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Key indicators

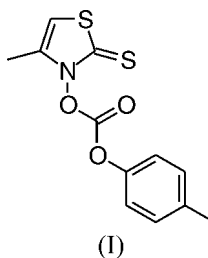
Single-crystal X-ray study
 $T = 293$ K
Mean $\sigma(\text{C}-\text{C}) = 0.011$ Å
 R factor = 0.071
 wR factor = 0.150
Data-to-parameter ratio = 12.1For details of how these key indicators were
automatically derived from the article, see
<http://journals.iucr.org/e>.4-Methyl-2-thioxo-2,3-dihydrothiazol-3-yl
4-methylphenyl carbonateThe *p*-cresyl substituent is inclined by -69.5 (10)° and the heterocyclic subunit is tilted by 88.4 (7)° with respect to the bridging carbonate functionality in the title compound, $\text{C}_{12}\text{H}_{11}\text{NO}_3\text{S}_2$.

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Comment

The title compound, (I), constitutes the first example of a carbonic acid derivative of *N*-hydroxy-4-methylthiazole-2(3*H*)-thione (Schneiders, 2004). Its identity was verified by X-ray crystallography (Fig. 1).

In (I), the endocyclic bond lengths decrease along the series $\text{C}5-\text{S}1 = 1.715$ (8) Å, $\text{C}2-\text{S}1 = 1.729$ (7) Å, $\text{N}3-\text{C}4 = 1.400$ (8) Å, $\text{N}3-\text{C}2 = 1.327$ (9) Å and $\text{C}4-\text{C}5 = 1.334$ (9) Å, whereas the angles increase along the series $\text{C}2-\text{S}1-\text{C}5 = 92.7$ (3)°, $\text{N}3-\text{C}2-\text{S}1 = 105.6$ (4)°, $\text{C}5-\text{C}4-\text{N}3 = 107.8$ (6)°, $\text{C}4-\text{C}5-\text{S}1 = 113.0$ (5)° and $\text{C}2-\text{N}3-\text{C}4 = 120.8$ (6)°. These parameters show that the heterocyclic ring is distorted from a regular pentagon. The $\text{C}2-\text{S}2$ distance [1.648 (6) Å] is close to the thiocarbonyl bond lengths observed in structurally related cyclic thiohydroxamates (Bond & Jones, 2000; Hartung *et al.*, 1996, 2003). The $\text{N}3-\text{O}1$ bond is 1.407 (7) Å, longer

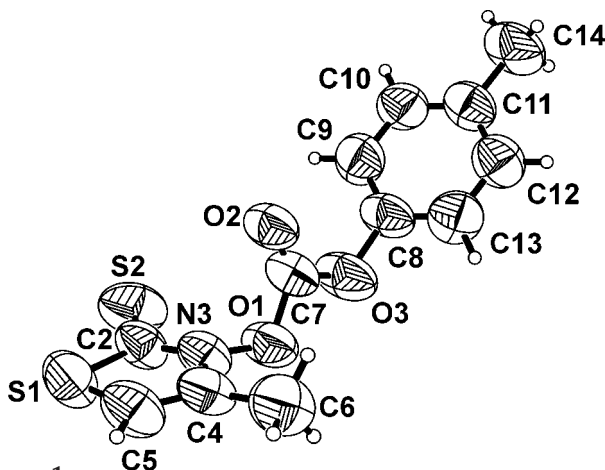


Figure 1
The molecular structure of (I). Displacement ellipsoids are drawn at the 50% probability level.

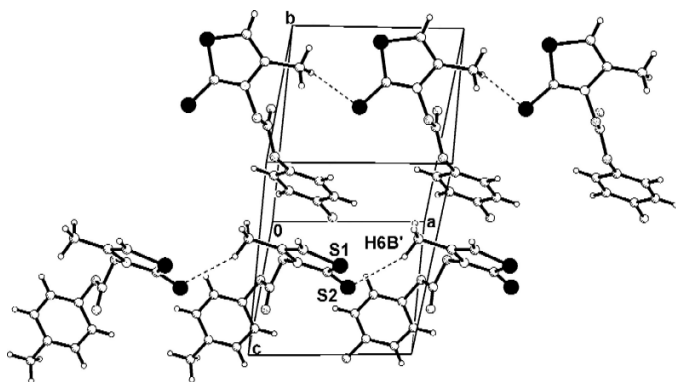


Figure 2
View of the close H6B...S2 contacts along [100] in the crystal structure of (I).

than corresponding values in *O*-alkyl esters of thiohydroxamic acids (Hartung *et al.*, 1999, 2003). It comes close to the value determined for the N–O bond in *N*-(acetyloxy)-4-(*p*-chlorophenyl)thiazole-2(3*H*)-thione (Hartung *et al.*, 1999). The angles associated with the carbonate functionality decrease from O2–C7–O3 = 130.6 (6)° via O1–C7–O2 = 128.3 (7)° to O1–C7–O3 = 100.9 (6)°. The distance C7–O2 = 1.139 (8) Å is unexpectedly short for a Csp²=O bond (Allen *et al.*, 1987). The two substituents of the carbonic acid ester functionality are connected via a shorter [C7–O3 = 1.347 (9) Å] and a longer bond C–O bond to C7 [C7–O1 = 1.383 (8) Å]. The four atoms of the carbonate subunit form a plane [deviation of O1 from O2/C7/O3 is 0.13 (3) Å], which is inclined by C2–N3–O1–C7 = 88.4 (7)° to the plane of the thiazolethione subunit [N3–C4–C5–S1 = –0.1 (8)° and C5–S1–C2–N3 = –1.6 (6)°] and by C9–C8–O3–C7 = –69.5 (10)° to the *p*-cresyl plane [C8–C9–C10–C11 = –0.7 (13)° and C11–C12–C13–C8 = –0.4 (12)°].

The packing of (I) in the unit cell gives rise to short S2...H6B distances (S2...H6B = 2.99 Å), which, in combination with the associated S2...H6B–C6B angle (154°), points to a weak C–H...acceptor interaction between C=S and C6H₃ (Steiner, 1996; Hartung *et al.*, 2003) along [100] (Fig. 2).

Experimental

N-Hydroxy-4-methylthiazole-2(3*H*)thione potassium salt (908 mg, 5.01 mmol) was treated with *p*-methylphenyl chloroformate (855 mg, 5.01 mmol) (Horwell *et al.*, 1991) in anhydrous acetonitrile (30 ml) (Schneiders, 2004). The reaction mixture was stirred for 5 min at 298 K. The solids were filtered off and the solvent was removed under reduced pressure. The residue was crystallized from Et₂O to furnish (I) (591 mg, 42%). Crystals suitable for X-ray analysis were obtained from a saturated solution of (I) in diethyl ether (m.p. = 358 K). Analysis calculated for C₁₂H₁₁NO₃S₂: C 51.23, H 3.94, N 4.98%; found: C 51.22, H 4.08, N 5.01%; ¹H NMR (200 MHz, CDCl₃, p.p.m.): 2.31 (*d*, *J* = 1.3 Hz, 3H), 2.37 (*s*, 3H), 6.25 (*q*, *J* = 1.3, 1H), 7.21 (*m_c*, 4H); ¹³C (100 MHz, CDCl₃, p.p.m.): 13.2, 20.8, 102.2, 119.9, 130.2, 136.5, 136.9, 148.6, 149.9, 180.1; IR (KBr): 3106, 2922, 1816, 1600, 1342, 1322, 1228, 1175, 1160, 1135 cm⁻¹; MS (70 eV, EI): *m/z* (%) = 281 (8) [*M*⁺], 207 (100), 196 (47), 147 (35), 131 (80), 99 (51), 71 (73).

Crystal data

C₁₂H₁₁NO₃S₂
M_r = 281.34
 Monoclinic, *P*2₁
a = 7.1730 (14) Å
b = 12.267 (3) Å
c = 7.8680 (16) Å
 β = 100.75 (3)°
V = 680.2 (2) Å³
Z = 2

D_x = 1.374 Mg m⁻³
 Mo *K*α radiation
 Cell parameters from 6004 reflections
 θ = 2.6–24.1°
 μ = 0.39 mm⁻¹
T = 293 (2) K
 Prism, yellow
 0.45 × 0.30 × 0.20 mm

Data collection

Stoe IPDS diffractometer
 φ scans
 6164 measured reflections
 2015 independent reflections
 1299 reflections with *I* > 2σ(*I*)

*R*_{int} = 0.156
 θ_{\max} = 24.2°
h = –7 → 7
k = –14 → 14
l = –9 → 8

Refinement

Refinement on *F*²
R [*F*² > 2σ(*F*²)] = 0.071
wR (*F*²) = 0.150
S = 1.14
 2015 reflections
 166 parameters
 H-atom parameters constrained
 $w = 1/[\sigma^2(F_o^2) + (0.0152P)^2 + 0.158P]$
 where $P = (F_o^2 + 2F_c^2)/3$

(Δ/σ)_{max} < 0.001
 $\Delta\rho_{\max} = 0.16 \text{ e } \text{Å}^{-3}$
 $\Delta\rho_{\min} = -0.23 \text{ e } \text{Å}^{-3}$
 Extinction correction: *SHELXL97*
 Extinction coefficient: 0.053 (6)
 Absolute structure: Flack (1983),
 856 Friedel pairs
 Flack parameter = 0.28 (17)

Table 1

Hydrogen-bonding geometry (Å, °).

<i>D</i> –H... <i>A</i>	<i>D</i> –H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> –H... <i>A</i>
C6–H6B...S2 ⁱ	0.96	2.99	3.880 (9)	154

Symmetry code: (i) *x* – 1, *y*, *z*.

All H atoms were placed in geometrically idealized positions (C–H = 0.93–0.96 Å) and refined as riding, with *U*_{iso}(H) = 1.2 or 1.5 times *U*_{eq}(C). The high value of *R*_{int} is probably due to the fact that the crystal is a weak scatterer.

Data collection: *EXPOSE* (Stoe & Cie, 1998); cell refinement: *CELL* (Stoe & Cie, 1998); data reduction: *INTEGRATE* (Stoe & Cie, 1998); structure solution: *SHELXS97* (Sheldrick, 1997); structure refinement: *SHELXL97* (Sheldrick, 1997); molecular graphics and publication software: *SHELXTL-Plus* (Sheldrick, 1994).

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