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3-(4-Hydroxystyryl)-1,1-dimethylcyclohex-3-en-5-one

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Key indicators

Single-crystal X-ray study
T = 291 K
Mean σ(C–C) = 0.004 Å
R factor = 0.032
wR factor = 0.108
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.

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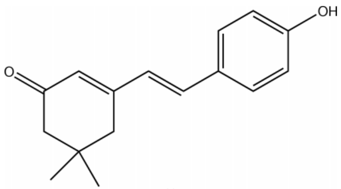
The crystal structure of the title compound, $C_{16}H_{18}O_2$, contains one molecule in the asymmetric unit. With the exception of the $C(CH_3)_2$ group, it is nearly planar. The intermolecular hydrogen bond formed by the hydroxy group with the O-carbonyl atom [O···O = 2.720 Å and O—H···O = 166°] links the molecules into infinite chains.

Comment

In the course of our spectroscopic and structural investigation of organic halochromic polymethine systems having non-linear optical and electro-optical properties (Chemla & Zyss, 1987; Nalwa & Miyata, 1997; Wolff & Wortmann, 1999), the crystal structure of the title compound, (I), was elucidated. Its vibrational (IR and Raman) spectra differ significantly from those expected, due to the formation of a strong hydrogen bond [ν(O—H) = 3220 cm^{-1}], which was confirmed by the crystal structure (Table 2). This hydrogen bond links the molecules into infinite chains in the crystal structure. The formation of a charge-transfer complex (CT) within the molecule is shown by the frequencies and intensities of the vibrational bands for the double bonds in the conjugated system; ν(O2=C11) = 1630 cm^{-1} and ν(C10=C9) is a doublet at 1598 and 1588 cm^{-1}. The most intensive band in the IR and Raman spectra appears at 1571 cm^{-1} [ν(C8=C7)]. The bond lengths O1—C1, C1—C2 and C1—C6 are equal (Table 1), due very probably to the CT formation, leading to bond-length alternation (Gorman & Marder, 1995; Marder *et al.*, 1994). This phenomenon characterizes the push–pull polymethine systems and is responsible for their halochromic properties. The yellow title compound forms red polymethine cations in basic media. The assignment of the bands in the IR and Raman spectra is in accordance with theoretically predicted frequencies, using RHF/6-31G** and B3LYP/6-31G** methods (Kolev & Stamboliyska, 2004).



(I)

Experimental

The title compound was prepared according to a published procedure (Lemke, 1970). 3,5,5-Trimethyl-2-cyclohexen-1-one (1.38 g, 10 mmol) and 4-hydroxybenzaldehyde (1.22 g, 10 mmol) were dissolved in 30 ml methanol, which was saturated with HCl. The solution was stirred under reflux for 5 h. The orange–red precipitate was purified

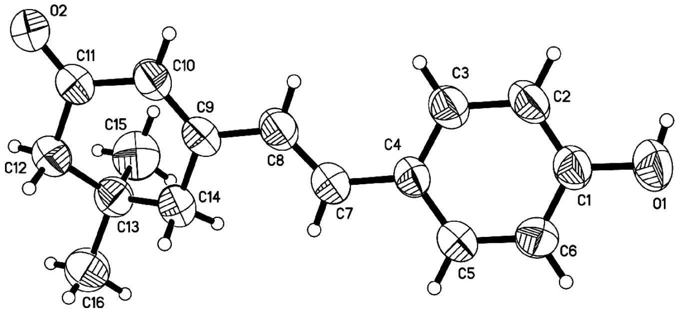


Figure 1
The molecular structure of the title compound, showing the labelling of all non-H atoms. Displacement ellipsoids are drawn at the 50% probability level.

by column chromatography on silica gel. The yellow solid was recrystallized twice, first from ethanol and then from anhydrous methanol; melting point 455–456 K. The IR and Raman spectra of the compound were measured after each recrystallization and did not show any changes. The purity of the compound was confirmed by elemental analysis, IR, UV–Vis and mass spectrometry. Crystals were grown from methanol by slow evaporation at room temperature over a period of a week.

Crystal data

$C_{16}H_{18}O_2$
$M_r = 242.30$
Monoclinic, $P2_1/n$
$a = 14.693$ (3) Å
$b = 6.0684$ (12) Å
$c = 15.266$ (3) Å
$\beta = 90.58$ (3)°
$V = 1361.1$ (5) Å^3
$Z = 4$

$D_x = 1.182$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 16335 reflections
$\theta = 1.9$–25.0°
$\mu = 0.08$ mm^{-1}
$T = 291$ (1) K
Needle, yellow
0.38 × 0.06 × 0.06 mm

Data collection

Nonius KappaCCD diffractometer
ω scans
16335 measured reflections
2351 independent reflections
616 reflections with $I > 2\sigma(I)$

$R_{\rm int} = 0.132$
$\theta_{\rm max} = 25.0°$
$h = -14 \rightarrow 17$
$k = -7 \rightarrow 7$
$l = -18 \rightarrow 18$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.032$
$wR(F^2) = 0.108$
$S = 0.96$
2351 reflections
167 parameters
H-atom parameters constrained

$w = \exp[8(\sin\theta/\lambda)^2)]/\sigma^2(F_o^2)$
$(\Delta/\sigma)_{\rm max} < 0.001$
$\Delta\rho_{\rm max} = 0.09$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.10$ e Å^{-3}
Extinction correction: *SHELXL*97
Extinction coefficient: 0.0087 (14)

Table 1
Selected geometric parameters (Å).

O1—C1	1.373 (4)	C1—C6	1.373 (4)
C1—C2	1.370 (4)		

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

D—H···A	D—H	H···A	D···A	D—H···A
O1—H1···O2$^{\rm i}$	0.82	1.91	2.718 (3)	166

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

The low proportion of observed data and the high $R_{\rm int}$ value presumably result from the relatively poor quality of the crystal and the fact that the data collection was performed at room temperature. H atoms were placed in calculated positions (C—H = 0.93–0.97 Å and O—H = 0.82 Å), with $U_{\rm iso}$ values constrained to be $1.5U_{\rm eq}$ of the carrier atom for methyl H and O—H, and $1.2U_{\rm eq}$ for the remaining H atoms. The methyl group and the O—H groups were allowed to rotate but not to tip.

Data collection: *COLLECT* (Nonius, 1998); cell refinement: *DENZO* and *SCALEPACK* (Otwinowski & Minor, 1997); data reduction: *DENZO* and *SCALEPACK*; program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1990); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *SHELXTL-Plus* (Sheldrick, 1991); software used to prepare material for publication: *SHELXL*97, *PARST*95 (Nardelli, 1995) and *PLATON* (Spek, 2001).

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