

Imidazolium-based ionic liquid salts: 3,3'-dimethyl-1,1'-(1,4-phenylenedimethylene)diimidazolium bis(tetrafluoroborate) and 3,3'-di-*n*-butyl-1,1'-(1,4-phenylenedimethylene)diimidazolium bis(trifluoromethanesulfonate)

Kilivelu Ganesan, Yatimah Alias and Seik Weng Ng*

Department of Chemistry, University of Malaya, 50603 Kuala Lumpur, Malaysia

Correspondence e-mail: seikweng@um.edu.my

Received 17 July 2008

Accepted 22 July 2008

Online 9 August 2008

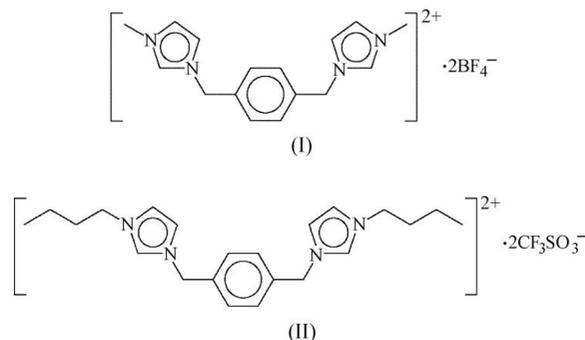
Crystallization of the ionic liquid 3,3'-dimethyl-1,1'-(1,4-phenylenedimethylene)diimidazolium bis(tetrafluoroborate), $C_{16}H_{20}N_4^{2+} \cdot 2BF_4^-$, (I), from its solution in water has permitted the first single-crystal study of an imidazolium-based ionic liquid having a tetrafluoroborate ion as counterion. Despite the expectation that the anion would not participate in nonclassical hydrogen bonding, the ionic liquid features C—H...F hydrogen bonds. The dication lies about a center of inversion. The ionic liquid 3,3'-di-*n*-butyl-1,1'-(1,4-phenylenedimethylene)diimidazolium bis(trifluoromethanesulfonate), $C_{22}H_{32}N_4^{2+} \cdot 2CF_3SO_3^-$, (II), features both C—H...F and C—H...O hydrogen bonds.

Comment

Some ionic liquids incorporate an imidazolium group, as this feature appears to confer limited crystallinity despite the homogenous appearance of these ionic liquids. An understanding of the liquid–crystalline state of such compounds has been provided by the crystal structure of the prototype ionic liquid 1-butyl-3-methylimidazolium chloride. The solid-state structure shows weak hydrogen bonding between the cations and chloride anions (Saha *et al.*, 2003). A better understanding of the solid-state *versus* liquid-state structures is furnished by the crystal structure of the hexafluorophosphate salt of 1-butyl-3-methylimidazolium (Dibrov & Kochi, 2006). As the hexafluorophosphate anion does not normally participate in nonclassical hydrogen bonding, the crystal structure probably better represents the inter-ionic interactions of the liquid–crystalline state.

Our interest in the 3,3'-dimethyl-1,1'-(1,4-phenylenedimethylene)diimidazolium dication arises from several reports on the applications of this class of ionic liquids. For example,

1-*n*-butyl-3-methylimidazolium tetrafluoroborate possesses an excellent gas-absorption property. As these studies have suggested that the nature of the anion influences this property (Aki *et al.*, 2004; Anthony *et al.*, 2005; Galán Sánchez *et al.*, 2007), we synthesized several 3,3'-dimethyl-1,1'-(1,4-phenylenedimethylene)diimidazolium salts, *viz.* with the hexafluorophosphate, tetrafluoroborate and trifluoromethylsulfonate anions, and examined their ^{13}C NMR properties in



various solvents (Ganesan & Alias, 2008). We expect this class of compounds, which possess a rigid phenylenedimethylene link between the imidazolium rings, to possess superior physical properties as studies on other compounds have shown the connection between chain length and physical properties (Holbrey & Seddon, 1999).

3,3'-Dimethyl-1,1'-(1,4-phenylenedimethylene)diimidazolium bis(tetrafluoroborate), (I), exists as a dication and a monoanion (Fig. 1) that interact weakly through C—H...F hydrogen bonding. The anion forms several contacts that are less than the sum of the van der Waals radii of hydrogen (1.2 Å) and fluorine (1.5 Å) (Table 1). Two of the three hydrogen bonds, both from the imidazolium group, are significantly short (2.33 and 2.37 Å); moreover, these two hydrogen bonds are almost linear (171 and 162°, respectively). All distances between adjacent phenylene rings or between adjacent imidazolium rings exceed 4 Å. The bond dimensions of the dication are similar to those found in the hexachloroplatinate(IV) (Li & Liu, 2003), tetrathiocyanatocadmate(II) (Liu *et al.*, 2002), tetraselenocyanatocadmate (Liu & Li, 2003) and tetrachloroargentate (Wang *et al.*, 2005) salts.

The bond dimensions of the tetrafluoroborate counterions are marginally different from those found in more flexible dications, *viz.* in 1,1'-methylenebis(3-methylimidazol-

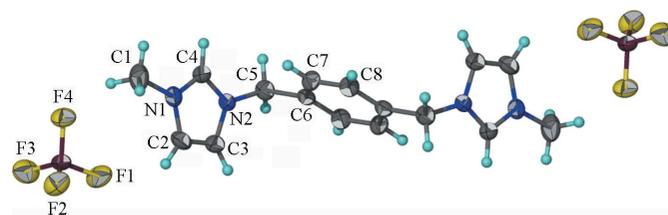


Figure 1

Displacement ellipsoid plot (Barbour, 2001) of (I) at the 70% probability level. H atoms are drawn as spheres of arbitrary radii. The dication lies on a center of inversion at $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$.

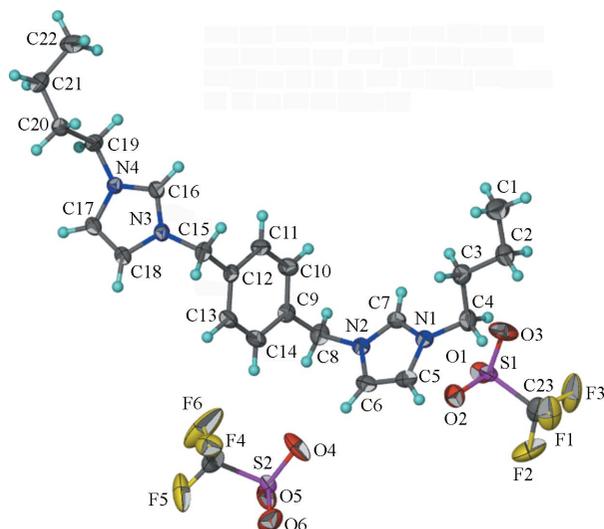


Figure 2
Displacement ellipsoid plot (Barbour, 2001) of (II) at the 70% probability level. H atoms are drawn as spheres of arbitrary radii.

ium) dipicrate (Jin *et al.*, 2006) and 3,3'-dimethyl-1,1'-ethylenediimidazolium dibromide (Jin *et al.*, 2007). The N—C_{methylene} distance [1.470 (3) Å] is lengthened compared with those found in the dipicrate salt [1.457 (2) and 1.458 (2) Å] and the N—C_{ethylene} distance found in the dibromide salt [1.461 (2) Å].

3,3'-Di-*n*-butyl-1,1'-(1,4-phenylenedimethylene)diimidazolium bis(trifluoromethanesulfonate), (II), also has the dication interacting with the monoanions (Fig. 2) through weak C—H···F hydrogen bonds. The imidazolium–phenylenedimethylene–imidazolium portion has a Z shape, with the butyl substituents at either end. One of the butyl groups has the usual zigzag shape, whereas the other has a U shape. The C—H···F interactions are somewhat longer and the hydrogen bonds more bent; however, two short linear C—H···O hydrogen bonds are present that are comparable with classical hydrogen bonds (Table 2).

In the present study, because the two anions do not engage in strong hydrogen bonding, the ionic liquid state then probably requires cation–anion interactions for long-range crystallinity.

Experimental

The syntheses of the title compounds have been detailed in the study by Ganesan & Alias (2008). Crystals of both (I) and (II) were grown from solutions in water.

Compound (I)

Crystal data

C₁₆H₂₀N₄²⁺·2BF₄[−]
M_r = 441.98
 Monoclinic, *P*2₁/*c*
a = 4.9517 (2) Å
b = 12.8674 (5) Å
c = 15.2828 (6) Å
 β = 92.806 (3)°

V = 972.58 (7) Å³
Z = 2
 Mo *K*α radiation
 μ = 0.14 mm^{−1}
T = 100 (2) K
 0.36 × 0.08 × 0.06 mm

Table 1
Hydrogen-bond geometry (Å, °) for (I).

<i>D</i> —H··· <i>A</i>	<i>D</i> —H	H··· <i>A</i>	<i>D</i> ··· <i>A</i>	<i>D</i> —H··· <i>A</i>
C2—H2···F1	0.95	2.59	3.367 (3)	140
C3—H3···F2 ⁱ	0.95	2.33	3.272 (3)	171
C4—H4···F3 ⁱⁱ	0.95	2.37	3.287 (3)	162
C4—H4···F4 ⁱⁱ	0.95	2.48	3.278 (3)	141

Symmetry codes: (i) $-x, -y, -z + 1$; (ii) $-x + 1, y + \frac{1}{2}, -z + \frac{1}{2}$

Data collection

Bruker SMART APEX
 diffractometer
 8044 measured reflections

2231 independent reflections
 1364 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.075$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.050$
 $wR(F^2) = 0.120$
 $S = 1.02$
 2231 reflections

137 parameters
 H-atom parameters constrained
 $\Delta\rho_{\text{max}} = 0.24 \text{ e \AA}^{-3}$
 $\Delta\rho_{\text{min}} = -0.30 \text{ e \AA}^{-3}$

Compound (II)

Crystal data

C₂₂H₃₂N₄²⁺·2CF₃SO₃[−]
M_r = 650.66
 Triclinic, *P* $\bar{1}$
a = 10.3833 (1) Å
b = 12.0470 (2) Å
c = 13.6933 (2) Å
 α = 100.752 (1)°
 β = 105.194 (1)°

$\gamma = 111.970 (1)^\circ$
V = 1453.36 (4) Å³
Z = 2
 Mo *K*α radiation
 $\mu = 0.27 \text{ mm}^{-1}$
T = 100 (2) K
 0.44 × 0.22 × 0.07 mm

Data collection

Bruker SMART APEX
 diffractometer
 Absorption correction: multi-scan
 (SADABS; Sheldrick, 1996)
 $T_{\text{min}} = 0.878, T_{\text{max}} = 0.982$

18621 measured reflections
 6636 independent reflections
 5673 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.035$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.035$
 $wR(F^2) = 0.101$
 $S = 1.02$
 6636 reflections

379 parameters
 H-atom parameters constrained
 $\Delta\rho_{\text{max}} = 0.61 \text{ e \AA}^{-3}$
 $\Delta\rho_{\text{min}} = -0.53 \text{ e \AA}^{-3}$

Table 2
Hydrogen-bond geometry (Å, °) for (II).

<i>D</i> —H··· <i>A</i>	<i>D</i> —H	H··· <i>A</i>	<i>D</i> ··· <i>A</i>	<i>D</i> —H··· <i>A</i>
C4—H4a···O3	0.99	2.50	3.397 (2)	150
C5—H5···O2 ⁱ	0.95	2.46	3.243 (2)	139
C6—H6···F1 ⁱ	0.95	2.45	3.261 (2)	143
C6—H6···O4	0.95	2.44	3.166 (2)	133
C7—H7···O1 ⁱⁱ	0.95	2.25	3.188 (2)	168
C10—H10···F3 ⁱⁱⁱ	0.95	2.47	3.365 (2)	157
C16—H16···O5 ⁱⁱⁱ	0.95	2.29	3.135 (2)	147
C18—H18···O3 ^{iv}	0.95	2.46	2.956 (2)	112

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

Carbon-bound H atoms were placed in calculated positions (C—H = 0.95–0.99 Å) and included in the refinement in the riding model approximation, with $U_{\text{iso}}(\text{H})$ values set at 1.2–1.5 $U_{\text{eq}}(\text{C})$.

For both compounds, data collection: *APEX2* (Bruker, 2007); cell refinement: *SAINT* (Bruker, 2007); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *X-SEED* (Barbour, 2001); software used to prepare material for publication: *publCIF* (Westrip, 2008).

The authors thank the University of Malaya for financial support of this study (Research University grant Nos. TA 0009/2007 A and TA 0009/2008 A).

Supplementary data for this paper are available from the IUCr electronic archives (Reference: SK3257). Services for accessing these data are described at the back of the journal.

References

- Aki, S. N. V., Mellein, B. R., Saurer, E. M. & Brennecke, J. F. (2004). *J. Phys. Chem. B*, **108**, 20355–20365.
- Anthony, J. L., Anderson, J. L., Maginn, E. J. & Brennecke, J. F. (2005). *J. Phys. Chem. B*, **109**, 6366–6374.
- Barbour, L. J. (2001). *J. Supramol. Chem.* **1**, 189–191.
- Bruker (2007). *APEX2* (Version 2.1-4) and *SAINT* (Version 7.34A). Bruker AXS Inc., Madison, Wisconsin, USA.
- Dibrov, S. M. & Kochi, J. K. (2006). *Acta Cryst.* **C62**, o19–o21.
- Galán Sánchez, L. N., Meindersma, G. & de Haan, A. B. (2007). *Trans. IChemE*, **85**, 31–39.
- Ganesan, K. & Alias, Y. (2008). *Int. J. Mol. Sci.* **9**, 1207–1213.
- Holbrey, J. D. & Seddon, K. R. (1999). *J. Chem. Soc. Dalton Trans.* pp. 2133–2139.
- Jin, C.-M., Wu, L.-Y., Han, D.-Y. & Hu, Y.-J. (2006). *Acta Cryst.* **E62**, o5619–o5620.
- Jin, H.-S., Wang, H.-J., Zhang, Y., Zuo, Y.-J. & Zhong, C.-M. (2007). *Acta Cryst.* **E63**, o1880–o1881.
- Li, D.-C. & Liu, D.-J. (2003). *Anal. Sci.* **19**, 1089–1090.
- Liu, D.-J. & Li, D. C. (2003). *Appl. Organomet. Chem.* **17**, 811–812.
- Liu, F.-H., Chen, W.-Z. & You, X.-Z. (2002). *J. Solid State Chem.* **169**, 199–207.
- Saha, S., Hayashi, S., Kobayashi, A. & Hamaguchi, H. (2003). *Chem. Lett.* **32**, 740–741.
- Sheldrick, G. M. (1996). *SADABS*. University of Göttingen, Germany.
- Sheldrick, G. M. (2008). *Acta Cryst.* **A64**, 112–122.
- Wang, J.-W., Xu, F.-B., Li, Q.-S., Song, H.-B. & Zhang, Z.-Z. (2005). *Acta Cryst.* **E61**, m367–m369.
- Westrip, S. P. (2008). *publCIF*. In preparation.