

4-Chloro-2-[(4-phenylthiazol-2-yl)hydrazonomethyl]-phenol: a polymorph with $Z' = 2$ Cemile Dağ,^a Hümeyra Paşaoğlu,^a Çiğdem Yüksektepe,^{a*} Alaaddin Cukurovalı^b and Ebru Murat^b^aDepartment of Physics, Arts and Sciences Faculty, Ondokuz Mayıs University, 55139 Samsun, Turkey, and ^bDepartment of Chemistry, Arts and Sciences Faculty, Firat University, 23119 Elazığ, Turkey

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Key indicators

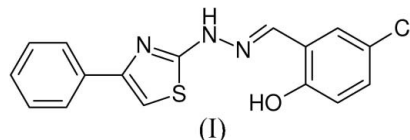
Single-crystal X-ray study
 $T = 296$ K
Mean $\sigma(\text{C}-\text{C}) = 0.003$ Å
 R factor = 0.046
 wR factor = 0.123
Data-to-parameter ratio = 13.6For details of how these key indicators were automatically derived from the article, see <http://journals.iucr.org/e>.

The title compound, β - $\text{C}_{16}\text{H}_{12}\text{ClN}_3\text{OS}$, crystallizes with two independent molecules in the asymmetric unit, both of which show a similar twisted conformation. It is polymorphic with α - $\text{C}_{16}\text{H}_{12}\text{ClN}_3\text{OS}$ [Çalışkan, Dağ, Yüksektepe, Cukurovalı & Murat (2006). *Acta Cryst.* E62, o4889–o4890]; both forms crystallize in the same space group. The two independent molecules in β - $\text{C}_{16}\text{H}_{12}\text{ClN}_3\text{OS}$ are linked into dimers by pairs of $\text{N}-\text{H}\cdots\text{N}$ hydrogen bonds.

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Comment

We have recently reported the crystal structure of 4-chloro-2-[(4-phenyl-thiazol-2-yl)-hydrazonomethyl]phenol, $\text{C}_{16}\text{H}_{12}\text{ClN}_3\text{OS}$ (Çalışkan *et al.*, 2006), which is hereafter described as the α modification of this material. We now report a second crystalline polymorph, (I), hereafter called β - $\text{C}_{16}\text{H}_{12}\text{ClN}_3\text{OS}$. Both polymorphs crystallize in space group $P2_1/c$; in the α form there is one independent molecule in the asymmetric unit, and in the β form there are two (Fig. 1).



The two molecules in (I) adopt similar conformations. The main backbones of both molecules are close to planar and in both cases the phenyl ring is twisted in the same sense (Table 1). The dihedral angle between the N1 and C1 rings is 29.13 (14°); the equivalent value for the N4 and C17 rings is 30.25 (13°). In α - $\text{C}_{16}\text{H}_{12}\text{ClN}_3\text{OS}$ (Çalışkan *et al.*, 2006) the unique molecule is almost planar.

Both molecules in (I) adopt an *E* geometry about the azomethine $\text{C}=\text{N}$ double bond, with $\text{N}2-\text{N}3-\text{C}10-\text{C}11 = 177.8$ (2°) and $\text{N}5-\text{N}6-\text{C}26-\text{C}27 = -175.5$ (2°). The *E* configuration of the double bond allows the formation of an intramolecular $\text{O}-\text{H}\cdots\text{N}$ hydrogen bond in both molecules (Table 2). Adjacent molecules are then linked into dimeric pairs by the two $\text{N}-\text{H}\cdots\text{N}$ bonds, resulting in an $R_2^2(8)$ loop (Bernstein *et al.*, 1995; Yüksektepe *et al.*, 2005). The dimers are arranged into (001) layers (Fig. 2).

Experimental

Thiosemicarbazide (0.9113 g, 10 mmol) was added in portions to a stirred solution of 5-chlorosalicylaldehyde (1.5657 g, 10 mmol) in 30 ml of ethanol. Subsequently, a solution of phenacyl chloride (1.5459 g, 10 mmol) in 20 ml of ethanol was added dropwise. After the addition of the haloketone, the temperature was kept at 323–

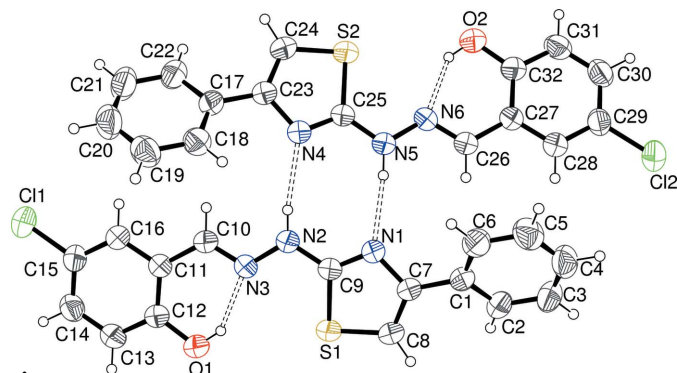


Figure 1
The asymmetric unit of (I) showing 40% displacement ellipsoids (arbitrary spheres for the H atoms). The hydrogen bonds are indicated by dashed lines.

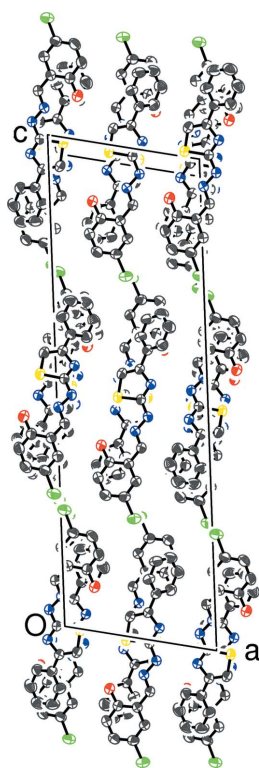


Figure 2
The packing of (I) with H atoms omitted for clarity.

328 K for 2 h more. After cooling to room temperature the solution was made alkaline with an aqueous solution of NH_3 (5%), and a light yellow precipitate separated. The precipitate was filtered off, washed with aqueous NH_3 solution several times and dried in air. Diffraction quality crystals of (I) were obtained by slow evaporation of its ethanol solution. Yield 85%, m.p. 505 K. IR (cm^{-1}): 3280 ν (O—H), 3120 ν (N—H), 1614 ν (C=N azomethine), 1604 ν (C=N thiazole), 676 ν (C—S—C thiazole). ^1H NMR (CDCl_3 , p.p.m.): δ 6.96 (s, 1H, thiazole), 7.20–7.89 (m, 8H, aromatics), 8.31 (s, 1H, azomethine), 10.40 (s, 1H, —NH—), 12.20 (s, 1H, —OH). ^{13}C NMR shifts (CDCl_3 , p.p.m.): δ 125.05 (C_1), 156.41 (C_2), 119.74 (C_3), 131.57 (C_4), 123.93 (C_5), 130.39 (C_6), 139.38 (C_7), 169.69 (C_8), 105.31 (C_9), 152.2 (C_{10}), 136.22 (C_{11}), 126.69 (C_{12}), 127.33 (C_{13}), 129.37 (C_{14}).

Crystal data

$\text{C}_{16}\text{H}_{12}\text{ClN}_3\text{OS}$
 $M_r = 329.80$
Monoclinic, $P2_1/c$
 $a = 10.8757$ (4) Å
 $b = 8.2302$ (5) Å
 $c = 34.9645$ (13) Å
 $\beta = 101.144$ (3) $^\circ$
 $V = 3070.6$ (2) Å 3

$Z = 8$
 $D_x = 1.427$ Mg m $^{-3}$
Mo $K\alpha$ radiation
 $\mu = 0.39$ mm $^{-1}$
 $T = 296$ K
Prism, pale yellow
 $0.60 \times 0.51 \times 0.31$ mm

Data collection

Stoe IPDS-2 diffractometer
 ω scans
Absorption correction: integration
(*X-RED32*; Stoe & Cie, 2002)
 $T_{\text{min}} = 0.765$, $T_{\text{max}} = 0.904$

36136 measured reflections
5398 independent reflections
3603 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.064$
 $\theta_{\text{max}} = 25.0^\circ$

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.046$
 $wR(F^2) = 0.123$
 $S = 0.99$
5398 reflections
398 parameters
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0772P)^2]$
where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\text{max}} = 0.001$
 $\Delta\rho_{\text{max}} = 0.75$ e Å $^{-3}$
 $\Delta\rho_{\text{min}} = -0.70$ e Å $^{-3}$
Extinction correction: *SHELXL97*
Extinction coefficient: 0.0204 (13)

Table 1

Selected torsion angles ($^\circ$).

C6—C1—C7—N1	29.0 (3)	C18—C17—C23—N4	30.0 (3)
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Table 2

Hydrogen-bond geometry (Å, $^\circ$).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
N2—H2A \cdots N4	0.86	2.11	2.967 (3)	171
N5—H5A \cdots N1	0.86	2.11	2.962 (3)	170
O1—H1 \cdots N3	0.82	1.94	2.661 (2)	146
O2—H2B \cdots N6	0.82	1.95	2.661 (2)	144

All H atoms were placed in idealized positions (C—H = 0.93 Å, N—H = 0.86 Å, O—H = 0.82 Å) and then treated as riding atoms, with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C}, \text{N})$ or $1.5U_{\text{eq}}(\text{O})$.

Data collection: *X-Area* (Stoe & Cie, 2002); cell refinement: *X-Area*; data reduction: *X-RED32* (Stoe & Cie, 2002); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP-3* (Farrugia, 1997); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

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