

## Methyl 2,6-dicarboxybenzoate

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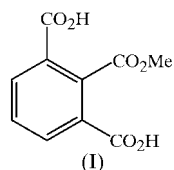
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Regioselective methylation of hemimellitic acid in basic MeOH yields the title 2-methyl ester,  $C_{10}H_8O_6$ , of the parent acid. The asymmetric unit contains one complete molecule, which packs with the methyl ester groups lying between zigzag chains produced by hydrogen bonding, utilizing the head-to-tail carboxylic acid–acid dimer motif.

## Comment

Derivatives of hemimellitic acid (benzene-1,2,3-tricarboxylic acid) have been little studied using single-crystal X-ray diffraction, with only eight crystal structures in the Cambridge Structural Database (September 2002 update; Allen, 2002), of which three are determinations of the commercially available dihydrate (Fornies-Marquina *et al.*, 1972; Takusagawa & Shimada, 1973; Mo & Adman, 1975). The successful use of many of the other members of the benzenepolycarboxylic acid family, such as trimesic and terephthalic acids, in the formation of supramolecular organic (*e.g.* Sharma & Zaworotko, 1996) and metal-inorganic (*e.g.* Groeneman *et al.*, 1999) networks has inspired us to investigate the relatively inexpensive hemimellitic acid as a potential supramolecular building block and metal ligand. Hemimellitic acid possesses three adjacent carboxylic acid groups, providing the opportunity for coordination to metal cations as well as the creation of extended networks through hydrogen bonding.



The reaction of hemimellitic acid with 0.5 equivalents of  $M_2CO_3$  ( $M$  is Li, Na or K) in the mixed solvent MeOH– $H_2O$  (9:1) under reflux conditions affords, surprisingly, regioselective methylation at the 2-position. The title compound, (I), is produced as X-ray quality colourless crystals in almost quantitative yield by the slow evaporation of the cooled solution. In contrast, similar reactions with phthalic acid in pure  $H_2O$  have

been shown to yield the expected group 1 metal salts (Smith, 1975*a,b*).

Compound (I) has previously been synthesized from the reaction of hemimellitic anhydride with MeOH and characterized only by  $^1H$  NMR spectroscopy (Hurst & Bender, 1971), but here, both the single-crystal X-ray structure and  $^1H$  and  $^{13}C$  NMR data are presented. NMR spectroscopic analysis of the bulk sample indicated a single product, showing that the isomeric 1-ester and the possible di- and tri-esters (Kasina & Nematollahi, 1978; Reval *et al.*, 1983) had not been produced.

The asymmetric unit of (I) contains one complete molecule (Fig. 1). The outer carboxylic acid substituents at C1 and C3 form hydrogen bonds to one symmetry-related neighbour each, *via* the expected head-to-tail  $R_2^2(8)$  carboxylic acid–acid synthon (Etter, 1990; Etter *et al.*, 1990; Bernstein *et al.*, 1995) (Table 2), producing zigzag chains (Fig. 2) reminiscent of the packing of isophthalic acid (Derissen, 1974). One outer carboxylic acid group of the parent acid dihydrate (Takusagawa & Shimada, 1973) adopts the  $R_2^2(8)$  dimer motif, but, in contrast to (I), the other also forms a hydrogen bond to a water of crystallization. Protection of the central carboxylic

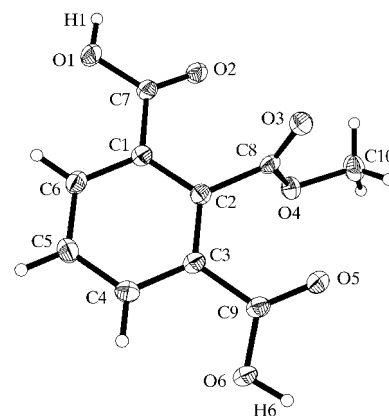


Figure 1

A view of the molecule of (I), showing the atom-labelling scheme and the selective methylation at the central position. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radii.

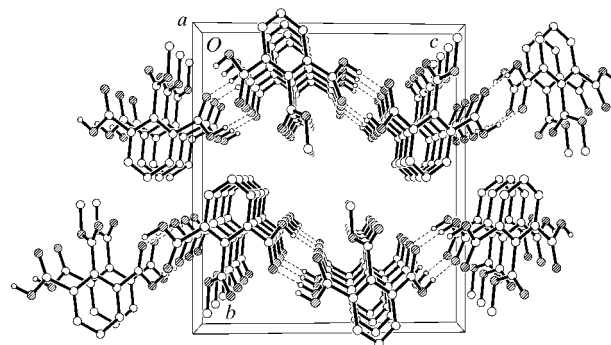


Figure 2

A packing plot for (I), viewed down the crystallographic  $a$  axis, showing the head-to-tail carboxylic acid–acid hydrogen-bonded dimers forming chains. H atoms bonded to C atoms have been omitted for clarity. Hydrogen bonding between molecules is indicated by dashed lines.

acid group as the methyl ester prevents its involvement in strong hydrogen bonding and also modifies the angle of rotation of this carboxyl group with respect to the plane of the aromatic ring, from 86.8° in the parent acid to 76.7° in (I), allowing the methyl group to lie between the chains. Weak C—H···O interactions [C···O = 3.2681 (15)–3.6564 (16) Å; Desiraju & Steiner, 1999] between the zigzag chains produce sheets, and interactions between these sheets produce a loosely held three-dimensional structure.

## Experimental

Hemimellitic acid dihydrate (1 equivalent) was refluxed overnight with  $M_2CO_3$  ( $M$  is Li, Na and K; 0.5 equivalents) in a 9:1 mixture of MeOH–H<sub>2</sub>O. The solutions were allowed to cool and then left to evaporate. X-ray quality colourless crystals formed and single-crystal X-ray analysis indicated that compound (I) had been synthesized in all three cases (m.p. 478–482 K; literature value 478–483 K; Hurst & Bender, 1971). Spectroscopic analysis, IR (KBr,  $\nu_{\max}$ , cm<sup>-1</sup>): 3500–2500 (*br*, OH), 3087, 3046 and 3006 (aromatic C–H), 2948, 2884 and 2837 ( $C_{sp^3}$ –H), 1742 (C=O, ester), 1711 and 1692 (C=O, acid), 1586 (C=C, aromatic), 1466, 1453, 1430 and 1415 ( $C_{sp^3}$ –H), 1308, 1275, 1123 and 1072 (C–O), 776 (aromatic C–H), 688; <sup>1</sup>H NMR (400 MHz,  $d_6$ -DMSO,  $\delta$ ): 8.13 (2H, *d*,  $J$  = 8 Hz), 7.68 (1H, *t*,  $J$  = 7.6 Hz), 3.77 (3H, *s*, Me); <sup>13</sup>C NMR (100 MHz,  $d_6$ -DMSO,  $\delta$ ): 167.9 ( $C_{quat}$ , C=O, ester), 166.17 ( $2C_{quat}$ , C=O, acid), 135.6 ( $C_{quat}$ , Ar), 133.4 (2CH, Ar), 129.8 (CH, Ar), 129.6 ( $2C_{quat}$ , Ar), 52.2 (CH<sub>3</sub>). The <sup>1</sup>H NMR results above correspond to previously reported data (Hurst & Bender, 1971).

### Crystal data

$C_{10}H_8O_6$   
 $M_r$  = 224.16  
 Monoclinic,  $P2_1/c$   
 $a$  = 5.0242 (3) Å  
 $b$  = 14.6263 (10) Å  
 $c$  = 12.9024 (9) Å  
 $\beta$  = 93.835 (2)°  
 $V$  = 946.02 (11) Å<sup>3</sup>  
 $Z$  = 4

$D_x$  = 1.574 Mg m<sup>-3</sup>  
 Mo  $K\alpha$  radiation  
 Cell parameters from 3989 reflections  
 $\theta$  = 2.8–28.5°  
 $\mu$  = 0.13 mm<sup>-1</sup>  
 $T$  = 150 (2) K  
 Column, colourless  
 0.37 × 0.16 × 0.13 mm

### Data collection

Bruker SMART1000 CCD area-detector diffractometer  
 $\omega$  rotation scans with narrow frames  
 Absorption correction: multi-scan (SADABS; Sheldrick, 2001)  
 $T_{\min}$  = 0.910,  $T_{\max}$  = 0.983  
 8271 measured reflections

2287 independent reflections  
 1847 reflections with  $I > 2\sigma(I)$   
 $R_{\text{int}}$  = 0.017  
 $\theta_{\text{max}}$  = 29°  
 $h$  = -6 → 6  
 $k$  = -19 → 18  
 $l$  = -16 → 16

### Refinement

Refinement on  $F^2$   
 $R[F^2 > 2\sigma(F^2)]$  = 0.033  
 $wR(F^2)$  = 0.094  
 $S$  = 1.03  
 2287 reflections  
 160 parameters  
 H atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.049P)^2 + 0.304P]$   
 where  $P = (F_o^2 + 2F_c^2)/3$   
 $(\Delta/\sigma)_{\text{max}} < 0.001$   
 $\Delta\rho_{\text{max}} = 0.35 \text{ e \AA}^{-3}$   
 $\Delta\rho_{\text{min}} = -0.19 \text{ e \AA}^{-3}$

Aromatic H atoms were placed in geometric positions (with a C—H distance of 0.95 Å) and refined using a riding model, while the coordinates of the methyl and hydroxy H atoms were freely refined.  $U_{\text{iso}}$  values were set at 1.2 $U_{\text{eq}}$ (C) for aryl H atoms and 1.5 $U_{\text{eq}}$ (C,O) for methyl and hydroxy H atoms.

**Table 1**  
 Selected bond lengths (Å).

C7—O2	1.2233 (15)	O4—C10	1.4424 (16)
C7—O1	1.3177 (14)	C9—O5	1.2256 (15)
C8—O3	1.2019 (15)	C9—O6	1.3156 (15)
C8—O4	1.3359 (15)		

**Table 2**  
 Hydrogen-bonding and short-contact geometry (Å, °).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
O1—H1···O5 <sup>i</sup>	0.91 (2)	1.71 (2)	2.6131 (13)	172 (2)
O6—H6···O2 <sup>ii</sup>	0.91 (2)	1.74 (2)	2.6433 (13)	173 (2)
C4—H4···O3 <sup>iii</sup>	0.95	2.65	3.2681 (15)	123
C5—H5···O1 <sup>iv</sup>	0.95	3.19	3.6564 (16)	112
C5—H5···O3 <sup>iii</sup>	0.95	2.66	3.2725 (15)	122
C5—H5···O5 <sup>iii</sup>	0.95	2.65	3.5594 (16)	160
C6—H6A···O1 <sup>iv</sup>	0.95	2.58	3.3627 (15)	140

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

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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Supplementary data for this paper are available from the IUCr electronic archives (Reference: BM1520). Services for accessing these data are described at the back of the journal.

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