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Benzene-1,2,4,5-tetracarboxylic acid dimethyl sulfoxide disolvate: a redetermination at 150 K

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The title compound, $C_{10}H_6O_8.2C_2H_6OS$, one of the few known examples of the cocrystallization of pyromellitic acid with common organic solvents, has been previously analysed by single-crystal X-ray diffraction at 296 K [Jin, Pan, Shen, Li & Hu (2003). *Acta Cryst.* C**59**, o205–o206]. We present here a redetermination at low temperature (150 K). The centrosymmetric compound crystallizes in space group $P\overline{1}$ and exhibits co-operative strong (acid)O—H···O(solvent) and weaker (solvent)C—H···O(acid) hydrogen-bonding interactions, giving rise to a one-dimensional ribbon structure along the *bc* diagonal of the unit cell.

Key indicators

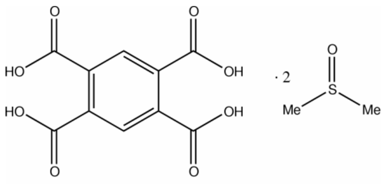
Single-crystal X-ray study
T = 150 K
Mean σ(C–C) = 0.002 Å
R factor = 0.028
wR factor = 0.075
Data-to-parameter ratio = 16.8

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

Comment

While pyromellitic acid (H_4PMA, benzene-1,2,4,5-tetracarboxylic acid) is commonly used as a ligand in coordination chemistry (Poleti *et al.*, 1988; Zhang *et al.*, 2003) and as a molecular tecton in hydrogen-bonding arrays (Mrvoš-Sermek *et al.*, 1996; Biradha & Zaworotko, 1998) due to its four carboxylic acid groups, few crystal structures have been published comprising H_4PMA cocrystallized solely with common organic solvents.

A search of the Cambridge Structural Database (Version 5.24 plus two updates, April 2003; Allen, 2002) has shown that H_4PMA has previously been cocrystallized with pyridine and various alkyl-substituted pyridines (Biradha & Zaworotko, 1998), as well as polyalkylamines, such as triethylenetetramine (Su *et al.*, 2001, 2002), with OH proton transfer to the basic N atoms resulting in the formation of salts. A more recent paper (Jin *et al.*, 2003) reported the single-crystal structure of the title compound, determined at 296 K.


(I)

We and other authors have investigated the inclusion of solvent molecules capable of hydrogen bonding in the solid-state structure of the related compound trimesic acid (benzene-1,3,5-tricarboxylic acid) (Dale & Elsegood, 2003*a*; Chatterjee *et al.*, 2000; Herbstein & Kapon, 1978; Herbstein *et al.*, 1978). Our investigations using H_4PMA have led us to the redetermination of $H_4PMA{\cdot}2H_2O$ (Dale & Elsegood, 2003*b*), and here we present a low-temperature (150 K) redetermination of the crystal structure of $H_4PMA{\cdot}2DMSO$ (DMSO =

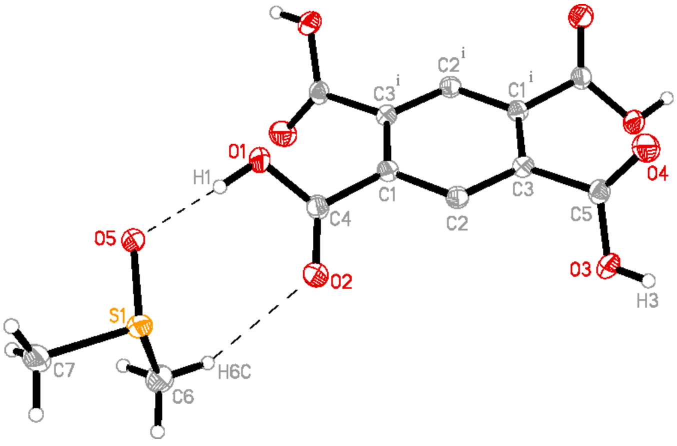


Figure 1
View of (I), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 50% probability level, H atoms are represented by circles of arbitrary radius and hydrogen bonding is shown by dashed lines. Aromatic H atoms have been removed for clarity. [Symmetry code: (i) $1 - x, 2 - y, -z$.]

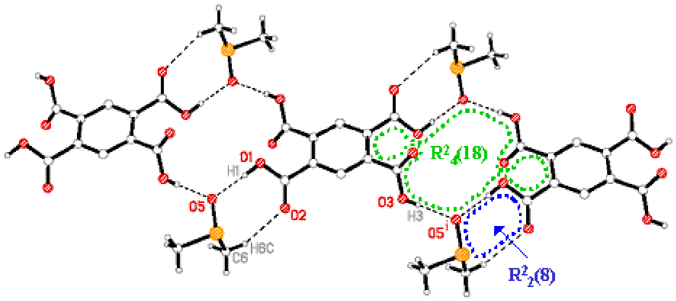


Figure 2
One-dimensional hydrogen-bonded tapes of (I). Atoms are represented by circles of arbitrary radius and hydrogen bonding is shown by dashed lines. Aromatic H atoms have been removed for clarity. [Symmetry code: (i) $x, y + 1, z - 1$.]

dimethyl sulfoxide), (I). It is worthy of mention that, prior to this study, trimesic acid was the only member of the benzenepolycarboxylic acid family to have been cocrystallized successfully with DMSO (Herbstein & Kapon, 1978), producing a two-dimensional sheet structure. During our investigations, we have also found that both isophthalic (benzene-1,3-dicarboxylic) and terephthalic (benzene-1,4-dicarboxylic) acids do not cocrystallize with DMSO, only the pure acid crystallizing from DMSO solutions.

Our redetermination shows good agreement with the original structure (Jin *et al.*, 2003), the use of a lower temperature in the analysis of (I) giving an improvement in the precision of the structure $\{R[F^2 > 2\sigma(F^2)] = 0.028$ at 150 K compared with 0.032 at 296 K$\}$ and also an improvement in the location of the H atoms within the O—H···O hydrogen bonds. The geometry of the centrosymmetric H_4PMA molecule is as expected (Table 1), with steric hindrance between adjacent carboxyl substituents resulting in dihedral angles of 34.42 (19)° (C4/O1/O2) and 57.42 (13)° (C5/O3/O4) with respect to the plane of the aromatic ring [C1/C3^i; symmetry code: (i) $1 - x, 2 - y, -z$], a feature common to the neutral H_4PMA molecule (Dale & Elsegood, 2003*b*).

The two independent carboxyl groups each have a unique binding mode to the single, crystallographically independent, DMSO molecule (Fig. 2), preventing the formation of the common head-to-tail carboxylic acid–carboxylic acid $R^2_2(8)$ graph-set motif (Etter, 1990; Etter & MacDonald, 1990; Bernstein *et al.*, 1995). One carboxyl group interacts with the DMSO molecule through an almost linear O—H···O interaction (Table 2). The second utilizes multipoint recognition (Nangia & Desiraju, 1999), *via* an O—H···O hydrogen bond and a weaker C—H···O interaction using a methyl group of the DMSO molecule, giving an $R^2_2(8)$ motif and a close O2···S1 contact distance of 3.227 (1) Å. The original authors rightly noted the ordered nature of the DMSO molecule and this could be attributed to the co-operative hydrogen bonding observed.

The hydrogen-bonding interactions in Table 2 lead to ribbons (Fig. 2) which propagate along the *bc* diagonal of the unit cell with the formation of $R^2_4(18)$ graph-set ring motifs.

Experimental

X-ray quality colourless crystals of (I) were obtained from a dimethyl sulfoxide solution of pyromellitic acid upon slow evaporation over a period of three months at room temperature (m.p. 419–422 K). Analysis calculated for $C_{14}H_{18}O_{10}S_2$: C 40.97, H, 4.42%; found: C 40.67, H 4.24%; IR (KBr, ν_{max}, cm^{-1}): 3100–2500 (br, OH), 3063 and 3027 (aromatic C—H), 2931 (sp^3 C—H), 1712 (C═O), 1502 (aromatic C═C), 1436, 1413 and 1359 (sp^3 C—H), 1321, 1298, 1254 (strong), 1143 and 1117 (C—O), 990 (S═O), 926, 813 and 757 (aromatic C—H).

Crystal data

$C_{10}H_6O_8\cdot 2C_2H_6OS$
$M_r = 410.40$
Triclinic, $P\bar{1}$
$a = 7.3283$ (6) Å
$b = 7.3331$ (6) Å
$c = 8.9456$ (8) Å
$\alpha = 80.510$ (2)°
$\beta = 81.124$ (2)°
$\gamma = 75.474$ (2)°
$V = 455.77$ (7) Å^3

$Z = 1$
$D_x = 1.495$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 3039 reflections
$\theta = 2.3$–29.0°
$\mu = 0.34$ mm^{-1}
$T = 150$ (2) K
Block, colourless
0.47 × 0.23 × 0.21 mm

Data collection

Bruker SMART 1000 CCD diffractometer
Narrow-frame ω scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 2001)
$T_{min} = 0.849$, $T_{max} = 0.931$
4046 measured reflections

2112 independent reflections
1918 reflections with $I > 2\sigma(I)$
$R_{int} = 0.010$
$\theta_{max} = 29.1°$
$h = -9 \rightarrow 9$
$k = -9 \rightarrow 9$
$l = -11 \rightarrow 11$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.028$
$wR(F^2) = 0.075$
$S = 1.07$
2112 reflections
126 parameters
H atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.0387P)^2 + 0.1844P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.38$ e Å^{-3}
$\Delta\rho_{min} = -0.26$ e Å^{-3}

Table 1
Selected geometric parameters (Å).

C1—C2	1.3947 (17)	C4—O1	1.3184 (15)
C1—C3^{i}	1.4013 (16)	C5—O4	1.2056 (16)
C1—C4	1.5022 (16)	C5—O3	1.3178 (15)
C2—C3	1.3922 (17)	S1—O5	1.5403 (9)
C3—C5	1.5066 (16)	S1—C6	1.7808 (14)
C4—O2	1.2120 (15)	S1—C7	1.7825 (14)

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

Table 2
Hydrogen-bonding geometry (Å, °).

D—H⋯*A*	*D*—H	H⋯*A*	*D*⋯*A*	*D*—H⋯*A*
O1—H1⋯O5	0.87 (2)	1.76 (2)	2.6317 (13)	173.9 (18)
O3—H3⋯O5^{ii}	0.78 (2)	1.84 (2)	2.6146 (13)	173 (2)
C6—H6*C*⋯O2	0.98	2.67	3.3595 (18)	127

Symmetry code: (ii) $x, 1 + y, z - 1$.

Aromatic H (C—H distance = 0.95 Å) and methyl H (C—H distance = 0.98 Å) atoms were placed in calculated positions using a riding model, while the H atoms of the OH groups were initially placed in calculated positions, and later their coordinates were freely refined. $U_{\rm iso}$ values were set to $1.2U_{\rm eq}$ of the parent atom for aromatic H ($1.5U_{\rm eq}$ for methyl H and OH).

Data collection: *SMART* (Siemens, 1994); cell refinement: *SAINT* (Siemens, 1994); data reduction: *SAINT*; program(s) used to solve structure: *SHELXTL* (Bruker, 1997); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL* and local programs.

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