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3-Hydroxy-1,3-di-*p*-tolylpropenone

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The title molecule, $C_{17}H_{16}O_2$, lies on a crystallographic twofold rotation axis. The dihedral angle between the planes of the two symmetry-related benzene rings is 15.56 (4)°. The molecular structure is stabilized by intramolecular $O—H\cdots O$ and $C—H\cdots O$ hydrogen bonds.

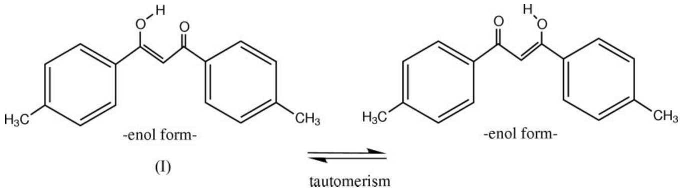
Key indicators

Single-crystal X-ray study
T = 150 K
Mean σ(C–C) = 0.001 Å
Disorder in main residue
R factor = 0.039
wR factor = 0.117
Data-to-parameter ratio = 14.1

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

Comment

1,3-Dicarbonyl compounds (*e.g.* 1,3-diones, diaroylmethanes, symmetrical diaryl β-diketones) and some cyclic diketone derivatives have been the subject of much research due to their importance in synthetic chemistry and their widespread potential biological, medicinal and agricultural activities, such as anti-algal properties (Cizmarikova *et al.*, 2000) and effects on the central nervous system (Wolskaa & Heroldb, 2002). The presence of the adjacent carbonyl groups polarizes the methylene group, rendering the C—H bonds somewhat acidic (Artico *et al.*, 1998; Sarhan *et al.*, 1997). 1,3-Diones are important synthetic intermediates for the synthesis of various useful compounds, such as flavonols (Fougerousse *et al.*, 2000), lamellarin alkaloids (Ruchirawat & Mutarapat, 2001), fluorescence 3-hydroxychromones (Klymchenko *et al.*, 2001) and many other compounds (Appleton *et al.*, 1977). Studies describing the reactions demonstrating the synthetic potential of this class of compounds have been reported (Rubinov *et al.*, 1999).



(I)

β-Diketones have been studied extensively because of their interesting properties as both enol and diketo forms. A 1,3-arrangement of two carbonyl groups leads to a situation in which the keto and enol forms are of comparable stability. The two principal structural features that stabilize the enol form of a 1,3-dicarbonyl compound are: (i) conjugation of its double bond with the remaining carbonyl group and (ii) the presence of a strong intramolecular hydrogen bond between the enolic hydroxyl group and the carbonyl O atom. 1,3-Diones, which are starting materials for synthesizing many heterocycles, show keto–enol tautomerism and the proportion of the tautomers depends on the temperature and solvent used (Norman, 1978). The cyclocondensation reaction of symmetric disubstituted 1,3-diones with oxalyl halides regiospecifically afforded 2,3-dihydro-2,3-furandiones in good yields, similar to

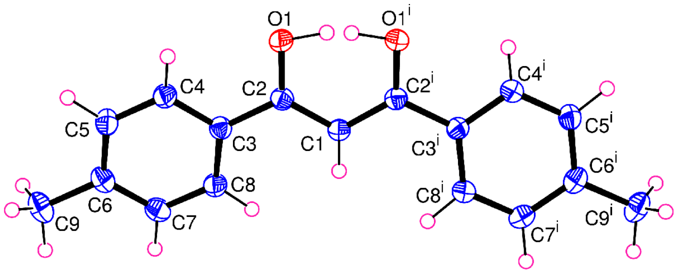


Figure 1
An *ORTEP*-3 (Farrugia, 1997) plot of (I), showing the atomic numbering. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as spheres of arbitrary radii [symmetry code: (i) $1 - x, y, \frac{1}{2} - z$]. H atoms attached to O1 and O1^i each have site occupancy of 0.50.

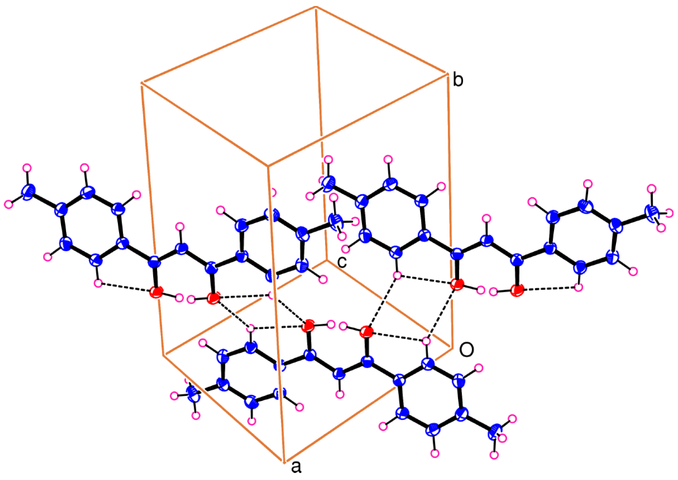


Figure 2
The crystal packing of (I). Dashed lines indicate C—H···O hydrogen bonds.

those reported by Ziegler, Eder *et al.* (1967) and Ziegler, Kollenz *et al.* (1971). Some analogs of the compound (I) were obtained from sodium methoxide and 2,3-dihalo-1,3-diaryl-1-propanone as pale yellow crystals which are formed easily by the Claisen–Schmidt condensation reaction of benzaldehyde and acetophenone derivatives (Dinçer *et al.*, 2004; Hökelek *et al.*, 2002; Yıldırım *et al.*, 2002). In view of these important properties, we have undertaken the X-ray diffraction study of the title compound, (I).

Molecules of (I) lie on crystallographic twofold rotation axes and the asymmetric unit therefore contains one-half of a molecule; atoms C1 and H1*C* lie on the twofold axis (Fig. 1). The molecule is in the enol tautomeric form. The dihedral angle between the planes of the two symmetry-related benzene rings is 15.56 (4)° and each of these two rings forms an angle of 8.30 (4)° with the central hydroxypropenal linkage. Hydroxyl atom H1O is disordered across the twofold rotation axis and hence attached to both O1 and O1^i [symmetry code (i): $1 - x, y, \frac{1}{2} - z$] with a site occupancy of 0.5. As a result of conjugation, the C1—C2 [1.3998 (11) Å] and C2—O1 [1.2934 (12) Å] bonds are longer than the corresponding double bonds and shorter than the corresponding single bonds. The hydroxy H atom is involved in an intramolecular O—H···O hydrogen bond and an intramolecular C—H···O hydrogen bond is also observed in the molecular structure (Table 2 and Fig. 2). Molecules related by a centre of symmetry are linked by intermolecular C—H···O hydrogen bonds (Table 2), resulting in the formation of a chain along [101].

Experimental

Starting materials were purchased from Merck, Fluka, Aldrich and Acros Chemical Co., and used without further purification. To a solution of sodium hydroxide (22 g, 0.55 mol) in a mixture of ethanol (140 ml) and water (200 ml) was added *p*-methylacetophenone (67.0 ml) dropwise with stirring at room temperature. *p*-Methylbenzaldehyde (58.8 ml) was poured into the mixture and stirred for 5 h and then kept in a refrigerator overnight. The crude precipitate was filtered off, washed with ethanol solution and dried to yield 116.0 g (96%) of pure *p,p'*-dimethylbenzalacetophenone. Then, to the solution of *p,p'*-dimethylbenzalacetophenone (11.53 g, 0.05 mol) in dichloromethane (150 ml) was added bromine (7.8 g, 0.05 mol) dropwise with stirring at about 263 K for 2 h. After filtering, the crude orange product was washed with ethanol and dried to afford 9.23 g (60%). To a solution of 2,3-dibromo-1,3-bis(4-methylphenyl)-1-propanone (20 g, 0.05 mol) in methanol (50 ml) fresh sodium methoxide was added. Fresh sodium methoxide was prepared before each reaction by slowly adding small pieces of freshly cut sodium metal (0.50 g, 0.02 mol) to dry methanol (15 ml), followed by stirring for 1 h at 323–333 K. After cooling to room temperature, the solution was acidified by adding concentrated hydrochloric acid (~22 ml; pH = 1). The precipitate was kept in a refrigerator for 1 h to ensure complete product formation, filtered off, washed with water and recrystallized from methanol to give 1.62 g (51%) of pure (I) (m.p. 395 K). FT–IR (KBr, cm^{-1}): ν = 3060–2900 (aromatic and aliphatic C—H stretching, respectively), 2850 (enolic O—H stretching), 1612, 1609 (C=O); ^{1}H NMR (CDCl$_3$): δ 7.94–7.21 (two *m*, 8H, Ar-H), 6.83 (enolic O—H), 4.59, 3.50 (weak peaks, tautomeric protons), 2.42, 241 (*s*, 6H, CH$_3$); ^{13}C NMR (CDCl$_3$): δ 187.47 (Ar–C=O), 145.16, 134.85, 131.42, 129.21 (aromatic C's), 94.45 (*s*, enolic =CH—, C-2), 23.65 (*s*, CH$_3$). Analysis calculated for $C_{17}H_{16}O_3$: C 80.93, H 6.39%; found: C 81.09, H 6.33%.

Crystal data

$C_{17}H_{16}O_2$
M_r = 252.30
Monoclinic, $C2/c$
a = 11.280 (5) Å
b = 11.884 (5) Å
c = 10.657 (5) Å
β = 114.169 (5)°
V = 1303.4 (10) Å^3
Z = 4

D_x = 1.286 Mg m$^{-3$}
Mo $K\alpha$ radiation
Cell parameters from 9667 reflections
θ = 2.1–29.1°
μ = 0.08 mm^{-1}
T = 150 K
Prism, colourless
0.40 × 0.35 × 0.31 mm

Data collection

Stoe IPDS-II diffractometer
ω scans
Absorption correction: by integration (*X-RED*32; Stoe & Cie, 2002)
$T_{\min}$ = 0.971, $T_{\max}$ = 0.983
10 682 measured reflections

1705 independent reflections
1490 reflections with $I > 2\sigma(I)$
$R_{\rm int}$ = 0.090
$\theta_{\max}$ = 28.9°
$h = -15 \rightarrow 15$
$k = -16 \rightarrow 16$
$l = -14 \rightarrow 14$

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Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.039$
$wR(F^2) = 0.117$
$S = 1.09$
1705 reflections
121 parameters
All H-atom parameters refined

$w = 1/[\sigma^2(F_o^2) + (0.0703P)^2 + 0.2674P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = 0.001$
$\Delta\rho_{\max} = 0.32$ e Å^{-3}
$\Delta\rho_{\min} = -0.16$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

O1—C2	1.2934 (12)	C4—C5	1.3849 (13)
C1—C2	1.3998 (11)	C5—C6	1.3942 (14)
C2—C3	1.4791 (12)	C6—C7	1.3910 (14)
C3—C8	1.3925 (13)	C6—C9	1.5015 (13)
C3—C4	1.3999 (12)	C7—C8	1.3876 (13)
O1—C2—C3	116.33 (7)	C1—C2—C3	123.16 (9)
C2^{i}—C1—C2—O1	−0.89 (5)	C1—C2—C3—C8	−8.22 (12)
C2^{i}—C1—C2—C3	179.28 (8)	O1—C2—C3—C4	−7.60 (11)
O1—C2—C3—C8	171.94 (8)	C1—C2—C3—C4	172.24 (7)

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

Table 2
Hydrogen-bonding geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
O1—H1O···O1^{i}	0.97 (5)	1.49 (5)	2.436 (1)	163 (2)
C4—H4*C*···O1	0.94 (1)	2.40 (1)	2.733 (1)	100 (1)
C4—H4*C*···O1^{ii}	0.94 (1)	2.57 (1)	3.364 (2)	143 (1)

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

All H atoms were located in a difference Fourier map and were refined isotropically. Atom H1O was found to be disordered over two positions related by a crystallographic twofold rotation axis. The O—H distance is 0.97 (5) Å and the C—H distances range from 0.93 (2) to 1.02 (2) Å.

Data collection: *X-AREA* (Stoe & Cie, 2002); cell refinement: *X-AREA*; data reduction: *X-RED*32 (Stoe & Cie, 2002); program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *ORTEP*-3 *for Window*s (Farrugia, 1997) and *PLATON* (Spek, 2003); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

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