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5-(4-Methoxyphenyl)-4-methylthiazole-2(3*H*)-thione

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Key indicators

Single-crystal X-ray study
T = 299 K
Mean σ(C–C) = 0.005 Å
R factor = 0.041
wR factor = 0.088
Data-to-parameter ratio = 15.9

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

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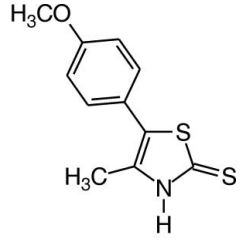
The molecules of the title compound, $C_{11}H_{11}NOS_2$, form hydrogen-bonded dimers in the solid state. The amide H atom serves as hydrogen-bond donor and the thiocarbonyl S atom of a neighbouring molecule serves as acceptor. The *p*-methoxyphenyl substituent is tilted by 7.3 (5)° from the thiazole-2(3*H*)-thione plane.

Comment

5-(*p*-Methoxyphenyl)-4-methylthiazole-2(3*H*)-thione, (I), is formed as a minor product in the photochemical reaction between *N*-hydroxy-5-(*p*-methoxyphenyl)-4-methylthiazole-2(3*H*)-thione and Bu_3SnH (Hartung, Gottwald *et al.*, 2005). The identity of compound (I) was established by X-ray diffraction analysis.



(I)

The methoxy group is situated in the plane of the aryl substituent, presumably for reasons of maximum overlap between one of the non-bonding electron pairs of oxygen and the aromatic π-system [C11—C10—O1—C13 = 5.0 (5)°]. The *p*-methoxyphenyl substituent is tilted by C4—C5—C7—C8 = 7.3 (5)° from the thiazole-2(3*H*)-thione plane defined by atoms S1, C2, N3, C4 and C5 [deviation of 0.002 (7) Å for atom C2 and 0.009 (7) Å for N3] (Fig. 1). This value is significantly smaller than the corresponding dihedral angle in both *N*-benzoyloxy-5-(*p*-methoxyphenyl)-4-methylthiazole-2(3*H*)-thione [51.6 (3)°; Hartung, Altermann *et al.*, 2005 and *N*-hydroxy-5-(*p*-methoxyphenyl)-4-methylthiazole-2(3*H*)-thione [51.8 (4)°; Hartung, Špehar *et al.*, 2005]. The C2—S2 bond length in (I) [1.679 (3) Å] is comparable to the C=S distance in, for example, *N*-hydroxy-5-(*p*-methoxyphenyl)-4-methylthiazole-2(3*H*)-thione [1.676 (3) Å], *N*-isopropoxy-5-(*p*-methoxyphenyl)-4-methylthiazole-2(3*H*)-thione [1.659 (2) Å] and *N*-pentoxy-5-(*p*-methoxyphenyl)-4-methylthiazole-2(3*H*)-thione [1.671 (7) Å; Hartung, Gottwald *et al.*, 2005. The bond lengths within the heterocyclic core increase along the series C2—N3 = 1.340 (3) Å < C4—C5 = 1.347 (4) Å < C4—N3 = 1.390 (3) Å < C2—S2 = 1.679 (3) Å < C2—S1 = 1.720 (3) Å < C5—S1 = 1.758 (3) Å. The endocyclic bond angles of the 1,3-thiazolidine subunit (Table 1) are, within

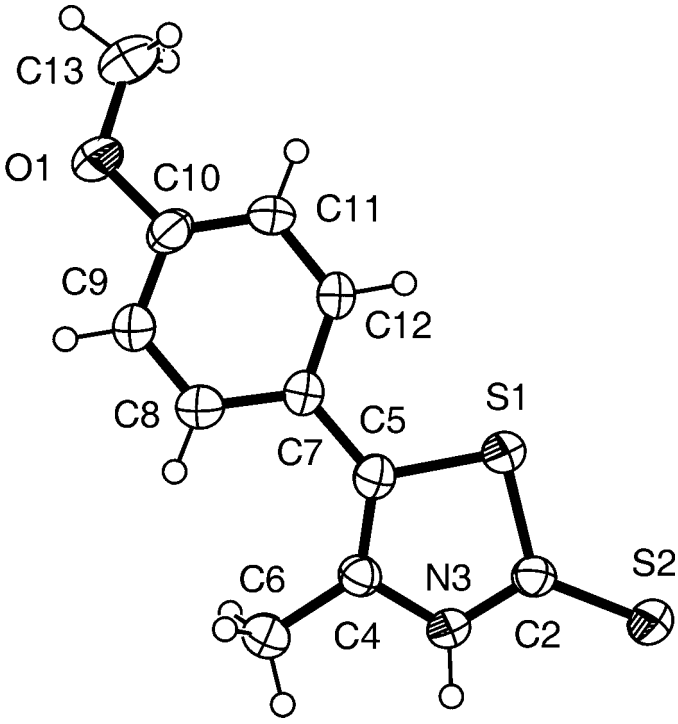


Figure 1
The molecular structure of (I). Displacement ellipsoids are drawn at the 50% probability level.

experimental error, identical to the values reported for *N*-hydroxy-5-(*p*-methoxyphenyl)-4-methylthiazole-2(3*H*)-thione (Hartung, Špehar *et al.*, 2005). An intermolecular N—H···S hydrogen bond links the molecules into hydrogen-bonded dimers (Fig. 2), where the amide H atom serves as hydrogen-bond donor and the thiocarbonyl S atom of a neighbouring molecule serves as an acceptor (Table 2). This type of hydrogen bonding is usual for heterocyclic thioamides (Penfold, 1953; Reynolds *et al.*, 1995; Nalini & Desiraju, 1987; Polonski *et al.*, 1999; Linden *et al.*, 2001; Kunimoto *et al.*, 2002; Zhong *et al.*, 2003).

Experimental

A solution of *N*-hydroxy-5-(*p*-methoxyphenyl)-4-methylthiazole-2(3*H*)-thione (96.0 mg, 0.36 mmol) (Hartung *et al.*, 2003) and Bu_3SnH (103.3 mg, 0.36 mmol) in anhydrous C_6H_6 (5 ml) was photolyzed (λ = 350 nm) for 10 min under Ar (293 K). The solvent was evaporated under reduced pressure. The residue was purified by column chromatography (SiO_2, petroleum ether/acetone 2:1 *v*/*v*) to afford 5-(*p*-methoxyphenyl)-4-methyl-2-(tributylstannylsulfanyl)thiazole (129 mg, 68%) (Hartung, Gottwald *et al.*, 2005) and 5-(*p*-methoxyphenyl)-4-methylthiazole-2(3*H*)thione, (I) (20.5 mg, 24%). Compound (I) crystallizes from MeOH as pale yellow plates, which were suitable for X-ray diffraction. Analysis calculated for $C_{11}H_{11}NOS_2$: C 55.67, H 4.67, N 5.90, S 27.02%; found C 55.43, H 4.51, N 5.75, S 26.13%. MS (EI, 70 eV), *m*/*z* (%) = 237 [M^+, (100)], 222 (17), 178 (5), 163 (14). HR MS: calculated 237.0282, found 237.0282. ^{1}H NMR ($CDCl_3$, 250 MHz) δ_H = 2.31 (*s*, 3H), 3.84 (*s*, 3H), 6.94 (Ar-*d*, 2H, *J* = 8.6 Hz), 7.25 (Ar-*d*, 2H, *J* = 8.6 Hz). ^{13}C NMR ($CDCl_3$, 63 MHz) δ_C = 33.7, 36.6, 55.4, 114.4, 130.0, 159.8, 171.5. UV/Vis (CH_3CN): λ (log ε) = 284 nm (4.23 *sh*).

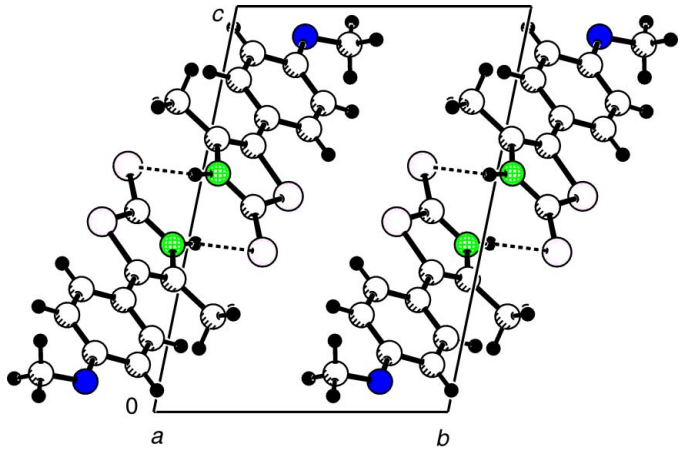


Figure 2
Visualization of the hydrogen bonding (dashed lines) in the unit cell of (I), viewed along [100].

Crystal data

$C_{11}H_{11}NOS_2$
M_r = 237.33
Triclinic, $P\overline{1}$
a = 6.227 (1) Å
b = 8.360 (1) Å
c = 11.624 (3) Å
α = 76.00 (2)°
β = 78.40 (2)°
γ = 75.05 (2)°
V = 561.0 (2) Å^3
Z = 2
D_x = 1.405 Mg m^{-3}
Mo *K*α radiation
Cell parameters from 1180 reflections
θ = 2.7–22.9°
μ = 0.45 mm^{-1}
T = 299 (2) K
Plate, pale yellow
0.52 × 0.28 × 0.06 mm

Data collection

Oxford Diffraction Xcalibur diffractometer with Sapphire CCD detector
ω scans
Absorption correction: analytical *CrysAlis RED* (Oxford Diffraction, 2002)
T_{min} = 0.801, T_{max} = 0.974
6413 measured reflections
2209 independent reflections
1140 reflections with $I > 2\sigma(I)$
R_{int} = 0.047
θ_{max} = 26.4°
h = −7 → 7
k = −8 → 10
l = −14 → 14

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.041
$wR(F^2)$ = 0.088
S = 0.86
2209 reflections
139 parameters
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.031P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.023
$\Delta\rho_{max}$ = 0.19 e Å^{-3}
$\Delta\rho_{min}$ = −0.19 e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

C2—N3	1.340 (3)	C4—N3	1.390 (3)
C2—S2	1.679 (3)	C4—C6	1.501 (4)
C2—S1	1.720 (3)	C5—C7	1.468 (4)
C4—C5	1.347 (4)	C5—S1	1.758 (3)
N3—C2—S1	107.9 (2)	C2—N3—C4	117.6 (3)
C5—C4—N3	112.3 (3)	C2—S1—C5	92.95 (15)
C4—C5—S1	109.3 (2)		
N3—C4—C5—S1	0.4 (3)	N3—C2—S1—C5	−0.3 (2)
S1—C2—N3—C4	0.5 (3)	C4—C5—S1—C2	−0.1 (2)
C5—C4—N3—C2	−0.6 (4)		

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

D—H···A	D—H	H···A	D···A	D—H···A
N3—H3···S2^{i}	0.89 (3)	2.45 (3)	3.333 (3)	172 (2)

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

Atom H3 was located in a difference Fourier map. The atomic coordinates of H3 were refined with U_{iso}(H) = 1.2U_{eq}(N3). All other H atoms were positioned geometrically and treated as riding atoms (C—H = 0.93–0.96 Å), with U_{iso}(H) = 1.2U_{eq}(C).

Data collection: *CrysAlis CCD* (Oxford Diffraction Limited, 2002); cell refinement: *CrysAlis RED* (Oxford Diffraction Limited, 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* (Farrugia, 1997, 2005); software used to prepare material for publication: *SHELXL97*.

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