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COMMUNICATION

Manifestations of noncovalent interactions in the solid state. Dimeric and polymeric self-assembly in imidazolium salts via face-to-face cation–cation π-stacking

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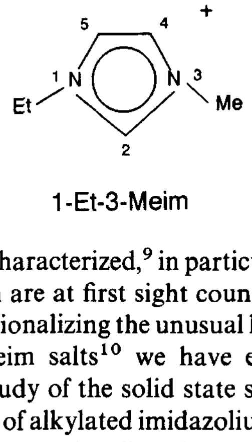
X-ray crystallographic investigation of the tertiary structure of simple 1-methylimidazolium (1-Meim) salts reveals that cation–cation face-to-face π-stacking with interplanar separations in the range typically seen for molecule–molecule and molecule–cation interactions are possible. Two salts are reported. 1-Meim-CF_3SO_3, 1, exists as a centrosymmetric dimer with an interplanar separation of only 3.16 Å. The two imidazolium rings are slipped to the extent that the interaction can be regarded as a manifestation of C–H ... C–H dipole interactions. 1-Meim-NO_3 exists as a one-dimensional (1-D) polymer with interplanar separations of 3.65 Å. The cations are not as severely slipped as for 1 and the interactions can be regarded as the result of cation–cation and anion–anion complementary electrostatics. Semi-empirical calculations are used to rationalize the π-π stacking in both 1 and 2. Crystal data: 1-Meim-CF_3SO_3, 1, triclinic, $P\bar{1}$, $a = 6.416(3)$ Å, $b = 7.617(4)$ Å, $c = 9.569(4)$ Å, $\alpha = 85.36(4)°$, $\beta = 86.08(3)°$, $\gamma = 85.18(4)°$, $V = 463.6(4)$ Å,^{3} $Z = 2$, $D_c = 1.66\ \mathrm{g\,cm^{-3}}$, $\mu = 3.7\ \mathrm{cm^{-1}}$, $T = 17°C$, $R = 0.054$ and $R_w = 0.076$ for 1241 reflections; 1-Meim-NO_3, 2, monoclinic, $P2_1/c$, $a = 9.009(7)$ Å, $b = 9.988(6)$ Å, $c = 7.308(5)$ Å, $\beta = 94.93(6)°$, $V = 655.2(8)$ Å,^{3} $Z = 4$, $D_c = 1.47\ \mathrm{g\,cm^{-3}}$, $\mu = 1.2\ \mathrm{cm^{-1}}$, $T = 17°C$, $R = 0.060$ and $R_w = 0.068$ for 483 reflections.



1-Et-3-Meim

That π–π interactions, which typically induce face-to-face interplanar (ie d–d) separations of the order of 3.4–3.8 Å, play a major role in many aspects of biological,[1] solid-state[2] and host–guest/supramolecular chemistry[3] is now generally accepted. The rationale behind, and hence predictability of, such interactions in the absence of electron donor–acceptor chemistry[4,5] continues to be a matter of great interest, with significant advances having been made in recent years via analysis of electrostatic effects as determined by semi-empirical[6,7] or *ab initio*[8] computational methods. However, solid state interionic interactions are less well characterized,[9] in particular cation–cation effects, which are at first sight counterintuitive. In the context of rationalizing the unusual low melting nature of 1-Et-3-Meim salts[10] we have embarked upon a systematic study of the solid state structure of a wide range of salts of alkylated imidazolium and pyridinium cations. Such a study offers the potential to delineate both cation–cation and cation–anion π–π interactions in the absence of the other binding forces[11] and geometric constraints/rigidity typically imposed by the host in host–guest chemistry (which have provided the bulk of the crystallographic data on π–π inter-actions). Salts also offer the virtue of structural simplicity and diversity. Our first X-ray structural study focussed upon salts of 1-Et-3-Meim, and d–d spacings were observed to be > 4.5 Å, beyond the range indicative of attractive interactions.[10c] In this study we demonstrate that short range face-to-face cation–cation stacking can occur in imidazolium salts that are not as sterically crowded, affording d–d distances in the order of those observed for molecule–molecule and molecule–cation attractions. Figures 1 and 2 reveal that 1-Meim cations in 1-Meim-CF_3SO_3,[12] 1, and 1-Meim-NO_3,[13] 2, adopt face-to-face, staggered and slipped orientations.

MOPAC[14] calculations support the idea that the short face-to-face contacts represent optimized electrostatic interactions. Figure 3 reveals that even though

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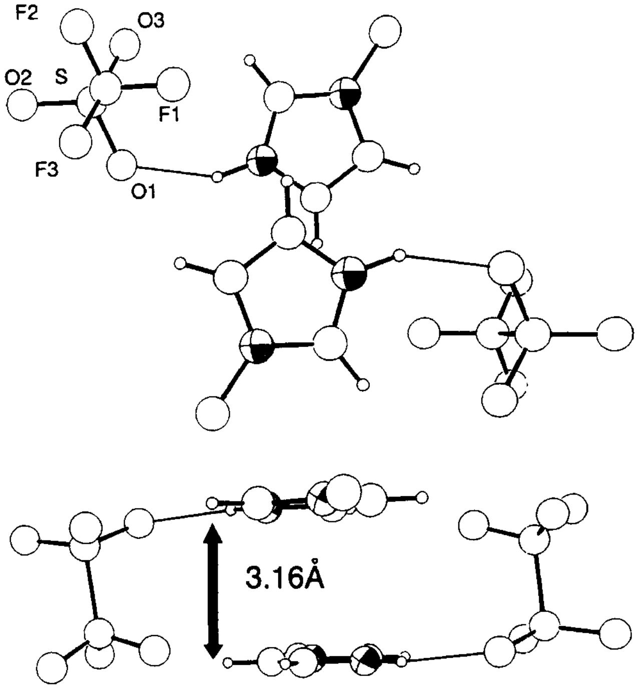

Figure 1 (a) Overhead and (b) perspective, views of the dimeric stacking in 1-Meim-CF_3SO_3.

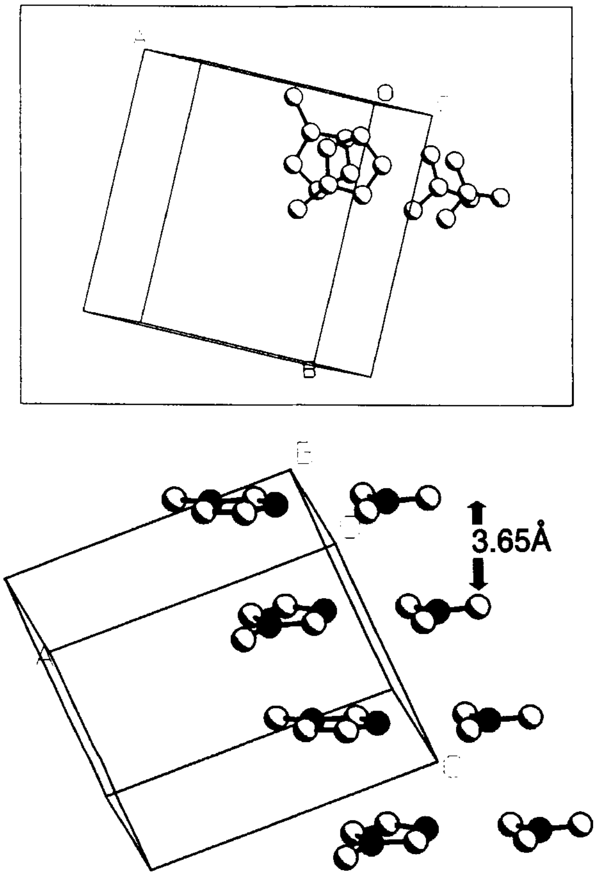

Figure 2 (a) Overhead and (b) perspective, views of the polymeric stacking in 1-Meim-NO_3.

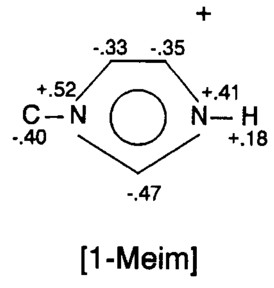

Figure 3 Calculated electrostatic potential charges (ie charge at van der Waals radius) for the 1-Meim cation. The balance of the charge is held by hydrogen atoms.

the imidazolium ring possesses a net charge of $+1$, the carbon atoms in 1-Meim are calculated to retain significant negative electrostatic potential charges at the van der Waals radius. **1** exists as a centrosymmetric dimer with a d–d spacing of only 3.16 Å, which is remarkably short even by the standards of electron donor–acceptor interactions.[15] **2** is effectively a 1-D polymer with d–d spacings of 3.65 Å and the nitrate anions are also slipped so as to facilitate N...O interactions. The geometry of **1** is remarkably similar to that of the most stable face-to-face interaction determined for the benzene dimer, which has been calculated to be of slightly higher energy than an edge-to-face interaction.[8b] Both **1** and **2** contain a localized interionic N–H...O hydrogen bond, with N...O distances of 2.886(5) and 2.729(6) Å, respectively. The only other interionic contact of note is a C–H...O contact of 2.40 Å in **1**. The interionic interactions in **1** and **2** bear some resemblance to the hinged synthetic receptor–thymine interactions observed by Hamilton *et al.*,[4d,16] which also contain a combination of localized H-bonding and π–π interactions. However, it must be noted that the apparent π–π interactions in **1** and **2** are cation–cation (rather than molecule–molecule) and the H bond is not directed towards the same species as the π–π interactions. The stacking and short d–d spacings observed in the solid state structures of **1** and **2** can therefore be at least partially attributed to complementary cation–cation (**1**) and anion–anion (**2**) electrostatic interactions. In summary, imidazolium cations appear predisposed to engage in face-to-face cation–cation stacking as a consequence of complementary electrostatic interactions. This observation is relevant to the structure[17] of imidazolium-based room temperature, ionic liquids since, whereas it precludes a conventional ionic structure, it does not preclude C–H...X hydrogen bonding.[10c,18] The results reported herein are also relevant to other fields such as biochemistry, where the imidazole moiety is prevalent, and crystal engineering, which could have important consequences for materials science.[2,5,19]

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REFERENCES AND NOTES

1 (a) Burley, S.K.; Petsko, G.A.; *Science* **1985**, *229*, 23. (b) Saenger, W.; *Principles of Nucleic Acid Structure*, Springer-Verlag, New York, **1984**.

2 Desiraju, G.R.; *Crystal Engineering. The Design of Organic Solids*, Elsevier, Amsterdam, **1989**.

3 (a) Diederich, F.; *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 362. (b) Cram, D.J.; *Nature* **1992**, *356*, 29. (c) Miller, S.P.; Whitlock, H.W. Jr.; *J. Am. Chem. Soc.* **1984**, *106*, 1492. (d) Muehldorf, A.V.; Van Engen, D.V.; Warner, J.C.; Hamilton, A.D.; *J. Am. Chem. Soc.* **1988**, *110*, 6561.

4 Donor–acceptor complexes have previously been characterized with both neutral and cationic hosts: Molecular host: (a) Zimmerman, S.C.; VanZyl, C.M.; Jamilton, G.S.; *J. Am. Chem. Soc.* **1989**, *111*, 1373. (b) Zimmerman, S.C.; Mrksich, M.; Baloga, M.; *J. Am. Chem. Soc.* **1989**, *111*, 8528. Cationic host: (c) Ortholand, J.-Y.; Slawin, A.M.Z.; Spencer, N.; Stoddart, J.F.; Williams, D.J.; *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 1394.

5 Donor–acceptor interactions have also been encountered in self-assembled rotaxanes and catenanes: Anelli, P.L.; Ashton, P.R.; Ballardini, R.; Balzani, V.; Delgado, M.; Gandolfi, M.T.; Goodnow, T.T.; Kaifer, A.E.; Philp, D.; Pietraszkiewicz, M.; Prodi, L.; Reddington, M.V.; Slawin, A.M.Z.; Spencer, N.; Stoddart, J.F.; Vicent, C.; Williams, D.J.; *J. Am. Chem. Soc.* **1992**, *114*, 193, and references therein.

6 MNDO has been utilized to determine electronic charge distributions and thereby rationalize the π–π interaction between thymine and a hinged artificial receptor: see reference 3(d).

7 IEH calculations have been utilized to model charge distribution in π-systems, thereby predicting and rationalizing observed geometrical requirements for interactions between aromatic molecules: Hunter, C.A.; Sanders, J.K.M.; *J. Am. Chem. Soc.* **1990**, *112*, 5525.

8 *Ab initio* methods have been employed to determine electrostatic potential functions for aromatic molecules and ultimately preferred structures of dimers or host–guest interactions: (a) Price, S.L.; Stone, A.J.; *J. Chem. Phys.* **1987**, *86*, 2859. (b) Jorgensen, W.L.; Severance, D.L.; *J. Am. Chem. Soc.* **1990**, *112*, 4768. (c) Jorgensen, W.L.; Nguyen, T.B.; Sanford, E.M. Chao, I.; Houk, K.N.; Diederich, F. *J. Am. Chem. Soc.* **1992**, *114*, 4003.

9 Solution phase interactions between organic ion pairs have been studied: Schneider, H.-J.; Schiestel, T.; Zimmermann, P.; *J. Am. Chem. Soc.* **1992**, *114*, 7698, and references therein.

10 Wilkes, J.S.; Levisky, J.A.; Wilson, R.A.; Hussey, C.L.; *Inorg. Chem.* **1982**, *21*, 1263. (b) Sanders, J.R.; Ward, E.H.; Hussey, C.L.; *J. Electrochem. Soc.* **1986**, *133*, 325. (c) Wilkes, J.S.; Zaworotko, M.J.; *J. Chem. Soc., Chem. Commun.* **1992**, 965.

11 Donor–acceptor interactions (see references 4 and 5) and π hydrogen bonds have been invoked in host–guest chemistry. For work on the effects of π hydrogen bonds see: (a) Atwood, J.L.; Hamada, F.; Robinson, K.D.; Orr, W.G.; Vincent, R.L.; *Nature* **1991**, *349*, 683. (b) Cochran, J.E. Parrott, T.J.; Whitlock, B.J.; Whitlock, H.W.; *J. Am. Chem. Soc.* **1992**, *114*, 2269.

12 Meim-CF_3SO_3, **1**: triclinic, $P\text{-}\bar{1}$, $a = 6.416(3)$ Å, $b = 7.617(4)$ Å, $c = 9.569(4)$ Å, $\alpha = 85.36(6)°$, $\beta = 86.08(3)°$, $\gamma = 85.18(4)°$, $V = 463.6(4)$ Å,^{3} $Z = 2$, $D_c = 1.66\ \text{g cm}^{-3}$, $\mu = 3.7\ \text{cm}^{-1}$, $T = 17°\text{C}$. Data were collected on a Siemens P3/PC diffractometer using the omega/2θ mode. Refinement with anisotropic thermal parameters for all non-hydrogen atoms and hydrogen atoms fixed in calculated (ring C–H) or located (methyl C–H) positions gave $R = 0.054$ and $R_w = 0.076$ for 1241 independent, observed $[I > 3\sigma(I)]$ and absorption-corrected reflections.

13 Meim-NO_3, **2**: monoclinic, $P2_1/c$, $a = 9.009(7)$ Å, $b = 9.988(6)$ Å, $c = 7.308(5)$ Å, $\beta = 94.93(6)°$, $V = 655.2(8)$ Å,^{3} $Z = 4$, $D_c = 1.47\ \text{g cm}^{-3}$, $\mu = 1.2\ \text{cm}^{-1}$, $T = 17°\text{C}$. Data were collected on a Siemens P3/PC diffractometer using the $\theta/2\theta$ mode. Refinement as for **1** gave $R = 0.060$ and $R_w = 0.068$ for 483 reflections.

14 *MOPAC: A General Molecular Orbital Package*, Stewart, J.J.P. (Ed.), QCPE No. 455, **1983**, Version 6, **1990**. A comparison of MNDO, MINDO/3, AM1 and PM3 affords widely differing results. The PM3 (Stewart, J.J.P.; *J. Comp. Chem.* **1989**, *10*, 221) and AM1 (Dewar, M.J.S.; Zoebisch, E.G.; Healy, E.F.; Stewart, J.J.P.; *J. Am. Chem. Soc.* **1985**, *107*, 3902) parameter sets yield results that are both intuitively correct (charge distribution) and consistent (charge magnitude) whereas MINDO/3 and, particularly, MNDO produce less realistic results. This is a significant observation since it has already been noted that MNDO does not lead to realistic measures of binding energy in the host–guest context (reference 6). However, even if the electrostatic charge distributions are only qualitatively correct the negative potentials associated with the ring carbon atoms justify the observed stacking in **1** and **2**.

15 Similar interionic contacts were reported (although not fully rationalized) between benzyl and pyridinium rings in the charge transfer salt *N*,*N*′-dibenyl-4,4′-bipyridylium diiodide: Russell, J.H.; Wallwork, S.C.; *Acta Cryst.* **1969**, *B25*, 2473. Anion–cation contacts of around 3.3 Å in the tetraphenylborate salt of paraquat have also been reported: Moody, G.J.; Owusu, R.K.; Slawin, A.M.Z.; Spencer, N.; Stoddart, J.F.; Thomas, J.D.R.; Williams, D.J.; *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 890. Separations in the order of 3.4–3.6 Å were observed between $[(\text{arene})_2\text{Fe}]^{2+}$ acceptors and ferrocene or arene donors: Lehmann, R.E.; Kochi, J.K.; *J. Am. Chem. Soc.* **1991**, *113*, 501; whereas related donor acceptor contacts in host–guest, rotaxane and catenane chemistry, which are typically defined by the geometry of the host, are usually longer (see references 4 and 5).

16 Hamilton, A.D.; Van Engen, D.; *J. Am. Chem. Soc.* **1987**, *109*, 5035.

17 A stacked structure for basic room temperature ionic liquids has already been proposed, but with chloride anions sandwiched between imidazolium cations: Dieter, K.M.; Dymek, Jr., C.J.; Heimer, N.E.; Rovang, J.W.; Wilkes, J.S.; *J. Am. Chem. Soc.* **1988**, *110*, 2722.

18 There is strong spectroscopic support for C–H…X^- hydrogen bonding in imidazolium-based ionic liquids: (a) see reference 17. (b) Wilkes, J.S.; Hussey, C.L.; Sanders, J.R., *Polyhedron* **1988**, *5*, 1567. (c) Carper, W.R.; W.R.; Pflug, J.L.; Elias, A.M.; Wilkes, J.S.; *J. Phys. Chem.* **1992**, *96*, 3828.

19 (a) Marder, S.R.; Perry, J.W.; Schaefer, W.P.; *Science* **1989**, *245*, 626. (b) Aakeroy, C.B.; Hitchcock, P.B.; Seddon, K.R.; *J. Chem. Soc., Chem. Commun.* **1992**, 553.