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5-Ethyl-5-methyl-4-phenyl-5*H*-1,2,4-triazol-3(4*H*)-thione

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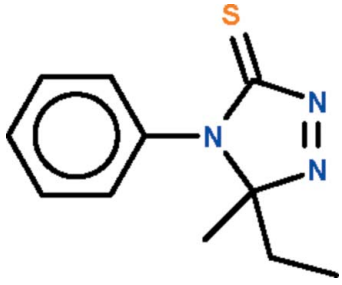
Key indicators: single-crystal X-ray study; T = 100 K; mean σ(C–C) = 0.008 Å; R factor = 0.065; wR factor = 0.186; data-to-parameter ratio = 14.6.

The five-membered ring of the title compound Δ^1-1,2,4-triazoline-5-thione, $C_{11}H_{13}N_3S$, is almost planar (r.m.s. deviation = 0.009 Å); the phenyl ring is aligned at 84.6 (2)° with respect to the five-membered ring. The crystal studied was a racemic twin with an approximate 20% minor twin component. Weak intermolecular C—H···N hydrogen bonding is present in the crystal structure.

Related literature

For the synthesis of this and other Δ^1-[1,2,4]-triazoline-5-thiones, see: Kabashima *et al.* (1991); Landquist (1970); Tripathi & Dhar (1986). For the crystal structure of the related compound 5,5-dimethyl-4-phenyl-1,2,4-triazol-3-thione, see: Katritzky *et al.* (1984).



Experimental

Crystal data

$C_{11}H_{13}N_3S$
M_r = 219.30
Tetragonal, $P\bar{4}2_1c$
a = 17.962 (4) Å
c = 6.9992 (14) Å
V = 2258.2 (6) Å^3
Z = 8
Mo $K\alpha$ radiation
μ = 0.26 mm^{-1}
T = 100 K
0.30 × 0.05 × 0.05 mm

Data collection

Bruker SMART APEX diffractometer
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
T_{min} = 0.927, T_{max} = 0.987
10418 measured reflections
1987 independent reflections
1546 reflections with $I > 2\sigma(I)$
R_{int} = 0.087

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.065
$wR(F^2)$ = 0.186
S = 1.07
1987 reflections
136 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.69 e Å^{-3}
$\Delta\rho_{min}$ = −0.31 e Å^{-3}
Absolute structure: Flack (1983), 837 Friedel pairs
Flack parameter: −0.2 (2)

Table 1
Hydrogen-bond geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
C9—H9A···N2^{i}	0.98	2.56	3.519 (9)	165

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

Data collection: *APEX2* (Bruker, 2009); cell refinement: *SAINT* (Bruker, 2009); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *X-SEED* (Barbour, 2001); software used to prepare material for publication: *publCIF* (Westrip, 2010).

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: XU5008).

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supplementary materials

Acta Cryst. (2010). E**66**, o2224 [**doi:10.1107/S1600536810030503**]

5-Ethyl-5-methyl-4-phenyl-5*H*-1,2,4-triazol-3(4*H*)-thione

K. W. Tan, M. J. Maah and S. W. Ng

Comment

3-Phenyl-Δ^1-[1,2,4]-triazoline-5-thiones are synthesized by the heterocyclization of the Schiff base condensation product of the reaction between phenylthiosemicarbazide and a ketone in the presence of chlorocarbonylsulfenyl chloride (Kabashima *et al.*, 1991), chlorosulfonyl isocyanate (Tripathi & Dhar, 1986) and manganese dioxide (Landquist, 1970). In the present study, the oxidizing agent is 1,10-phenanthroline-5,6-dione, commonly known as phendione. 4-Phenyl thiosemicarbazide condensed with methyl ethyl ketone to form the initial Schiff base, which was then oxidized to the title compound by phendione (Scheme I, Fig. 1). Intermolecular weak C—H···N hydrogen bonding is present in the crystal structure (Table 1).

Experimental

4-Phenyl thiosemicarbazide (2 mmol, 0.33 g) and 1,10-phenanthroline-5,6-dione (1 mmol, 0.21 g) were heated in a mixture of methyl ethyl ketone (5 ml) and ethanol (10 ml). The yellow precipitate that formed was removed by filtration. Slow evaporation of the orange filtrate afforded the title compound.

Refinement

Carbon-bound H-atoms were placed in calculated positions (C—H 0.95–0.99 Å) and were included in the refinement in the riding model approximation, with *U*(H) set to 1.2–1.5*U*(C).

Figures

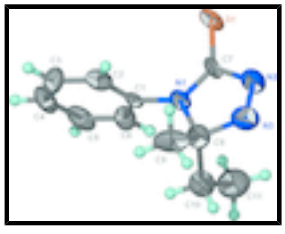

Fig. 1. Thermal ellipsoid plot (Barbour, 2001) of $C_{11}H_{13}N_3S$ at the 70% probability level; hydrogen atoms are drawn as spheres of arbitrary radius.

5-Ethyl-5-methyl-4-phenyl-5*H*-1,2,4-triazol-3(4*H*)-thione

Crystal data

$C_{11}H_{13}N_3S$	D_x = 1.290 Mg m^{-3}
M_r = 219.30	Mo *K*α radiation, λ = 0.71073 Å
Tetragonal, $P\bar{4}2_1c$	Cell parameters from 926 reflections
Hall symbol: P -4 2n	θ = 2.5–18.5°
a = 17.962 (4) Å	μ = 0.26 mm^{-1}

c = 6.9992 (14) Å	T = 100 K
V = 2258.2 (6) Å^3	Prism, orange
Z = 8	0.30 × 0.05 × 0.05 mm
F(000) = 928	

Data collection

Bruker SMART APEX diffractometer	1987 independent reflections
Radiation source: fine-focus sealed tube	1546 reflections with $I > 2\sigma(I)$
graphite	R_{int} = 0.087
ω scans	θ_{max} = 25.0°, θ_{min} = 2.3°
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)	h = −21→20
T_{min} = 0.927, T_{max} = 0.987	k = −21→21
10418 measured reflections	l = −8→5

Refinement

Refinement on F^2	Secondary atom site location: difference Fourier map
Least-squares matrix: full	Hydrogen site location: inferred from neighbouring sites
$R[F^2 > 2\sigma(F^2)]$ = 0.065	H-atom parameters constrained
$wR(F^2)$ = 0.186	$w = 1/[\sigma^2(F_o^2) + (0.0992P)^2 + 1.8759P]$ where $P = (F_o^2 + 2F_c^2)/3$
S = 1.07	$(\Delta/\sigma)_{max}$ = 0.001
1987 reflections	$\Delta\rho_{max}$ = 0.69 e Å^{-3}
136 parameters	$\Delta\rho_{min}$ = −0.31 e Å^{-3}
0 restraints	Absolute structure: Flack (1983), 837 Friedel pairs
Primary atom site location: structure-invariant direct methods	Flack parameter: −0.2 (2)

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2)

	x	y	z	U_{iso}*/U_{eq}
S1	0.47452 (8)	0.23341 (7)	1.2411 (2)	0.0351 (4)
N1	0.4463 (3)	0.2810 (3)	0.8841 (6)	0.0351 (11)
N2	0.4094 (3)	0.3589 (3)	1.1143 (7)	0.0531 (15)
N3	0.3934 (3)	0.3924 (3)	0.9623 (8)	0.0511 (14)
C1	0.4778 (3)	0.2198 (2)	0.7806 (6)	0.0237 (10)
C2	0.5518 (3)	0.2275 (3)	0.7230 (8)	0.0353 (13)
H2	0.5801	0.2706	0.7530	0.042*
C3	0.5823 (3)	0.1677 (3)	0.6175 (9)	0.0441 (15)
H3	0.6323	0.1704	0.5738	0.053*
C4	0.5409 (4)	0.1065 (3)	0.5785 (8)	0.0480 (17)
H4	0.5623	0.0671	0.5066	0.058*
C5	0.4687 (4)	0.1003 (3)	0.6404 (8)	0.0435 (15)
H5	0.4406	0.0568	0.6136	0.052*

C6	0.4381 (3)	0.1576 (3)	0.7413 (9)	0.0351 (12)
H6	0.3881	0.1537	0.7846	0.042*
C7	0.4431 (3)	0.2869 (3)	1.0741 (7)	0.0371 (14)
C8	0.4127 (3)	0.3477 (3)	0.7940 (8)	0.0398 (14)
C9	0.4652 (4)	0.3911 (3)	0.6695 (9)	0.0525 (17)
H9A	0.5098	0.4041	0.7429	0.079*
H9B	0.4407	0.4367	0.6254	0.079*
H9C	0.4794	0.3607	0.5590	0.079*
C10	0.3418 (3)	0.3257 (4)	0.6851 (9)	0.0528 (18)
H10A	0.3210	0.3707	0.6231	0.063*
H10B	0.3554	0.2902	0.5828	0.063*
C11	0.2824 (4)	0.2911 (5)	0.8070 (11)	0.073 (2)
H11A	0.2391	0.2789	0.7276	0.109*
H11B	0.2675	0.3262	0.9072	0.109*
H11C	0.3017	0.2455	0.8659	0.109*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
S1	0.0531 (8)	0.0347 (6)	0.0174 (6)	−0.0009 (6)	−0.0038 (7)	0.0016 (7)
N1	0.051 (3)	0.033 (2)	0.021 (2)	0.014 (2)	−0.004 (2)	−0.001 (2)
N2	0.069 (4)	0.058 (3)	0.033 (3)	0.025 (3)	−0.008 (3)	−0.007 (3)
N3	0.058 (3)	0.048 (3)	0.047 (3)	0.010 (3)	−0.015 (3)	−0.009 (3)
C1	0.035 (2)	0.024 (2)	0.012 (2)	0.0085 (19)	−0.006 (2)	0.000 (2)
C2	0.042 (3)	0.031 (3)	0.032 (3)	−0.009 (2)	−0.009 (3)	0.000 (3)
C3	0.036 (3)	0.055 (4)	0.041 (4)	0.012 (3)	0.015 (3)	0.008 (3)
C4	0.088 (5)	0.034 (3)	0.022 (3)	0.023 (3)	0.001 (3)	0.002 (3)
C5	0.072 (4)	0.029 (3)	0.029 (3)	−0.006 (3)	−0.010 (3)	−0.003 (2)
C6	0.038 (3)	0.038 (3)	0.030 (3)	−0.001 (2)	0.006 (3)	0.001 (3)
C7	0.053 (4)	0.042 (3)	0.016 (3)	0.019 (2)	−0.002 (2)	−0.008 (2)
C8	0.044 (3)	0.039 (3)	0.037 (4)	0.006 (2)	−0.001 (3)	−0.001 (3)
C9	0.059 (4)	0.048 (3)	0.051 (4)	−0.006 (3)	−0.019 (3)	0.021 (3)
C10	0.047 (4)	0.066 (4)	0.046 (4)	0.004 (3)	−0.003 (3)	−0.009 (3)
C11	0.045 (4)	0.101 (6)	0.072 (6)	−0.004 (4)	−0.009 (4)	−0.012 (5)

Geometric parameters (Å, °)

S1—C7	1.614 (5)	C5—C6	1.364 (8)
N1—C7	1.335 (7)	C5—H5	0.9500
N1—C1	1.433 (6)	C6—H6	0.9500
N1—C8	1.483 (7)	C8—C9	1.502 (8)
N2—N3	1.255 (7)	C8—C10	1.535 (8)
N2—C7	1.456 (7)	C9—H9A	0.9800
N3—C8	1.466 (8)	C9—H9B	0.9800
C1—C6	1.355 (7)	C9—H9C	0.9800
C1—C2	1.396 (7)	C10—C11	1.502 (10)
C2—C3	1.415 (8)	C10—H10A	0.9900
C2—H2	0.9500	C10—H10B	0.9900
C3—C4	1.355 (9)	C11—H11A	0.9800

C3—H3	0.9500	C11—H11B	0.9800
C4—C5	1.372 (9)	C11—H11C	0.9800
C4—H4	0.9500		
C7—N1—C1	125.5 (5)	N2—C7—S1	122.3 (4)
C7—N1—C8	110.0 (5)	N3—C8—N1	101.3 (4)
C1—N1—C8	124.5 (4)	N3—C8—C9	109.3 (5)
N3—N2—C7	110.9 (5)	N1—C8—C9	114.2 (5)
N2—N3—C8	111.4 (4)	N3—C8—C10	110.1 (5)
C6—C1—C2	121.7 (4)	N1—C8—C10	109.9 (5)
C6—C1—N1	121.8 (5)	C9—C8—C10	111.5 (5)
C2—C1—N1	116.5 (4)	C8—C9—H9A	109.5
C1—C2—C3	116.4 (5)	C8—C9—H9B	109.5
C1—C2—H2	121.8	H9A—C9—H9B	109.5
C3—C2—H2	121.8	C8—C9—H9C	109.5
C4—C3—C2	120.6 (5)	H9A—C9—H9C	109.5
C4—C3—H3	119.7	H9B—C9—H9C	109.5
C2—C3—H3	119.7	C11—C10—C8	114.4 (6)
C3—C4—C5	121.4 (5)	C11—C10—H10A	108.7
C3—C4—H4	119.3	C8—C10—H10A	108.7
C5—C4—H4	119.3	C11—C10—H10B	108.7
C6—C5—C4	119.0 (5)	C8—C10—H10B	108.7
C6—C5—H5	120.5	H10A—C10—H10B	107.6
C4—C5—H5	120.5	C10—C11—H11A	109.5
C1—C6—C5	121.0 (5)	C10—C11—H11B	109.5
C1—C6—H6	119.5	H11A—C11—H11B	109.5
C5—C6—H6	119.5	C10—C11—H11C	109.5
N1—C7—N2	106.3 (5)	H11A—C11—H11C	109.5
N1—C7—S1	131.2 (5)	H11B—C11—H11C	109.5
C7—N2—N3—C8	0.9 (7)	C8—N1—C7—S1	−176.6 (5)
C7—N1—C1—C6	85.0 (7)	N3—N2—C7—N1	0.5 (7)
C8—N1—C1—C6	−95.6 (6)	N3—N2—C7—S1	175.9 (5)
C7—N1—C1—C2	−94.8 (7)	N2—N3—C8—N1	−1.9 (6)
C8—N1—C1—C2	84.7 (6)	N2—N3—C8—C9	−122.7 (6)
C6—C1—C2—C3	1.5 (7)	N2—N3—C8—C10	114.5 (6)
N1—C1—C2—C3	−178.8 (4)	C7—N1—C8—N3	2.2 (6)
C1—C2—C3—C4	−0.7 (8)	C1—N1—C8—N3	−177.3 (5)
C2—C3—C4—C5	−0.5 (9)	C7—N1—C8—C9	119.6 (6)
C3—C4—C5—C6	0.9 (9)	C1—N1—C8—C9	−60.0 (7)
C2—C1—C6—C5	−1.1 (8)	C7—N1—C8—C10	−114.3 (5)
N1—C1—C6—C5	179.1 (5)	C1—N1—C8—C10	66.2 (7)
C4—C5—C6—C1	−0.1 (9)	N3—C8—C10—C11	−50.8 (8)
C1—N1—C7—N2	177.8 (5)	N1—C8—C10—C11	60.0 (7)
C8—N1—C7—N2	−1.8 (7)	C9—C8—C10—C11	−172.4 (6)
C1—N1—C7—S1	2.9 (10)		

Hydrogen-bond geometry (Å, °)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*

C9—H9A···N2^{i}	0.98	2.56	3.519 (9)	165

Symmetry codes: (i) −*y*+1, *x*, −*z*+2.

Fig. 1