Crystal structures of imidazolium bis(trifluoromethanesulfonyl)imide ‘ionic liquid’ salts: the first organic salt with a cis-TFSI anion conformation†

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Crystal structures of two examples of an important class of ionic liquids, 1,3-dimethylimidazolium and 1,2,3-triethylimidazolium bis(trifluoromethanesulfonyl)imide have been characterized by single crystal X-ray diffraction. The anion in the 1,3-dimethylimidazolium example (mp 22 °C), adopts an unusual cis-geometry constrained by bifurcated cation–anion C–H⋯O hydrogen-bonds from the imidazolium cation to the anion resulting in the formation of fluorinated layers within the solid-state structure. In contrast, in the 1,2,3-triethylimidazolium salt (mp 57 °C), the ions are discretely packed with only weak C–H⋯O contacts between the ions close to the van der Waals separation distances, and with the anion adopting the twisted conformation observed for all other examples from the limited set of organic bis(trifluoromethanesulfonyl)imide crystal structures. The structures are discussed in terms of the favorable physical properties that bis(trifluoromethanesulfonyl)imide anions impart in ionic liquids.

Introduction

Ionic liquids (ILs) are salts, comprised of organic cations combined with anions having typically diffuse negative charges, which have low melting points. The current interest in ionic liquids as non-volatile solvents for electrochemical, chemical, separations, and materials applications has been thoroughly reviewed.1,2 The importance of the anion in determining the physical properties of ionic liquids has also been noted.3–5

Ionic liquids containing inorganic perfluorinated sulfonylimide anions are of great interest as anions for the formation of hydro-lytically stable, ‘hydrophobic’ ionic liquids with low viscosity and high electrical conductivity. The most widely studied example is the bis(trifluoromethanesulfonyl)imide (TFSI) anion which is generally regarded as charge-diffuse and weakly coordinating. Delocalization of negative charge along the S-N-S core of the anion, which is additionally shielded by steric features of the non-charge carrying sulfonyl oxygens and trifluoromethane groups, reduces the capacity for ion–ion interactions. This apparent lack of strong cation–anion interactions results in the suppression of liquid-crystallinity in long-chain 1-alkyl-3-methylimidazolium salts and enables the formation of low melting, fluid ionic liquids with a wide range of cations; example salts have been reported with ammonium, pyridinium, imidazolium, and pyrrolidinium cations.

Determining hydrogen-bonding environments is critical to understanding the modes of interaction and conformational influences of ionic liquid anions and cations on the lattice energies, melting points, and general behavior of the salts.

However, the favorable properties of the ILs, especially low melting points, restricts structural studies that would provide valuable information about ion conformations and interactions, and which would allow them to be compared to other structurally characterized alkylimidazolium ionic liquids including chloride,6 hexafluorophosphate,4,7 alkyl sulfate,8 carborane,9 and functionalized tetraphenylborate10 salts.

MacFarlane and co-workers have made excellent inroads isolating and determining the crystal structures of a number of examples from the key cation groups of interest; namely 1-benzyl-2-ethyl-3-methylimidazolium,11 N-methyl-1-methylpyrrolidinium,12 N,N-dimethylpyrrolidinium,13 triethylammonium,14 and teta(p-propyl)ammonium.14 Three of these salts have melting points below 100 °C, with triethylammonium (mp 79–81 °C) and 1-benzyl-2-ethyl-3-methylimidazolium (mp ~55 °C) being the lowest melting.13,14 It is worth noting, that these are the only published crystallographically characterized examples of organic TFSI salts, and an equally small number of known inorganic examples are known.15

The TFSI anion is generally considered as non-coordinating and usually acts as a discrete non-coordinating anion.16 However, the TFSI salts of the oxophilic Group 1 metal cations exhibit strong metal–anion interactions to the sulfonyl oxygens, resulting in the formation of extended catenar network structures.17

Given the importance of the TFSI anion for formation of ionic liquids (especially the interest in imidazolium TFSI ionic liquids) and the scarcity of structural information on these systems, further information on the cation–anion and lattice interactions would be invaluable. Here, two low-melting alkylimidazolium TFSI salts with only aliphatic substituents on the heterocyclic cation: 1,3-dimethylimidazolium (I) and 1,2,3-triethylimidazolium (II) have been isolated as crystalline solids and the single crystal structures have been determined by X-ray crystallography. I contains the first example of an imidazolium TFSI salt bearing a hydrogen substituent on the imidazolium C(2) position that has been crystallographically characterized and is the first example of an organic TFSI salt to exhibit a cis-anion geometry.

Results and discussion

Two low-melting substituted alkylimidazolium TFSI salts, 1,3-dimethylimidazolium bis(trifluoromethanesulfonyl)imide (I) and 1,2,3-triethylimidazolium bis(trifluoromethanesulfonyl)imide (II), have been prepared and their crystal structures determined. I was prepared by metathesis of 1,3-dimethylimidazolium methyl sulfate18 with Li[TFSI], the resulting colorless liquid solidifying on cooling to 0 °C. DSC analysis showed a broad melting transition at 22 °C consistent with the literature,2 and on cooling, a sharp crystallization transition. No lower temperature solid–solid phase transitions were observed. Slow cooling of biphasic mixtures of the molten salt I and water from 30 to 4 °C resulted in the growth of crystals from the supercooled ionic liquid phase into the upper aqueous phase. Crystals were taken, and mounted for X-ray analysis
using a liquid-nitrogen cooled block to prevent melting. I is the lowest melting ionic liquid (and the first imidazolium TFSI salt with only a hydrogen at the C(2) position of the imidazolium ring) that has been crystallographically characterized.

The new salt, II, was prepared by dialkylation of 2-ethylimidazole with two equivalents of diethyl sulfate, followed by metathesis with Li(TFSI), and was isolated as a colorless crystalline solid, which melted at 57 °C to a colorless hydrophobic liquid. Crystals suitable for X-ray analysis were also obtained by slow cooling of biphasic mixtures of the molten salt and water at 60 °C to room temperature. Crystal data for I and II is shown in Table 1.

I crystallizes in a triclinic lattice with two crystallographically distinct, but structurally equivalent cations and anions in the asymmetric unit (Fig. 1). Overlaying the two cations, and two anions, respectively, in the asymmetric unit shows that the ions are conformationally identical, but occupy different environments and positions within the crystallographic asymmetric unit. The crystal lattice (Fig. 2) consists of alternating two-dimensional sheets with an –AA–B–AA– pattern comprised of charge-bearing double layers of cations and anions separated by fluororous regions formed from the –CF₃ groups on the anions. In the charged planes, the TFSI anion of I is hydrogen-bonded to three equatorially arrayed 1,3-dimethylimidazolium cations through C–H–O and C–H–N contacts between the cations and anions (Fig. 3) with an additional imidazolium cation below each anion, from the next layer of the double layer. Each cation, and each anion, are constrained by seven hydrogen-bonding interactions from hydrogen atoms of the cations to either oxygen or nitrogen atoms of the anions. The difference between the two cation/anion pairs in the asymmetric unit is the formation of a single hydrogen bond, C(14)–H4C–O1 (2.57(4) Å, 126(3)°) that is not observed from the corresponding position, C(7), in the other cation.

The anion conformation in I is directed by the formation of a bifurcated hydrogen bond from the acidic imidazolium C(2)–H hydrogen of one cation to sulfonate oxygen atoms of two anions and also from C–H–O and C–H–N hydrogen-bonding from a second cation in the same plane to the anion. One feature of this extended hydrogen-bonding between cations and anions in I, is stabilization of the anion in an unusual higher energy conformation with the two S–CF₃ groups cis to one another, caused apparently by structural constraints of the extensive C–H–O cation–anion hydrogen-bonding in the lattice. This results in the formation of domain separated fluororous layers in the structure (Fig. 2).

II crystallizes in a monoclinic lattice, with a more conventional organic salt structure, consisting of alternating layers of cations and anions with only weak cation–anion interactions (similar to the organic TFSI salts reported by MacFarlane and co-workers). One ion pair is present in the crystallographic asymmetric unit and is shown in Fig. 1.

In the 1,2,3-triethylimidazolium cation, the three ethyl groups may all reside on one side of the planar ring, alternate ‘up-down-up’, have an asymmetric ‘up-up-down’ arrangement, or have rotational fluxionality. The internal bond lengths and angles of the 1,2,3-triethylimidazolium cation are comparable with other imidazolium crystal structures, with a planar heterocyclic ring, and alkyl substituents orientated out of the plane of the ring. It is interesting to note that the low symmetry cation conformation with the ethyl groups in the ‘up-up-down’ arrangement is observed in the crystal structure of II, with a relatively large degree of thermal motion in the ethyl substituents.

Anion conformations in the two crystal structures are shown in Fig. 1, and are compared with data for other examples in the CSD database in Table 2. The TFSI anion conformation in I differs from

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<th>Chemical formula</th>
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<td>17.113(14)</td>
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<tr>
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<td>90</td>
</tr>
<tr>
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</tr>
<tr>
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<td>90</td>
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<td>1803(3)</td>
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<td>7811</td>
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<tr>
<td>Independent reflections,</td>
<td>4074, 0.020</td>
<td>2590, 0.041</td>
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**Table 1** Crystal and refinement data for I and II

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that observed in the organic TFSI salt structures previously reported,13,14 and has the two S–CF3 groups oriented cis to one another (C–S–S–C torsion angle 31.47(13)° and 32.88(13)° in the two anions in the asymmetric unit). A result of this interaction and the resulting anion conformation is the formation of fluorous layers, as all the −CF3 groups interact, separating layers of cations and the hydrogen-bonded sulfonylimide portion of the anions (Fig. 3). The extended structure shows alternating sheets of cations and anions in the ab plane, with the cation heterocycle ring tilted at approximately 45° to the a-axis.

Compared to the trans-anion conformation, this cis-conformer has a higher energy and has only previously been crystallographically characterized in the Li, Na, K, and Cs salts,17 in which the anion conformation is locked in the cis-structure (although in these salts with an average dihedral angle of 13.59°) by an extensive series of strong metal–oxygen bonds from the cation to anion, which result in catenar lattices. It should be noted that all the characterized highly oxophilic alkali metal salts of the TFSI anion form highly coordinated structures.

The TFSI anion in II adopts the lower energy trans conformation (S–N–S bond angle, 127.78(3)°; C–S–S–C torsion angle 175.67(16)°), consistent with π→π charge delocalization within the S–N–S moiety and comparable to the other organic TFSI salts which have been reported by MacFarlane and co-workers.13,14 The trans conformation and twist of the anion in II allows the charge bearing region of the (S–N–S) to remain close to the cation, and enables the –CF3 groups of adjacent anions to interact forming an-ionic ribbons through the crystal (Fig. 2) and alternating cation and anion sheets along the ab plane. The imidazolium cations are tilted relative to the anion sheets.

In comparison to the extensive hydrogen-bonding interactions observable in the crystal structure of I, there are only four identifiable hydrogen-bonding interactions between the cation and anions in II (Table 3): the imidazolium-ring hydrogen atoms form strong hydrogen-bonding contacts to N and O atoms of two anions, bridging between chains of anions, additional contacts between the α-hydrogen of the N-ethyl substituent to TFSI oxygen atoms, and a third short hydrogen-contact between the mobile terminal methyl group (C(11)–H) of the lone ethyl substituent on one side of the ring-plane are observed (Fig. 4).

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### Table 2

<table>
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<tbody>
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<td>I</td>
<td>1.833(6)</td>
<td>1.430(6)</td>
<td>1.574(4)</td>
<td>126.33(18)</td>
<td>32(1)</td>
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<tr>
<td>II</td>
<td>1.831(4)</td>
<td>1.422(5)</td>
<td>1.571(4)</td>
<td>124.97(13)</td>
<td>175.67(16)</td>
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<td>cis</td>
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<td>1.428 (1.407–1.477)</td>
<td>1.562 (1.477–1.580)</td>
<td>127.8 (126.4–130.8)</td>
<td>13.59 (0–17.68)</td>
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<tr>
<td>trans</td>
<td>1.831 (1.808–1.850)</td>
<td>1.422 (1.401–1.446)</td>
<td>1.597 (1.563–1.675)</td>
<td>125.7 (121.9–135.6)</td>
<td>170.7 (163.2–174.5)</td>
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</table>

**Fig. 2** Packing diagrams for I (left) and II (right). Both structures exhibit two-dimensional layered structures; in I, separated fluorous and ‘ionic’ layers, and in II, more conventional alternating sheets of cations and anions.

**Fig. 3** Cation⋯anion hydrogen bonding in I, showing the three in-plane cations surrounding each anion resulting in the cis-anion conformation with all the anion–CF3 groups in each hydrogen-bonded sheet projecting from the same side of the layer.

**Fig. 4** Nearest neighbor close contacts around each anion of II, showing only three C–H⋯O hydrogen bonds from the cations to anions which allows the anions to form extended arrays with end-to-end CF3 to CF3 fluorous grouping.

All other remaining close contacts of the imidazolium cation and anion between the sulfonyl oxygen atoms and C–H bonds of the cation approximate to the van der Waals atomic separations indicating that the cations are held in pockets within the crystal lattice formed by the anions, with no strong hydrogen bonding to the anions. In addition, a reasonably large degree of thermal motion in the anion and cation is observed, this is particularly evident for the anion oxygen atoms, and the terminal atoms of the three ethyl substituents of the cation (Fig. 1).
The single crystal structures of I and II show different packing modes for the ions depending on the nature of the hydrogen-bond donors available on the cation. I displays the formation of two-dimensional hydrogen-bonded sheets maintained by C–H...O hydrogen bonded sandwiched sheets of cations and anions in the solid state. The structure of II however, shows a layered ionic lattice of alternating sheets of anions and cations with few significant hydrogen-bonding interactions, consistent with the structures of other organic TFSI salts reported in the literature. The observation of the apparently anomalous high melting point of I. Dashed lines show the positions of apparent discontinuities in the melting point transitions.

The melting points for several 1-alkyl-3-methylimidazolium TFSI salts are plotted in Fig. 5. It should first be noted that for alkyl chains between 2–10 carbons in length, the melting points are below room temperature, and were determined by DSC on second heating cycles, these are room temperature liquidics, and that the destabilization of the crystal structures (indicated by the decrease in melting point) is essentially linear with n. From n = 12 upwards, a net stabilization from the cumulative increase in cation...cation alkyl chain van der Waals interactions, and a switch to a microphobic layered structures contributes additional crystal stabilization. The 1,3-dimethylimidazolium salt (I) appears anomalous in having an apparent ~20 °C stabilization in melting point compared to the longer-chain congeners. This could be attributed to a number of factors, including the higher symmetry of the cation, but it is appealing to suggest that the formation of the layered crystal structure, with separation of fluorous and ‘organic’ regions leads to increased net stability despite imposing the less stable anion cis-conformation. The identified conformational flexibility of the TFSI anion may play a key role and account for many of the low melting properties of these and related salts, and the ready observation of plasticity and double melting phenomena in the salts. Finally, II gives a further example of a low melting point C(2)-alkylated imidazolium TFSI ionic liquid.

Summary

Crystal structures of two low melting point substituted imidazolium bistriylfimide structures have been reported. The TFSI anion in the lower melting I adopts a higher energy, less stable cis conformation than the trans conformation observed for II and all other characterized organic TFSI salts. The observation of the cis and trans anion conformations in the different crystalline salts described here may have important implications in developing a better understanding of the factors governing the crystal–liquid transition (melting point and lattice energies) in these and other ionic liquids and low melting organic salts. Despite this apparently less stable anion conformation, the solid state of I appears to be stabilized by approximately 20 °C relative to the longer alkyl-chain homologs, possibly through the formation of alternating charged (ionic) and fluorous sheets in the crystal. These results provide direct evidence for conformational flexibility of the TFSI anion in the crystalline state, and for the contribution of this with respect to of anion flexibility and hydrogen-bonding contributions to the melting points and stability of the crystalline phase of organic TFSI salts.

Experimental

Reagents were used as received. Lithium bis(trifluoromethane-sulfonyl)imide (Li[TFSI]) was a gift from 3M (St. Paul, MN). 1-Methylimidazole, 2-ethylimidazole, dimethyl sulfate and diethyl sulfate were purchased from Aldrich (St. Louis, MO). 1H and 13C NMR spectra were recorded on Bruker AM360 spectrometer in DMSO-d6 (I) and CDCl3 (II). Melting points were determined by differential scanning calorimetry (TA 2620 DSC equipped with cryostat cooling, 5–20 mg samples, 5 °C min⁻¹ heating and cooling rates) and were consistent over multiple heating cycles.

1,3-Dimethylimidazolium bis(trifluoromethanesulfonyl)imide (I) was prepared by alkylation of 1-methylimidazole with dimethyl sulfate following literature procedures, followed by metathesis with Li[TFSI] in water at 25 °C. The ionic liquid separated as a lower phase from solution and the upper aqueous phase was decanted. The ionic liquid was washed once with water (10 mL) and solidified on cooling to 0 °C (mp 22 °C). 1H and 13C NMR were consistent with the literature.
1,2,3-Triethylimidazolium bis(trifluoromethanesulfonyl)imide (II) was prepared by alkylation of 2-ethylimidazole (1.0 g, 10.4 mmol) with 2 eq. of diethyl sulfate (3.2 g, 20.8 mmol), followed by dissolution in water (10 mL) and metathesis with Li[TFSI] (3.26 g, 12 mmol). The colorless salt precipitated from solution and was collected by filtration, washed with water, and dried under vacuum (mp 57 °C). H NMR, δ (360 MHz, CDCl 3) 7.32 (2H, s, C(4)-H), 4.165 (4H, q, J 7.7 Hz, C(2)-CH 2), 1.524 (6H, t, J 7.3 Hz, NCH 2CH 3), 1.319 (3H, t, J 7.7 Hz, C(2)-CH 3). Samples of I and II were recrystallized by slow cooling of melts of the respective ionic liquids in contact with water to approximately 20 °C below the respective melting points. Crystals suitable for X-ray characterization grew from the supercooled dense ionic liquid phase into the aqueous layer. Single crystals were mounted on a Siemens SMART diffractometer with a CCD area detector, using graphite monochromated Mo-Kα radiation. The SHELXTL software, version 5, was used for solution and refinement. Absorption corrections were made with SADABS. Each structure was refined by full-matrix least-squares on F2.

In each structure, the atoms were readily located and the highest thermal motion was observed in the fluoride atoms, and the ethyl substituents in II characteristic of alkyl groups with high mobility and little or no hydrogen-bonded conformational restrictions. The positions of all non-hydrogen atoms were refined anisotropically. The hydrogen atoms were added in approximated positions and allowed to refine unconstrained in order to obtain proper close contact interactions, except for the hydrogens on the carbon atoms C10 and C11 of the ethyl group in II which were refined with fixed positions.

CCDC reference numbers 236629 and 236630. See http://www.ccdc.cam.ac.uk/contents/structures.html for crystallographic data in CIF or other electronic format.

Acknowledgement
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References


15 The Cambridge Structural Database (F. H. Allen, Acta Crystallogr., Sect. B, 2002, 58, 380;) currently holds coordinates for 14 structures containing the TFSI group (codes in parentheses), these can be broken down as five group I metal catenar salts (GYIBOF, TURZAH, TURZEL, TURZOV, TURZUB), five organic salts (JOSIXZ, XOMDAE, XOMDEI, XOMDIM, XOMDOS), one hydrated metal salt (ZURWIS), and three structures containing the TFSI anion coordinated through the N atom to a proton (ZURWEQ), phenyl (PUYQOP) and [Cu(CO 3) 2](QAPHOE) moieties, respectively. A further three structures are reported without coordinates (IGIQY, IGIQOE, PUSPUO). After submission of this manuscript, the structure of a Zn[TFSI] 2 was also published (M. J. Earle, U. Hakalab, B. J. McCauley, M. Nieuwenhuyzen, A. Ramania and K. R. Seddon, Chem. Commun., 2004, 1368.


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