

## 2,3-Methylenedioxybenzoic acid

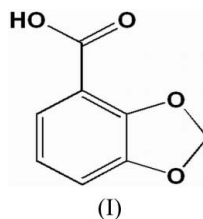
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## Key indicators

Single-crystal X-ray study  
 $T = 173$  K  
Mean  $\sigma(\text{C}-\text{C}) = 0.004$  Å  
 $R$  factor = 0.063  
 $wR$  factor = 0.176  
Data-to-parameter ratio = 10.0For details of how these key indicators were  
automatically derived from the article, see  
<http://journals.iucr.org/e>.The title compound,  $\text{C}_8\text{H}_6\text{O}_4$ , consists of a cyclic diether fused to benzoic acid and crystallizes as a hydrogen-bonded carboxylic acid dimer.Received 3 May 2006  
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## Comment

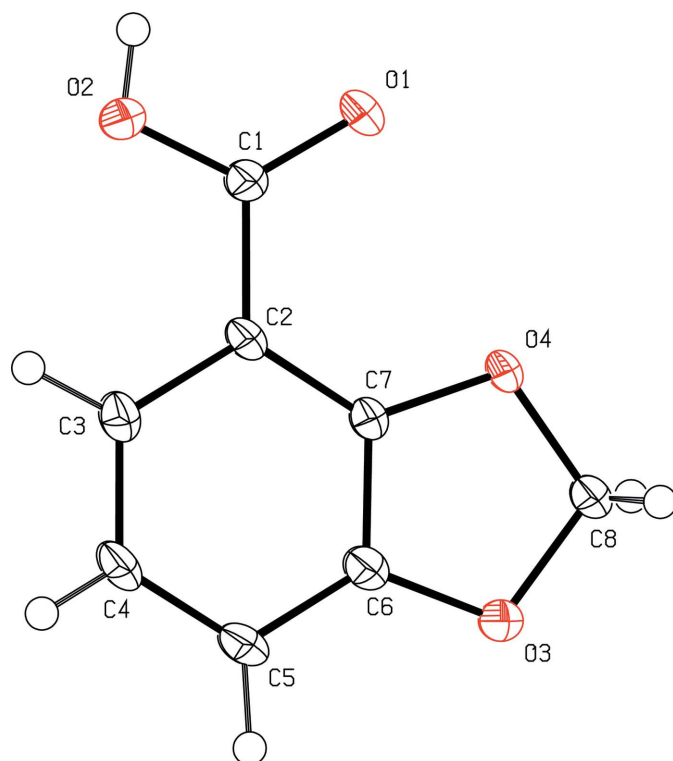
Methylenedioxybenzoic acids play an important role in the pharmaceutical industry because of their use as precursors for the synthesis of tamoxifen, which is widely used in the treatment of breast cancer (Zhang *et al.*, 2000; Wu *et al.*, 1997; Kelly & Beckett 1969; Lester *et al.*, 1979). Compound (I), and related compounds having the methylenedioxybenzene ring system, are also reported to have biological activity against malaria (Lester *et al.*, 1979).

The molecular structure of (I) is illustrated in Fig. 1, and selected bond distances and angles are given in Table 1. The methylenedioxy group is inclined to the benzene ring by only  $0.60$  ( $13$ )°. The mean plane through the acid group (O1/O2/C1/C2) is inclined to the benzene ring by  $8.24$  ( $12$ )°. The bond lengths and angles are consistent with the values given by Pálincó (1999) for similar systems. The presence of the methylenedioxy ring has no significant effect on the bond lengths and angles in the benzene ring.

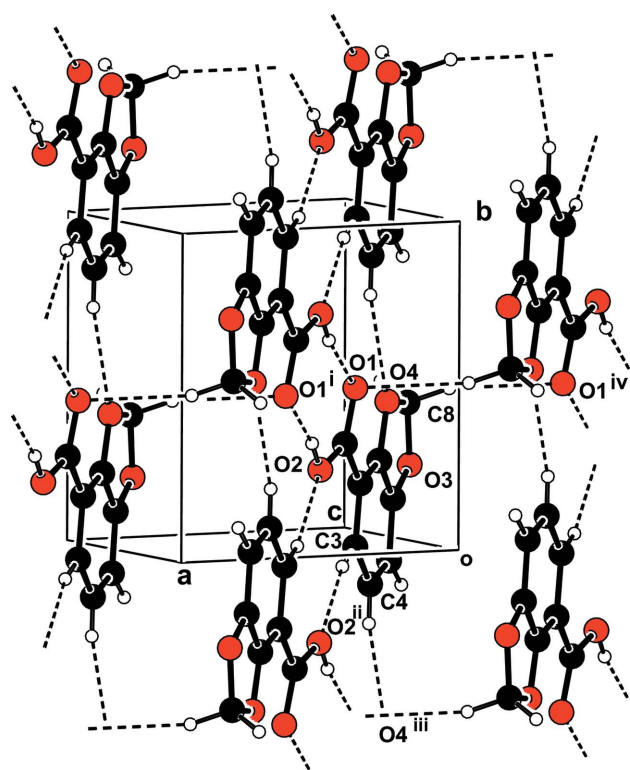
The compound crystallizes as hydrogen-bonded centrosymmetric carboxylic acid dimers with a strong intermolecular  $\text{O}-\text{H}\cdots\text{O}$  hydrogen bond (Table 2 and Fig. 2) These dimers are further linked by  $\text{C}-\text{H}\cdots\text{O}$  hydrogen bonds to form a sheet-like structure.

## Experimental

To 300 ml of water was added 2,3-methylenedioxybenzaldehyde (5.0 g, 1 mmol), and the mixture was heated to 318–323 K. The solution was stirred mechanically and potassium permanganate (12.5 g, mmol) in water (100 ml) was run in slowly until the odour of the aldehyde was no longer perceptible. Excess of the latter was removed by the addition of a little ethanol. The mixture was then filtered hot and the filtrate acidified with hydrochloric acid. The title acid separated out as the solution cooled and was recrystallized from chloroform to give colourless crystals.



**Figure 1**  
The molecular structure of compound (I), showing the atomic numbering scheme and displacement ellipsoids drawn at the 50% probability level.



**Figure 2**  
A crystal packing diagram of compound (I), showing the presence of the carboxylic acid dimers involving the  $O2-H2 \cdots O1^i$  hydrogen bond. The hydrogen bonds are shown as dashed lines and symmetry operations correspond to those given in Table 2.

#### Crystal data

$C_8H_6O_4$   
 $M_r = 166.13$   
 Monoclinic,  $P2_1/c$   
 $a = 9.7327$  (13) Å  
 $b = 7.2600$  (7) Å  
 $c = 12.394$  (2) Å  
 $\beta = 129.395$  (11)°  
 $V = 676.77$  (16) Å<sup>3</sup>

$Z = 4$   
 $D_x = 1.630$  Mg m<sup>-3</sup>  
 Mo  $K\alpha$  radiation  
 $\mu = 0.13$  mm<sup>-1</sup>  
 $T = 173$  (2) K  
 Prism, colourless  
 $0.50 \times 0.40 \times 0.20$  mm

#### Data collection

Stoe IPDS diffractometer  
 $\varphi$  scans  
 Absorption correction: none  
 4940 measured reflections

1302 independent reflections  
 957 reflections with  $I > 2\sigma(I)$   
 $R_{int} = 0.154$   
 $\theta_{max} = 25.9^\circ$

#### Refinement

Refinement on  $F^2$   
 $R[F^2 > 2\sigma(F^2)] = 0.063$   
 $wR(F^2) = 0.176$   
 $S = 1.02$   
 1302 reflections  
 130 parameters

H atoms treated by a mixture of independent and constrained refinement  
 $w = 1/[\sigma^2(F_o^2) + (0.1155P)^2]$   
 where  $P = (F_o^2 + 2F_c^2)/3$   
 $(\Delta/\sigma)_{max} < 0.001$   
 $\Delta\rho_{max} = 0.33$  e Å<sup>-3</sup>  
 $\Delta\rho_{min} = -0.54$  e Å<sup>-3</sup>

**Table 1**

Selected geometric parameters (Å, °).

O1—C1	1.256 (3)	O3—C8	1.437 (3)
O2—C1	1.289 (4)	O4—C7	1.367 (3)
O3—C6	1.380 (4)	O4—C8	1.433 (5)
C6—O3—C8	105.7 (2)	O3—C6—C7	109.8 (2)
C7—O4—C8	106.4 (2)	O3—C6—C5	128.0 (3)
O1—C1—O2	123.4 (3)	O4—C7—C2	128.7 (3)
O2—C1—C2	116.5 (2)	O4—C7—C6	109.9 (3)
O1—C1—C2	120.1 (3)	O3—C8—O4	108.2 (2)

**Table 2**

Hydrogen-bond geometry (Å, °).

$D-H \cdots A$	$D-H$	$H \cdots A$	$D \cdots A$	$D-H \cdots A$
$O2-H2 \cdots O1^i$	0.84	1.79	2.622 (3)	171
$C3-H3 \cdots O2^{ii}$	0.98 (3)	2.49 (3)	3.448 (4)	164 (2)
$C4-H4 \cdots O4^{iii}$	0.87 (3)	2.58 (3)	3.365 (3)	150 (3)
$C8-H8A \cdots O1^{iv}$	0.98 (4)	2.56 (4)	3.495 (4)	161 (3)

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

The crystal diffracted poorly beyond  $45^\circ$  in  $2\theta$  and with a large mosaic spread, hence the  $R_{int}$  value was found to be  $> 0.10$ . The OH H atom was included in a calculated position and treated as a riding atom [ $O-H = 0.84$  Å and  $U_{eq}(H) = 1.5U_{eq}(O)$ ]. The remainder of the H atoms were located in difference Fourier maps and refined isotropically [ $C-H = 0.87$  (3)– $0.98$  (4) Å].

Data collection: *EXPOSE* in *IPDS Software* (Stoe & Cie, 2000); cell refinement: *CELL* in *IPDS Software*; data reduction: *INTEGRATE* in *IPDS Software*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *PLATON* (Spek, 2003); software used to prepare material for publication: *SHELXL97*.

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## References

- Kelly, R. B. & Beckett, A. B. (1969). *Can. J. Chem.* **47**, 2501–2504.
- Lester, A. M., Daniel, L. F., Eugene Gracey, H. & Steven, D. D. (1979). *J. Med. Chem.* **22**, 1354–1357.
- Pálinkó, I. (1999). *Acta Cryst.* **B55**, 216–220.
- Sheldrick, G. M. (1997). *SHELXS97* and *SHELXL97*. University of Göttingen, Germany.
- Spek, A. L. (2003). *J. Appl. Cryst.* **36**, 7–13.
- Stoe & Cie (2000). *IPDS Software*. Stoe & Cie GmbH, Darmstadt, Germany.
- Wu, C., Chan, M. F., Stavros, F., Raju, B., Okun, I., Mong, S., Keller, K. M., Brock, T., Kogan, T. P. & Dixon, R. A. F. (1997). *J. Med. Chem.* **40**, 1690–1697.
- Zhang, F., Fan, P. W., Liu, X., Shen, L., van Breemen, R. B. & Bolton, J. L. (2000). *Chem. Res. Toxicol.* **13**, 53–62.