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3-(1-Methyl-1-phenylethoxy)-1,3-thiazole-2(3*H*)-thione: a tertiary thiohydroxamic acid *O*-ester

Jens Hartung,* Nina Schneiders and Uwe Bergsträsser

Organische Chemie, Fachbereich Chemie, Technische Universität Kaiserslautern, Erwin-Schrödinger-Strasse, D-67663 Kaiserslautern, Germany

Correspondence e-mail: hartung@chemie.uni-kl.de

Key indicators

Single-crystal X-ray study
T = 293 K
Mean σ(C–C) = 0.004 Å
Disorder in main residue
R factor = 0.035
wR factor = 0.085
Data-to-parameter ratio = 13.6

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

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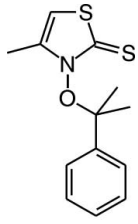
The steric demand of a tertiary alkyl substituent attached to the thiohydroxamate O atom in the title compound, $C_{13}H_{15}NOS_2$, is reflected in a widening of the associated N—O—C angle [116.4 (2)°]. Close contacts along [100] indicate C—H···S interactions in the crystal structure.

Comment

3-(1-Methyl-1-phenylethoxy)-1,3-thiazole-2(3*H*)-thione, (I), is a photolabile compound that undergoes facile *N*,*O*-homolysis upon UV–vis photolysis or if heated in the presence of a free radical initiator (Hartung *et al.*, 2006). The compound was prepared and investigated by X-ray diffraction in order to study the hitherto unknown geometry of tertiary thiohydroxamic acid *O*-esters.



(I)

The cumyl substituent of (I) is rotated by 95.6 (2)° from the plane defined by the thiohydroxamate entity and the *N*,*C*-bridging vinyl–thiyl subunit, as measured by the appropriate torsion angles (Table 1). The unit cell comprises a 1:1 mixture of *P*- and *M*-rotamers with respect to the configuration about the stereogenic N—O axis. In $CDCl_3$ solution (298 K), a fast rotation about this axis occurs, as is evident from the topomerization of prochiral substituents, *i.e.* $C8H_3$ and $C9H_3$.

Bond lengths and angles within the heterocyclic core and those associated with the thiohydroxamate functionality

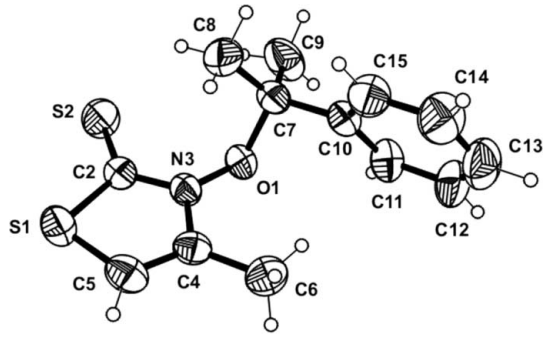


Figure 1
The molecular structure of (I). Displacement ellipsoids are plotted at the 50% probability level. Only one disorder component is shown.

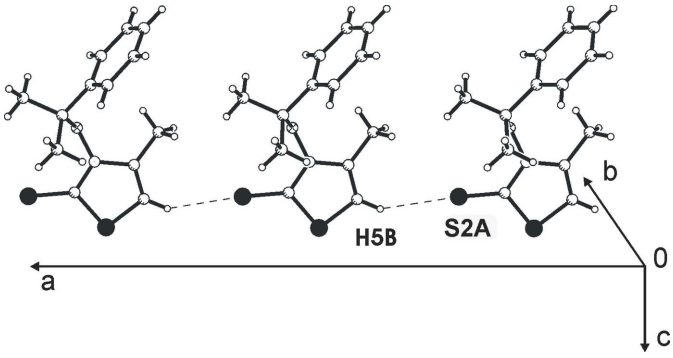


Figure 2
The packing of (I) in the crystal structure, viewed approximately along [010]. Hydrogen bonds are drawn as dashed lines.

(Table 1) correspond to values reported previously for a secondary *N*-alkoxy (Hartung *et al.*, 2003) and an *N*-(alkoxycarbonyloxy) (Hartung *et al.*, 2005) derivative of *N*-hydroxy-4-methylthiazole-2(3*H*)thione. The major difference between the reference data and those of compound (I) is due to a significant widening of the N3—O1—C7 angle [116.4 (2) °]. The origin of this feature is probably associated with the steric demand of the cumyl substituent attached to O1.

The packing of (I) in the unit cell (Z = 4, $P2_1/c$) leads to close H5*B*···S2^{i} (2.93 Å) contacts along [100] (Fig. 2 and Table 2). The separation of these atoms and the associated angle at H5*B* indicate C—H···acceptor interactions between C5H and C═S (Steiner, 1996; Hartung *et al.*, 2005).

Experimental

2-Phenyl-2-propanol (1.10 g, 8.08 mmol), CuCl (16.0 mg, 0.162 mmol) and diisopropyl carbodiimide (1.02 g, 8.08 mmol) were stirred in anhydrous dichloromethane (5 ml) for 24 h. A solution of *N*-hydroxy-4-methylthiazole-2(3*H*)-thione (1.31 g, 8.89 mmol) (Barton *et al.*, 1986) in anhydrous dichloromethane (20 ml) was added at 203 K. The reaction mixture was stirred at 293 K for 45 h. The solids were filtered off and the solvent was removed under reduced pressure. The residue was purified by column chromatography [SiO_2, pentane–diethyl ether, 2:1 (*v*/*v*), R_f = 0.44] to afford colourless crystals of (I) (yield 70.0 mg, 0.26 mmol, 3%). Crystals suitable for X-ray analysis were obtained from a saturated solution of (I) in diethyl ether (m.p. 379 K). Analysis, calculated for $C_{13}H_{15}NOS_2$: C 58.83, H 5.70, N 5.28%; found: C 58.98, H 5.68, N 5.26%.

Crystal data

$C_{13}H_{15}NOS_2$
M_r = 265.38
Monoclinic, $P2_1/c$
a = 7.7504 (16) Å
b = 18.363 (4) Å
c = 9.788 (2) Å
β = 102.16 (3)°
V = 1361.9 (5) Å^3
Z = 4
D_x = 1.294 Mg m^{-3}
Mo $K\alpha$ radiation
μ = 0.37 mm^{-1}
T = 293 (2) K
Prism, colourless
0.35 × 0.25 × 0.20 mm

Data collection

Stoe IPDS diffractometer
φ scans
Absorption correction: none
10870 measured reflections
2099 independent reflections
1278 reflections with $I > 2\sigma(I)$
R_{int} = 0.090
θ_{max} = 24.2°

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.035
$wR(F^2)$ = 0.085
S = 0.92
2099 reflections
154 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0355P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.19 e Å^{-3}
$\Delta\rho_{min}$ = −0.22 e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

S1—C2	1.720 (3)	C2—N3	1.362 (3)
S1—C5	1.727 (3)	N3—C4	1.406 (3)
O1—N3	1.370 (2)	C4—C5	1.317 (4)
O1—C7	1.511 (3)	C4—C6	1.487 (4)
S2—C2	1.654 (2)		
C2—S1—C5	91.99 (13)	C2—N3—C4	116.9 (2)
N3—O1—C7	116.41 (16)	O1—N3—C4	121.86 (19)
N3—C2—S2	128.04 (19)	C5—C4—N3	110.2 (2)
N3—C2—S1	107.55 (16)	C5—C4—C6	129.0 (2)
S2—C2—S1	124.40 (15)	N3—C4—C6	120.7 (2)
C2—N3—O1	120.20 (18)	C4—C5—S1	113.1 (2)
S2—C2—N3—O1	−5.9 (3)	C7—O1—N3—C2	95.6 (2)

Table 2
Hydrogen-bond geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
C5—H5···S2^{i}	0.93	2.93	3.713 (3)	142

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

The H-atom sites at C6 are disordered, probably due to a 0.5:0.5 population of CH_3 rotamers with a skew angle of 60°. The group was refined as a disordered methyl group with six half-occupied geometrically idealized positions for the H atoms. All other H atoms were positioned geometrically and treated as riding atoms, with C—H distances set to 0.96 (for CH_3) or 0.93 Å (Csp^2—H) and with U_{iso}(H) = 1.2U_{eq}(Csp^2—H) or 1.5U_{eq}(CH_3).

Data collection: *EXPOSE* in *IPDS Software* (Stoe & Cie, 1998); cell refinement: *EXPOSE*; data reduction: *EXPOSE*; 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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