

Orthorhombic form of 6-phenylhex-5-ene-2,4-dione

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Key indicators

Single-crystal X-ray study

T = 123 K

Mean $\sigma(\text{C}-\text{C}) = 0.002 \text{ \AA}$

R factor = 0.041

wR factor = 0.137

Data-to-parameter ratio = 14.2

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

The title compound, $\text{C}_{12}\text{H}_{12}\text{O}_2$, crystallizes in at least two polymorphic forms, one monoclinic and the other orthorhombic. In the orthorhombic polymorph, the enol group is asymmetric with the H atom bonded to the O atom closest to the most electronegative substituent, and the molecule displays the longest possible conjugation. The molecular packing is dominated by weak $\text{C}-\text{H}\cdots\text{O}$ interactions.

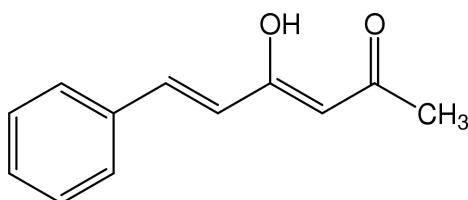
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Comment

The 6-phenylhex-5-ene-2,4-dione molecule has been studied by X-ray methods in the course of a systematic study on the position of the enol H atom and the conjugation in β,β' -diketo compounds. This compound crystallizes in at least two polymorphic forms: one is orthorhombic, which is presented here, and the other is monoclinic, with $a = 13.822 (1)$, $b = 5.8033 (6)$, $c = 25.239 (3) \text{ \AA}$ and $\beta = 99.663 (4)^\circ$ in space group $P2_1/c$. The enolized molecule, 4-hydroxy-6-phenylhexa-3,5-diene-2-one, (I), is shown in Fig. 1 with the atom-numbering scheme.



(I)

The enol-H atom is found to be positioned at the O atom closest to the most electronegative substituent; this is also consistent with the longest possible conjugation in the molecule. To our knowledge, there is no information about any existing keto tautomer of this molecule in solution. The molecular packing is dominated by a number of $\text{C}-\text{H}\cdots\text{O}$ contacts where at least one, $\text{C}8-\text{H}8\cdots\text{O}1(\frac{1}{2} + x, \frac{1}{2} - y, 2 - z)$ is a clear-cut intermolecular hydrogen bond. The $\text{C}-\text{H}\cdots\text{O}$ short contacts observed between molecules related by a center of symmetry [$\text{H}\cdots\text{O}$ distances of $3.00 (2)$ and $3.19 (2) \text{ \AA}$] are similar to a mode seen in the crystal structures of related molecules (Mostad, 1994; Arrieta *et al.*, 1995, 2000). In the solid state, the phenyl rings pack along the cell direction b forming an angle of 72.5° . The distance from the H atoms H11 and H12 in one phenyl group to the C atom C8 in the next are $3.03 (2)$ and $3.02 (2) \text{ \AA}$, respectively. This is a commonly found interaction between aromatic moieties.

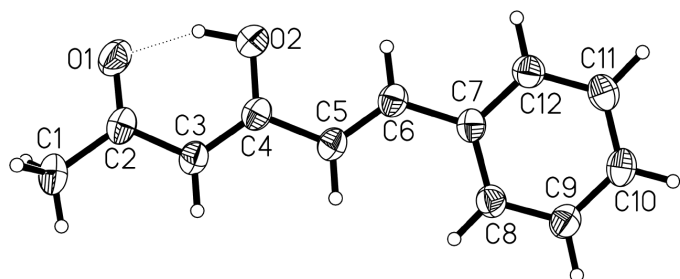


Figure 1
Molecular structure and crystallographic numbering scheme for (I); displacement ellipsoids are shown at the 50% probability level.

Experimental

The title compound was synthesized by boiling ethyl-2-*trans*-cinnamoyl acetate (Arrieta & Mostad, 2001) 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. Usually this procedure results in the formation of thin needle crystals showing a monoclinic unit cell. However, in one experiment, one large-sized crystal with a different morphology was grown, and a small part of that was used for the present study.

Crystal data

$C_{12}H_{12}O_2$
 $M_r = 188.22$
Orthorhombic, *Pbca*
 $a = 8.9118$ (18) Å
 $b = 9.4953$ (19) Å
 $c = 23.628$ (5) Å
 $V = 1999.4$ (7) Å³
 $Z = 8$
 $D_x = 1.251$ Mg m⁻³

Mo $K\alpha$ radiation
Cell parameters from 1024 reflections
 $\theta = 4.9$ – 56.6°
 $\mu = 0.08$ mm⁻¹
 $T = 123$ (2) K
Prismatic, yellow
 $0.5 \times 0.5 \times 0.5$ mm

Data collection

Bruker SMART 1000
diffractometer
 ω scans
22303 measured reflections
2484 independent reflections
2117 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.022$
 $\theta_{\text{max}} = 28.3^\circ$
 $h = -11 \rightarrow 11$
 $k = -12 \rightarrow 12$
 $l = -31 \rightarrow 31$

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.041$
 $wR(F^2) = 0.137$
 $S = 1.12$
2484 reflections
175 parameters
All H-atom parameters refined

$w = 1/[\sigma^2(F_o^2) + (0.0786P)^2 + 0.3676P]$
where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\text{max}} = 0.001$
 $\Delta\rho_{\text{max}} = 0.27$ e Å⁻³
 $\Delta\rho_{\text{min}} = -0.20$ e Å⁻³

Table 1

Selected geometric parameters (Å, °).

O2—C4	1.3286 (16)	C7—C6	1.4687 (16)
C5—C6	1.3397 (17)	C3—C4	1.3729 (17)
C5—C4	1.4589 (16)	C3—C2	1.4337 (16)
O1—C2	1.2571 (17)	C2—C1	1.4960 (19)
C6—C5—C4	122.26 (12)	O2—C4—C5	116.09 (11)
C12—C7—C6	118.86 (11)	C3—C4—C5	122.74 (12)
C8—C7—C6	122.75 (11)	O1—C2—C3	121.02 (12)
C4—C3—C2	120.81 (12)	O1—C2—C1	118.96 (11)
C5—C6—C7	126.63 (12)	C3—C2—C1	120.02 (12)
O2—C4—C3	121.16 (11)		
C4—C5—C6—C7	−175.97 (11)	C6—C5—C4—O2	3.09 (18)
C12—C7—C6—C5	−176.01 (12)	C6—C5—C4—C3	−178.16 (12)
C8—C7—C6—C5	6.1 (2)	C4—C3—C2—O1	0.79 (19)
C2—C3—C4—O2	0.35 (19)	C4—C3—C2—C1	−178.74 (11)
C2—C3—C4—C5	−178.34 (11)		

Table 2

Hydrogen-bonding geometry (Å, °).

$D-H \cdots A$	$D-H$	$H \cdots A$	$D \cdots A$	$D-H \cdots A$
O2—H20 \cdots O1	0.99 (3)	1.59 (3)	2.5085 (14)	152 (2)
C8—H8 \cdots O1 ⁱ	0.951 (18)	2.471 (18)	3.4159 (17)	172.0 (14)

Symmetry code: (i) $\frac{1}{2} + x, \frac{1}{2} - y, 2 - z$.

H atoms were located from a difference map and both positional and isotropic displacement parameters were refined. For H atoms, the C—H range is 0.94 (2)–1.002 (17) Å, while the intramolecular O—H distance is 0.99 (3) Å. The deviation of the C2—C1—H1c angle [116.3 (15)°] from 109° is believed to be a result of the eclipsed position of the H1c atom relative to the C3—H3 bond. Similar considerations may explain the closing of the C7—C6—H6 angle [114.2 (9)°] and the C4—C5—H5 angle [115.9 (9)°]. The sum of the angles around C6 and C5 is 360° in both cases.

Data collection: *SMART* (Bruker, 1998); cell refinement: *SMART*; data reduction: *SAINT* (Bruker, 1998); 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: *SHELXL97*.

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