

Three-dimensional networks in bis(imidazolium) 2,2'-dithiodibenzoate and 4-methylimidazolium 2-[(2-carboxyphenyl)disulfanyl]-benzoate

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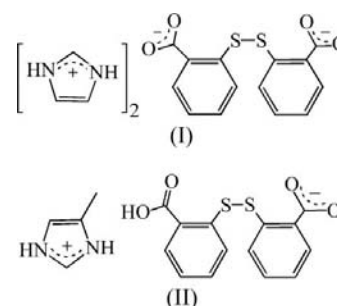
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Cocrystallization of imidazole or 4-methylimidazole with 2,2'-dithiodibenzoic acid from methanol solution yields the title 2:1 and 1:1 organic salts, $2\text{C}_3\text{H}_5\text{N}_2^+\cdot\text{C}_{14}\text{H}_{10}\text{O}_4\text{S}_2^{2-}$, (I), and $\text{C}_4\text{H}_7\text{N}_2^+\cdot\text{C}_{14}\text{H}_{10}\text{O}_4\text{S}_2^{2-}$, (II), respectively. Compound (I) crystallizes in the monoclinic $C2/c$ space group with the midpoint of the S—S bond lying on a twofold axis. The component ions in (I) are linked by intermolecular N—H...O hydrogen bonds to form a two-dimensional network, which is further linked by C—H...O hydrogen bonds into a three-dimensional network. In contrast, by means of N—H...O, N—H...S and O—H...O hydrogen bonds, the component ions in (II) are linked into a tape and adjacent tapes are further linked by π - π , C—H...O and C—H... π interactions, resulting in a three-dimensional network.

Comment

2,2'-Dithiodibenzoic acid (H_2DTBB), possessing two carboxyl groups, has often been employed in coordination complexes (Wang *et al.*, 2007, 2008; Murugavel *et al.*, 2001). However, due to its poor solubility in water, molecular adducts based on H_2DTBB have been reported for only a few cases to date (Meng *et al.*, 2008; Li *et al.*, 2001; Cai *et al.*, 2006; Kang *et al.*, 2002; Hu *et al.*, 2004). In order to investigate crystal engineering involving two hydrogen-bonded R -COOH groups and an N-containing heterocycle in the solid state, we used H_2DTBB and imidazole (Im) or 4-methylimidazole (4-MeIm) as potential cocrystallization agents in our experiments. According to the ΔpK_a rule (Meng *et al.*, 2009; Childs *et al.*, 2007), a 1:1 type of organic salt for the combination of H_2DTBB and Im, and a 1:2 organic salt (acid to base) for

H_2DTBB and 4-MeIm, should both exist theoretically [for a 1:1 salt, $\Delta pK_{a1} = 11.1$ and $\Delta pK_{a2} = 10.4$; for a 1:2 salt, $\Delta pK_{a1} = 11.5$ and $\Delta pK_{a2} = 10.8$]. However, when H_2DTBB and Im were mixed and stirred in methanol solution in a molar ratio of 1:1, only some of the H_2DTBB was dissolved, showing that the preparation of the target compound was hampered by the poor solubility of H_2DTBB in methanol. For the second combination, although H_2DTBB and 4-MeIm can be easily dissolved in methanol in a molar ratio of 1:2, the result is an oil-like compound when the humidity level in the air exceeds 20%. Further research on this will be carried out for the 1:1 and 1:2 organic salts. We report here the crystal structures of the title salts, $2(4\text{-MeIm}^+)\cdot\text{DTBB}^{2-}$, (I), and $4\text{-MeIm}^+\cdot\text{HDTBB}^-$, (II).



In (I), half of a 2,2'-dithiodibenzoate dianion (DTBB^{2-}) and one imidazolium (Im^+) cation, linked by an $\text{N1}-\text{H1}\cdots\text{O1}$ hydrogen bond (see Fig. 1 and Table 1), comprise the asymmetric unit. The two halves of the DTBB^{2-} ion are related by a twofold axis lying across the mid-point of the S—S bond. Both the dihedral angle between the two benzene rings [$76.80(11)^\circ$] and the bridging S—S bond length [$2.0476(10) \text{ \AA}$] are comparable with those observed in some analogous compounds [Cambridge Structural Database (CSD, Version 5.30 of November 2008; Allen 2002) refcodes MIPVAI (Li *et al.*, 2001), MUFNIK (Bi *et al.*, 2002), WUBHOQ (Kang *et al.*, 2002), XEBDEO (Cai *et al.*, 2006) and XEXFOV (Basiuk *et al.*, 1999)]. The deprotonation of the H_2DTBB molecule and protonation of imidazole were very clearly shown in difference maps and the relevant dimensions are fully in accord with this: $\text{C7}-\text{O1} = 1.259(2) \text{ \AA}$ and $\text{C7}-\text{O2} = 1.250(2) \text{ \AA}$, and $\text{C2}'-\text{N1} = 1.315(3) \text{ \AA}$ and $\text{C2}'-\text{N3} =$

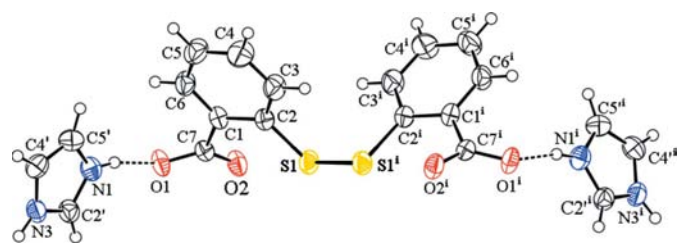
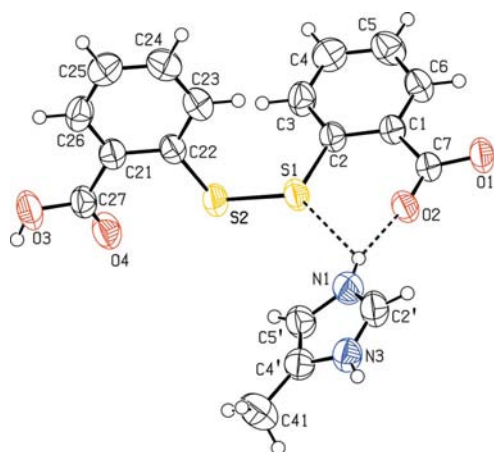
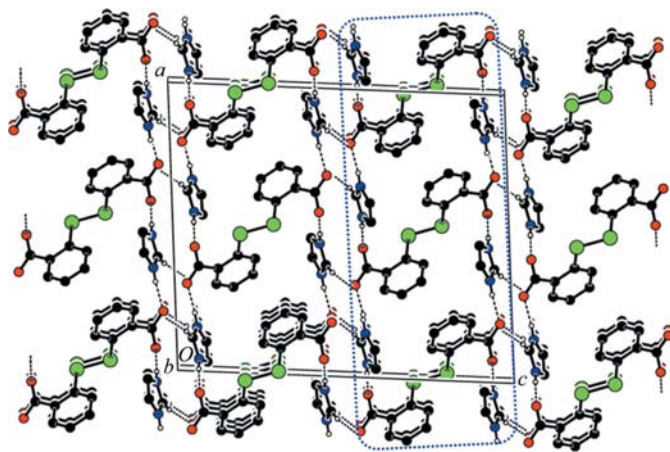


Figure 1

The molecular structure of (I), showing the atom-numbering scheme. 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) $1 - x, y, \frac{3}{2} - z$.]


Figure 2

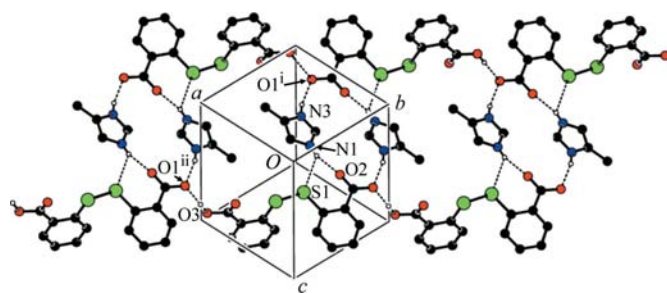
The molecular structure of (II), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radii. Hydrogen bonds are shown as dashed lines.


Figure 3

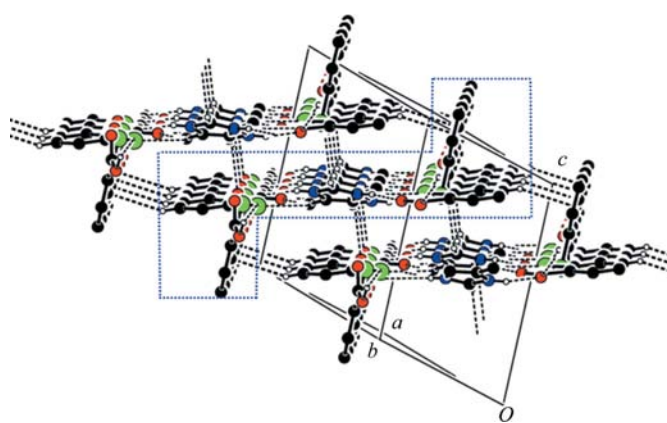
Part of the crystal structure of (I), showing the three-dimensional network formed only by N—H...O and C—H...O hydrogen bonds. Hydrogen bonds are shown as short dashed lines. For the sake of clarity, H atoms not involved in the motif have been omitted. The area outlined by a dotted line shows the (001) layer in the domain $0.530 < z < 0.970$.

1.316 (3) Å. Compound (I) can be regarded as a binary 2:1 organic salt, according to Aakerøy & Salmon (2005).

The asymmetric unit of (II) (Fig. 2) contains a 4-methylimidazolium (4-MeIm⁺) ion and a hydrogen 2,2'-dithiobenzoate anion (HDTBB⁻), both lying in general positions, forming a 1:1 salt. The dihedral angle between the two benzene rings and the disulfide bridge are 73.50 (10) and 2.0504 (8) Å. As with (I), the H atoms involved in the hydrogen bonding were unequivocally located from difference map plots and the resulting ion dimensions are fully in accord with these H-atom locations: at the deprotonated carboxyl group, C7—O1 = 1.264 (3) Å and C7—O2 = 1.239 (3) Å. For the carboxyl group, the main bond lengths are C27—O3(H) = 1.320 (3) Å and C27—O4 = 1.205 (3) Å, again in accord with the location of the carboxyl H atom at O3. In the 4-MeIm⁺ cation, the C2'—N1 and C2'—N3 bond lengths of 1.315 (4) and 1.310 (4) Å, respectively, are almost the same as those


Figure 4

Part of the crystal structure of (II), showing the formation of the one-dimensional tape running parallel to the $[1\bar{1}0]$ direction. Hydrogen bonds are shown as dashed lines. For the sake of clarity, H atoms not involved in the motif have been omitted. See Table 2 for symmetry codes.


Figure 5

Part of the crystal structure of (II), showing the formation of the three-dimensional network. Hydrogen bonds are shown as short dashed lines. For the sake of clarity, H atoms not involved in the motif have been omitted. The area outlined by a continuous dotted line shows part of the $[1\bar{1}0]$ tape.

found in (I), consistent with the delocalization of the imidazole ring.

In the crystal packing of (I), the DTBB²⁻ anion and the Im⁺ cation are linked into a two-dimensional network by the N1—H1...O1 and N3—H3...O2ⁱ hydrogen bonds (see Table 1 and Fig. 3; symmetry code as in Table 1) running parallel to the (001) plane in the domain $0.530 < z < 0.970$. These adjacent networks are linked by a C2'—H2'...O1ⁱⁱ hydrogen bond, resulting in a three-dimensional network (Fig. 3; symmetry code as in Table 1). PLATON (Spek, 2009) calculations show that there are no significant C—H...π or π—π interactions in the packing of (I).

In the structure of (II), the HDTBB⁻ anion and 4-MeIm⁺ cation are linked by N—H...O, N—H...S and O—H...O hydrogen bonds to generate a tape extending in the $[1\bar{1}0]$ direction (shown in Fig. 4 and with details in Table 2). The N3—H3...O1ⁱⁱⁱ (symmetry code as in Table 2) and N1—H1...O2 hydrogen bonds serve to generate a centrosymmetric $R_4^4(16)$ ring (Bernstein *et al.*, 1995). These $R_4^4(16)$ rings are linked by an O3—H3...O1^{iv} (symmetry code as in Table 2) hydrogen bond to form the tape shown in Fig. 4. These tapes are further linked to form a three-dimensional network (Fig. 5)

by a combination of π - π interactions [$Cg1 \cdots Cg1(-x, 1 - y, 2 - z)$, with a centroid-centroid distance of 3.9798 (17) Å and an interplanar spacing of 3.6820 (12) Å, where $Cg1$ is the centroid of the C1-C6 ring], a $C2' - H2' \cdots O4^v$ interaction (symmetry code as in Table 2) and a $C4 - H4 \cdots Cg2$ interaction [$H4 \cdots Cg2 = 2.94$ Å and $C4 - H4 \cdots Cg2 = 136^\circ$, where $Cg2$ is the centroid of the C21-C26 ring at $(x - 1, y, z)$].

Experimental

2,2'-Dithiodibenzoic acid (0.2 mmol, 0.0612 g) and imidazole (0.2 mmol, 0.0136 g) were dissolved in 95% methanol (10 ml). The resulting clear solution was kept in air for 3 d. Colourless plate-shaped crystals of (I) suitable for single-crystal X-ray diffraction analysis were grown by slow evaporation from the solution (yield 17.7 mg, 40%, based on 1:2 cocrystallization). Similarly, colourless block-shaped crystals of compound (II) were obtained by mixing equivalent molar amounts of 2,2'-dithiodibenzoic acid (0.2 mmol, 0.0612 g) and 4-methylimidazole (0.2 mmol, 0.0164 g) in 95% methanol (10 ml) (yield 43.5 mg, 56%, based on 1:1 cocrystallization).

Compound (I)

Crystal data

$2C_3H_5N_2^+ \cdot C_{14}H_8O_4S_2^{2-}$	$V = 1996.9$ (3) Å ³
$M_r = 442.50$	$Z = 4$
Monoclinic, $C2/c$	Mo $K\alpha$ radiation
$a = 17.0142$ (13) Å	$\mu = 0.30$ mm ⁻¹
$b = 5.9064$ (4) Å	$T = 297$ K
$c = 19.9254$ (15) Å	$0.30 \times 0.30 \times 0.04$ mm
$\beta = 94.228$ (1)°	

Data collection

Bruker SMART APEX CCD area-detector diffractometer	10805 measured reflections
Absorption correction: multi-scan (SADABS; Sheldrick, 1997)	2283 independent reflections
$T_{\min} = 0.905$, $T_{\max} = 0.988$	1721 reflections with $I > 2\sigma(I)$
	$R_{\text{int}} = 0.038$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.046$	136 parameters
$wR(F^2) = 0.129$	H-atom parameters constrained
$S = 1.06$	$\Delta\rho_{\text{max}} = 0.38$ e Å ⁻³
2283 reflections	$\Delta\rho_{\text{min}} = -0.26$ e Å ⁻³

Compound (II)

Crystal data

$C_4H_7N_2^+ \cdot C_{14}H_9O_4S_2^{2-}$	$\gamma = 81.285$ (1)°
$M_r = 388.45$	$V = 882.81$ (9) Å ³
Triclinic, $P\bar{1}$	$Z = 2$
$a = 8.2486$ (5) Å	Mo $K\alpha$ radiation
$b = 10.1528$ (6) Å	$\mu = 0.33$ mm ⁻¹
$c = 11.3724$ (7) Å	$T = 300$ K
$\alpha = 70.359$ (1)°	$0.20 \times 0.20 \times 0.10$ mm
$\beta = 82.112$ (2)°	

Data collection

Bruker SMART APEX CCD area-detector diffractometer	9067 measured reflections
Absorption correction: multi-scan (SADABS; Sheldrick, 1997)	3427 independent reflections
$T_{\min} = 0.927$, $T_{\max} = 0.968$	2884 reflections with $I > 2\sigma(I)$
	$R_{\text{int}} = 0.021$

Table 1

Hydrogen-bond geometry (Å, °) for (I).

$D-H \cdots A$	$D-H$	$H \cdots A$	$D \cdots A$	$D-H \cdots A$
$N1-H1 \cdots O1$	0.86	1.81	2.643 (2)	162
$N3-H3' \cdots O2^i$	0.86	1.86	2.710 (2)	172
$C2'-H2' \cdots O1^{ii}$	0.93	2.27	3.185 (3)	167

Symmetry codes: (i) $x - \frac{1}{2}, y - \frac{1}{2}, z$; (ii) $-x + \frac{1}{2}, -y - \frac{1}{2}, -z + 1$.

Table 2

Hydrogen-bond geometry (Å, °) for (II).

$D-H \cdots A$	$D-H$	$H \cdots A$	$D \cdots A$	$D-H \cdots A$
$N1-H1 \cdots O2$	0.86	1.94	2.764 (3)	161
$N1-H1 \cdots S1$	0.86	2.80	3.408 (2)	129
$N3-H3' \cdots O1^{iii}$	0.86	1.90	2.720 (3)	159
$O3-H3' \cdots O1^{iv}$	0.82	1.81	2.613 (3)	168
$C2'-H2' \cdots O4^v$	0.93	2.57	3.209 (3)	127

Symmetry codes: (iii) $-x + 1, -y + 2, -z + 1$; (iv) $x + 1, y - 1, z$; (v) $x, y + 1, z$.

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.041$	236 parameters
$wR(F^2) = 0.136$	H-atom parameters constrained
$S = 1.13$	$\Delta\rho_{\text{max}} = 0.34$ e Å ⁻³
3427 reflections	$\Delta\rho_{\text{min}} = -0.24$ e Å ⁻³

For both compounds, all H atoms were clearly visible in difference maps and were subsequently allowed for as riding atoms in the refinements: C-H = 0.93 Å for aromatic or 0.96 Å for methyl H atoms, with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{aromatic C})$ or $1.5U_{\text{eq}}(\text{methyl C})$, N-H = 0.86 Å, with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{N})$, and O-H = 0.82 Å, with $U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{O})$.

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, 2009); software used to prepare material for publication: PLATON.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: FG3123). Services for accessing these data are described at the back of the journal.

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