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Ethyl (1-methyl-3-phenyl-5-thioxo-4,5-dihydro-1*H*-1,2,4-triazol-4-yl)acetate

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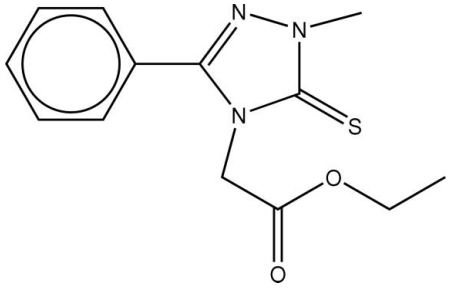
Key indicators: single-crystal X-ray study; T = 290 K; mean σ(C–C) = 0.004 Å; R factor = 0.040; wR factor = 0.120; data-to-parameter ratio = 16.4.

All interatomic distances in the title compound, $C_{13}H_{15}N_3O_2S$, are normal. The 1,2,4-triazole ring is planar and is inclined at 46.50 (6)° to the phenyl ring. The ethoxycarbonylmethyl group is also close to being planar and is inclined at 87.54 (9)° to the 1,2,4-triazole ring. The crystal was an inversion twin with a twin ratio 0.88 (3):0.12 (3).

Related literature

For potential applications, see: Bohn and Karow (1981), Potts (1961), Santus (1980). For structures of other 1,4,5-substituted 2,4-dihydro-3*H*-1,2,4-triazole-3-thiones, see: Dinçer *et al.*, (2005), El-Gazzar *et al.*, (1999), Saghiyan *et al.*, (2006). For general synthesis procedures, see: Bany and Dobosz (1972), Veverka and Marchalin (1987).



Experimental

Crystal data

$C_{13}H_{15}N_3O_2S$
M_r = 277.34
Orthorhombic, $P2_12_12_1$
a = 7.6493 (8) Å
b = 12.8459 (10) Å
c = 14.2061 (11) Å
V = 1395.9 (2) Å^3
Z = 4
Cu $K\alpha$ radiation
μ = 2.09 mm^{-1}
T = 290 (2) K
0.40 × 0.20 × 0.20 mm

Data collection

Kuma KM-4 diffractometer
Absorption correction: numerical (*X-RED*; Stoe & Cie, 1999)
T_{min} = 0.489, T_{max} = 0.681
3095 measured reflections
2887 independent reflections
2386 reflections with $I > 2\sigma(I)$
R_{int} = 0.035
3 standard reflections
every 100 reflections
intensity decay: 4.7%

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.040
$wR(F^2)$ = 0.120
S = 1.05
2887 reflections
176 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.21 e Å^{-3}
$\Delta\rho_{min}$ = −0.26 e Å^{-3}
Absolute structure: Flack (1983), 1112 Friedel pairs
Flack parameter: 0.12 (3)

Table 1
Selected torsion angles (°).

N3—C10—C11—O1	162.9 (3)	C10—C11—O2—C12	−177.40 (19)
N3—C10—C11—O2	−18.2 (3)	C11—O2—C12—C13	−177.5 (2)

Data collection: *KM-4 Software* (Kuma, 1993); cell refinement: *KM-4 Software*; data reduction: *DATAPROC* (Gałdecki *et al.*, 1998); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1990*a*); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *XP* in *SHELXTL/PC* (Sheldrick, 1990*b*) and *ORTEP-3 for Windows* (Version 1.062; Farrugia 1997); software used to prepare material for publication: *SHELXL97* and *PLATON* (Spek, 2003).

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: BT2537).

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supplementary materials

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Ethyl (1-methyl-3-phenyl-5-thioxo-4,5-dihydro-1*H*-1,2,4-triazol-4-yl)acetate

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Comment

The title compound (I) is a member of 1,2,4-triazoline-3-thione derivatives family, known to posses antibacterial, anitimycotical and antivirostatical activity (Veverka and Marchalin, 1987; Bohn and Karow, 1981; Potts, 1961; Santus, 1980).

All interatomic distances in (I) are normal. The 1,2,4-triazoline ring of (I) can be considered as planar in the range of experimental error. The most deviating C2 atom derives 0.0046 (12) Å from weighted least squares plane of the ring. The C3, C9, C10, S1 atoms deviate respectively −0.021 (4), 0.006 (5), 0.254 (4), −0.009 (4) from this plane. The phenyl ring is inclined at 46.50 (6)° to above mentioned heteroatomic ring. The ethoxycarbonylmethyl moiety is close to planarity (Table 1) and the most deviating atom is C12 [0.038 (3) Å from weighted O1, O2, C10, C11, C12, C13 least-squares plane]. This plane is inclined at 87.54 (9)° to weighted least squares plane of 1,2,4-triazoline ring. In the structure can not be found any unusual intermolecular contacts. The crystal was a racemic twin with the twin ratio of 0.88 (3):0.12 (3).

Experimental

The title compound was synthesized according to method of Bany and Dobosz (1972). Crystals were obtained by crystallization from mixture of water, methanol, ethanol and 2-butanone (1:2:3:1).

Refinement

The hydrogen atoms were placed in calculated positions after four cycles of anisotrophic refinement and were refined as riding on adjacent atom with U_{iso}(H) = 1.2U_{eq}(*C*-non-methyl) and U_{iso}(H) = 1.5U_{eq}(*C*-methyl). The methyl groups were allowed to rotate about their local threefold axis (AFIX 137).

Figures

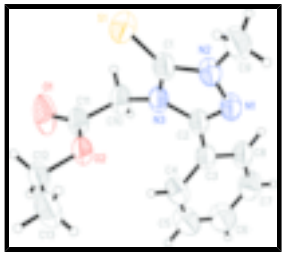

Fig. 1. Molecular structure of the title compound (I). Displacement ellipsoids are drawn at the 50% probability level.

Ethyl (1-methyl-3-phenyl-5-thioxo-4,5-dihydro-1*H*-1,2,4-triazol-4-yl)acetate

Crystal data

$C_{13}H_{15}N_3O_2S$ F_{000} = 584

M_r = 277.34	D_x = 1.320 Mg m^{-3}
Orthorhombic, $P2_12_12_1$	Cu $K\alpha$ radiation λ = 1.54178 Å
Hall symbol: P 2ac 2ab	Cell parameters from 99 reflections
a = 7.6493 (8) Å	θ = 5–60º
b = 12.8459 (10) Å	μ = 2.09 mm^{-1}
c = 14.2061 (11) Å	T = 290 (2) K
V = 1395.9 (2) Å^3	Prism, colourless
Z = 4	0.40 × 0.20 × 0.20 mm

Data collection

Kuma KM-4 diffractometer	R_{int} = 0.035
Radiation source: fine-focus sealed tube	θ_{max} = 80.7º
Monochromator: graphite	θ_{min} = 4.6º
T = 290(2) K	h = −8→9
ω–2θ scans	k = 0→16
Absorption correction: numerical (X-RED; Stoe & Cie, 1999)	l = 0→18
T_{min} = 0.489, T_{max} = 0.681	3 standard reflections
3095 measured reflections	every 100 reflections
2887 independent reflections	intensity decay: 4.7%
2386 reflections with $I > 2\sigma(I)$	

Refinement

Refinement on F^2	H-atom parameters constrained
Least-squares matrix: full	$w = 1/[\sigma^2(F_o^2) + (0.0798P)^2 + 0.0731P]$ where $P = (F_o^2 + 2F_c^2)/3$
$R[F^2 > 2\sigma(F^2)]$ = 0.040	$(\Delta/\sigma)_{max}$ = 0.001
$wR(F^2)$ = 0.120	$\Delta\rho_{max}$ = 0.21 e Å^{-3}
S = 1.05	$\Delta\rho_{min}$ = −0.25 e Å^{-3}
2887 reflections	Extinction correction: SHELXL97 (Sheldrick, 1997), $Fc^*=kFc[1+0.001xFc^2\lambda^3/\sin(2\theta)]^{-1/4}$
176 parameters	Extinction coefficient: 0.0114 (11)
Primary atom site location: structure-invariant direct methods	Absolute structure: Flack (1983), 1112 Friedel pairs
Secondary atom site location: structure-invariant direct methods	Flack parameter: 0.12 (3)
Hydrogen site location: inferred from neighbouring sites	

Special details

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations

between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

Refinement. Refinement of F^2 against ALL reflections. The weighted *R*-factor *wR* and goodness of fit S are based on F^2, conventional *R*-factors *R* are based on F, with F set to zero for negative F^2. The threshold expression of $F^2 > 2\text{sigma}(F^2)$ is used only for calculating *R*-factors(gt) *etc*. and is not relevant to the choice of reflections for refinement. *R*-factors based on F^2 are statistically about twice as large as those based on F, and R– factors based on ALL data will be even larger.

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

	x	*y*	*z*	U_{iso}*/U_{eq}
N1	0.8202 (2)	0.79745 (12)	0.41689 (13)	0.0570 (4)
N2	0.8363 (3)	0.74693 (13)	0.33226 (13)	0.0591 (4)
C1	0.8901 (3)	0.64742 (15)	0.34141 (16)	0.0578 (5)
S1	0.92489 (10)	0.55811 (4)	0.25886 (5)	0.0790 (2)
N3	0.9083 (2)	0.63576 (11)	0.43724 (12)	0.0526 (4)
C2	0.8658 (3)	0.72900 (13)	0.47946 (16)	0.0521 (4)
C3	0.8649 (3)	0.74947 (14)	0.58079 (16)	0.0539 (5)
C4	0.7864 (4)	0.68126 (19)	0.64452 (17)	0.0671 (6)
H4	0.7373	0.6192	0.6235	0.081*
C5	0.7821 (4)	0.7066 (2)	0.7389 (2)	0.0802 (7)
H5	0.7313	0.6609	0.7817	0.096*
C6	0.8528 (4)	0.7995 (2)	0.7705 (2)	0.0807 (7)
H6	0.8478	0.8163	0.8341	0.097*
C7	0.9310 (4)	0.86738 (19)	0.70771 (19)	0.0727 (6)
H7	0.9785	0.9297	0.7290	0.087*
C8	0.9382 (3)	0.84203 (15)	0.61283 (17)	0.0616 (5)
H8	0.9921	0.8870	0.5706	0.074*
C9	0.7969 (4)	0.80072 (19)	0.2454 (2)	0.0782 (7)
H9A	0.7208	0.8584	0.2583	0.117*
H9C	0.7405	0.7537	0.2026	0.117*
H9B	0.9034	0.8258	0.2178	0.117*
C10	0.9964 (3)	0.54664 (15)	0.47858 (19)	0.0618 (5)
H10A	1.0397	0.5667	0.5401	0.074*
H10B	1.0970	0.5299	0.4399	0.074*
C11	0.8880 (3)	0.44955 (15)	0.48975 (16)	0.0579 (5)
O1	0.9562 (3)	0.36687 (13)	0.5025 (2)	0.1044 (8)
O2	0.7171 (2)	0.46454 (9)	0.48593 (10)	0.0537 (3)
C12	0.6098 (3)	0.37176 (15)	0.50081 (17)	0.0598 (5)
H12A	0.6298	0.3440	0.5634	0.072*
H12B	0.6402	0.3185	0.4552	0.072*
C13	0.4237 (4)	0.4017 (2)	0.4899 (3)	0.0881 (9)
H13A	0.3506	0.3428	0.5032	0.132*
H13B	0.4034	0.4247	0.4265	0.132*
H13C	0.3966	0.4571	0.5328	0.132*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
N1	0.0613 (11)	0.0365 (7)	0.0731 (11)	0.0006 (6)	0.0050 (8)	0.0019 (7)
N2	0.0666 (11)	0.0399 (8)	0.0708 (10)	−0.0017 (8)	0.0048 (8)	0.0053 (7)
C1	0.0555 (13)	0.0393 (9)	0.0785 (12)	−0.0046 (8)	0.0038 (10)	0.0006 (8)
S1	0.0924 (5)	0.0536 (3)	0.0909 (4)	−0.0013 (3)	0.0131 (4)	−0.0149 (3)
N3	0.0492 (9)	0.0319 (7)	0.0767 (10)	−0.0004 (6)	0.0013 (8)	0.0021 (6)
C2	0.0477 (10)	0.0337 (8)	0.0748 (12)	−0.0017 (7)	0.0019 (9)	0.0028 (7)
C3	0.0491 (10)	0.0380 (8)	0.0746 (12)	−0.0004 (7)	−0.0013 (9)	0.0028 (8)
C4	0.0678 (14)	0.0546 (11)	0.0789 (14)	−0.0177 (11)	−0.0024 (11)	0.0063 (10)
C5	0.0914 (19)	0.0750 (15)	0.0743 (15)	−0.0184 (14)	0.0008 (15)	0.0112 (12)
C6	0.094 (2)	0.0781 (16)	0.0697 (14)	−0.0080 (15)	−0.0040 (13)	−0.0019 (12)
C7	0.0771 (16)	0.0537 (11)	0.0872 (16)	−0.0054 (11)	−0.0106 (12)	−0.0093 (11)
C8	0.0603 (13)	0.0396 (9)	0.0850 (14)	−0.0014 (8)	−0.0005 (11)	0.0004 (9)
C9	0.1017 (19)	0.0573 (12)	0.0755 (14)	−0.0040 (12)	0.0010 (16)	0.0159 (11)
C10	0.0517 (12)	0.0387 (9)	0.0950 (16)	0.0038 (8)	−0.0103 (10)	0.0011 (10)
C11	0.0544 (13)	0.0369 (8)	0.0825 (13)	0.0048 (8)	−0.0091 (10)	0.0064 (8)
O1	0.0733 (12)	0.0404 (8)	0.200 (3)	0.0123 (8)	−0.0145 (14)	0.0236 (11)
O2	0.0547 (8)	0.0332 (6)	0.0732 (8)	−0.0004 (5)	−0.0051 (7)	0.0067 (5)
C12	0.0671 (14)	0.0365 (8)	0.0759 (13)	−0.0059 (9)	0.0022 (10)	0.0089 (8)
C13	0.0627 (16)	0.0563 (13)	0.145 (3)	−0.0130 (11)	−0.0068 (17)	0.0213 (15)

Geometric parameters (Å, °)

N1—C2	1.298 (3)	C7—H7	0.9300
N1—N2	1.372 (3)	C8—H8	0.9300
N2—C1	1.349 (2)	C9—H9A	0.9600
N2—C9	1.445 (3)	C9—H9C	0.9600
C1—N3	1.377 (3)	C9—H9B	0.9600
C1—S1	1.662 (2)	C10—C11	1.506 (3)
N3—C2	1.378 (2)	C10—H10A	0.9700
N3—C10	1.452 (2)	C10—H10B	0.9700
C2—C3	1.463 (3)	C11—O1	1.197 (2)
C3—C8	1.391 (3)	C11—O2	1.322 (3)
C3—C4	1.396 (3)	O2—C12	1.463 (2)
C4—C5	1.381 (4)	C12—C13	1.483 (4)
C4—H4	0.9300	C12—H12A	0.9700
C5—C6	1.385 (4)	C12—H12B	0.9700
C5—H5	0.9300	C13—H13A	0.9600
C6—C7	1.383 (4)	C13—H13B	0.9600
C6—H6	0.9300	C13—H13C	0.9600
C7—C8	1.388 (3)		
C2—N1—N2	104.81 (16)	C3—C8—H8	119.9
C1—N2—N1	113.02 (18)	N2—C9—H9A	109.5
C1—N2—C9	126.8 (2)	N2—C9—H9C	109.5
N1—N2—C9	120.20 (18)	H9A—C9—H9C	109.5

N2—C1—N3	103.25 (18)	N2—C9—H9B	109.5
N2—C1—S1	129.41 (18)	H9A—C9—H9B	109.5
N3—C1—S1	127.34 (15)	H9C—C9—H9B	109.5
C1—N3—C2	108.18 (16)	N3—C10—C11	116.10 (18)
C1—N3—C10	122.18 (18)	N3—C10—H10A	108.3
C2—N3—C10	128.20 (19)	C11—C10—H10A	108.3
N1—C2—N3	110.74 (19)	N3—C10—H10B	108.3
N1—C2—C3	123.40 (17)	C11—C10—H10B	108.3
N3—C2—C3	125.83 (18)	H10A—C10—H10B	107.4
C8—C3—C4	119.9 (2)	O1—C11—O2	124.5 (2)
C8—C3—C2	118.26 (19)	O1—C11—C10	120.7 (2)
C4—C3—C2	121.83 (19)	O2—C11—C10	114.80 (16)
C5—C4—C3	119.5 (2)	C11—O2—C12	115.50 (15)
C5—C4—H4	120.2	O2—C12—C13	108.19 (17)
C3—C4—H4	120.2	O2—C12—H12A	110.1
C4—C5—C6	120.5 (2)	C13—C12—H12A	110.1
C4—C5—H5	119.7	O2—C12—H12B	110.1
C6—C5—H5	119.7	C13—C12—H12B	110.1
C7—C6—C5	120.2 (2)	H12A—C12—H12B	108.4
C7—C6—H6	119.9	C12—C13—H13A	109.5
C5—C6—H6	119.9	C12—C13—H13B	109.5
C6—C7—C8	119.7 (2)	H13A—C13—H13B	109.5
C6—C7—H7	120.1	C12—C13—H13C	109.5
C8—C7—H7	120.1	H13A—C13—H13C	109.5
C7—C8—C3	120.1 (2)	H13B—C13—H13C	109.5
C7—C8—H8	119.9		
N3—C10—C11—O1	162.9 (3)	C10—C11—O2—C12	−177.40 (19)
N3—C10—C11—O2	−18.2 (3)	C11—O2—C12—C13	−177.5 (2)

Fig. 1