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Amel Djedouani, Abderrahmen Bendaas, Sihem Boufas, Magali Allain, Gilles Bouet, et al.. Zwitterionic (E)-6-methyl-2-oxo-3-[1-(p -tolyliminio)ethyl]-2 H -pyran-4-olate. Acta Crystallographica Section E: Structure Reports Online [2001-2014], 2007, 63 (3), pp.o1271-o1273. 10.1107/S1600536807006083 . hal-03232157

HAL Id: hal-03232157

<https://univ-angers.hal.science/hal-03232157>

Submitted on 31 May 2021

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Acta Crystallographica Section E

Structure Reports

Online

ISSN 1600-5368

Editors: W. Clegg and D. G. Watson

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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
 $T = 173\text{ K}$
 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.

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 $\text{C7}=\text{N1}$ 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 $\text{C4}-\text{O2}$ bond distance is relatively short compared with the corresponding distances of 1.283 (3) and 1.316 (2) Å in the

Received 24 December 2006
 Accepted 5 February 2007

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

C₁₅H₁₅NO₃
M_r = 257.28
Monoclinic, *P*2₁/*c*
a = 14.131 (2) Å
b = 7.8128 (6) Å
c = 12.841 (2) Å
β = 109.92 (2)°
V = 1332.9 (3) Å³

Z = 4
D_x = 1.282 Mg m^{−3}
Mo *K*α 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* > 2σ(*I*)
*R*_{int} = 0.040
θ_{max} = 26.0°

Refinement

Refinement on *F*²
R [*F*² > 2σ(*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 $P = (F_o^2 + 2F_c^2)/3$
(Δ/σ)_{max} < 0.001
Δρ_{max} = 0.11 e Å^{−3}
Δρ_{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, °).

<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 ⁱ	0.93	2.57	3.354 (3)	142
C8—H8A...O1	0.96	2.35	2.773 (3)	106
C8—H8C...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) = 1.2*U*_{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) = 1.2*U*_{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.

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