

Ribbons of hydrogen-bonded rings in the 1:2 complex of pyromellitic acid and dimethyl sulfoxide

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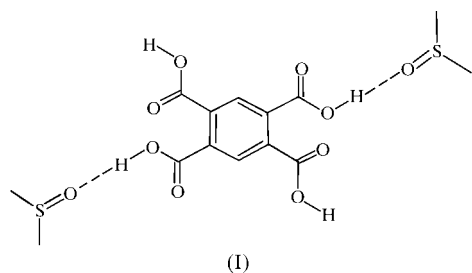
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In the title complex, pyromellitic acid–dimethyl sulfoxide (1/2), $C_{10}H_6O_8 \cdot 2C_2H_6OS$, molecules of pyromellitic acid (1,2,4,5-benzenetetracarboxylic acid) and dimethyl sulfoxide, the latter being well ordered, are linked to each other by $O-H \cdots O$ hydrogen bonds. The formula unit displays crystallographic inversion symmetry. The packing consists of ribbons of hydrogen-bonded rings that can be described by graph set $C_2^1(10)R_4^2(18)$.

Comment

Until now, only a few supramolecular structures involving pyromellitic acid (PMA) have been determined (Mrvoš-Sermek *et al.*, 1996; Biradha & Zaworotko, 1998; Lough *et al.*, 2000). From these known cases, it was impossible to predict the supramolecular hydrogen-bonding behaviour of PMA, even at the gross connectivity level (Lough *et al.*, 2000). Thus, it is desirable to search for new examples of hydrogen-bonding



motifs of PMA. Dimethyl sulfoxide (DMSO) is a versatile solvent which can dissolve various organic substances, and can form crystalline solvates in which it is either disordered (Deetz *et al.*, 2000; Harper *et al.*, 2001) or well ordered (TranQui *et al.*, 1998). In this context, the title complex, pyromellitic acid–

dimethyl sulfoxide (1/2), (I), has been synthesized and its hydrogen-bonding pattern elucidated.

Fig. 1 shows the inversion-symmetric formula unit of (I). The carboxyl groups display normal bond lengths and angles. It has been noted previously that the dihedral angles between the benzene ring and carboxyl groups in PMA are disposed at random (Biradha & Zaworotko, 1998). In (I), these dihedral angles are $58.6(2)$ and $35.0(3)^\circ$, respectively, for the C5 and C4 carboxyl groups.

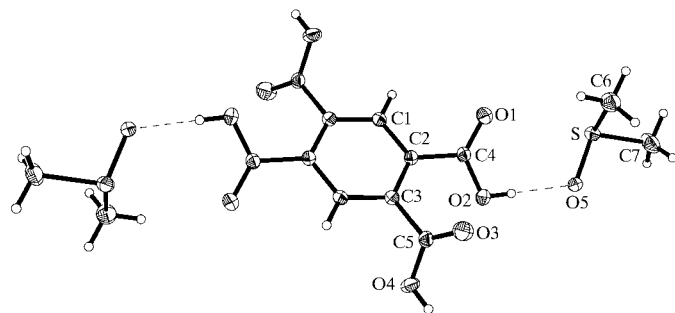


Figure 1

The cell unit of the title complex, showing the atom-numbering scheme and displacement ellipsoids at the 30% probability level. Hydrogen bonds are illustrated with dashed lines.

Disordered DMSO has been previously observed in cases where DMSO is held by a host molecule *via* only one $O-H \cdots O$ hydrogen bond (Deetz *et al.*, 2000; Harper *et al.*, 2001). In (I), where atom O5 is hydrogen bonded through both O2 and O4, the DMSO molecules are well ordered.

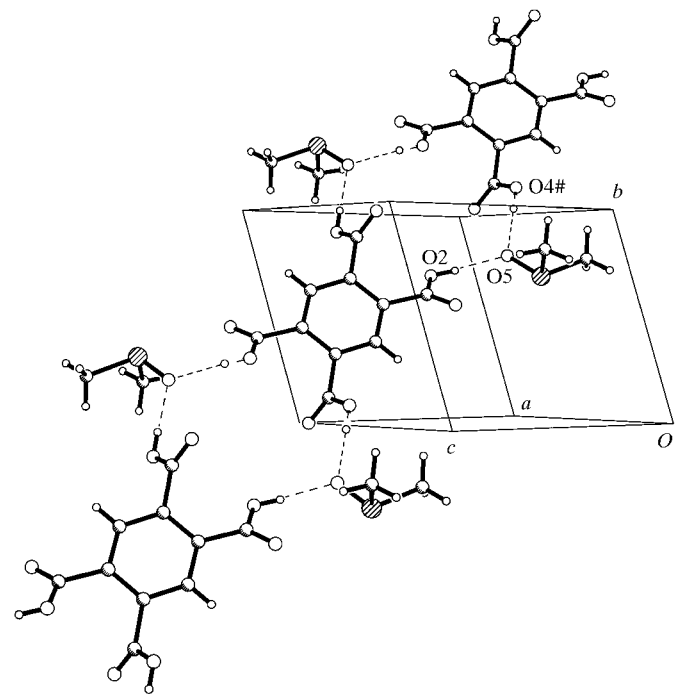


Figure 2

Part of the title crystal structure, showing the formation of one of the hydrogen-bond sheets of graph set $C_2^1(10)R_4^2(18)$. For the sake of clarity, only a small number of molecular components are drawn. The atom marked with a hash (#) is at the symmetry position $(1-x, 2-y, 1-z)$.

As seen in Fig. 2, molecules of DMSO and PMA are linked to each other by $O2 \cdots O5$ and $O4 \cdots O5(1-x, 2-y, 1-z)$ hydrogen bonds (Table 2) to form a hydrogen-bonded ring that can be described by graph set $R_4^2(18)$. The centre of the PMA molecule and the hydrogen-bonded rings are at $(\frac{1}{2}, \frac{1}{2}, 0)$ and $(\frac{1}{2}, 1, \frac{1}{2})$, respectively. While the dihedral angle between $C7-S-O5$ and $O1-C4-O2$ planes is $11.9(1)^\circ$, that between $C6-S-O5$ and $O3-C5-O4$ at $(1-x, -y, 1-z)$ is $14.0(3)^\circ$. This means that the methyl groups of DMSO are arranged so as to comply with the hydrogen-bonding requirements of both carboxyl groups.

A ribbon motif is formed by propagation of the hydrogen-bonded ring along the [011] direction, and may be depicted by graph set $C_2^1(10)R_4^2(18)$. Such a ribbon is translated repeatedly for one unit along the b or c axis to generate a layer parallel to the (100) plane. The nearest face-to-face distance of benzene-ring centroids between neighboring layers is $7.377(1) \text{ \AA}$, indicating no π - π -stacking interactions. There are many $C-H \cdots O$ hydrogen bonds playing subordinate roles in the crystal packing; some of the shorter ones are listed in Table 2.

Experimental

PMA (0.01 mol), DMSO (0.04 mol) and water (0.02 mol) were mixed and heated to form a clear solution. Crystals of the title complex formed by gradual concentration over a period of one week at 293 K.

Crystal data

$C_{10}H_6O_8 \cdot 2C_2H_6OS$	$D_x = 1.467 \text{ Mg m}^{-3}$
$M_r = 410.40$	Mo $K\alpha$ radiation
Triclinic, $P\bar{1}$	Cell parameters from 25 reflections
$a = 7.377(1) \text{ \AA}$	$\theta = 3.4\text{--}14.2^\circ$
$b = 7.424(1) \text{ \AA}$	$\mu = 0.34 \text{ mm}^{-1}$
$c = 8.934(1) \text{ \AA}$	$T = 296(2) \text{ K}$
$\alpha = 80.07(1)^\circ$	Prism, colourless
$\beta = 80.97(1)^\circ$	$0.50 \times 0.50 \times 0.44 \text{ mm}$
$\gamma = 76.15(1)^\circ$	
$V = 464.51(10) \text{ \AA}^3$	
$Z = 1$	

Data collection

Siemens P4 diffractometer	$h = 0 \rightarrow 8$
ω scans	$k = -8 \rightarrow 8$
1775 measured reflections	$l = -10 \rightarrow 10$
1634 independent reflections	3 standard reflections
1413 reflections with $I > 2\sigma(I)$	every 97 reflections
$R_{int} = 0.013$	intensity decay: 3.6%
$\theta_{max} = 25.0^\circ$	

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0447P)^2 + 0.1816P]$
$R[F^2 > 2\sigma(F^2)] = 0.032$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.086$	$(\Delta/\sigma)_{max} < 0.001$
$S = 1.05$	$\Delta\rho_{max} = 0.26 \text{ e \AA}^{-3}$
1634 reflections	$\Delta\rho_{min} = -0.24 \text{ e \AA}^{-3}$
129 parameters	Extinction correction: <i>SHELXL97</i>
H atoms: see below	Extinction coefficient: 0.129 (10)

Table 1

Selected interatomic distances (\AA).

O1—C4	1.204 (2)	O4—C5	1.312 (2)
O2—C4	1.306 (2)	C1—C3 ⁱ	1.387 (3)
O3—C5	1.192 (2)	C2—C3	1.402 (2)

Symmetry code: (i) $1-x, 1-y, 2-z$.

Table 2

Hydrogen-bonding geometry ($\text{\AA}, ^\circ$).

$D-H \cdots A$	$D-H$	$H \cdots A$	$D \cdots A$	$D-H \cdots A$
O2—H2O \cdots O5	0.89 (2)	1.76 (2)	2.647 (2)	174 (3)
O4—H4O \cdots O5 ⁱ	0.89 (2)	1.73 (2)	2.622 (2)	175 (2)
C6—H6B \cdots O1	0.96	2.71	3.391 (3)	128
C6—H6C \cdots O1 ⁱⁱ	0.96	2.68	3.386 (4)	130
C7—H7C \cdots O1 ⁱⁱ	0.96	2.67	3.379 (4)	131

Symmetry codes: (i) $1-x, 2-y, 1-z$; (ii) $-x, 1-y, 1-z$.

The O—H distances of the hydroxyl groups, the H atoms of which were located in difference Fourier maps, were refined with O—H distance restraints; otherwise these H atoms were refined freely. All remaining H atoms were placed in calculated positions, with their U_{iso} values set at $1.2U_{eq}$ of the parent atoms.

Data collection: *XSCANS* (Siemens, 1996); cell refinement: *XSCANS*; data reduction: *SHELXTL-Plus* (Sheldrick, 1990); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL-Plus*; software used to prepare material for publication: *SHELXTL-Plus*.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: *JZ1542*). Services for accessing these data are described at the back of the journal.

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