

Crystal structure of 1-ethylpyrazolo[3,4-*d*]pyrimidine-4(5*H*)-thione

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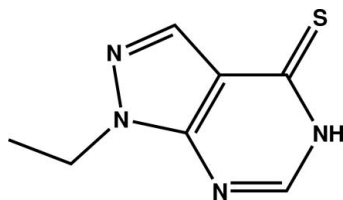
In the title compound, C₇H₈N₄S, the methyl C atom is displaced by 1.232 (7) Å from the mean plane of the pyrazolo[3,4-*d*]pyrimidine ring system (r.m.s. deviation = 0.007 Å). The N–N–C–C_m (m = methyl) torsion angle is –60.3 (6)°. In the crystal, molecules are linked by N–H···S hydrogen bonds, generating [010] chains, which are reinforced by C–H···N interactions. The chains are cross-linked by weak C–H···S hydrogen bonds, generating (001) sheets.

Keywords: crystal structure; pyrazolo[3,4-*d*]pyrimidine; biological activity; hydrogen bonding.

CCDC reference: 1018657

1. Related literature

For the biological activity of pyrazolo[3,4-*d*]pyrimidine derivatives, see: Rashad *et al.* (2008, 2011); Ballell *et al.* (2007). For related structures, see: El Fal *et al.* (2013); Radi *et al.* (2013); Alsubari *et al.* (2011).



2. Experimental

2.1. Crystal data

C₇H₈N₄S

M_r = 180.23

Monoclinic, *P*₂₁
a = 4.472 (4) Å
b = 5.353 (4) Å
c = 17.573 (12) Å
β = 93.71 (4)°
V = 419.8 (5) Å³

Z = 2
Mo *Kα* radiation
μ = 0.33 mm^{−1}
T = 296 K
0.38 × 0.34 × 0.29 mm

2.2. Data collection

Bruker X8 APEX CCD diffractometer
Absorption correction: multi-scan (*SADABS*; Bruker, 2009)
T_{min} = 0.578, *T_{max}* = 0.746

4028 measured reflections
1704 independent reflections
1242 reflections with *I* > 2σ(*I*)
R_{int} = 0.059

2.3. Refinement

R[*F*² > 2σ(*F*²)] = 0.053
wR(*F*²) = 0.139
S = 1.01
1704 reflections
109 parameters
1 restraint
H-atom parameters constrained

Δρ_{max} = 0.29 e Å^{−3}
Δρ_{min} = −0.36 e Å^{−3}
Absolute structure: Flack & Bernardinelli (2000), 652 Friedel pairs
Absolute structure parameter: −0.11 (16)

Table 1

Hydrogen-bond 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>
N1–H1···S1 ⁱ	0.89	2.48	3.333 (4)	161
C5–H5···S1 ⁱⁱ	0.93	2.75	3.685 (5)	179
C3–H3···N2 ⁱⁱⁱ	0.93	2.60	3.528 (6)	174

Symmetry codes: (i) $-x, y + \frac{1}{2}, -z + 1$; (ii) $x - 1, y + 1, z$; (iii) $x + 1, y - 1, z$.

Data collection: *APEX2* (Bruker, 2009); cell refinement: *SAINT-Plus* (Bruker, 2009); data reduction: *SAINT-Plus*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 2012); software used to prepare material for publication: *PLATON* (Spek, 2009) and *pubCIF* (Westrip, 2010).

Acknowledgements

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Supporting information for this paper is available from the IUCr electronic archives (Reference: HB7262).

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supporting information

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Crystal structure of 1-ethylpyrazolo[3,4-*d*]pyrimidine-4(5*H*)-thione

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S1. Comment

Pyrazolo [3,4-*d*] pyrimidine derivatives have attracted considerable attention from researchers due to their bioactive and pharmaceutical properties. Many members of this family are widely used as antiviral (Rashad *et al.*, 2008); anti-mycobacterial (Ballell *et al.* 2007) and anticancer agents (Rashad *et al.* 2011). The present paper is a continuation of our research work devoted to the development of pyrazolo [3,4-*d*] pyrimidine derivatives with potential pharmacological activities (El Fal *et al.*, 2013; Radi *et al.*, 2013; Alsubari *et al.*, 2011).

The molecule of the title compound is build up from two fused five- and six-membered heterocycles linked to an ethyl group and to S atom as shown in Fig.1. The pyrazolo[3,4-*d*]pyrimidine ring is nearly perpendicular to the ethyl group as indicated by the torsion angle C7C6N3N4 of -60.3 (6)°.

In the crystal, the molecules are linked together by a weak intermolecular N1–H1···S1, C5–H5···S1 and C3–H3···N2 interactions, in the way to build a two-dimensional network (see Fig.2 and Table 1).

S2. Experimental

(0,54 g, 3.04 mmol) of 1-ethyl-pyrazolo [3, 4 - d] pyrimidin-4 (5*H*)-one and (0,84 g, 3.65 mmol) of phosphorus pentasulfide were refluxed in pyridine for 4 h. Then the solvent is evaporated under reduced pressure; the precipitate formed is washed with hot water and recrystallized from ethanol solution to afford the title compound as yellow blocks.

S3. Refinement

The H atoms were located in a difference map and treated as riding with C—H = 0.93 Å (aromatic), C—H = 0.97 Å (methylene) and C—H = 0.96 Å, (methyl). All hydrogen with $U_{\text{iso}}(\text{H}) = 1.2 U_{\text{eq}}$ (aromatic and methylene) and $U_{\text{iso}}(\text{H}) = 1.5 U_{\text{eq}}$ for the methyl.

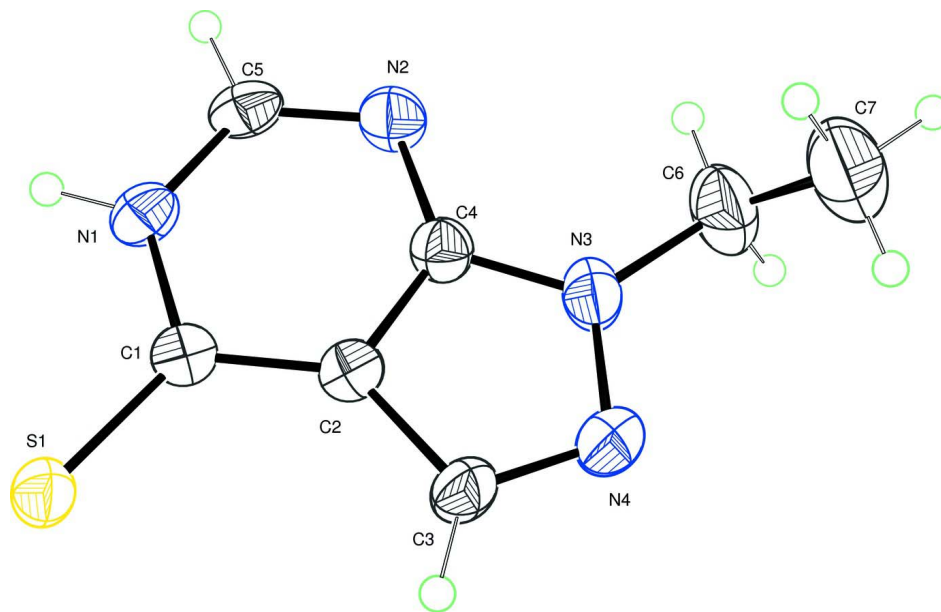


Figure 1

Molecular structure of the title compound with displacement ellipsoids drawn at the 50% probability level.

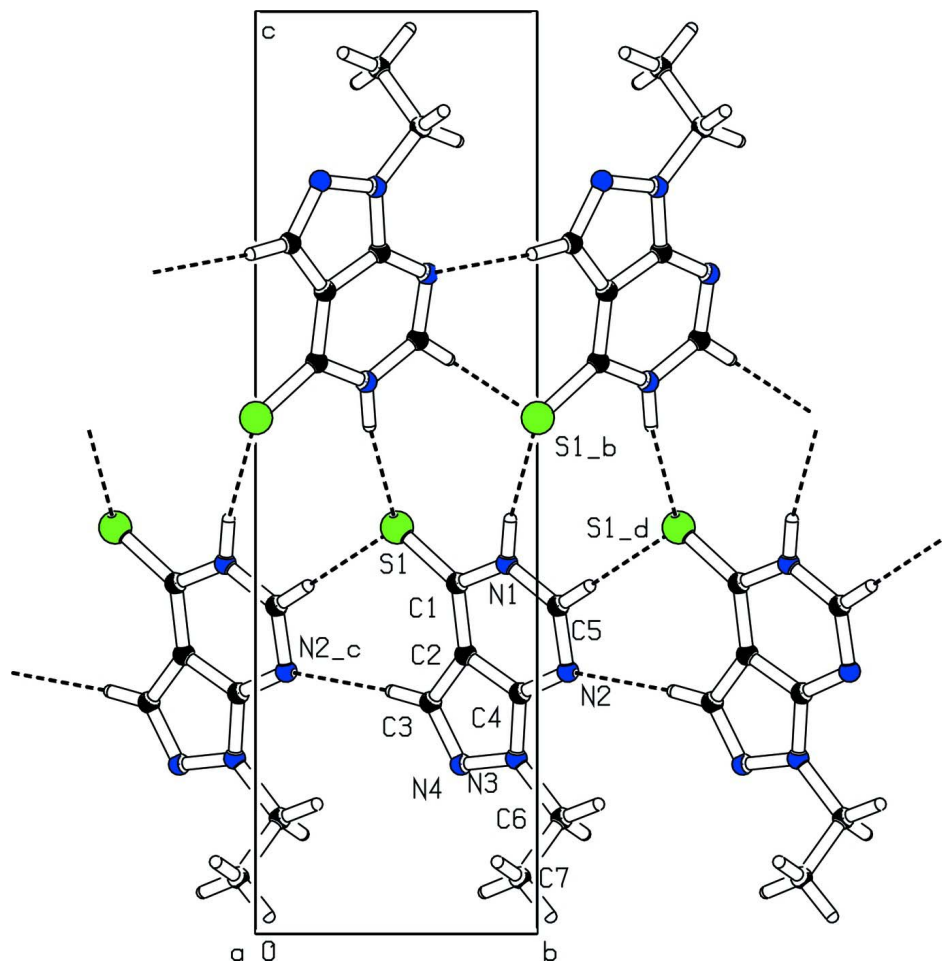


Figure 2

Structure projection along (0 1 1) of the title compound, showing molecules linked through hydrogen bonds (dashed lines).

1-Ethylpyrazolo[3,4-*d*]pyrimidine-4(5*H*)-thione

Crystal data

$C_7H_8N_4S$

$M_r = 180.23$

Monoclinic, $P2_1$

Hall symbol: P 2yb

$a = 4.472$ (4) Å

$b = 5.353$ (4) Å

$c = 17.573$ (12) Å

$\beta = 93.71$ (4)°

$V = 419.8$ (5) Å³

$Z = 2$

$F(000) = 188$

$D_x = 1.426$ Mg m⁻³

Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å

Cell parameters from 1704 reflections

$\theta = 3.5$ – 27.5 °

$\mu = 0.33$ mm⁻¹

$T = 296$ K

Block, yellow

$0.38 \times 0.34 \times 0.29$ mm

Data collection

Bruker X8 APEX CCD

diffractometer

Radiation source: fine-focus sealed tube

Graphite monochromator

φ and ω scans

Absorption correction: multi-scan

(*SADABS*; Bruker, 2009)

$T_{\min} = 0.578$, $T_{\max} = 0.746$

4028 measured reflections
 1704 independent reflections
 1242 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.059$

$\theta_{\text{max}} = 27.5^\circ$, $\theta_{\text{min}} = 3.5^\circ$
 $h = -5 \rightarrow 5$
 $k = -6 \rightarrow 5$
 $l = -22 \rightarrow 22$

Refinement

Refinement on F^2
 Least-squares matrix: full
 $R[F^2 > 2\sigma(F^2)] = 0.053$
 $wR(F^2) = 0.139$
 $S = 1.01$
 1704 reflections
 109 parameters
 1 restraint
 Primary atom site location: structure-invariant
 direct methods
 Secondary atom site location: difference Fourier
 map

Hydrogen site location: inferred from
 neighbouring sites
 H-atom parameters constrained
 $w = 1/[\sigma^2(F_o^2) + (0.P)^2]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\text{max}} < 0.001$
 $\Delta\rho_{\text{max}} = 0.29 \text{ e } \text{\AA}^{-3}$
 $\Delta\rho_{\text{min}} = -0.36 \text{ e } \text{\AA}^{-3}$
 Absolute structure: Flack & Bernardinelli
 (2000), 652 Friedel pairs
 Absolute structure parameter: $-0.11 (16)$

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 $F^2 > \sigma(F^2)$ 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 (\AA^2)

	x	y	z	$U_{\text{iso}}^*/U_{\text{eq}}$
C1	0.2656 (8)	0.2169 (7)	0.6200 (2)	0.0340 (9)
C2	0.3666 (8)	0.2465 (8)	0.6972 (2)	0.0349 (9)
C3	0.5729 (9)	0.1222 (9)	0.7490 (2)	0.0421 (10)
H3	0.6856	-0.0166	0.7370	0.050*
C4	0.2506 (9)	0.4396 (7)	0.7391 (2)	0.0386 (10)
C5	-0.0448 (9)	0.5752 (8)	0.6444 (2)	0.0438 (11)
H5	-0.1874	0.6853	0.6230	0.053*
C6	0.3360 (13)	0.5872 (10)	0.8749 (3)	0.0669 (16)
H6A	0.1925	0.7165	0.8595	0.080*
H6B	0.5229	0.6675	0.8919	0.080*
C7	0.2207 (15)	0.4383 (15)	0.9390 (3)	0.091 (3)
H7A	0.1876	0.5471	0.9810	0.137*
H7B	0.3652	0.3131	0.9550	0.137*
H7C	0.0355	0.3592	0.9221	0.137*
N1	0.0543 (7)	0.3928 (6)	0.59849 (19)	0.0407 (9)
H1	-0.0256	0.4046	0.5509	0.049*
N2	0.0419 (8)	0.6091 (7)	0.71546 (19)	0.0435 (9)
N3	0.3849 (9)	0.4260 (7)	0.80986 (17)	0.0482 (10)
N4	0.5830 (8)	0.2300 (8)	0.81616 (19)	0.0513 (10)

S1	0.3799 (2)	0.0022 (2)	0.55937 (5)	0.0413 (3)
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Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C1	0.0340 (18)	0.030 (2)	0.038 (2)	-0.0022 (18)	0.0034 (16)	0.0046 (17)
C2	0.0340 (18)	0.030 (2)	0.040 (2)	-0.0013 (19)	0.0000 (15)	0.0005 (18)
C3	0.046 (2)	0.039 (2)	0.040 (2)	0.011 (2)	-0.0064 (17)	0.0030 (19)
C4	0.041 (2)	0.036 (3)	0.038 (2)	-0.0003 (19)	0.0021 (16)	-0.0011 (17)
C5	0.036 (2)	0.038 (3)	0.056 (3)	0.0102 (19)	-0.0030 (18)	0.005 (2)
C6	0.089 (4)	0.067 (4)	0.045 (3)	0.002 (3)	0.005 (2)	-0.017 (2)
C7	0.094 (4)	0.128 (8)	0.053 (3)	-0.003 (5)	0.016 (3)	-0.009 (3)
N1	0.0406 (18)	0.037 (2)	0.0440 (19)	0.0066 (17)	-0.0044 (15)	0.0078 (16)
N2	0.050 (2)	0.034 (2)	0.046 (2)	0.0076 (18)	0.0027 (16)	-0.0015 (16)
N3	0.059 (2)	0.052 (3)	0.0337 (17)	0.0086 (19)	0.0001 (15)	-0.0048 (16)
N4	0.051 (2)	0.058 (3)	0.044 (2)	0.015 (2)	-0.0072 (16)	-0.0002 (18)
S1	0.0449 (5)	0.0390 (6)	0.0388 (5)	0.0052 (6)	-0.0053 (4)	-0.0052 (5)

Geometric parameters (Å, °)

C1—N1	1.370 (5)	C5—H5	0.9300
C1—C2	1.410 (5)	C6—N3	1.459 (5)
C1—S1	1.669 (4)	C6—C7	1.499 (7)
C2—C4	1.390 (5)	C6—H6A	0.9700
C2—C3	1.419 (6)	C6—H6B	0.9700
C3—N4	1.312 (5)	C7—H7A	0.9600
C3—H3	0.9300	C7—H7B	0.9600
C4—N3	1.347 (5)	C7—H7C	0.9600
C4—N2	1.348 (5)	N1—H1	0.8900
C5—N2	1.296 (5)	N3—N4	1.373 (5)
C5—N1	1.359 (5)		
N1—C1—C2	111.1 (3)	N3—C6—H6B	109.5
N1—C1—S1	122.1 (3)	C7—C6—H6B	109.5
C2—C1—S1	126.8 (3)	H6A—C6—H6B	108.1
C4—C2—C1	119.1 (4)	C6—C7—H7A	109.5
C4—C2—C3	104.9 (3)	C6—C7—H7B	109.5
C1—C2—C3	136.0 (4)	H7A—C7—H7B	109.5
N4—C3—C2	110.8 (4)	C6—C7—H7C	109.5
N4—C3—H3	124.6	H7A—C7—H7C	109.5
C2—C3—H3	124.6	H7B—C7—H7C	109.5
N3—C4—N2	125.4 (4)	C5—N1—C1	125.2 (3)
N3—C4—C2	106.9 (4)	C5—N1—H1	112.4
N2—C4—C2	127.7 (3)	C1—N1—H1	122.4
N2—C5—N1	125.7 (4)	C5—N2—C4	111.2 (3)
N2—C5—H5	117.1	C4—N3—N4	111.2 (3)
N1—C5—H5	117.1	C4—N3—C6	127.6 (4)
N3—C6—C7	110.5 (5)	N4—N3—C6	121.2 (4)

N3—C6—H6A	109.5	C3—N4—N3	106.2 (3)
C7—C6—H6A	109.5		

Hydrogen-bond geometry (Å, °)

<i>D—H...A</i>	<i>D—H</i>	<i>H...A</i>	<i>D...A</i>	<i>D—H...A</i>
N1—H1...S1 ⁱ	0.89	2.48	3.333 (4)	161
C5—H5...S1 ⁱⁱ	0.93	2.75	3.685 (5)	179
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