

Weak intermolecular interactions in sulfonamide salts: structure of 1-ethyl-2-methyl-3-benzyl imidazolium bis[(trifluoromethyl)sulfonyl]amide

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The crystal structure of a 1,2,3-trisubstituted imidazolium salt of the bis[(trifluoromethyl)sulfonyl]amide ion is presented; this salt is a prototype for similar, room temperature liquid, imidazolium salts; the structure shows that the anion and cation interact weakly, with little if any hydrogen bonding present.

The use of molten organic salts as electrolytes in a variety of electrochemical devices, such as photo-electrochemical cells,¹ is becoming more widespread. As these applications become more varied,² the need for a variety of new, low melting point, fluid, ionic liquids is apparent. In the investigation of novel ionic liquids, interactions between the anion and cation are of great interest, as are the conformational states of each component of the salt, since the key transport properties (conductivity and diffusivity) are determined to a significant extent by these interactions. The relationship between structure and physical characteristics of many ionic liquids is yet to be fully quantified. The direct insight into the spatial relationship between cation and anion afforded by the elucidation of crystal structures provides a basis from which features of the ionic liquid itself can be understood, since the short range order and interactions of related, non-crystalline compounds may be similar to those of the crystalline form.

It is becoming clear¹⁻³ that anions (and cations) with diffuse charges and negligible hydrogen bonding yield the lowest melting points and hence have the greatest potential to produce ionic compounds that are liquid at room temperature. For example, the bis[(trifluoromethyl)sulfonyl]amide ion, $(\text{CF}_3\text{SO}_2)_2\text{N}^-$, has been found to produce low melting point (sub-room temperature in some cases, and completely non-crystalline in others) salts which are also characterized by their high fluidity and high ionic conductivity relative to other molten salts.³ Owing to a lack of structural information on these types of complexes, the origins of these two important effects (low mp and high fluidity) are not well understood. In this work we present crystal structure data for a low melting (mp $\approx 50^\circ\text{C}$) organic salt, 1-ethyl-2-methyl-3-benzyl imidazolium bis[(trifluoromethyl)sulfonyl]amide **1**.^{‡§}

In the only previously reported crystal structure⁴ determination of a salt of this anion {magnesium hexaaquobis[(trifluoromethyl)sulfonyl]amide dihydrate}, the anion was subject to molecular distortions⁴ due to hydrogen bonding to the water molecules coordinated to the $[\text{Mg}(\text{H}_2\text{O})_6]^{2+}$ cation. The structure presented here allows a clearer picture of the geometric features of this anion to be observed, in the absence of the hydrogen-bonding interactions which are present in the previous structure.

Fig. 1 shows the crystal structure of **1**. The imidazolium ring lies above the amide nitrogen, with the $-\text{SO}_2\text{CF}_3$ groups positioned away from the benzyl group. The distances between oxygen, nitrogen or fluorine and the closest hydrogen atoms approximate to van der Waals separations (*ca.* 2.6, 2.7 and 2.55 Å, respectively) indicating no evidence of the presence of strong

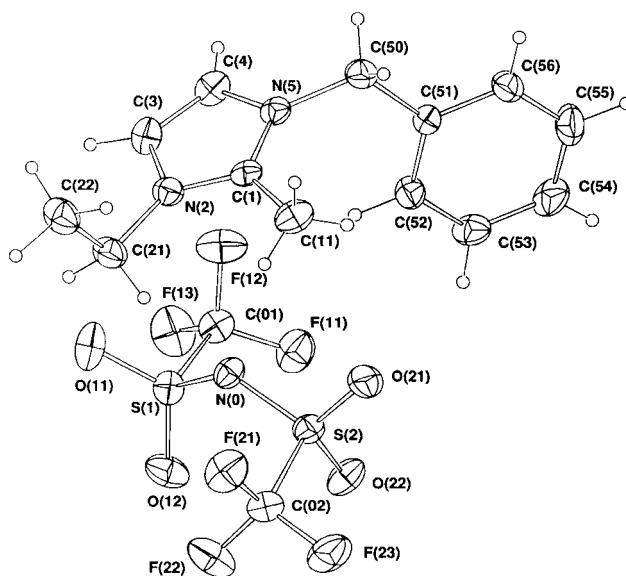
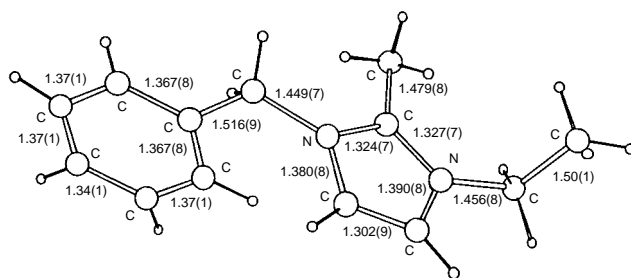


Fig. 1 Projection of the salt **1**. 20% Thermal ellipsoids are shown for the non-hydrogen atoms, hydrogen atoms having arbitrary radii of 0.1 Å.

hydrogen bonding in the crystal lattice.⁵ The large degree of thermal motion evident in both ions is also consistent with the absence of any strong interaction between the anion and cation. This implies that ionic, rather than covalent, interactions hold the salt in a low melting point crystalline form.

Bond length and angle data for the 1-ethyl-2-methyl-3-benzyl imidazolium cation in this salt (Fig. 2), agree with previously reported imidazolium cations⁵⁻⁷ (the majority of which are unsubstituted in the 2-position). The imidazole ring remains planar and the bond lengths in the imidazolium ring show strong residual double bond character at C(3)–C(4) with only partial delocalization of the positive charge, as previously reported.⁵⁻⁷ It is perhaps not surprising that this and related trisubstituted imidazolium salts (*i.e.* 1-alkyl-2-methyl-3-benzyl imidazolium salts) do not easily form salts which are liquid at



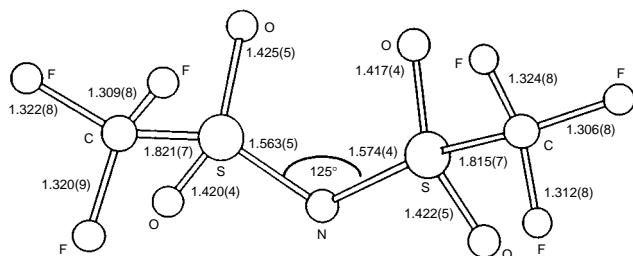


Fig. 3 Ball and stick representation of the bis[(trifluoromethyl)sulfonyl]amide anion including bond lengths (Å)

room temperature, when the influence of the size and orientation of the benzyl group, perpendicular to the plane of the imidazole ring [dihedral angle $86.7(3)^\circ$], are taken into account.

Fig. 3 shows the bond lengths and spatial arrangement of the anion. The anion as a whole has near C_2 symmetry, and the sulfonyl moieties have distorted tetrahedral symmetry with bond angles ranging from 102 to 115° .

Previous investigations of sulfonyl amide anions^{4,8} have supported Cruickshank's⁹ description, which proposed $d_{\pi}-p_{\pi}$ interaction between neighbouring sulfur and nitrogen atoms. This interaction effectively delocalizes the negative charge across the S–N–S moiety but not necessarily onto the sulfonyl oxygens, as might have been expected on the basis of simpler models. The structure determined in this work supports this model, the S–O bond lengths all being quite characteristic of the S–O double bond in SO_2 (1.43 Å) and showing no evidence of lengthening due to charge delocalization onto the sulfonyl oxygens. The lengthening of the S–O bonds (0.07 Å) observed by Haas *et al.*⁴ when the sulfonyl amine was converted to the amide can be partially explained by the increased charge density across the S–N–S moiety. Given the strong hydrogen bonding present in their compound, no conclusive evidence of charge delocalization onto the sulfonyl oxygens can be deduced from that structure. On the other hand, the S–N bond lengths shown in Fig. 3 (1.56 – 1.57 Å) are significantly shorter than typical S–N single bonds (≈ 1.75 Å) as a result of the S–N–S charge delocalization, hence charge delocalization onto the sulfurs is clearly indicated.

The key features of this anion in promoting a low melting point in its compounds, concomitant with high fluidity, would therefore appear to be this charge delocalization coupled with the lack of hydrogen bonding. The slightly larger than trigonal S–N–S angle (125°) will also, combined with the bulk of the $-SO_2CF_3$ groups, provide steric impediments to close interactions with neighbouring cations.

The crystal structure presented here provides a contrasting view of the interaction of organic cations, vs. solvated inorganic cations, *e.g.* aquo ions, with this anion. In the case of $[Mg(H_2O)_6][N(SO_2CF_3)_2]_2$, the intermolecular hydrogen bonding distorted the geometric features of the anion. In the structure presented here, however, the relatively unperturbed intramolecular features of the anion have been elucidated. This has been possible because only weak electrostatic interactions are evident between the sulfonamide anion and the imidazolium cation.

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Notes and References

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‡ *Crystal data:* $C_{15}H_{17}F_6N_3O_4S_2$, $M = 481.4$. Monoclinic, space group $P2_1/n$, $a = 8.862(2)$, $b = 11.051(3)$, $c = 21.271(7)$ Å, $\beta = 98.42(2)^\circ$, $U = 2061$ Å³, D_c ($Z = 4$) = 1.552 g cm⁻³. $F(000) = 984$. $\mu_{Mo} = 3.4$ cm⁻¹; specimen: $0.50 \times 0.26 \times 0.17$ mm; $A_{min,max}^*$ (gaussian correction) 1.05, 1.10. 1795 'observed' [$I > 3(I)$] out of 3612 independent four-circle diffractometer reflections (monochromatic Mo-K α radiation, $\lambda = 0.71073$ Å; $2\theta_{max} = 50^\circ$; $T = 295$ K) refining to conventional R on $|F|$ 0.050, R_w (statistical weights) = 0.059. (x, y, z, U_{iso})_H refined; anisotropic thermal parameter forms refined for non-hydrogen atoms (full-matrix). CCDC 182/881.

§ After reacting ethyl iodide with 1-benzyl-2-methylimidazole, the resultant iodide salt was converted to a nitrate (using $AgNO_{3(aq)}$), and subsequently $LiN(SO_2CF_3)_2$ was added in a minimum of EtOH. The hydrophobic salt **1** was isolated and dissolved in CH_2Cl_2 [to remove residual $LiN(SO_2CF_3)_2$] and dried over $MgSO_4$. Crystals were grown from a CH_2Cl_2 – $C_2H_5Cl_3$ – $MeCN$ mixture.

- 1 P. Bonhote, A. Dias, N. Papageorgiou, K. Kalyanasundaram and M. Gratzel, *Inorg. Chem.*, 1996, **35**, 1168.
- 2 K. R. Seddon, *J. Chem. Technol. Biotechnol.*, 1997, **68**, 351.
- 3 J. Sun, D. Macfarlane and M. Forsyth, *Proceedings of 5th International Symposium on Molten salt Chemistry and Technology*, Dresden, in press. V. R. Koch, C. Nanjundah, G. Battista Appetecchi and B. Scrosati, *J. Electrochem. Soc.*, 1995, **142**, L116.
- 4 A. Haas, Ch. Klare, P. Betz, C. Kruger, Y.-H. Tsay and F. Aubke, *Inorg. Chem.*, 1996, **35**, 1918.
- 5 A. K. Abdul-Sada, A. M. Geenway, P. B. Hitchcock, T. J. Mohammed, K. R. Seddon and J. A. Zora, *J. Chem. Soc., Chem. Commun.*, 1986, 1753.
- 6 J. S. Wilkes and M. J. Zaworotko, *J. Chem. Soc., Chem Commun.*, 1986, 965.
- 7 J. Fuller, R. T. Carlin, H. C. De Long and D. Haworth, *J. Chem. Soc., Chem. Commun.*, 1994, 299.
- 8 F. A. Cotton and P. F. Stokely, *J. Am. Chem. Soc.*, 1970, **92**, 294.
- 9 D. W. J. Cruickshank, *J. Chem. Soc.*, 1961, 5486.

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