Acta Crystallographica Section E
**Structure Reports**
**Online**

ISSN 1600-5368

# Monoclinic form of 6-phenylhex-5-ene-2,4-dione

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Received 11 December 2001
Accepted 17 January 2002
Online 25 January 2002

The orthorhombic form was published in *Acta Cryst.* (2001). E**57**, o1198–o1199.

**Key indicators**

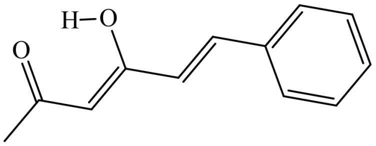
Single-crystal X-ray study
*T* = 150 K
Mean $\sigma$(C–C) = 0.005 Å
*R* factor = 0.070
*wR* factor = 0.228
Data-to-parameter ratio = 10.2

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

The asymmetric unit in the crystal structure of the monoclinic form of 6-phenylhex-5-ene-2,4-dione, $C_{12}H_{12}O_2$, consists of two independent molecules. Both molecules exist in the enolized form and show a strong asymmetric intramolecular hydrogen bond. The intermolecular C—H···O contacts represent the most prominent feature of the crystal packing of the compound.

## Comment

6-Phenylhex-5-ene-2,4-dione (PHD) crystallizes in an orthorhombic (Arrieta & Mostad, 2001*a*), as well as a monoclinic form with two independent molecules in the asymmetric unit, as indicated in Fig. 1, which also shows the atom numbering. The precision of the present structure determination is significantly lower than that of the orthorhombic form as it proved difficult to grow good crystals of the monoclinic modification. Nevertheless, the geometry of the molecules in the two polymorphic forms is remarkably similar. In both polymorphs, the molecules exist in the enolized form typical for 1,3-diketo-derivatives (Emsley, 1984; Bertolasi *et al.*, 1991), and there are no significant differences in the geometry of the enol groups in the two modifications of PHD. As one would expect, the keto-group closest to the olefin bond is enolized, thus allowing for the greatest possible conjugation in the molecules. This asymmetry is in accordance with the results of the neutron diffraction study of benzoylacetone (Madsen, 1998).



(I)

As the molecules of neither the orthorhombic nor the monoclinic form of the title compound, (I), are engaged in intermolecular hydrogen bonds of the conventional O—H···O type, they provide convenient systems for studying the impact of weak interactions on the packing mode. In both forms, the most prominent intermolecular contacts seem to be of the C—H···O-type described for the orthorhombic form, as well as for several other similar structures (Gørbitz *et al.*, 1986; Mostad, 1994; Arrieta & Mostad, 2001). Besides the C—H···O contact within the asymmetric unit shown in Fig. 1, there are two other intermolecular contacts, C10*A*—H10*A*···O1*A*(*x*, 3/2−*y*, 1/2+*z*) and C10*B*—H10*B*···O1*B*(*x*, 1/2−*y*, 1/2+*z*), the geometry of which is given in Table 2.

DOI: 10.1107/S1600536802000995

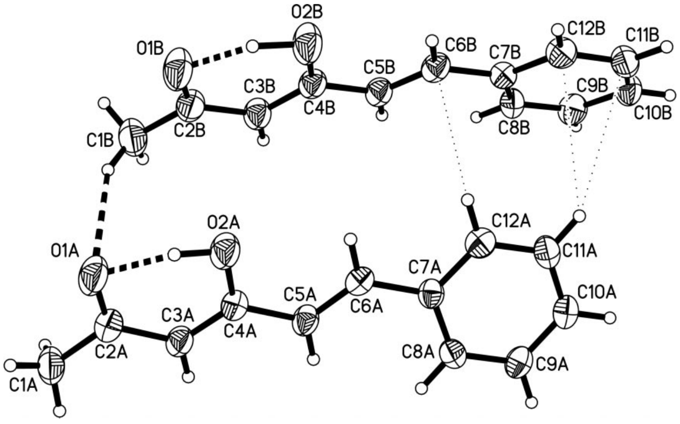


**Figure 1**

The atom numbering in the PHD molecules in the asymmetric unit of (I) with displacement ellipsoids drawn at the 50% probability level. The dashed solid lines show the hydrogen bonds and C—H···O contact, and the dotted lines indicate the interaction between H atoms and the $\pi$-electron system in the aromatic unit.

Finally, the relationship between the aromatic fragments is also indicated in Fig. 1. The angle between the aromatic rings in the asymmetric unit is 50.81 (9)°, and the distances from H11*A* to atoms C11*B* and C12*B* are 3.22 and 3.21 Å, respectively, whereas the distance from H12*A* to C6*B* is 2.82 Å. This relationship between the aromatic moieties is similar to that found in the orthorhombic form, as well as in other structures containing aromatic fragments (Bakke & Mostad, 1980; Mostad *et al.*, 1983, 1984; Mostad, 1994; Arrieta *et al.*, 1995; Arrieta & Mostad, 2001). The contacts described above connect the asymmetric units into double molecular layers in the directions of the *b* and *c* axes, whereas there seem to be only van der Waals interactions between these layers in the direction of the *a* axis. This may explain the difficulty in growing large crystals.

## Experimental

The title compound was synthesized by refluxing ethyl 2-*trans*-cinnamoylacetate (Arrieta & Mostad, 2001*b*) with water according to a known procedure (Borsche & Lewinsohn, 1933). The melting point was found to be 355–356 K. The crystals were grown by cooling a saturated warm solution in toluene.

### *Crystal data*

$C_{12}H_{12}O_2$
$M_r = 188.22$
Monoclinic, $P2_1/c$
$a = 13.8222\ (14)$ Å
$b = 5.8033\ (6)$ Å
$c = 25.240\ (3)$ Å
$\beta = 99.663\ (4)^\circ$
$V = 1995.9\ (4)$ Å$^3$
$Z = 8$

$D_x = 1.253$ Mg m$^{-3}$
Mo $K\alpha$ radiation
Cell parameters from 1024 reflections
$\theta = 2.0$–$23.0^\circ$
$\mu = 0.08$ mm$^{-1}$
$T = 150\ (2)$ K
Needle, yellow
$0.2 \times 0.1 \times 0.1$ mm

### *Data collection*

Bruker SMART diffractometer
$\omega$ scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1997)
$T_{\min} = 0.983$, $T_{\max} = 0.992$
14 200 measured reflections
2874 independent reflections

2017 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.083$
$\theta_{\max} = 23.3^\circ$
$h = -15 \rightarrow 15$
$k = -5 \rightarrow 6$
$l = -28 \rightarrow 28$

### *Refinement*

Refinement on $F^2$
$R[F^2 > 2\sigma(F^2)] = 0.070$
$wR(F^2) = 0.228$
$S = 1.08$
2874 reflections
283 parameters
H atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.1069P)^2 + 3.0387P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = 0.007$
$\Delta\rho_{\max} = 0.27$ e Å$^{-3}$
$\Delta\rho_{\min} = -0.32$ e Å$^{-3}$

**Table 1**

Selected geometric parameters (Å, °).

| | | | |
|---|---|---|---|
| O1*A*—C2*A* | 1.267 (5) | O1*B*—C2*B* | 1.255 (5) |
| O2*A*—C4*A* | 1.337 (4) | O2*B*—C4*B* | 1.326 (5) |
| O2*A*—H2O*A* | 0.95 (5) | O2*B*—H2O*B* | 1.05 (5) |
| C1*A*—C2*A* | 1.486 (6) | C1*B*—C2*B* | 1.500 (6) |
| C2*A*—C3*A* | 1.426 (5) | C2*B*—C3*B* | 1.426 (5) |
| C3*A*—C4*A* | 1.364 (5) | C3*B*—C4*B* | 1.367 (5) |
| C4*A*—C5*A* | 1.451 (5) | C4*B*—C5*B* | 1.450 (5) |
| C5*A*—C6*A* | 1.336 (5) | C5*B*—C6*B* | 1.337 (5) |
| C6*A*—C7*A* | 1.461 (5) | C6*B*—C7*B* | 1.471 (5) |
| C7*A*—C12*A* | 1.391 (5) | C7*B*—C8*B* | 1.391 (5) |
| C7*A*—C8*A* | 1.397 (5) | C7*B*—C12*B* | 1.398 (5) |
| C8*A*—C9*A* | 1.386 (5) | C8*B*—C9*B* | 1.388 (5) |
| C9*A*—C10*A* | 1.386 (6) | C9*B*—C10*B* | 1.387 (6) |
| C10*A*—C11*A* | 1.377 (6) | C10*B*—C11*B* | 1.372 (6) |
| C11*A*—C12*A* | 1.382 (5) | C11*B*—C12*B* | 1.378 (5) |
| | | | |
| C4*A*—O2*A*—H2O*A* | 100 (3) | C4*B*—O2*B*—H2O*B* | 100 (3) |
| O1*A*—C2*A*—C3*A* | 120.2 (4) | O1*B*—C2*B*—C3*B* | 120.4 (4) |
| O1*A*—C2*A*—C1*A* | 119.0 (3) | O1*B*—C2*B*—C1*B* | 118.6 (4) |
| C3*A*—C2*A*—C1*A* | 120.9 (4) | C3*B*—C2*B*—C1*B* | 120.9 (4) |
| C4*A*—C3*A*—C2*A* | 121.6 (4) | C4*B*—C3*B*—C2*B* | 122.0 (4) |
| O2*A*—C4*A*—C3*A* | 120.7 (3) | O2*B*—C4*B*—C3*B* | 120.3 (3) |
| O2*A*—C4*A*—C5*A* | 115.5 (3) | O2*B*—C4*B*—C5*B* | 116.2 (3) |
| C3*A*—C4*A*—C5*A* | 123.8 (3) | C3*B*—C4*B*—C5*B* | 123.5 (3) |
| C6*A*—C5*A*—C4*A* | 123.7 (3) | C6*B*—C5*B*—C4*B* | 122.9 (4) |
| C5*A*—C6*A*—C7*A* | 127.5 (4) | C5*B*—C6*B*—C7*B* | 127.1 (4) |
| C12*A*—C7*A*—C6*A* | 119.5 (3) | C8*B*—C7*B*—C6*B* | 122.8 (3) |
| C8*A*—C7*A*—C6*A* | 123.5 (3) | C12*B*—C7*B*—C6*B* | 119.1 (3) |

**Table 2**

Hydrogen-bonding geometry (Å, °).

| *D*—H···*A* | *D*—H | H···*A* | *D*···*A* | *D*—H···*A* |
|---|---|---|---|---|
| O2*A*—H2O*A*···O1*A* | 0.95 (5) | 1.59 (5) | 2.495 (4) | 159 (4) |
| O2*B*—H2O*B*···O1*B* | 1.05 (5) | 1.50 (5) | 2.505 (4) | 158 (4) |
| C1*B*—H1*B*1···O1*A* | 1.02 (7) | 2.55 (7) | 3.520 (7) | 157 (5) |
| C10*B*—H10*B*···O1*B*$^{\rm i}$ | 0.95 | 2.53 | 3.434 (5) | 159 |
| C10*A*—H10*A*···O1*A*$^{\rm ii}$ | 0.95 | 2.53 | 3.423 (5) | 158 |

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

The positions of all H atoms were located from Fourier maps. However, whereas the positions of the enol and methyl H atoms were refined with isotropic displacement parameters, giving distances O—H = 0.95 (5) and 1.05 (5) Å, and C—H = 0.81–1.03 Å.; the rest of the H atoms were placed in geometrically calculated positions and included in the refinement in the riding-motion approximation. The displacement parameters of the H atoms were set to $1.2U_{\rm eq}$, where $U_{\rm eq}$ is the equivalent isotropic displacement parameter of the carrier non-H atom.

Data collection: *SMART* (Bruker, 1998); cell refinement: *SMART*; data reduction: *SAINT* (Bruker, 1998); program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics:

*SHELXL*97; software used to prepare material for publication: *SHELXL*97.

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