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Key indicators

Single-crystal X-ray study
 $T = 100\text{ K}$
Mean $\sigma(\text{C}-\text{C}) = 0.007\text{ \AA}$
 R factor = 0.066
 wR factor = 0.171
Data-to-parameter ratio = 11.2For details of how these key indicators were
automatically derived from the article, see
<http://journals.iucr.org/e>.Methoxycarbonylmethyl 3-hydroxy-2-(methoxy-
carbonyl)benzo[*b*]furan-6-carboxylateThe title compound, $\text{C}_{14}\text{H}_{12}\text{O}_8$, exists in the crystal structure in
the enol form, as hydrogen-bonded dimers.

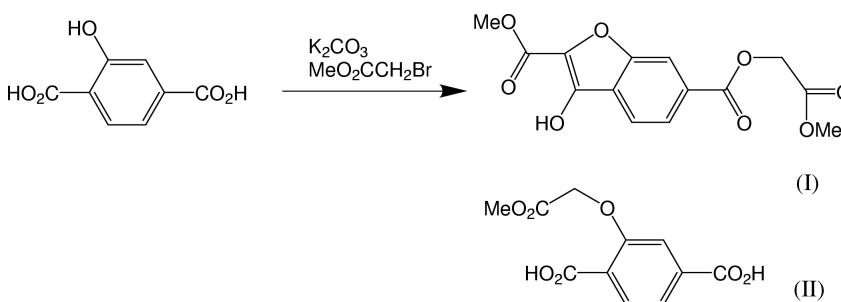
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Comment

The title compound, (I), was obtained unintentionally during the synthesis of (II) (see *Scheme*), an intermediate on the synthetic route to new tetracyanoquinodimethanes functionalized with a carboxylic acid group in the side chain. We were preparing (II) by alkylation of the tripotassium salt of hydroxyterephthalic acid with methyl bromoacetate. While the reaction proceeds smoothly with an equimolar amount of methyl bromoacetate, with an excess of the latter it yields mainly the cyclization product (I).



Compound (I) is potentially a keto–enol tautomeric substance. Like its analogue ethyl 3-hydroxybenzo[*b*]furan-2-carboxylate, or 3-hydroxycumarilate (Gould *et al.*, 1998), (I) exists in the crystal structure in the enol form (Fig. 1). Two molecules, related *via* an inversion centre (at $\frac{1}{2}, \frac{1}{2}, \frac{1}{2}$), are linked into a dimer by hydrogen bonds, *viz.* $\text{O}2-\text{H}02 \cdots \text{O}8^i$ (Table 2) and its inversion equivalent. The ester substituents in positions 2 and 6 are slightly inclined to the planar benzofuran system [by 3.6 (2) and 6.9 (1)°, respectively]. The dihedral angle between the $\text{O}6/\text{C}11/\text{O}5/\text{C}12$ and $\text{C}12/\text{C}13/\text{O}7/\text{O}8/\text{C}14$ planes is 76.5 (2)°.

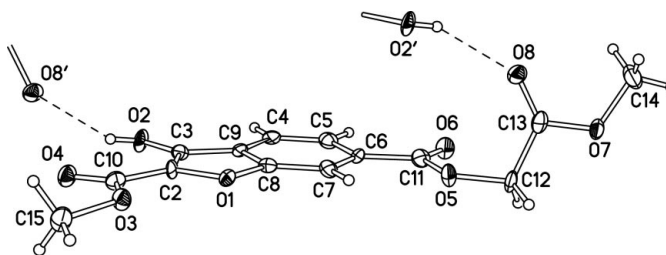


Figure 1

The molecular structure of (I), showing atomic displacement ellipsoids at the 50% probability level and intermolecular hydrogen bonds to fragments of a second molecule. Primed atoms are generated by the inversion ($1-x, 1-y, 1-z$) (code *i* in Table 2).

Experimental

Potassium carbonate (270 mg, 1.96 mmol) was suspended in a solution of hydroxyterephthalic acid (90 mg, 0.50 mmol) in dimethyl sulfoxide, and methyl bromoacetate (0.10 ml, 1.2 mmol) was added. The reaction mixture was stirred at room temperature for 16 h and the solvent was removed *in vacuo*. The residue was triturated with an HCl/ice mixture, and the resultant white precipitate was filtered off, washed with water and recrystallized from 50% aqueous EtOH (7 ml), yielding pure (I) (76 mg, 50%), m.p. 403 K; m/z (EI): 308 (M^+ , 100%); ^1H NMR (δ , p.p.m., DMSO- d_6): 11.16 (s, 1H), 8.15 (s, 1H), 8.06 (d, 1H, $J = 8$ Hz), 7.93 (d, 1H, $J = 8$ Hz), 4.98 (s, 2H), 3.72 (s, 3H); ^{13}C NMR (δ , p.p.m., DMSO- d_6): 168.0, 164.9, 159.2, 151.7, 146.3, 129.3, 128.5, 125.9, 123.3, 121.7, 113.5, 61.4, 52.0, 51.4.

Crystal data

| | |
|--|---|
| $\text{C}_{14}\text{H}_{12}\text{O}_8$ | $Z = 2$ |
| $M_r = 308.24$ | $D_x = 1.554 \text{ Mg m}^{-3}$ |
| Triclinic, $P\bar{1}$ | Mo $K\alpha$ radiation |
| $a = 6.862$ (1) Å | Cell parameters from 180 reflections |
| $b = 7.335$ (1) Å | $\theta = 10.3\text{--}21.1^\circ$ |
| $c = 13.323$ (3) Å | $\mu = 0.13 \text{ mm}^{-1}$ |
| $\alpha = 80.73$ (1)° | $T = 100$ (2) K |
| $\beta = 85.30$ (1)° | Needle, colourless |
| $\gamma = 86.60$ (1)° | $0.40 \times 0.06 \times 0.02 \text{ mm}$ |
| $V = 658.9$ (2) Å ³ | |

Data collection

| | |
|---|------------------------------------|
| SMART 1K CCD area-detector diffractometer | $R_{\text{int}} = 0.094$ |
| ω scans | $\theta_{\text{max}} = 25.1^\circ$ |
| 3856 measured reflections | $h = -8 \rightarrow 7$ |
| 2328 independent reflections | $k = -8 \rightarrow 8$ |
| 1173 reflections with $I > 2\sigma(I)$ | $l = -15 \rightarrow 14$ |
| | Intensity decay: none |

Refinement

| | |
|---------------------------------|--|
| Refinement on F^2 | H atoms treated by a mixture of independent and constrained refinement |
| $R[F^2 > 2\sigma(F^2)] = 0.066$ | $w = 1/[\sigma^2(F_o^2) + (0.0618P)^2]$ |
| $wR(F^2) = 0.171$ | where $P = (F_o^2 + 2F_c^2)/3$ |
| $S = 0.99$ | $(\Delta/\sigma)_{\text{max}} < 0.001$ |
| 2328 reflections | $\Delta\rho_{\text{max}} = 0.32 \text{ e \AA}^{-3}$ |
| 207 parameters | $\Delta\rho_{\text{min}} = -0.34 \text{ e \AA}^{-3}$ |

Table 1

Selected interatomic distances (Å).

| | | | |
|--------|-----------|---------|-----------|
| O1—C8 | 1.367 (6) | O8—C13 | 1.212 (6) |
| O1—C2 | 1.384 (5) | C2—C3 | 1.380 (6) |
| O2—H02 | 0.77 (6) | C2—C10 | 1.431 (7) |
| O2—C3 | 1.345 (6) | C3—C9 | 1.421 (7) |
| O3—C10 | 1.342 (5) | C4—C5 | 1.374 (7) |
| O3—C15 | 1.457 (6) | C4—C9 | 1.390 (7) |
| O4—C10 | 1.221 (6) | C5—C6 | 1.409 (7) |
| O5—C11 | 1.353 (6) | C6—C7 | 1.395 (6) |
| O5—C12 | 1.432 (5) | C6—C11 | 1.485 (7) |
| O6—C11 | 1.205 (6) | C7—C8 | 1.386 (7) |
| O7—C13 | 1.348 (6) | C8—C9 | 1.411 (6) |
| O7—C14 | 1.448 (6) | C12—C13 | 1.506 (7) |

Table 2

Hydrogen-bonding geometry (Å, °).

| $D\text{—}H\cdots A$ | $D\text{—}H$ | $H\cdots A$ | $D\cdots A$ | $D\text{—}H\cdots A$ |
|---------------------------------|--------------|-------------|-------------|----------------------|
| O2—H02 \cdots O8 ⁱ | 0.77 (6) | 2.13 (6) | 2.768 (5) | 141 (6) |

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

The rotational orientations of the methyl groups were obtained from a circular Fourier synthesis and refined with a rigid-body model ($C\text{—}H = 0.978$ Å). The hydroxy H atom was located in a difference Fourier synthesis and refined in isotropic approximation. Other H atoms were treated as riding in idealized positions, assuming $Csp^2\text{—}H = 0.948$ Å and $Csp^3\text{—}H = 0.988$ Å.

Data collection: *SMART* (Bruker, 1999); cell refinement: *SMART*; data reduction: *SAINTE* (Bruker, 1999); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL* (Bruker, 1998); software used to prepare material for publication: *SHELXTL*.

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