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5-(4-Chlorophenyl)-3-hydroxy-4-methylthiazole-2(3*H*)-thione: an instance of bifurcated hydrogen bonding

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Key indicators

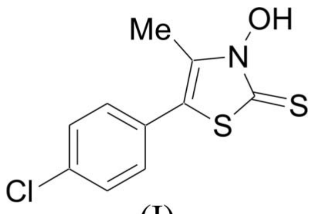
Single-crystal X-ray study
T = 291 K
Mean σ(C–C) = 0.003 Å
R factor = 0.030
wR factor = 0.082
Data-to-parameter ratio = 12.7

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

The asymmetric unit of the title compound, $C_{10}H_8ClNOS_2$, comprises two unique molecules. Aggregation occurs *via* intermolecular bifurcated hydrogen bonding between the thiohydroxamate H atom and the thiocarbonyl S atoms of the same and of an adjacent molecule.

Comment

The title compound, (I), was prepared in order to probe, in a combined experimental and computational study, the effect of a *p*-chlorophenyl substituent at position 5 on the UV–VIS absorption of 5-aryl-4-methyl-3-hydroxythiazole-2(3*H*)-thiones (Hartung *et al.*, 2004, 2007). Compound (I) (Fig. 1) separates as yellow prisms from its saturated solution in diethyl ether–petroleum ether and was investigated by X-ray diffraction in order to compare its computed and experimental structures.



(I)

There are two molecules in the asymmetric unit of (I), which show similar but not identical geometric parameters. The acidic H atom of (I) is located within the thiohydroxamate plane [H—O1—N3—C2 = 1.50 (5)°], to form an intramolecular hydrogen bond with the thiocarbonyl S atom (O1H···S2 = 2.51 Å) and a second one with the thione S atom of an adjacent molecule (O1H···S2′*B* = 2.56 Å) (Fig. 2 and Table 1). O—H···S hydrogen bonds link adjacent molecules to form inversion-related dimers with respect to the stereogenic axis along C5—C51 [C4—C5—C51—C56 = 37.7 (3) and −36.8 (3)°].

The mode of hydrogen bonding in (I) is distinctly different from that observed in *N*-(hydroxy)pyridine-2(1*H*)-thione (Hartung *et al.*, 1999*a*) and in hitherto investigated substituted derivatives of *N*-(hydroxy)thiazole-2(3*H*)-thione. In the former instance, only intramolecular hydrogen bonding is found. In *N*-hydroxy derivatives of 4-methyl-, 4-(4-chlorophenyl)- and 4-methyl-5-(4-methoxyphenyl)thiazole-2(3*H*)-thione, the thiohydroxamate H atom is offset from the thiazolethione plane, thus disfavouring intramolecular hydrogen bonding (Hartung *et al.*, 1999*b*, 2004, 2005; Bond *et al.*, 2000). Hence, intermolecular hydrogen bonds form, with H···S

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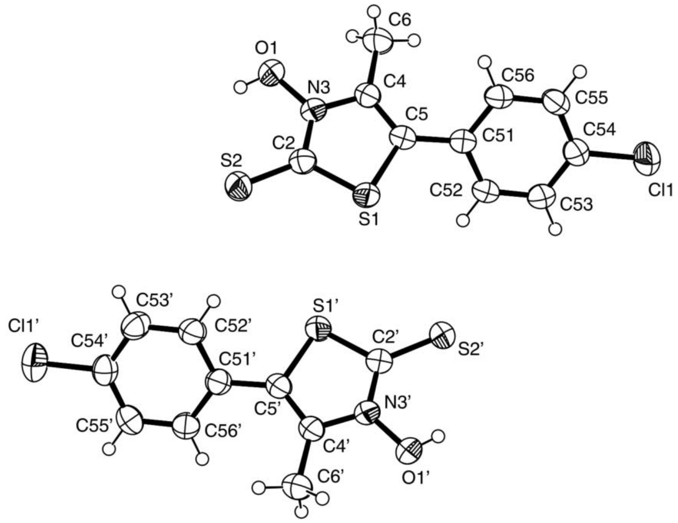

Figure 1
The asymmetric unit of (I). Displacement ellipsoids are plotted at the 50% probability level.

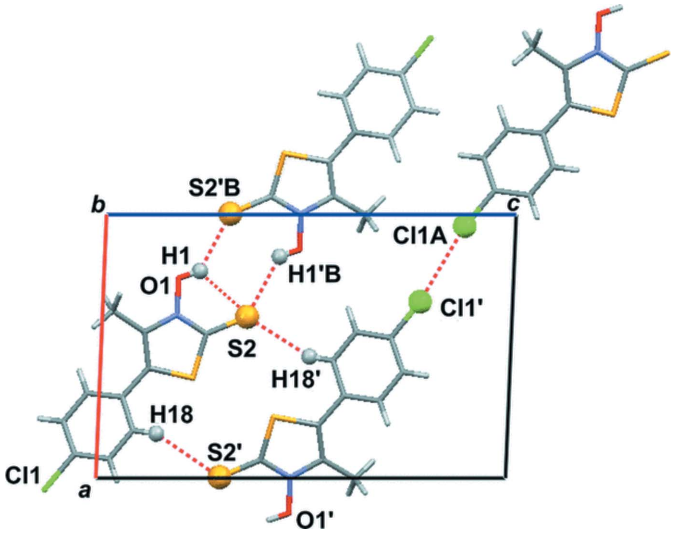

Figure 2
The hydrogen bonding (dashed lines) of (I) in the solid state, projected along [010]. S atoms are depicted in yellow, Cl in green, O in red, N in blue and H in white. The suffix A denotes atoms generated by the symmetry operator $(-1 + x, y, z)$ and B the symmetry operator $(-1 + x, y, 1 + z)$.

distances shorter than those observed for (I) [*e.g.* 2.26 (3) Å for *N*-(hydroxy)-4-methyl-5-(4-methoxyphenyl)thiazole-2(3*H*)-thione; Hartung *et al.*, 2004].

The packing of (I) in the unit cell gives rise to two additional close contacts. Short S2···H—C52 (2.87 Å) distances associated with an S2···H—C52 bond angle of 146.8° indicate weak C—H···acceptor interactions (Steiner, 1996). Furthermore, the separation between Cl atoms in adjacent molecules [Cl1*A*···Cl1′ = 3.402 (4) Å] is shorter than twice the van der Waals radius of Cl (1.75 Å; Bondi, 1964). This, combined with a C54—Cl1···Cl1A angle of 158.1° (symmetry code as in Fig. 2), indicates a Cl···Cl bonding interaction (Politzer *et al.*, 2007) between molecules of (I).

Experimental

To an ice-cooled solution (273 K) of KOH (950 mg, 16.9 mmol) in H_2O (15 ml) was added a solution of *O*-ethyl-*S*-[2-hydroxyimino-1-(*p*-chlorophenyl)propyl]xanthogenate (1.15 g, 3.80 mmol) in CH_2Cl_2 (15 ml) over a period of 20 min. Stirring was continued at 295 K for 2.5 h. Water (20 ml) was added and the phases were separated. The aqueous layer was washed with dichloromethane (15 ml), carefully acidified with aqueous HCl (37%) to a pH of 1.5–2.5, and extracted with CH_2Cl_2 (3 × 50 ml). The combined CH_2Cl_2 layer and organic washings were concentrated under reduced pressure to afford a residue, which was purified by recrystallization from a mixture of Et_2O–petroleum ether (b.p. 303–323 K) (10:1 *v*/*v*) at 253 K to afford (I) as yellow prisms (641 mg, 2.23 mmol, 59%; m.p. 413–414 K). Crystals suitable for X-ray diffraction were grown by allowing pentane to diffuse slowly into a saturated solution of (I) in Et_2O at 298 K.

Crystal data

$C_{10}H_8ClNOS_2$
$M_r = 257.74$
Monoclinic, $P2_1/c$
$a = 9.843$ (2) Å
$b = 14.707$ (3) Å
$c = 15.312$ (3) Å
$\beta = 92.34$ (3)°
$V = 2214.7$ (8) Å^3
$Z = 8$
Mo $K\alpha$ radiation
$\mu = 0.69$ mm^{-1}
$T = 291$ (2) K
0.30 × 0.25 × 0.20 mm

Data collection

Stoe IPDS diffractometer
Absorption correction: none
25254 measured reflections
3499 independent reflections
3008 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.054$
$\theta_{\rm max} = 24.1$°

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.030$
$wR(F^2) = 0.082$
$S = 1.04$
3499 reflections
275 parameters
H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{\rm max} = 0.26$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.25$ e Å^{-3}

Table 1
Hydrogen-bond geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
O1′—H1′···S2^{i}	0.78	2.63	3.2266 (18)	135
O1—H1···S2′^{ii}	0.85	2.55	3.1452 (18)	128
C52—H18···S2′	0.93	2.87	3.688 (2)	147
C52′—H18′···S2	0.93	2.88	3.763 (2)	158

Symmetry codes: (i) $x + 1, y, z$; (ii) $x - 1, y, z$.

Atoms H1 and H1′ were placed in geometrically idealized positions as riding atoms and then refined with fixed isotropic displacement parameters [$U_{\rm iso}$(H) = 1.5$_{\rm eq}$(O)]. All other H atoms were positioned geometrically and treated as riding atoms, with C—H = 0.93–0.96 Å and with $U_{\rm iso}$(H) = 1.2 or 1.5 times $U_{\rm eq}$(C).

Data collection: *EXPOSE* in *IPDS Software* (Stoe & Cie, 1998); cell refinement: *CELL* in *IPDS Software*; data reduction: *INTEGRATE* in *IPDS Software*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL-Plus*

(Sheldrick, 1994); software used to prepare material for publication: *SHELXTL-Plus*.

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