

## 4-(4-Chlorophenyl)-3-(4-phenylpent-4-enyloxy)-1,3-thiazole-2(3H)-thione

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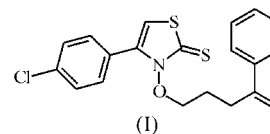
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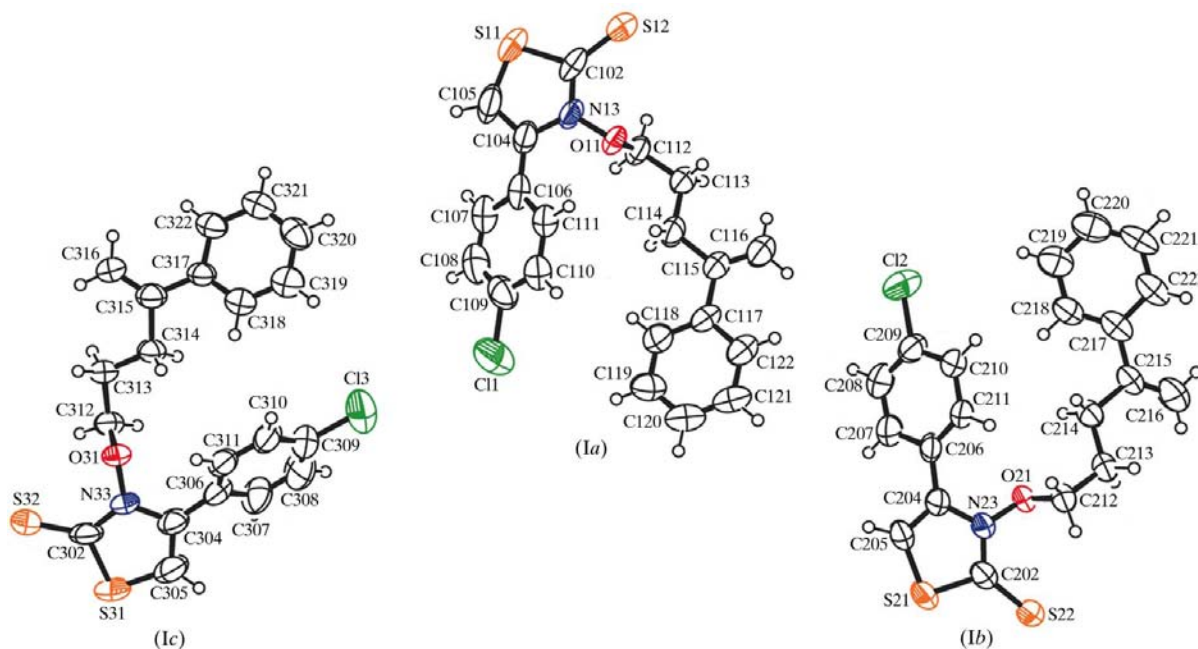
The title compound, C<sub>20</sub>H<sub>18</sub>ClNOS<sub>2</sub>, is a thiazole-derived thiohydroxamic acid O-ester. The value of *Z'* is 3 and the asymmetric unit comprises three molecules of identical helicity along the N—O bond. Two of these show an *anti* and the third a *syn* arrangement of substituents attached in positions 3 and 4 to the 1,3-thiazole nucleus.

### Comment

The title compound, (I), furnishes 3-phenyltetrahydropyran as the major non-thiazole-derived product if photolyzed in the presence of reactive H-atom donors. The 4-methyl derivative of (I), *i.e.* 4-(4-chlorophenyl)-3-(4-methylpent-4-enyloxy)thiazole-2(3H)-thione, affords 2,2-dimethyltetrahydrofuran as the major cyclic ether under identical conditions (Hartung *et al.*, 1999, 2004). This unexpected complementary selectivity initiated a series of experimental and theoretical studies directed toward elucidating polar and steric substituent effects in the underlying ring closure, *i.e.* the 4-penten-1-oxyl radical cyclization (Gottwald *et al.*, 2004; Hartung *et al.*, 2004). In order to correlate regioselectivities with conformational preferences, NOE experiments were conducted in CDCl<sub>3</sub> solution, however, without leading to decisive results. In view of these difficulties, the crystal structure of 4-(4-chlorophenyl)-3-(4-phenylpent-4-enyloxy)thiazole-2(3H)-thione, (I), was investigated. The results of the study are outlined below.



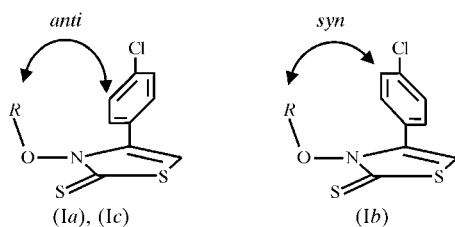
Compound (I) forms colorless hexagonal rods and crystallizes in the trigonal space group *P*31c. The trigonal symmetry of the racemic crystal structure is evident from a projection of the unit cell (*Z* = 18) along [001]. The asymmetric unit comprises three molecules, denoted (Ia), (Ib) and (Ic), and chosen to have identical helicity with respect to the stereo-



**Figure 1**

The molecular structures of crystallographically independent molecules (Ia)–(Ic) in the solid state. Displacement ellipsoids are drawn at the 50% probability level. H atoms are shown as small circles of arbitrary radius.

genic N—O axis (Table 1 and Fig. 1). Geometrical details of the 1,3-thiazolidinethione substructure of molecules (Ia)–(Ic) are similar to those reported for 3-acetoxy-4-(4-chlorophenyl)-1,3-thiazole-2(3*H*)-thione, 4-(4-chlorophenyl)-3-hydroxy-1,3-thiazole-2(3*H*)-thione, and two secondary 3-(alkoxy)-4-(4-chlorophenyl)-1,3-thiazole-2(3*H*)-thiones (Hartung *et al.*, 1999). Marked differences, however, were noted for bond angles at *On*1 ( $n = 1–3$ ), which are smaller than the reference data for secondary derivatives and 3-acetoxy-4-(4-chlorophenyl)-1,3-thiazole-2(3*H*)-thione. The values determined for molecules (Ia)–(Ic), on the other hand, are larger than the N—O—H angle found in the crystal structure of 4-(4-chlorophenyl)-3-hydroxy-1,3-thiazole-2(3*H*)-thione (Hartung *et al.*, 1999). It is therefore tempting to interpret this sequencing of angles in terms of differences in steric congestion caused by substituents at oxygen in cyclic thiohydroximates of this type. The dihedral angle associated with the offset of *Cn*12 is slightly larger than the tilt of the 1,3-thiazolidinethione plane from the 4-chlorophenyl plane (Table 1). The relative orientation of the two substituents is *anti* in molecules (Ia) and (Ic), and *syn* in (Ib) (Fig. 2). A survey of the literature indicated that a *syn* arrangement has hitherto not been reported for solid-state geometries of *O*-acyl or *O*-alkyl derivatives of 4-(4-chlorophenyl)-3-hydroxy-1,3-thiazole-2(3*H*)-thione (Hartung *et al.*, 1999, 2006). The situation is different in isotropic media. In solution, both conformers exist. This argumentation originates from a topomerization of substituents due to rotation about the N—O bond (Hartung *et al.*, 2001). Data from a computational study on the *N*-methoxy derivative of (I) predict that the *anti* arrangement is lower in conformational free energy than the *syn* rotamer, at least in the applied model that refers to the gas phase (Hartung *et al.*, 2006). The alkenoxy chain, *i.e.* the reactive part of the molecule upon UV–Vis excitation, shows a +synclinal positioning of atoms *On*1—*Cn*12—*Cn*13—*Cn*14, antiperiplanar for *Cn*12—*Cn*13—*Cn*14—*Cn*15, and synperiplanar for *Cn*13—*Cn*14—*Cn*15—*Cn*16 in thiones (Ia)–(Ic) (Table 1). This orientation gives rise to a notable distance between atoms that undergo C—O bond formation upon N—O homolysis [*O*11...*C*116 = 5.028 (8) Å for (Ia), *O*21...*C*216 = 4.986 (8) Å for (Ib) and *O*31...*C*316 = 5.013 (8) Å for (Ic)]. The only conformational change that is, however, necessary in order to convert the side-chain arrangement seen in the crystal structure of (I) into a geometry that closely resembles the calculated lowest energy



**Figure 2**

Visualization of the *anti* and *syn* arrangements of substituents attached to the thiazole-2(3*H*)-thione entity in (I) ( $R = 4\text{-phenyl-4-penten-1-yl}$ ).

transition structure of the 6-*endo*-trig 4-phenyl-4-pentenyl-1-oxyl radical ring closure, is a rotation about the *Cn*13—*Cn*14 ( $n = 1–3$ ) bond. Torsional movements like this are readily feasible at 298 K in solution. In view of the planar solid-state geometry of  $\alpha$ -methylstyrene (Bond & Davies, 2002), it was surprising to note that the planes of the olefinic  $\pi$ -bond and the phenyl group are tilted by 20.1 (1) $^\circ$  in (Ia),  $-31.9$  (9) $^\circ$  in (Ib) and  $-31.9$  (9) $^\circ$  in (Ic), as measured by appropriate torsion angles (Table 1). This finding, however, correlates with the calculated dihedral angle in the equilibrium structure of the 4-phenylpent-4-enyl-1-oxyl radical in the gas phase (40.3 $^\circ$ ; Hartung *et al.*, 2004). This feature is an important aspect in the model that was established for interpreting the origin of the 6-*endo* selectivity in cyclizations of 4-substituted pent-4-en-1-oxyl radicals on the basis of relative orbital energies (Hartung *et al.* 2004).

## Experimental

Crystals suitable for X-ray diffraction analysis (see supplementary material) were obtained from a saturated solution of 4-(4-chlorophenyl)-3-(4-phenyl-4-pentenyl-1-oxyl)thiazole-2(3*H*)-thione (Hartung *et al.*, 1999) in diethyl ether, which was stored at 293 K under an atmosphere saturated with *n*-pentane vapour.

### Crystal data

$C_{20}H_{18}ClNOS_2$	$D_x = 1.331 \text{ Mg m}^{-3}$
$M_r = 387.92$	Mo $K\alpha$ radiation
Trigonal, $P31c$	$\mu = 0.42 \text{ mm}^{-1}$
$a = 36.2171$ (1) Å	$T = 293$ (2) K
$c = 7.6695$ (1) Å	Hexagonal rod, colourless
$V = 8712.14$ (12) Å <sup>3</sup>	$0.48 \times 0.20 \times 0.20 \text{ mm}$
$Z = 18$	

### Data collection

Bruker SMART CCD area-detector diffractometer	10106 independent reflections
$\omega$ and $\varphi$ scans	8858 reflections with $I > 2\sigma(I)$
49608 measured reflections	$R_{\text{int}} = 0.036$
	$\theta_{\text{max}} = 25.7^\circ$

### Refinement

Refinement on $F^2$	$w = 1/[\sigma^2(F_o^2) + (0.0132P)^2 + 4.1632P]$
$R[F^2 > 2\sigma(F^2)] = 0.049$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.096$	$(\Delta/\sigma)_{\text{max}} = 0.001$
$S = 1.30$	$\Delta\rho_{\text{max}} = 0.14 \text{ e \AA}^{-3}$
10106 reflections	$\Delta\rho_{\text{min}} = -0.16 \text{ e \AA}^{-3}$
677 parameters	Absolute structure: Flack (1983)
H-atom parameters constrained	Flack parameter: 0.11 (7)

All H atoms were positioned geometrically and treated as riding atoms ( $C-H = 0.93–0.98$  Å), with  $U_{\text{iso}}(\text{H})$  values set at  $1.2U_{\text{eq}}$  of the parent atom.

Data collection: *SMART* (Bruker, 1999); cell refinement: *SMART*; data reduction: *SMART* and *SHELXTL* (Bruker, 1998); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *PLATON* (Spek, 2003) and *ORTEP-3* (Farrugia, 1997, 2005); software used to prepare material for publication: *SHELXL97*.

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**Table 1**

Selected geometric parameters (Å, °).

O11–N13	1.387 (4)	N23–C204	1.397 (6)
C102–N13	1.356 (6)	C204–C205	1.336 (6)
C102–S12	1.650 (6)	C205–S21	1.724 (6)
C102–S11	1.737 (5)	O31–N33	1.387 (4)
N13–C104	1.393 (6)	C302–N33	1.360 (6)
C104–C105	1.350 (7)	C302–S32	1.646 (5)
C105–S11	1.706 (7)	C302–S31	1.742 (4)
O21–N23	1.391 (4)	N33–C304	1.400 (6)
C202–N23	1.336 (6)	C304–C305	1.350 (7)
C202–S22	1.669 (6)	C305–S31	1.697 (7)
C202–S21	1.733 (5)		
N13–C102–S11	105.7 (4)	C205–C204–N23	110.4 (4)
C102–N13–C104	118.7 (4)	C204–C205–S21	111.8 (4)
C105–C104–N13	110.2 (5)	C205–S21–C202	92.3 (2)
C104–C105–S11	111.6 (4)	N33–C302–S31	105.6 (3)
C105–S11–C102	93.7 (3)	C302–N33–C304	119.1 (4)
N23–C202–S21	107.2 (4)	C305–C304–N33	109.0 (5)
C202–N23–C204	118.1 (4)	C304–C305–S31	113.1 (4)
C112–O11–N13–C102	–84.3 (5)	C212–C213–C214–C215	173.6 (5)
N13–C104–C106–C111	40.1 (8)	C213–C214–C215–C216	10.7 (9)
O11–C112–C113–C114	71.3 (6)	C216–C215–C217–C222	–31.9 (9)
C112–C113–C114–C115	173.9 (5)	C312–O31–N33–C302	–82.9 (5)
C113–C114–C115–C116	–0.8 (10)	N33–C304–C306–C311	47.4 (8)
C116–C115–C117–C122	20.1 (10)	O31–C312–C313–C314	69.9 (5)
C212–O21–N23–C202	–77.0 (6)	C312–C313–C314–C315	172.8 (4)
N23–C204–C206–C211	–47.4 (8)	C313–C314–C315–C316	10.6 (9)
O21–C212–C213–C214	64.6 (5)	C316–C315–C317–C322	–31.7 (9)

Supplementary data for this paper are available from the IUCr electronic archives (Reference: HJ1090). Services for accessing these data are described at the back of the journal.

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