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Key indicators

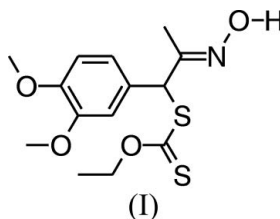
Single-crystal X-ray study
 $T = 299$ K
Mean $\sigma(\text{C}-\text{C}) = 0.006$ Å
 R factor = 0.071
 wR factor = 0.220
Data-to-parameter ratio = 16.4For details of how these key indicators were
automatically derived from the article, see
<http://journals.iucr.org/e>.O-Ethyl S-[1-(3,4-dimethoxyphenyl)-2-(hydroxy-
imino)propyl] dithiocarbonate

The stereogenic centre in the title compound, $\text{C}_{14}\text{H}_{19}\text{NO}_4\text{S}_2$, is substituted with a dithiocarbonate, an ethyloximino and a 3,4-dimethoxyphenyl group, as well as an H atom. Tandem hydrogen-bonding occurs between enantiomers to produce dimers, in which the oxime H atom serves as donor toward the oxime N atom of an adjacent molecule.

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Comment

The title compound, (I), is the starting material for the synthesis of *N*-hydroxy-5-(3,4-dimethoxyphenyl)-4-methylthiazole-2(3*H*)-thione, a molecule of notable interest for investigating substituent effects on the location of absorption bands caused by visible to near-UV light excitations in heterocyclic alkoxy radical precursors (Hartung, Špehar *et al.*, 2005). Compound (I) has been crystallized and studied by X-ray diffraction in order to gain an understanding of its structural details in the solid state.



The stereogenic centre, atom C4, is substituted by three virtually planar groups, *viz* a 3,4-dimethoxyphenyl, an *O*-ethyl dithiocarbonate and an ethyloximino group, and by one H atom (Fig. 1). The heteroatoms and the central C atom of the dithiocarbonate group are located in a plane [deviation of O2 = 0.012 (1) Å]. The stereogenic bonds associated with the latter entity adopt an (*E*) arrangement for C1–S2 and (*Z*) geometry for C1–O2. The C1–S1 distance [1.639 (4) Å] is smaller than the mean value for the C=S double bond in *O,S*-dialkyldithiocarbonates [1.67 (2) Å; Abrahamsson & Innes, 1974; Allen *et al.*, 1987; Duarte *et al.*, 1989]. The connectivities S2–C1 and S2–C4 differ in length due to different hybridization of the associated C atoms (Zhang *et al.*, 2003, Hartung, Schmidt *et al.*, 2005). The oxime group adopts an (*E*) configuration. The distances N1–O1 and N1=C3 agree with mean values for both types of connectivities (Allen *et al.*, 1987; Hartung *et al.*, 2004).

The unit cell ($Z = 4$) contains a 1:1 mixture of (*S*) and (*R*) enantiomers. A view along [001] indicates that these enantiomers are linked *via* a tandem hydrogen bond to provide dimers. The oxime H atom serves as the donor toward the oxime N atom of an adjacent molecule (Fig. 2 and Table 2).

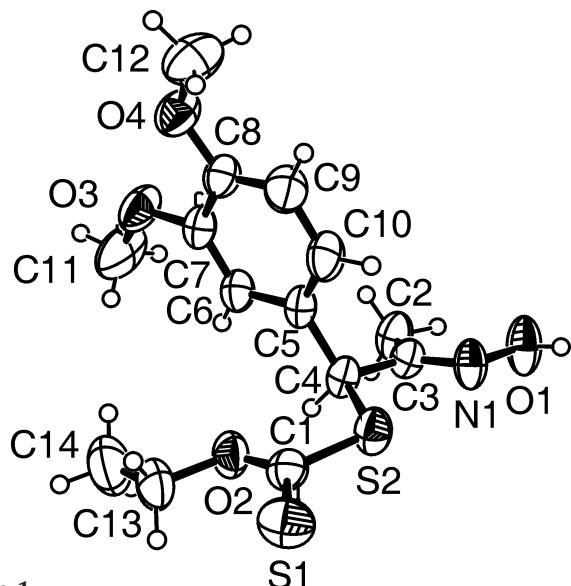


Figure 1
The molecular structure of (I). Displacement ellipsoids are drawn at the 50% probability level.

Experimental

Crystals of (I) suitable for X-ray diffraction were obtained by slowly concentrating a saturated solution of (I) in CH_2Cl_2 at 298 K. (m.p. 375–377 K). $R_f = 0.35$ [SiO_2 , petroleum ether/ $\text{Et}_2\text{O} = 2/1$ (v/v)]. Analysis, calculated for $\text{C}_{14}\text{H}_{19}\text{NO}_4\text{S}_2$: C 51.04, H 5.81, N 4.25, S 19.47%; found: C 51.21, H 5.63, N 4.33, S 19.31%. MS (70 eV, EI): m/z (%) 329 (1), 300 (3), 208 (100), 191 (33), 182 (30). ^1H NMR (CDCl_3 , 400 MHz, δ , p.p.m.): 1.38 (t, 3H, $J = 7.2$ Hz), 1.91 (s, 3H), 3.86 (s, 3H), 3.87 (s, 3H), 4.61 (q, 2H, $J = 7.1$ Hz), 5.50 (s, 1H), 6.81 (d, 1H, $J = 8.2$ Hz), 6.88 (d, 1H, $J = 1.9$ Hz), 6.93 (dd, 1H, $J = 1.9, 8.2$ Hz). ^{13}C NMR (CDCl_3 , 100 MHz, δ , p.p.m.): 13.9, 14.1, 56.3, 56.4, 58.6, 70.6, 111.6, 112.0, 121.5, 128.8, 149.4, 156.4, 213.6 (C=O).

Crystal data

$\text{C}_{14}\text{H}_{19}\text{NO}_4\text{S}_2$	$D_x = 1.297 \text{ Mg m}^{-3}$
$M_r = 329.42$	Mo $K\alpha$ radiation
Monoclinic, $P2_1/c$	Cell parameters from 1190 reflections
$a = 9.114$ (2) Å	$\theta = 2.6$ – 22.0°
$b = 7.319$ (2) Å	$\mu = 0.33 \text{ mm}^{-1}$
$c = 25.575$ (6) Å	$T = 299$ (2) K
$\beta = 98.66$ (2)°	Prism, light brown
$V = 1686.5$ (7) Å ³	$0.66 \times 0.60 \times 0.24 \text{ mm}$
$Z = 4$	

Data collection

Oxford Diffraction Xcalibur CCD diffractometer	1809 reflections with $I > 2\sigma(I)$
φ scans	$R_{\text{int}} = 0.047$
Absorption correction: none	$\theta_{\text{max}} = 26.4^\circ$
4733 measured reflections	$h = -11 \rightarrow 11$
3161 independent reflections	$k = -9 \rightarrow 8$
	$l = -31 \rightarrow 31$

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.124P)^2 + 1.166P]$
$R[F^2 > 2\sigma(F^2)] = 0.071$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.220$	$(\Delta/\sigma)_{\text{max}} = 0.002$
$S = 0.93$	$\Delta\rho_{\text{max}} = 0.40 \text{ e \AA}^{-3}$
3161 reflections	$\Delta\rho_{\text{min}} = -0.42 \text{ e \AA}^{-3}$
193 parameters	
H atoms treated by a mixture of independent and constrained refinement	

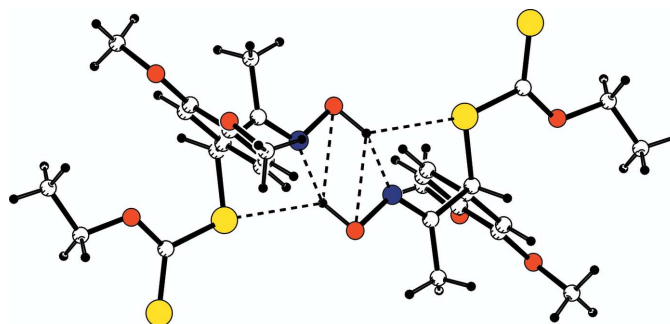


Figure 2
Visualization of the hydrogen bonding (dashed lines) between molecules of (I), viewed along [001]. O atoms are depicted in red, N atoms in blue and S atoms in yellow.

Table 1

Selected geometric parameters (Å, °).

C1–O2	1.309 (5)	C4–S2	1.831 (4)
C1–S1	1.639 (4)	C7–O3	1.370 (4)
C1–S2	1.741 (4)	C8–O4	1.377 (5)
C3–N1	1.278 (5)	N1–O1	1.417 (4)
O2–C1–S1	127.5 (3)	C3–C4–C5	110.1 (3)
O2–C1–S2	113.9 (3)	C3–C4–S2	109.5 (2)
S1–C1–S2	118.7 (2)	C5–C4–S2	112.9 (3)
N1–C3–C2	124.4 (3)	C3–N1–O1	111.8 (3)
N1–C3–C4	117.0 (3)	N1–O1–H1	93 (3)
C2–C3–C4	118.6 (3)		
C2–C3–N1–O1	−0.2 (6)	C8–C7–O3–C11	174.7 (5)
C4–C3–N1–O1	−180.0 (3)	C7–C8–O4–C12	172.8 (4)

Table 2

Hydrogen-bond geometry (Å, °).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
O1–H1 \cdots N1 ⁱ	0.91 (6)	1.90 (6)	2.786 (5)	164 (5)

Symmetry code: (i) $-x + 1, -y + 2, -z$.

Atom H1 was located in a difference Fourier map and its atomic coordinates were refined, with $U_{\text{iso}}(\text{H1}) = 1.2U_{\text{eq}}(\text{O1})$. All other H atoms were positioned geometrically and treated as riding atoms, with C–H distances in the range 0.93–0.96 Å and with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$.

Data collection: *CrysAlis CCD* (Oxford Diffraction, 2002); cell refinement: *CrysAlis RED* (Oxford Diffraction, 2002); data reduction: *CrysAlis RED*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *PLATON-2002* (Spek, 2003) and *ORTEP-3* (Farrugia, 1997); software used to prepare material for publication: *SHELXL97*.

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