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5-(4-Methoxyphenyl)-4-methyl-2-thioxo-2,3-dihydro-1,3-thiazol-3-yl benzoate at 100 K

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A Z arrangement of substituents about the carboxylate C—O bond causes a *syn* positioning of the carbonyl O atom and the heterocyclic part of the title compound, $C_{18}H_{15}NO_3S$. The carboxylate entity is inclined by −28.1 (3)° to the phenyl group. The planes of the thiazol-2(3*H*)-thione subunit and the carboxylate group are orthogonally arranged.

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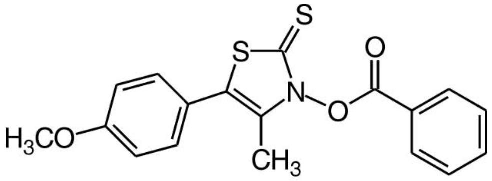
Key indicators

Single-crystal X-ray study
T = 100 K
Mean σ(C–C) = 0.003 Å
R factor = 0.037
wR factor = 0.090
Data-to-parameter ratio = 12.9

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

Comment

O-Alkyl derivatives of *N*-hydroxy-5-(4-methoxyphenyl)-4-methyl-1,3-thiazole-2(3*H*)-thione liberate oxygen-centered radicals if photolyzed with incandescent light (Hartung *et al.*, 2003, 2005). In a similar way, visible-light induced reactions of *N*-acyloxy-5-(*p*-methoxyphenyl)-4-methylthiazole-2(3*H*)-thiones are considered to afford acyloxyl radicals that upon decarboxylation furnish carbon radicals as valuable intermediates in organic synthesis (Crich Hartung *et al.*, 2005). In order to probe this hypothesis, 5-(4-methoxyphenyl)-4-methyl-2-thioxo-2,3-dihydro-1,3-thiazol-3-yl benzoate, (I), was prepared by adapting literature procedures (Barton *et al.*, 1985; Hartung *et al.*, 1999). The identity of the thermally and photochemically labile compound (I) was verified by X-ray diffraction analysis, which was performed at 100 K (Fig. 1).



(I)

The OCH$_3$ substituent is located in the plane of the attached aryl ring, presumably for reasons of a maximum overlap between one of the non-bonding electron pairs on the oxygen

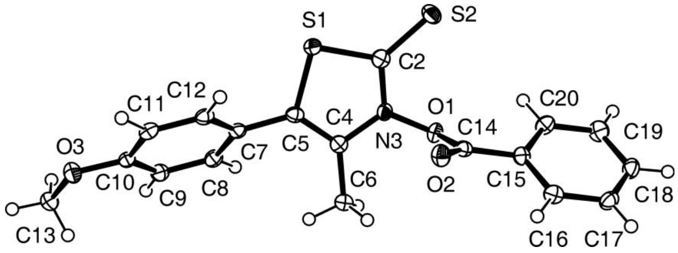


Figure 1
The molecular structure of (I). Displacement ellipsoids are drawn at the 50% probability level.

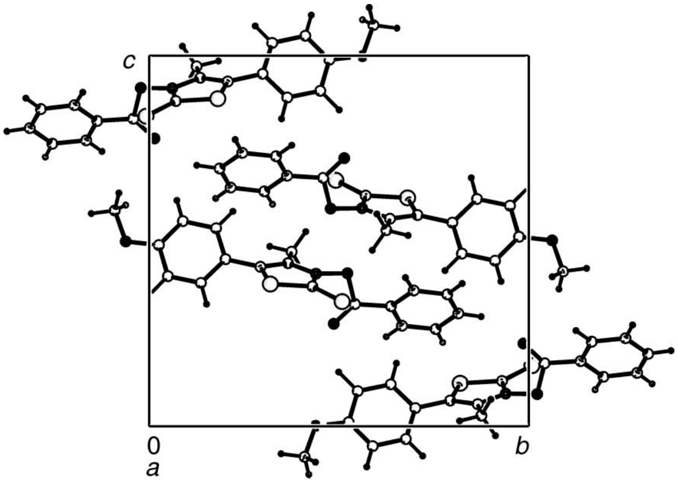


Figure 2
Packing of racemic (I) in the unit cell, viewed along [100]. The two *m*-configured molecules are located in the upper and the *p*-arranged enantiomers positioned in the lower section of the unit cell.

and the aromatic π-system [C9—C10—O3—C13 = 0.3 (3)°; Fig. 1]. The 4-methoxyphenyl group is tilted by C4—C5—C7—C8 = 51.3 (3)° from the thiazolethione plane that is defined by atoms S1, C2, N3, C4 and C5 [deviation of 0.002 (4) Å for C2 and 0.025 (4) Å for N3]. The N3—O1 bond [1.389 (2) Å] in (I) is longer and the distance C2—S2 [1.662 (2) Å] is shorter than the corresponding values reported for *N*-hydroxy-5-(4-methoxyphenyl)-4-methyl-1,3-thiazole-2(3*H*)-thione [N—O = 1.373 (3) Å and C═S = 1.676 (3) Å; Hartung *et al.*, 2005]. The carboxylate functionality exhibits Z geometry [O2—C14—O1—N3 = −16.8 (3)°]. It is tilted by O2—C14—C15—C16 = −28.0 (3)° from the plane of the phenyl ring and by C2—N3—O1—C14 = −89.7 (2) Å from the thiazole-2(3*H*)-thione plane. A view along 100 indicates that the unit cell ($Z = 4$) comprises a racemate of (I), *i.e.* a 1:1 mixture of P and M enantiomers with respect to the configuration at the stereogenic N3—O1 axis (Fig. 2) (Hartung *et al.*, 2001).

Experimental

A slurry of the *N*-hydroxy-5-(4-methoxyphenyl)-4-methyl-1,3-thiazole-2(3*H*)-thione sodium salt (554 mg, 2.02 mmol) (Hartung *et al.*, 2005) in CH_2Cl_2 (10 ml) was treated at 298 K with neat benzoyl chloride (283 mg, 2.0 mmol). The solids were removed by filtration. The filtrate was concentrated under reduced pressure to furnish a residue, which was crystallized from diethyl ether/*n*-pentane (2/1, *v*/*v*) to furnish 684 mg (95%) of (I) as light brown prisms. Crystals obtained from this crop were suitable for X-ray diffraction analysis. Calculated: C 60.50, H 4.20, N 3.92%; found: C 59.71, H 4.16, N 3.23%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.26 (*d*, $J = 7.5$ Hz, 2H), 7.73 (*t*, $J = 7.5$ Hz, 2H), 7.57 (*t*, $J = 7.5$ Hz, 1H), 7.30 (*d*, $J = 8.8$ Hz, 2H), 6.97 (*d*, $J = 8.8$ Hz, 2H), 3.84 (*s*, 3H), 2.27 (*s*, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 12.5, 55.9, 115.1, 119.5, 122.6, 125.6, 129.5, 130.4, 131.1, 132.2, 135.6, 160.5, 162.8, 179.7. UV/vis (CH_2Cl_2): λ (lg ε) = 318 (3.98), 231 (4.36) nm. IR (KBr): ν = 2963, 1175, 1510, 1301, 1257, 1174, 1036, 821 cm^{-1}.

Crystal data

$C_{18}H_{15}NO_3S_2$
$M_r = 357.43$
Monoclinic, $P2_1/c$
$a = 7.3037$ (5) Å
$b = 15.287$ (1) Å
$c = 14.985$ (1) Å
$\beta = 92.735$ (7)°
$V = 1671.2$ (2) Å^3
$Z = 4$
$D_x = 1.421$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 2804 reflections
$\theta = 2.8$–24.0°
$\mu = 0.33$ mm^{-1}
$T = 100$ (2) K
Prism, light brown
0.36 × 0.14 × 0.12 mm

Data collection

Oxford Diffraction Xcalibur diffractometer with a Sapphire CCD detector
ω scans
Absorption correction: none
10 562 measured reflections
3376 independent reflections
2885 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.037$
$\theta_{\rm max} = 26.4$°
$h = -9 \rightarrow 6$
$k = -19 \rightarrow 19$
$l = -18 \rightarrow 18$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.037$
$wR(F^2) = 0.090$
$S = 1.10$
3376 reflections
262 parameters
Only coordinates of H atoms refined
$w = 1/[\sigma^2(F_o^2) + (0.0392P)^2 + 0.8411P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\rm max} = 0.011$
$\Delta\rho_{\rm max} = 0.32$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.24$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

C2—N3	1.357 (2)	C5—C7	1.471 (3)
C2—S1	1.7290 (19)	C5—S1	1.7567 (18)
C4—C5	1.352 (3)	C14—O2	1.192 (2)
C4—N3	1.396 (2)	C14—O1	1.415 (2)
C4—C6	1.488 (3)	C14—C15	1.476 (3)
N3—C2—S1	106.09 (13)	C2—N3—O1	118.70 (14)
C5—C4—N3	109.99 (16)	C2—N3—C4	119.78 (15)
C4—C5—S1	110.83 (14)	N3—O1—C14	111.00 (13)
O2—C14—O1	121.73 (16)	C2—S1—C5	93.27 (9)

All H atoms were located in a difference Fourier map and refined. Their displacement parameters were constrained with $U_{\rm iso}$(H) values set at $1.2U_{\rm eq}$ of the parent atom.

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: *PLATON2003* (Spek, 2003) and *ORTEP-3 for Windows* (Farrugia, 1997, 2005); software used to prepare material for publication: *SHELXL97*.

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