

**Zwitterionic ( E )-6-methyl-2-oxo-3-[1-( p  
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Zwitterionic (*E*)-6-methyl-2-oxo-3-[1-(*p*-tolyl-iminio)ethyl]-2*H*-pyran-4-olate

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## Key indicators

Single-crystal X-ray study  
 T = 173 K  
 Mean  $\sigma(\text{C}-\text{C}) = 0.003 \text{ \AA}$   
 R factor = 0.040  
 wR factor = 0.110  
 Data-to-parameter ratio = 14.4

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

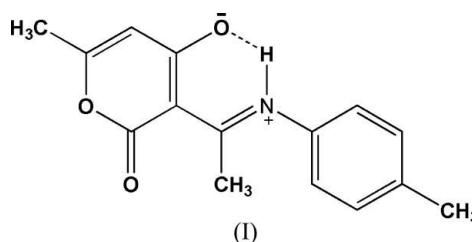
The title compound,  $\text{C}_{15}\text{H}_{15}\text{NO}_3$ , derived from the condensation of dehydroacetic acid and *p*-toluidine, crystallizes in a zwitterionic form with cationic iminium and anionic enolate groups, which complete a six-membered pseudocycle *via* an intramolecular  $\text{N}-\text{H}\cdots\text{O}$  hydrogen bond.  $\text{C}-\text{H}\cdots\text{O}$  interactions link the molecules into a two-dimensional network.

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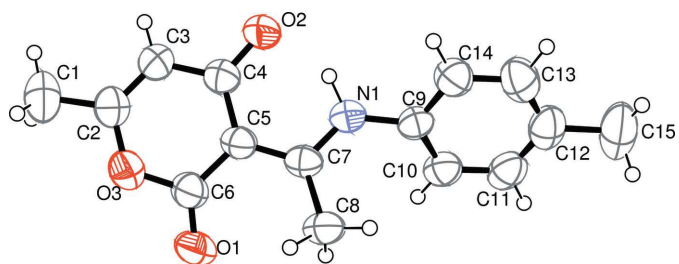
## Comment

Schiff base compounds have been of great interest for many years. These compounds play an important role in the development of coordination chemistry (Pfeiffer *et al.*, 1933). These compounds, with several donor atoms, have potential analytical application in water treatment, owing to their ability to readily form transition metal complexes (Abdou *et al.*, 2004; Hebbachi & Benali-Cherif, 2005; Issaâdi *et al.*, 2005) related to catalysis and enzymatic reactions (Venturini & González, 2002; Taggi *et al.*, 2002; Delpiccolo & Mata, 2002).

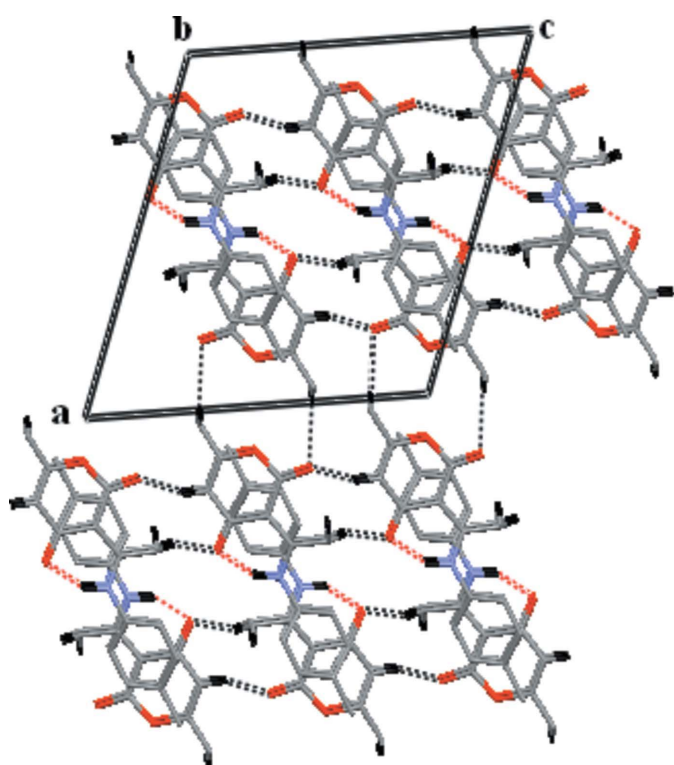
Our group is interested in the synthesis and coordination chemistry of Schiff bases prepared by the condensation of aromatic amines and diaromatic amines with carbonyl groups (Ghames *et al.*, 2006). As an extension of our work, the crystal structure of the title compound, (I), is reported here.



Schiff bases display two possible tautomeric forms, namely the phenol-imine ( $\text{O}-\text{H}\cdots\text{N}$ ) (Ünver, Yildiz *et al.*, 2002; Karadayı *et al.*, 2003) and keto-amine ( $\text{N}-\text{H}\cdots\text{O}$ ) forms (Ünver, Kabak *et al.*, 2002; Odabaşoğlu *et al.*, 2003). The interchange behaviour of these compounds has been described as a proton-transfer reaction between the phenol-imine and keto-amine tautomers. However, the title molecule has a zwitterionic form with cationic iminium and anionic enolate groups (Fig. 1). The length of the  $\text{C}7=\text{N}1$  iminium bond (Table 1) is comparable to the values of 1.314 (4) and 1.307 (3)  $\text{Å}$  observed in 1-dimethylamino-3-dimethylimino-1-phenylprop-1-ene perchlorate (Girija *et al.*, 2004), and 1-dimethylamino-3-dimethyliminio-2-(*p*-methoxyphenyl)prop-1-ene perchlorate (Girija & Begum, 2004), respectively. The  $\text{C}4-\text{O}2$  bond distance is relatively short compared with the corresponding distances of 1.283 (3) and 1.316 (2)  $\text{Å}$  in the



**Figure 1**  
The molecular structure of (I), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 50% probability level.



**Figure 2**  
The crystal packing of (I), viewed down the *b* axis. Dashed lines indicate the N—H...O and C—H...O interactions.

related zwitterionic compounds, (*E*)-2,4-dichloro-6-[(2-hydroxyethyliminio)-methyl]phenolate (Huang *et al.*, 2006) and (*E*)-2-hydroxy-6-[(*o*-tolyliminio)-methyl]phenolate 0.07-hydrate (Temel *et al.*, 2006), respectively. In (I), the dihedral angle between the benzene ring and dehydroacetic acid ring is 42.27 (10)°. The C4—C5—C7—N1 and C5—C7—N1—C9 torsion angles are −5.8 (2) and −173.64 (16), respectively.

The iminium atom, H1, in (I) participates in an intramolecular hydrogen bond with the enolate atom, O2 (Table 2), which generates an *S*(6) ring motif (Bernstein *et al.*, 1995). Similar intramolecular hydrogen bonds were reported in the above-mentioned zwitterionic phenolates (Huang *et al.*, 2006; Temel *et al.*, 2006). This six-membered pseudocycle is almost planar, the maximum deviation from the mean plane being 0.039 (2) Å for atom C7. The molecules are linked by weak

C—H...O hydrogen bonds (Table 2) into a two-dimensional network (Fig. 2).

## Experimental

Compound (I) was prepared by refluxing a mixture of a solution containing dehydroacetic acid (0.01 mmol) and *para*-toluidine (0.01 mmol) in ethanol (40 ml). The reaction mixture was stirred for 2 h under reflux. The solution was kept in air for 2 d and yellow prism-shaped crystals formed on slow evaporation of the solvent (yield 83%, m.p. 433 K).

### Crystal data

$C_{15}H_{15}NO_3$	$Z = 4$
$M_r = 257.28$	$D_x = 1.282 \text{ Mg m}^{-3}$
Monoclinic, $P2_1/c$	Mo $K\alpha$ radiation
$a = 14.131$ (2) Å	$\mu = 0.09 \text{ mm}^{-1}$
$b = 7.8128$ (6) Å	$T = 173$ (2) K
$c = 12.841$ (2) Å	Prism, yellow
$\beta = 109.92$ (2)°	$0.35 \times 0.05 \times 0.02 \text{ mm}$
$V = 1332.9$ (3) Å <sup>3</sup>	

### Data collection

Nonius KappaCCD diffractometer	2581 independent reflections
$\varphi$ scans	1487 reflections with $I > 2\sigma(I)$
Absorption correction: none	$R_{\text{int}} = 0.040$
10079 measured reflections	$\theta_{\text{max}} = 26.0^\circ$

### Refinement

Refinement on $F^2$	H atoms treated by a mixture of independent and constrained refinement
$R[F^2 > 2\sigma(F^2)] = 0.040$	$w = 1/[\sigma^2(F_o^2) + (0.0634P)^2]$
$wR(F^2) = 0.110$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 0.88$	$(\Delta/\sigma)_{\text{max}} < 0.001$
2581 reflections	$\Delta\rho_{\text{max}} = 0.11 \text{ e \AA}^{-3}$
179 parameters	$\Delta\rho_{\text{min}} = -0.13 \text{ e \AA}^{-3}$

**Table 1**  
Selected bond lengths (Å).

C4—O2	1.2637 (19)	C7—N1	1.324 (2)
C5—C7	1.419 (2)	C9—N1	1.427 (2)
C6—O1	1.208 (2)		

**Table 2**  
Hydrogen-bond geometry (Å, °).

<i>D</i> —H... <i>A</i>	<i>D</i> —H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> —H... <i>A</i>
N1—H1...O2	0.93 (2)	1.70 (2)	2.5396 (19)	148.4 (19)
C3—H3...O1 <sup>i</sup>	0.93	2.57	3.354 (3)	142
C8—H8A...O1	0.96	2.35	2.773 (3)	106
C8—H8C...O2 <sup>ii</sup>	0.96	2.50	3.414 (2)	160

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

The iminium H atom was located in a difference Fourier map and was refined isotropically. The methyl H atoms were constrained to an ideal geometry (C—H = 0.96 Å) with  $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$ , but were allowed to rotate freely about the C—C bonds. All remaining H atoms were placed in geometrically idealized positions (C—H = 0.93 Å) and constrained to ride on their parent atoms with  $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$ .

Data collection: *COLLECT* (Nonius, 1997); cell refinement: *SCALEPACK* (Otwinowski & Minor, 1997); data reduction: *SCALEPACK* and *DENZO* (Otwinowski & Minor, 1997); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 1997) and *Mercury* (Macrae *et al.*, 2006); software used to prepare material for publication: *WinGX* (Farrugia, 1999) and *PARST* (Nardelli, 1995).

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