plane of the imidazolium ring (the mean deviation is 0.0153 Å). The butyl chain, in which all four C atoms lie in a plane (the mean deviation is 0.0121 Å), propagates in the all-*trans* conformation. This chain is twisted with respect to the C5–N2 bond, as indicated by the N2–C5–C6–C7 torsion angle of  $-60.80$  (17)°. The butyl group makes an interplanar angle of 82.29 (5)° with the plane of the imidazolium ring.

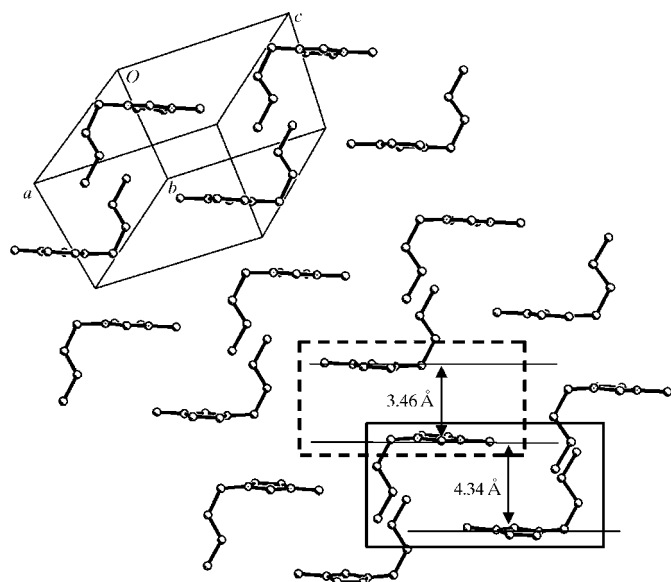
It is interesting to compare the cation packing of (I) with that of its short- and long-chain analogs. The series of 1-methyl-3-alkylimidazolium salts are arbitrarily categorized



**Figure 1**  
The molecular structure of (I). Displacement ellipsoids are drawn at the 50% probability level.

as either short-chain, the alkyl being methyl (Holbrey, Reichert, Nieuwenhuizen, Sheppard *et al.*, 2003) or ethyl (Fuller *et al.*, 1994), or long-chain, the alkyl being dodecyl (Gordon *et al.*, 1998) or tetradecyl (De Roche *et al.*, 2003); all have melting points above room temperature and are readily crystallized. X-ray crystallographic studies show that structures in short-chain ionic liquids are dominated by electrostatic cation–anion interactions that lead to salts with high lattice energy and higher melting points. In long-chain ionic liquids, significant hydrophobic alkyl chain–chain interactions govern the higher melting points. The *n*-butyl analog, (I), is the exception, the intermediate length of the alkyl chain disrupting the strong cation–anion interactions but being insufficient for chain–chain effects to be dominant. As such, (I) is the only structurally characterized imidazolium hexafluorophosphate that remains liquid at room temperature.

The supramolecular structure of the imidazolium rings of (I) shown in Fig. 2 represents a hybrid of both short- and long-chain structures. Two types of imidazolium interplanar arrangements are found; in one set, the butyl groups point into the space between the imidazolium rings (solid box), and in the other they point outwards (dashed box). The first motif is somewhat similar to those in the short-chain analogs, where cations are arranged in discrete pairs. In (I), these pairs propagate continuously. The centers of corresponding imidazolium rings of these pairs are shifted by 4.307 (4) Å. The imidazolium–imidazolium interplanar distance of these pairs is 4.3378 (15) Å, with a centroid-to-centroid separation of 6.113 (4) Å. Pairs of imidazolium rings with butyl chains pointing outwards form a set of planes similar to those found in the long-chain analogs. The alkyl chains of neighboring cations form interpenetrating regions along the crystallographic *b* axis with about 4 Å separation between the chains (Fig. 3), but this alkyl chain arrangement does not have a pronounced effect on the crystal structure of (I). Unlike in the



**Figure 2**

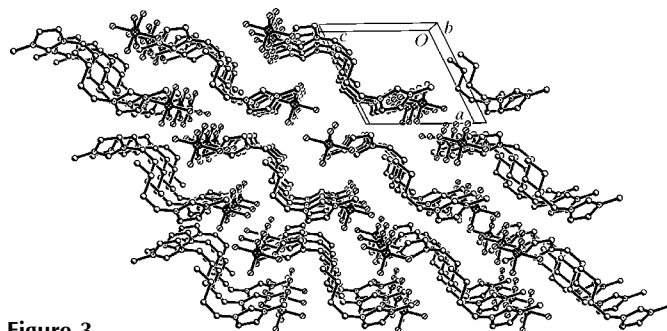
The two different types of interplanar arrangements of imidazolium cations in the room-temperature ionic liquid (I). H atoms have been omitted.

corresponding dodecyl and tetradecyl hexafluorophosphates, the imidazolium rings in (I) are all parallel, with a 3.4618 (14) Å interplanar distance and a 4.857 (4) Å centroid-to-centroid separation. The rings are also shifted with respect to each other by 3.407 (4) Å. Because of these shifts, there are no close  $\pi$ – $\pi$  interactions between the imidazolium rings. The hexafluorophosphate anions are positioned close to the imidazolium rings and lie in the channels between the imidazolium rings and butyl chains, as shown in Fig. 3.

The  $\text{PF}_6^-$  anion forms several  $\text{H}\cdots\text{F}$  contacts that are less than the sum of the van der Waals radii of H (1.2 Å) and F atoms (1.5 Å). All  $\text{H}\cdots\text{F}$  contacts with  $\text{C}\text{--}\text{H}\cdots\text{F}$  angles greater than  $90^\circ$  that match this criterion are listed in Table 1. The shortest contact is the  $\text{H2}\cdots\text{F1}$  distance of 2.36 Å, which is the shortest hydrogen–fluorine distance so far found in linear alkylimidazolium hexafluorophosphate ionic liquids (the corresponding distances for the methyl, ethyl, dodecyl and tetradecyl analogs are 2.64, 2.58, 2.58 and 2.47 Å, respectively). Nonetheless, it represents a very weak hydrogen bond according to published criteria (Hitchcock *et al.*, 1993; Gordon *et al.*, 1998; Desiraju, 2004).

With the detailed structural information of (I) in hand, it is now possible to draw conclusions about the structure of this ionic liquid in its fluid phase. Close examination of the crystal structure suggests that the previous structural assignment was only partially correct. The plane-to-plane and ring-to-ring solid-state distances of 4.3378 (15) and 6.113 (4) Å may be safely correlated with the 4.4 and 6.3 Å peaks observed by the SAXS method (Billard *et al.*, 2003). Concomitantly, the coherence distance of 15 Å is better described by two repetitions of alternating 4.3378 (15) and 3.4618 (14) Å imidazolium–imidazolium interplanar distances, giving a value of 15.6 Å (Fig. 2). It is also interesting to compare the electron density of the bulk  $\text{BMIM}^+\text{PF}_6^-$  liquid (with  $\rho = 0.42 \text{ e \AA}^{-3}$ ) and its surface (Solutskin *et al.*, 2005) (with  $\rho = 0.50 \text{ e \AA}^{-3}$ ) to the electron density of the crystalline sample (with  $\rho = 0.48 \text{ e \AA}^{-3}$ ). It seems plausible to suppose that structural features of the crystalline sample are also retained at the surface of a liquid sample to an even greater degree than in the bulk liquid.

In summary, the detailed structure of the widely used and extensively studied room-temperature ionic liquid (I) has been obtained. Given the precise X-ray crystal data, we are now able to interpret the structural data obtained previously



**Figure 3**

A view of the molecular arrangements of (I), showing the  $\text{PF}_6^-$  channels and interpenetrating alkyl chains. H atoms have been omitted.

by small-angle X-ray scattering and reflectivity on liquid samples, and to elucidate the structure of the ionic liquid (I) to a greater degree of certainty. By comparing the electron densities of the surface layer and the crystalline sample, it is clear that the structural information obtained will greatly facilitate the elucidation of the structural features of this material not only in the bulk but also at the liquid surface.

## Experimental

The sample of the title compound was supplied by Dr Baldelli (University of Houston). It was synthesized according to the method of Bortolini *et al.* (2003).

### Crystal data

$C_8H_{15}N_2^+ \cdot PF_6^-$	$Z = 2$
$M_r = 284.19$	$D_x = 1.560 \text{ Mg m}^{-3}$
Triclinic, $P\bar{1}$	Mo $K\alpha$ radiation
$a = 8.7549 (12) \text{ \AA}$	Cell parameters from 9189 reflections
$b = 8.9042 (12) \text{ \AA}$	$\theta = 2.5\text{--}30.0^\circ$
$c = 9.0128 (13) \text{ \AA}$	$\mu = 0.28 \text{ mm}^{-1}$
$\alpha = 95.810 (3)^\circ$	$T = 173 (2) \text{ K}$
$\beta = 114.955 (2)^\circ$	Plate, colorless
$\gamma = 103.061 (3)^\circ$	$0.50 \times 0.18 \times 0.01 \text{ mm}$
$V = 604.96 (15) \text{ \AA}^3$	

### Data collection

Bruker SMART diffractometer	2840 reflections with $I > 2\sigma(I)$
$\omega$ scans	$R_{\text{int}} = 0.020$
Absorption correction: multi-scan (SADABS; Bruker, 2003)	$\theta_{\text{max}} = 30.0^\circ$
$T_{\text{min}} = 0.889$ , $T_{\text{max}} = 1.000$	$h = -12 \rightarrow 12$
9189 measured reflections	$k = -12 \rightarrow 12$
3486 independent reflections	$l = -12 \rightarrow 12$

### Refinement

Refinement on $F^2$	$w = 1/[\sigma^2(F_o^2) + (0.0749P)^2 + 0.0074P]$
$R[F^2 > 2\sigma(F^2)] = 0.043$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.125$	$(\Delta/\sigma)_{\text{max}} = 0.001$
$S = 1.05$	$\Delta\rho_{\text{max}} = 0.41 \text{ e \AA}^{-3}$
3486 reflections	$\Delta\rho_{\text{min}} = -0.27 \text{ e \AA}^{-3}$
156 parameters	
H-atom parameters constrained	

**Table 1**

Hydrogen-bond geometry ( $\text{\AA}$ ,  $^\circ$ ).

$D-H \cdots A$	$D-H$	$H \cdots A$	$D \cdots A$	$D-H \cdots A$
$C2-H2 \cdots F1$	0.95	2.36	3.2264 (17)	152
$C2-H2 \cdots F5^i$	0.95	2.58	3.1721 (19)	121
$C3-H3 \cdots F6^{ii}$	0.95	2.43	3.3653 (19)	167
$C4-H4 \cdots F5^{iii}$	0.95	2.56	3.4008 (18)	147
$C5-H5B \cdots F4^{iii}$	0.99	2.52	3.2917 (19)	135
$C1-H1B \cdots F2^{ii}$	0.98	2.45	3.329 (2)	150
$C8-H8C \cdots F5^{iv}$	0.98	2.55	3.499 (2)	163

Symmetry codes: (i)  $-x + 1, -y + 2, -z + 1$ ; (ii)  $-x + 1, -y + 1, -z + 1$ ; (iii)  $x + 1, y, z + 1$ ; (iv)  $x, y, z + 1$ .

H atoms were placed in calculated positions and were treated as riding atoms, with C—H distances of 0.98 ( $\text{CH}_3$ ), 0.99 ( $\text{CH}_2$ ) and 0.95  $\text{\AA}$  ( $\text{CH}$ ); methyl groups were allowed to rotate freely.

Data collection: SMART (Bruker, 2003); cell refinement: SAINT (Bruker, 2003); data reduction: SAINT and SADABS (Bruker, 2003); program(s) used to solve structure: SHELXTL (Bruker, 2003); program(s) used to refine structure: SHELXTL; molecular graphics: XP (Bruker, 1999); software used to prepare material for publication: SHELXTL and XCIF (Bruker, 1999).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: JZ1769). Services for accessing these data are described at the back of the journal.

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