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

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electronic reprint

Acta Crystallographica Section E
Structure Reports
Online
ISSN 1600-5368
Editors: **W. Clegg and D. G. Watson**

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Key indicators

Single-crystal X-ray study
T = 173 K
Mean σ(C–C) = 0.003 Å
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.

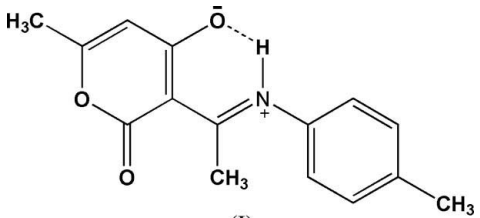
Received 24 December 2006
Accepted 5 February 2007

The title compound, $C_{15}H_{15}NO_3$, 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 N—H···O hydrogen bond. C—H···O interactions link the molecules into a two-dimensional network.

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.



(I)

Schiff bases display two possible tautomeric forms, namely the phenol–imine (O—H···N) (Ünver, Yildiz *et al.*, 2002; Karadayı *et al.*, 2003) and keto–amine (N—H···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 C7═N1 iminium bond (Table 1) is comparable to the values of 1.314 (4) and 1.307 (3) 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 C4—O2 bond distance is relatively short compared with the corresponding distances of 1.283 (3) and 1.316 (2) Å in the

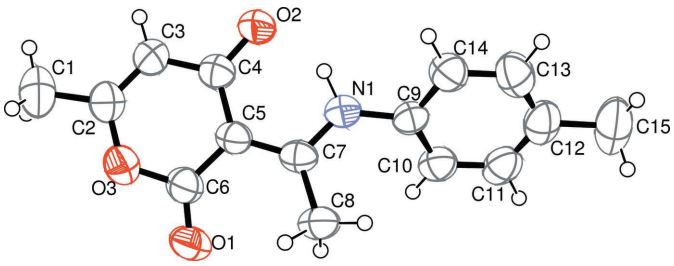


Figure 1
The molecular structure of (I), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 50% probability level.

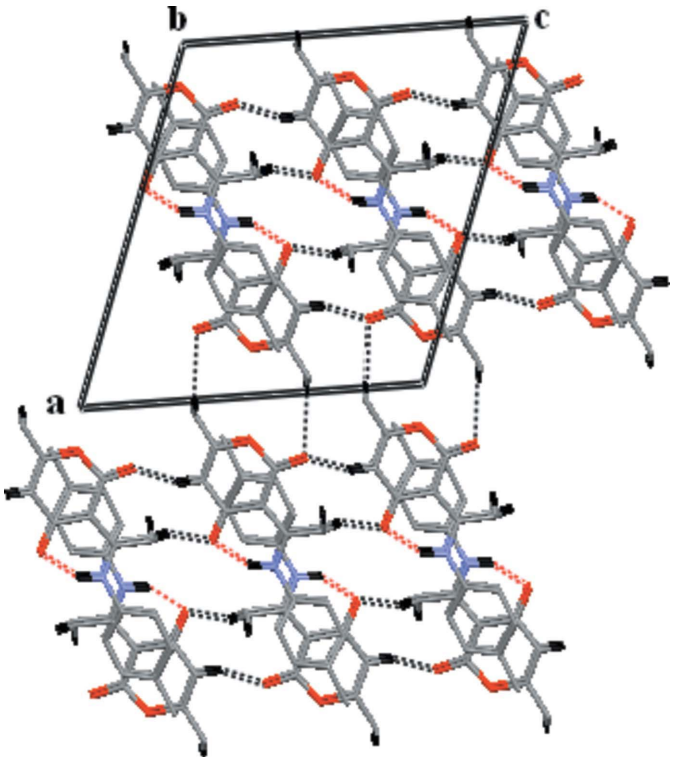


Figure 2
The crystal packing of (I), viewed down the *b* axis. Dashed lines indicate the N—H···O and C—H···O interactions.

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

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

Data collection

Nonius KappaCCD diffractometer
φ scans
Absorption correction: none
10079 measured reflections
2581 independent reflections
1487 reflections with $I > 2\sigma(I)$
R_{int} = 0.040
θ_{max} = 26.0°

Refinement

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

D—H···A	D—H	H···A	D···A	D—H···A
N1—H1···O2	0.93 (2)	1.70 (2)	2.5396 (19)	148.4 (19)
C3—H3···O1^{i}	0.93	2.57	3.354 (3)	142
C8—H8*A*···O1	0.96	2.35	2.773 (3)	106
C8—H8*C*···O2^{ii}	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_{iso}(H) = 1.2U_{eq}(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_{iso}(H) = 1.2U_{eq}(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).

This work was supported by Université Farhet Abbes de Sétif, Sétif, Algeria.

References

Abdou, S., El-Tabl Raffat, M. I. & Morsi, M. A. (2004). *Transition Met. Chem.* **29**, 543–549.

Bernstein, J., Davis, R. E., Shimoni, L. & Chang, N.-L. (1995). *Angew. Chem. Int. Ed. Engl.* **34**, 1555–1573.

Delpiccolo, C. M. L. & Mata, E. G. (2002). *Tetrahedron Asymmetry*, **13**, 905–910.

Farrugia, L. J. (1997). *J. Appl. Cryst.* **30**, 565.

Farrugia, L. J. (1999). *J. Appl. Cryst.* **32**, 837–838.

Ghames, A., Douadi, T., Haffar, D., Chafaa, S., Allain, M., Khan, M. A. & Bouet, G. M. (2006). *Polyhedron*, **25**, 3201–3208.

Girija, C. R. & Begum, N. S. (2004). *Acta Cryst.* E**60**, o535–o536.

Girija, C. R., Begum, N. S., Sridhar, M. A., Lokanath, N. K. & Prasad, J. S. (2004). *Acta Cryst.* E**60**, o586–o588.

Hebbachi, R. & Benali-Cherif, N. (2005). *Acta Cryst.* E**61**, m1188–m1190.

Huang, L., Chen, D.-B., Qiu, D. & Zhao, B. (2006). *Acta Cryst.* E**62**, o5239–o5240.

Issaâdi, S., Haffer, D., Douadi, T., Chafaa, S., Séraphin, D., Khan, M. A. & Bouet, G. M. (2005). *Synth. React. Inorg. Metal-Org. Nano-Metal Chem.* **35**, 875–882.

Karadayı, N., Gözüyeşil, S., Güzel, B., Kazak, C. & Büyükgüngör, O. (2003). *Acta Cryst.* E**59**, o851–o853.

Macrae, C. F., Edgington, P. R., McCabe, P., Pidcock, E., Shields, G. P., Taylor, R., Towler, M. & van de Streek, J. (2006). *J. Appl. Cryst.* **39**, 453–457.

Nardelli, M. (1995). *J. Appl. Cryst.* **28**, 659.

Nonius (1997). *COLLECT*. Nonius BV, Delft The Netherlands.

Odabaşoğlu, M., Albayrak, Ç., Büyükgüngör, O. & Goesmann, H. (2003). *Acta Cryst.* C**59**, o234–o236.

Otwinowski, Z. & Minor, W. (1997). *Methods in Enzymology*, Vol. 276, *Macromolecular Crystallography*, Part A, edited by C. W. Carter Jr & R. M. Sweet, pp. 307–326. New York: Academic Press.

Pfeiffer, P., Breith, E., Lulbbe, E. & Tsumaki, T. (1933). *Anal. Chem.* **503**, 84–129.

Sheldrick, G. M. (1997). *SHELXS97* and *SHELXL97*. University of Göttingen, Germany.

Taggi, A. E., Hafez, A. M., Wack, H., Young, B., Ferraris, D. & Lectka, T. (2002). *J. Am. Chem. Soc.* **124**, 6626–6635.

Temel, E., Albayrak, Ç., Büyükgüngör, O. & Odabaşoğlu, M. (2006). *Acta Cryst.* E**62**, o4484–o4486.

Ünver, H., Kabak, M., Zengin, D. M. & Durlu, T. N. (2002). *J. Chem. Crystallogr.* **31**, 203–209.

Ünver, H., Yildiz, M., Zengin, D. M., Özbey, S. & Kendi, E. (2002). *J. Chem. Crystallogr.* **31**, 211–216.

Venturini, A. & González, J. (2002). *J. Org. Chem.* **67**, 9089–9092.