

## Two three-dimensional networks in the binary molecular adducts 4-methylimidazolium hydrogen terephthalate and bis(4-methylimidazolium) terephthalate

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Received 18 April 2008

Accepted 2 May 2008

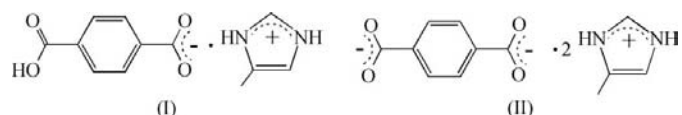
Online 14 May 2008

Both the 1:1 and 2:1 molecular adducts of 4-methylimidazole (4-MeIm) and terephthalic acid ( $H_2$ TPA) are organic salts, *viz.*  $C_4H_7N_2^+ \cdot C_8H_5O_4^-$ , (I), and  $2C_4H_7N_2^+ \cdot C_8H_4O_4^{2-}$ , (II), respectively. The component ions in (I) are linked by  $N-H \cdots O$  and  $O-H \cdots O$  hydrogen bonds into continuous two-dimensional layers built from  $R_6^4(32)$  hydrogen-bond motifs running parallel to the (100) plane. These adjacent two-dimensional layers are in turn linked by a combination of  $C-H \cdots O$ ,  $C-H \cdots \pi$  and  $\pi-\pi$  interactions into a three-dimensional network. In the crystal structure of (II), with the anion located on an inversion centre, only  $N-H \cdots O$  hydrogen bonds result in two-dimensional layers built from  $R_8^8(42)$  hydrogen-bond motifs running parallel to the (102) plane. Being similar to those in (I), these layers are also linked by means of  $C-H \cdots O$ ,  $C-H \cdots \pi$  and  $\pi-\pi$  interactions, forming a three-dimensional network. This study indicates that, on occasion, a change of the reactant concentration can exert a pivotal influence on the construction of supramolecular structures based on hydrogen bonds.

### Comment

Terephthalic acid ( $H_2$ TPA), a rod-like aromatic diacid, has often been used in the synthesis of metal-organic frameworks as a linker molecule (Serre *et al.*, 2007; Mukherjee *et al.*, 2004; Sun *et al.*, 2000; Zakaria *et al.*, 2001; Karanović *et al.*, 2002; Damgaard Poulsen *et al.*, 2006; Li *et al.*, 1998). Recently, with the increase in interest in controlling the crystalline structures of organic-based solid-state materials,  $H_2$ TPA is being increasingly employed in constructing supramolecular structures (Mei *et al.*, 2007; Dale *et al.*, 2004; Zhang & Chen, 2004; Lynch & Jones, 2004; Spencer *et al.*, 2004; Devi & Muthiah,

2007). However, the experimental conditions employed (such as the solvent, temperature, crystallization method and counter-ions) can all have an important impact on the structure of the final assembly (She *et al.*, 2008; Meng *et al.*, 2007, 2008; Childs *et al.*, 2007; Díaz *et al.*, 2006). In this paper, we chose 4-methylimidazole (4-MeIm) acting as a proton-accepting candidate to study further the influence of its concentration on cocrystals and/or organic salt structures containing  $H_2$ TPA. We obtained the title 1:1 and 2:1 binary molecular adducts, (I) and (II), respectively, and report their crystal structures here.



Compounds (I) and (II) crystallize in the space groups  $P\bar{1}$  and  $P2_1/c$ , respectively. In (I), the H atom of one carboxyl group O atom is transferred to an imidazole N atom, while the other remains as the acid. The carboxyl and carboxylate groups are distinctly twisted away from the benzene ring, with dihedral angles of  $5.7$  (1) and  $21.9$  (1)°, respectively. However, the imidazole ring makes a much larger dihedral angle of  $60.6$  (1)° with the benzene ring. The  $4-MeIm^+$  and  $HTPA^-$  component ions are joined together by two intermolecular  $N-H \cdots O$  hydrogen bonds (Fig. 2 and Table 1).

In contrast with (I), there is an inversion centre lying across the centre of the benzene ring of (II). Both carboxyl groups are deprotonated, with a carboxylate-benzene ring dihedral angle of  $3.3$  (1)° and an imidazole-benzene ring dihedral angle of  $30.7$  (1)°, roughly half of the corresponding values in (I). The component ions in (II) are linked together mainly by  $N-H \cdots O$  hydrogen bonds (Fig. 3 and Table 1).

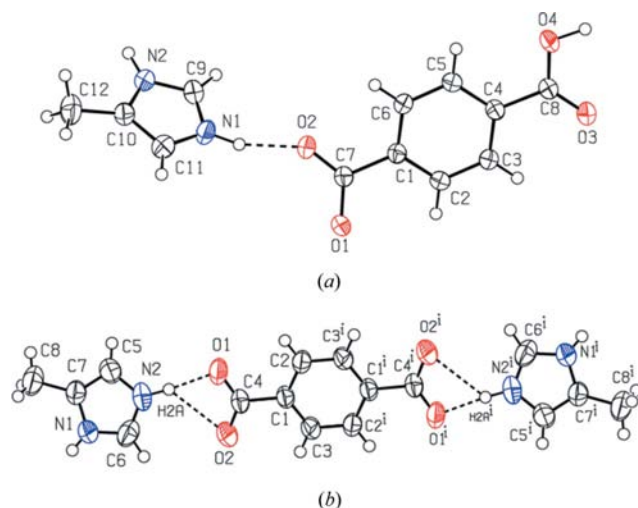
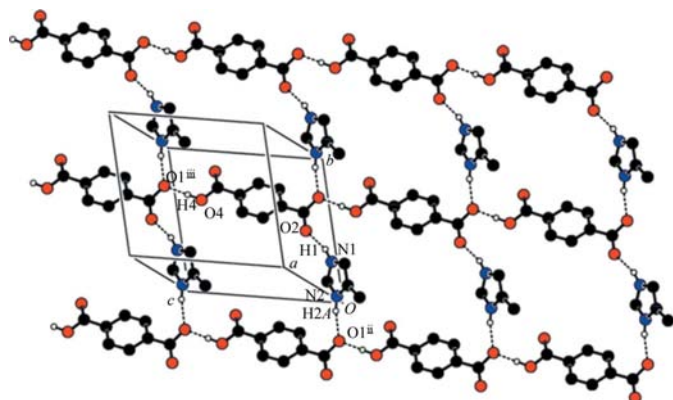


Figure 1

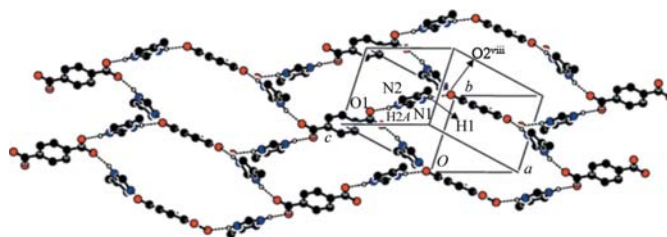
The molecular structures of (a) (I) and (b) (II), showing the atom-numbering schemes. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radii. Hydrogen bonds are shown as dashed lines. [Symmetry code: (i)  $-x, -y, 2-z$ .]

**Figure 2**

Part of the crystal structure of (I), showing the formation of the two-dimensional layer running parallel to the (100) plane. Hydrogen bonds are shown as dashed lines. For the sake of clarity, 4-MeIm<sup>+</sup> cations and H atoms not involved in the motif have been omitted. [Symmetry codes: (ii)  $x, y - 1, z$ ; (iii)  $x, y, z + 1$ ]

The carboxyl/carboxylate C—O bond lengths in both title compounds [C7—O1 = 1.275 (2) Å, C7—O2 = 1.229 (2) Å, C8—O3 = 1.210 (2) Å and C8—O4 = 1.310 (2) Å in (I); C4—O1 = 1.255 (2) Å and C4—O2 = 1.250 (2) Å in (II)] agree well with those tabulated by Allen *et al.* (1995) for a carboxyl [1.305 (20) and 1.226 (20) Å] and/or a carboxylate group [1.255 (10) Å] attached to a benzene ring. The bond distances and angles in the 4-MeIm<sup>+</sup> cation are also indicative of its protonation by drawing a comparison between (I), (II) and analogous compounds [Cambridge Structural Database, Version 5.29 (Allen, 2002; Macrae *et al.*, 2006); refcodes AHIJUW (Gossman *et al.*, 2002), FETDAK (Aakerøy *et al.*, 2005), HISTPA (Mata *et al.*, 2006), JAXMEB (Wang & Wei, 2005) and HILSAX (Tian, 2007)].

Although compounds (I) and (II) are both linked into their final three-dimensional networks by a combination of N—H...O, O—H...O and C—H...O hydrogen bonds and C—H... $\pi$  and  $\pi$ — $\pi$  interactions, the structural subunits are apparently different because of the concentration change of 4-MeIm. In (I), the supramolecular structure can be simply analyzed in terms of three substructures. Firstly, the HTPA<sup>−</sup> anions result in discrete one-dimensional  $C(8)$  (Bernstein *et al.*, 1995) chains *via* an O4—H4...O1<sup>iii</sup> hydrogen bond [symmetry code: (iii)  $x, y, z + 1$ ] running parallel to the [001] direction (Fig. 2). Secondly, these adjacent [001] chains are linked together by 4-MeIm<sup>+</sup> cations, forming two-dimensional layers built from  $R_6^4(32)$  hydrogen-bond motifs which are parallel to the (100) plane (Fig. 2). If these  $R_6^4(32)$  rings are regarded as the nodes of the resulting net, then this is of the (4,4)-type (Batten & Robson, 1998). Finally, these neighbouring two-dimensional layers are assembled into a three-dimensional network by means of two C—H...O hydrogen bonds and two C—H... $\pi$  interactions (Table 1), and  $\pi$ — $\pi$  interactions. One of the  $\pi$ — $\pi$  interactions occurs between centrosymmetrically related imidazole rings, with a ring centroid distance of 3.706 (2) Å, an interplanar spacing of 3.452 (2) Å and a ring offset of 1.348 (2) Å. However, another  $\pi$ — $\pi$  interaction is stronger and is formed between strictly

**Figure 3**

Part of the crystal structure of (II), showing the formation of the two-dimensional layer built from N—H...O hydrogen bonds. For the sake of clarity, H atoms not involved in the motif have been omitted. [Symmetry code: (viii)  $-x + 1, y + \frac{1}{2}, -z + \frac{3}{2}$ ]

parallel benzene rings; the ring centroid separation is 3.569 (2) Å, the interplanar spacing is 3.476 (2) Å and the ring offset is 0.807 (2) Å.

By comparison, the component ions in (II) are first linked by N1—H1A...O2<sup>viii</sup> [symmetry code: (iii)  $1 - x, \frac{1}{2} + y, \frac{3}{2} - z$ ] and N2—H2A...O1 hydrogen bonds, forming a two-dimensional layer built from centrosymmetric  $R_8^8(42)$  hydrogen-bonded rings running parallel to the (102) plane (Fig. 3). According to the topology classification for nets, this is a (6,3)-net, which is apparently larger than that in (I). These adjacent layers in (II) are in turn linked into a three-dimensional network by a combination of one C—H...O hydrogen bond and one C—H... $\pi$  interaction (Table 1), and  $\pi$ — $\pi$  interactions. The  $\pi$ — $\pi$  interactions in (II) only occur between the strictly parallel imidazole rings, with a ring centroid distance of 3.665 (2) Å, an interplanar spacing of 3.302 (2) Å and a ring offset of 1.591 (2) Å.

Both title compounds should be regarded as organic salts according to the definitions of cocrystals and organic salts (Aakerøy & Salmon, 2005). We might find some reasons from the  $\Delta pK_a$  rule [ $\Delta pK_a = pK_a(\text{base}) - pK_a(\text{acid})$ ; Childs *et al.*, 2007; Bhogala *et al.*, 2005] why cocrystallization of H<sub>2</sub>TPA and 4-MeIm from water yields the organic salt but not a cocrystal. It is generally accepted that reaction of an acid with a base will be expected to form a salt if  $\Delta pK_a$  is greater than 3 and will exclusively result in cocrystal formation if  $\Delta pK_a$  is less than 0. The  $pK_a$  value of 4-MeIm is 8.5 in aqueous solution at 303 K, calculated using SOLARIS (Advanced Chemistry Development, 2005). For H<sub>2</sub>TPA,  $pK_{a1} = 3.51$  and  $pK_{a2} = 4.82$ . Both the  $\Delta pK_{a1}$  (4.99) and  $\Delta pK_{a2}$  (3.68) values are greater than 3, indicating that the 1:1 and 2:1 organic salts are available.

In conclusion, H<sub>2</sub>TPA is a good participant in hydrogen-bonding networks for the formation of acid–base molecular adducts. With the aim of gaining more insight into crystal engineering based on hydrogen bonds, further organic salts and/or cocrystals containing H<sub>2</sub>TPA are expected to be obtained by means of the  $\Delta pK_a$  rule.

## Experimental

All reagents and solvents were used as obtained without further purification. Crystals of (I) were obtained by mixing equivalent molar quantities of 4-methylimidazole (0.2 mmol, 16.4 mg) and terephthalic acid (0.2 mmol, 33.2 mg) dissolved in water (10 ml). The mixture was stirred for 10 min at ambient temperature and then filtered. The

resulting colourless solution was kept in air for one week. Colourless plate-shaped crystals of (I) suitable for single-crystal X-ray diffraction analysis were grown by slow evaporation of the solution at the bottom of the vessel. The crystals were filtered off carefully, washed with distilled water and dried in air (yield 30%, 15.0 mg, based on the 1:1 organic salt).

Crystals of (II) were obtained by mixing 2:1 molar quantities of 4-methylimidazole (0.4 mmol, 32.8 mg) and terephthalic acid (0.2 mmol, 33.2 mg) in water (20 ml). The mixture was stirred for 30 min at ambient temperature and then filtered. The resulting colourless solution was kept in air for three weeks. Block-shaped colourless crystals of (II) suitable for single-crystal X-ray diffraction analysis were grown by slow evaporation of the solution at the bottom of the vessel. The crystals were filtered off carefully, washed with distilled water and dried in air (yield 50%, 33.0 mg, based on the 2:1 organic salt).

### Compound (I)

#### Crystal data

$C_4H_7N_2^+ \cdot C_8H_5O_4^-$   
 $M_r = 248.24$   
 Triclinic,  $P\bar{1}$   
 $a = 7.2649$  (5) Å  
 $b = 8.9459$  (7) Å  
 $c = 9.6844$  (7) Å  
 $\alpha = 75.406$  (1)°  
 $\beta = 72.731$  (1)°  
 $\gamma = 77.966$  (2)°  
 $V = 575.52$  (7) Å<sup>3</sup>  
 $Z = 2$   
 Mo  $K\alpha$  radiation  
 $\mu = 0.11$  mm<sup>-1</sup>  
 $T = 298$  (2) K  
 $0.30 \times 0.10 \times 0.04$  mm

#### Data collection

Bruker SMART APEX CCD area-detector diffractometer  
 Absorption correction: multi-scan (SADABS; Sheldrick, 1997)  
 $T_{\min} = 0.956$ ,  $T_{\max} = 0.996$   
 5915 measured reflections  
 2204 independent reflections  
 1820 reflections with  $I > 2\sigma(I)$   
 $R_{\text{int}} = 0.021$

#### Refinement

$R[F^2 > 2\sigma(F^2)] = 0.049$   
 $wR(F^2) = 0.155$   
 $S = 1.07$   
 2204 reflections  
 173 parameters  
 H atoms treated by a mixture of independent and constrained refinement  
 $\Delta\rho_{\text{max}} = 0.25$  e Å<sup>-3</sup>  
 $\Delta\rho_{\text{min}} = -0.29$  e Å<sup>-3</sup>

### Compound (II)

#### Crystal data

$2C_4H_7N_2^+ \cdot C_8H_4O_4^{2-}$   
 $M_r = 330.34$   
 Monoclinic,  $P2_1/c$   
 $a = 10.7759$  (7) Å  
 $b = 7.5608$  (5) Å  
 $c = 10.3254$  (7) Å  
 $\beta = 103.454$  (1)°  
 $V = 818.17$  (9) Å<sup>3</sup>  
 $Z = 2$   
 Mo  $K\alpha$  radiation  
 $\mu = 0.10$  mm<sup>-1</sup>  
 $T = 296$  (2) K  
 $0.36 \times 0.30 \times 0.10$  mm

#### Data collection

Bruker SMART APEX CCD area-detector diffractometer  
 Absorption correction: multi-scan (SADABS; Sheldrick, 1997)  
 $T_{\min} = 0.945$ ,  $T_{\max} = 0.990$   
 8924 measured reflections  
 1860 independent reflections  
 1491 reflections with  $I > 2\sigma(I)$   
 $R_{\text{int}} = 0.029$

#### Refinement

$R[F^2 > 2\sigma(F^2)] = 0.048$   
 $wR(F^2) = 0.150$   
 $S = 1.08$   
 1860 reflections  
 116 parameters  
 H atoms treated by a mixture of independent and constrained refinement  
 $\Delta\rho_{\text{max}} = 0.24$  e Å<sup>-3</sup>  
 $\Delta\rho_{\text{min}} = -0.21$  e Å<sup>-3</sup>

**Table 1**

Geometry of hydrogen bonds and C—H... $\pi$  interactions in the title compounds (Å, °).

Cg1 is the centroid defined by atoms N1/N2/C9–C11 in (I), and Cg2 and Cg3 are the centroids defined by the benzene rings in (I) and (II), respectively.

| D—H...A                      | D—H      | H...A      | D...A       | D—H...A    |
|------------------------------|----------|------------|-------------|------------|
| (I)                          |          |            |             |            |
| N1—H1...O2                   | 0.93 (2) | 1.749 (19) | 2.6536 (17) | 162.7 (18) |
| N2—H2A...O1 <sup>ii</sup>    | 0.98 (2) | 1.59 (2)   | 2.5657 (16) | 176.5 (19) |
| O4—H4...O1 <sup>iii</sup>    | 0.98 (2) | 1.59 (2)   | 2.5657 (16) | 176.5 (19) |
| C3—H3...O3 <sup>iv</sup>     | 0.93     | 2.53       | 3.2762 (19) | 138        |
| C9—H9...O3 <sup>v</sup>      | 0.93     | 2.27       | 3.155 (2)   | 160        |
| C2—H2...Cg1 <sup>vi</sup>    | 0.93     | 2.96       | 3.744 (2)   | 143        |
| C11—H11...Cg2 <sup>vii</sup> | 0.93     | 2.60       | 3.429 (2)   | 149        |
| (II)                         |          |            |             |            |
| N1—H1A...O2 <sup>viii</sup>  | 0.82 (2) | 1.90 (2)   | 2.6968 (18) | 161.0 (19) |
| N2—H2A...O1                  | 0.92 (2) | 1.74 (2)   | 2.6632 (17) | 171.8 (18) |
| C6—H6...O1 <sup>ix</sup>     | 0.93     | 2.30       | 3.164 (2)   | 154        |
| C8—H8C...Cg3 <sup>x</sup>    | 0.96     | 3.00       | 3.791 (2)   | 141        |

Symmetry codes: (ii)  $x, y - 1, z$ ; (iii)  $x, y, z + 1$ ; (iv)  $-x, -y + 2, -z + 1$ ; (v)  $-x, -y + 1, -z + 1$ ; (vi)  $-x, 1 - y, -z$ ; (vii)  $1 - x, 1 - y, -z$ ; (viii)  $-x + 1, y + \frac{1}{2}, -z + \frac{3}{2}$ ; (ix)  $x, -y + \frac{1}{2}, z - \frac{1}{2}$ ; (x)  $1 - x, -y, 2 - z$ .

For both compounds, H atoms bonded to C atoms were positioned geometrically, with C—H = 0.93 (aromatic) or 0.96 Å (methyl), and refined in riding mode, with  $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{aromatic C})$  or  $1.5U_{\text{eq}}(\text{methyl C})$ . H atoms bonded to N and O atoms were found in difference maps. N—H and O—H distances were refined freely (refined distances are given in Table 1), with  $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{N})$  or  $1.5U_{\text{eq}}(\text{O})$ .

For both compounds, data collection: SMART (Bruker, 2001); cell refinement: SMART; data reduction: SAINT-Plus (Bruker, 2001); program(s) used to solve structure: SHELXS97 (Sheldrick, 2008); program(s) used to refine structure: SHELXL97 (Sheldrick, 2008); molecular graphics: PLATON (Spek, 2003); software used to prepare material for publication: PLATON.

This work received financial support mainly from the National Key Fundamental Project (grant No. 2002-CCA00500).

Supplementary data for this paper are available from the IUCr electronic archives (Reference: SK3225). Services for accessing these data are described at the back of the journal.

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