Alkyl *vs.* alkoxy chains on ionic liquid cations†

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The crystal structures and thermal behavior of the 1-(2-methoxyethyl)-2,3-dimethylimidazolium chloride and hexafluorophosphate salts are compared with the analogous 1-butyl-2,3-dimethylimidazolium salts to examine the influence of the ether oxygen on salt thermal properties for a typical constituent cation used in the preparation of ionic liquids.

Ionic liquids (ILs)—salts or mixtures of salts which melt below 373 K (arbitrarily set at the boiling point of water)—are a topic of rapidly expanding research since these materials often possess unique combinations of physical properties not available in molecular solvents.[1,2] Frequently, ILs are referred to as 'tuneable', 'tailored', 'task-specific' or 'designer' solvents due to the ability to vary the ions, thereby modifying and optimizing a salt's physical properties for specific applications.[3–5] At present, this optimization is greatly hindered by a lack of knowledge regarding how ion structure affects salt properties. In particular, the addition of functional groups (*e.g.*, ether oxygens) to the ions may dramatically change a salt's thermal behavior.[6–9] Here we compare the 1-butyl-2,3-dimethylimidazolium salts of Cl⁻ and PF₆⁻ with the analogous salts of 1-(2-methoxyethyl)-2,3-dimethylimidazolium cations:
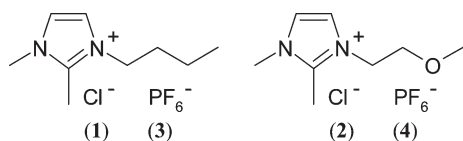
An ether oxygen, with its two electron lone-pairs, is comparable in size (slightly larger) and shape to a methylene group, suggesting that the two groups might have similar steric interactions with neighboring atoms. However, unlike the methylene group, the ether oxygen will exert repulsive interactions with neighboring anions and ether oxygens. Thus, a study of salts 1–4‡ represents an excellent opportunity to examine how minor structural changes affect ion crystal packing and how this, in turn, affects a salt's thermal properties. The crystal structures of **1** and **3** have been previously reported.[10,11] The crystal structures of **2** and **4** have been determined and are reported here for comparison (Table 1).

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† Electronic supplementary information (ESI) available: NMR spectra, structure determination information, DSC traces and schematic of PF₆⁻ disorder in **4**. See DOI: 10.1039/b606381k

Table 1 Crystallographic data of **1–4**

	1[6]	**2**[a]	**3**[7]	**4**[a]
Formula	C₉H₁₇ClN₂	C₈H₁₅ClN₂O	C₉H₁₇F₆N₂P	C₈H₁₅F₆N₂OP
Formula weight	188.69	190.67	298.22	300.19
T/K	213(1)	173(2)	213(1)	173(2)
Wavelength/Å	0.71073	0.71073	0.71073	0.71073
Crystal system	Monoclinic	Triclinic	Monoclinic	Triclinic
Space group	$P2_1/n$	$P\text{-}1$	Cc	$P\text{-}1$
a/Å	8.380(2)	7.3748(13)	15.389(3)	8.3405(13)
b/Å	11.710(2)	7.5274(13)	8.604(2)	8.7297(14)
c/Å	10.760(2)	10.1293(18)	11.730(2)	10.4831(16)
α/°	90	82.170(3)	90	67.755(2)
β/°	90.74(3)	76.176(3)	122.46(5)	69.073(2)
γ/°	90	65.881(3)	90	62.821(2)
Volume/Å³	1055.8(2)	497.88(15)	1310.4(5)	612.52(17)
Z	4	2	4	2
ρ_{calc}/g cm⁻³	1.187	1.272	1.512	1.628
μ/mm⁻¹		0.342		0.291
Reflns coll.		5689		6573
Reflns unique		2177		2665
R_{int}		0.0172		0.0194
$R1^b$		0.0296		0.0373
w$R2^b$		0.0841		0.1057

[a] CCDC 606677 and 606678. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b606381k. [b] $I > 2\sigma(I)$.

DSC heating traces of the four salts are shown in Fig. 1. The melting point (m.p.) of **1** is reported to be 370–377 K,[10–13] in agreement with the DSC data (Table 2). **2** exhibits a solid–solid phase transition that may correspond to the onset of ion disordering prior to the m.p. The m.p. of **3** is reported to be 313 K,[11] also in agreement with the DSC data (Table 2). However, several authors have previously reported the absence of a m.p. for **3**, perhaps due to slow kinetics hindering crystallization (see ESI†).[13,14] It is interesting to note that the m.p.s of the salts containing methoxyethyl groups are higher than those containing butyl groups, and that the melting transition for **2** occurs slowly over a wide temperature range (Fig. 1).
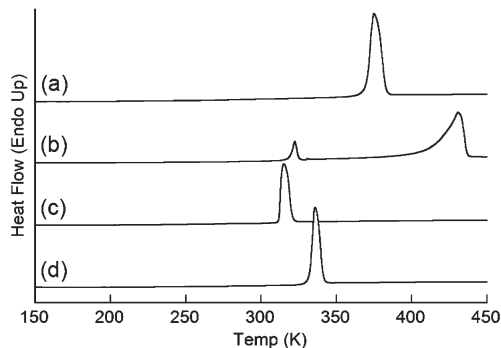
Fig. 1 DSC heating traces (5 K min⁻¹) of (a) **1**, (b) **2**, (c) **3** and (d) **4**.

Table 2 DSC thermal transition data from Fig. 1

| Salt	Peak/K	Onset/K	ΔH/kJ mol^{-1}	Transition type
1	373.0 ± 0.4	369.0 ± 0.6	14.53 ± 0.68	Melting
2	321.2 ± 1.3	317.2 ± 1.9	1.96 ± 0.38	Solid–solid
	430.0 ± 0.8	416.8 ± 0.1	24.04 ± 0.13	Melting
3	314.9 ± 0.3	311.8 ± 0.2	17.09 ± 0.18	Melting
4	336.2 ± 0.2	332.8 ± 0.4	22.03 ± 0.27	Melting

The ion crystal packing of **1**[10] and **2** are compared in Fig. 2. In **1**, the cations arrange themselves as pairs in layers, with the butyl groups oriented in opposite directions (Fig. 2(a)). The cation butyl groups adopt a right angle kink from the plane of the imidazole ring. This creates cavities between the cations where the Cl$^-$ anions reside.

In **2**, the cations again arrange themselves as oppositely-oriented pairs, forming layers (Fig. 2(b)), with the methoxyethyl groups adopting a right angle kink from the plane of the imidazole ring. In this respect, **1** and **2** are very similar. However, the orientation of these cation pairs within the layers differs between the two structures, as does the positioning of the Cl$^-$ anions. Although strong hydrogen bonds do exist between the anions and cations (for example, in **1**, a Cl$^-$ anion is bonded to the hydrogen at the 5-position on the cation ring, while another anion is bonded to the hydrogen at the 4-position on the cation ring and one of the methyl hydrogens), this appears to be only a contributing rather than a determining factor governing the crystal packing.

The ion crystal packing of **3**[11] and **4** are compared in Fig. 3. In **3**, the butyl group of the cation once again adopts a right angle kink from the plane of the imidazole ring, but now all the cations face in the same direction and no ionic layers are formed (Fig. 3(a)).

In **4**, as with the side chains of the other structures, the methoxyethyl group of the cation once again adopts a right angle kink from the plane of the imidazole ring. Half of the cations and half of the anions have the same orientation and positions found in **3**, but the other half of the cations are oriented in the opposite direction (creating cationic layers) (Fig. 3(b)). All of the PF$_6^-$ anions are disordered (not shown—see ESI†). Note that the PF$_6^-$ anions in **3** were reported to be disordered at 298 K but ordered at 213 K.[11] It is probable that the anion disorder in **4** was frozen into the structure from a room temperature disordered structure during a rapid cooling undergone prior to data collection.

Although the structures with the same anions have some close similarities, there are also dramatic differences between them. An examination of the ion crystal packing about the methylene –CH$_2$– segments (second from the end of the butyl chains) in **1** reveals that the hydrogens are not directed at the Cl$^-$ anions, but rather two such segments on neighboring cations are in close proximity (indicated by stars in Fig. 2(a)) (C–C distance of 4.1 Å). If these –CH$_2$– segments were replaced with ether oxygens, the electron lone pairs would repel one another. This explains the reorientation of the cations found in **2**. In this structure, the ether oxygens from two cations are directed towards one another (indicated by stars in Fig. 2(b)) but the distance separating them is greater (O–O distance of 5.1 Å), which is likely to reduce or eliminate altogether any repulsive interactions. Note that the cation pairs are offset, creating a tilt to the layers in **2** that is not found in **1**. This offset helps in separating the neighboring ether oxygens. The same butyl –CH$_2$– segment in **3** has one of the hydrogens directed at a neighboring PF$_6^-$ anion (indicated by stars in Fig. 3(a)). Thus, the replacement of this segment with an ether oxygen would result in strong
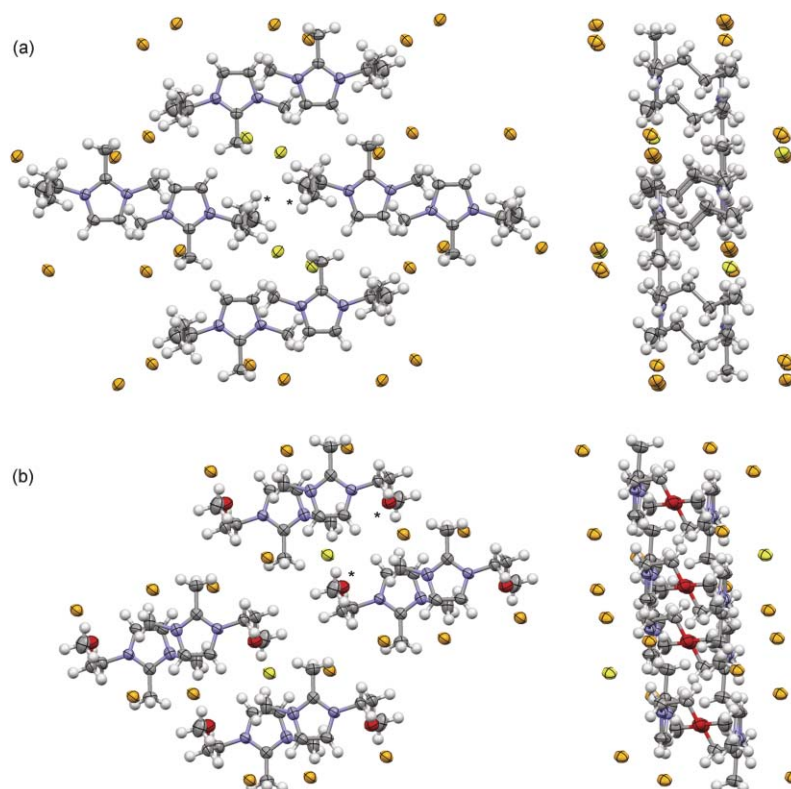
Fig. 2 Crystal packing of (a) **1**[10] and (b) **2** (N—blue, O—red, Cl—orange and yellow; two colors for the latter are used for clarity).
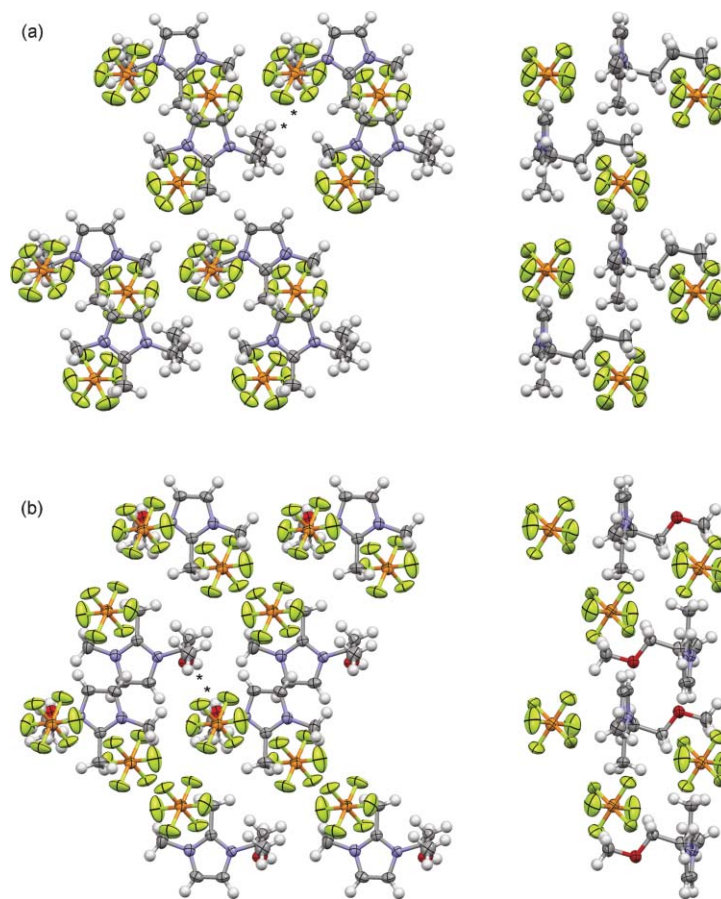
Fig. 3 Crystal packing of (a) **3**[11] and (b) **4** (N—blue, O—red, P—orange, F—green). The PF_6^- anion disorder in **4** is not shown.

electron lone pair repulsive interactions with the anion. Although the ether oxygens on neighboring cations in **4** are closely situated (indicated by stars in Fig. 3(b)) (O–O distance of 3.8 Å), their positions and orientation suggests that the electron lone pairs do not overlap significantly, thereby reducing or eliminating altogether any repulsive interactions.

In conclusion, a comparison of the structures of salts in which a methylene group is replaced by an ether oxygen indicates that oxygen electron lone pair repulsive interactions between neighboring ether oxygens or anions lead to significant ion crystal packing rearrangements which, in turn, result in notable differences in the thermal properties of salts.

Notes and references

‡ **1** was prepared as previously reported.[13] **2** was prepared by reacting equimolar amounts of 2-chloroethyl methyl ether (Aldrich, 98%) and 1,2-dimethylimidazole (Aldrich, 98%) in ethyl acetate with stirring under ambient conditions. The resulting chloride salt was purified by washing it repeatedly with hot ethyl acetate. **3** and **4** were prepared by reacting equimolar amounts of **1** or **2**, respectively, with NH_4PF_6 in de-ionized water. The resulting white salts were rinsed five times with fresh water. There was no evidence for the formation of HF impurities in the short contact times of the hexafluorophosphate salts with water. **1–4** were dried under vacuum (<200 mTorr) at 353 K for 24 h, then at 383 K for 5 h. The salts were stored and handled in a controlled atmosphere glove box. Thermal data were obtained from the DSC analysis of 2–5 different samples of each salt. Crystal packing images were drawn with Mercury 1.4.1.

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