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4-Amino-3-(4-pyridyl)-1,2,4-triazole-5(4*H*)-thione

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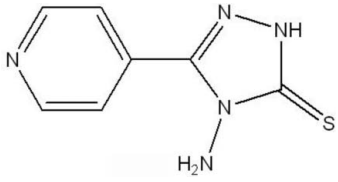
Key indicators: single-crystal X-ray study; T = 273 K; mean σ(C–C) = 0.005 Å; R factor = 0.065; wR factor = 0.169; data-to-parameter ratio = 13.8.

In the title molecule, $C_7H_7N_5S$, the pyridyl and triazole rings form a dihedral angle of 20.07 (6)°. Intermolecular N—H···N hydrogen bonds link the molecules into chains extended in the direction [10$\bar{1}$]. Further stability is provided by $\pi\cdots\pi$ stacking interactions, indicated by short distances between the centroids of triazole rings [3.480 (5) Å] and pyridyl rings [3.574 (5) Å] of neighbouring molecules.

Related literature

For the biological activities of related compounds, see: Eweiss *et al.* (1986); Awad *et al.* (1991). For a similar structure, see Kajdan *et al.* (2000).



Experimental

Crystal data

$C_7H_7N_5S$
M_r = 193.24
Monoclinic, $C2/c$
a = 7.722 (6) Å
b = 14.215 (11) Å
c = 15.068 (12) Å
β = 93.432 (15)°
V = 1651 (2) Å^3
Z = 8
Mo $K\alpha$ radiation
μ = 0.35 mm^{-1}
T = 273 (2) K
0.15 × 0.10 × 0.08 mm

Data collection

Bruker APEX area-detector diffractometer
Absorption correction: multi-scan (*SADABS*; Bruker, 2001)
T_{min} = 0.950, T_{max} = 0.973
4402 measured reflections
1626 independent reflections
1116 reflections with $I > 2\sigma(I)$
R_{int} = 0.060

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.065
$wR(F^2)$ = 0.169
S = 1.01
1626 reflections
118 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.29 e Å^{-3}
$\Delta\rho_{min}$ = −0.28 e Å^{-3}

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

D—H···A	D—H	H···A	D···A	D—H···A
N4—H4B···N1^{i}	0.86	1.91	2.772 (4)	175

Symmetry code: (i) $x-\frac{1}{2}, -y+\frac{3}{2}, z+\frac{1}{2}$.

Data collection: *SMART* (Bruker, 2001); cell refinement: *SAINT* (Bruker, 2001); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP-3* (Farrugia, 1997) and *ViewerPro* (Accelrys, 2001); software used to prepare material for publication: *SHELXL97*.

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: CV2366).

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supplementary materials

Acta Cryst. (2008). E**64**, o213 [**doi:10.1107/S1600536807064331**]

4-Amino-3-(4-pyridyl)-1,2,4-triazole-5(4*H*)-thione

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Comment

Amine- and thione-substituted triazoles have been studied as anti-inflammatory and antimicrobial agents (Eweiss *et al.*, 1986; Awad *et al.*, 1991). Herein, we report the structure of the title compound, (I).

In (I) (Fig. 1), the molecule exists as a thione tautomer. All bond lengths and angles are normal and comparable with those found in related compounds (Kajdan *et al.*, 2000). The dihedral angle between the pyridinyl and triazole rings is 20.07 (6)°.

In the crystal, intermolecular N—H···N hydrogen bonds (Table 1) link the molecules into chains extending in direction [10–1]. Further stability is provided by π···π stacking interactions supported by short distances between the centroids of pyridine (*Cg*1) and triazole (*Cg*2) rings, respectively - $Cg1\cdots Cg1^{ii}$ 3.574 (5) Å, $Cg2\cdots Cg2^{iii}$ 3.480 (5) Å [symmetry codes: (ii) 1/2 − *x*, 3/2 − *y*, −*z*; (iii) −*x*, *y*, 1/2 − *z*].

Experimental

Potassium hydroxide (8.4 g, 0.15 mol) in 100 ml of absolute ethanol was added to isonicotinohydrazide (13.7 g, 0.10 mol) under ice bath. The mixture was stirred until the solution became clear, and carbon disulfide (9.04 ml, 0.15 mol) was added. The solution was reacted for 12 h at room temperature and 100 ml dried ethyl ether were added to form a precipitate, which was filtered and washed with ethyl ether several times. The precipitate was mixed with hydrazine hydrate (8.0 g, 160 mmol) and 10 ml water. The solution was refluxed for 2 h until the colour of the solution became clear green. After cooling to room temperature, 100 ml ice water was added and neutralized with 3*M* hydrochloric acid to form the precipitate, which was isolated by filtration and purified by recrystallization from ethanol to give pure 3-pyridinyl-4-amino-5- -mercapto-1,2,4-triazole. Crystals suitable for X-ray diffraction analysis were obtained by slow evaporation of an Dimethylformamide solution.

Refinement

The hydrogen atoms were geometrically positioned (C—H 0.93 Å, N—H 0.86–0.90 Å) and were included in the refinement in the riding model approximation, with U_{iso}(H)=1.2–1.5Ueq of the parent atom.

Figures

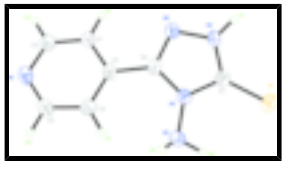

Fig. 1. The molecular structure of (I) showing the atomic numbering and 30% probability displacement ellipsoids.

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Crystal data

$C_7H_7N_5S$	F_{000} = 800
M_r = 193.24	D_x = 1.555 Mg m^{-3}
Monoclinic, *C*2/*c*	Mo *K*α radiation λ = 0.71073 Å
a = 7.722 (6) Å	Cell parameters from 1061 reflections
b = 14.215 (11) Å	θ = 2.7–23.8º
c = 15.068 (12) Å	μ = 0.35 mm^{-1}
β = 93.432 (15)º	*T* = 273 (2) K
V = 1651 (2) Å^3	Clubbed, colourless
Z = 8	0.15 × 0.10 × 0.08 mm

Data collection

Bruker APEX area-detector diffractometer	1626 independent reflections
Radiation source: fine-focus sealed tube	1116 reflections with $I > 2\sigma(I)$
Monochromator: graphite	R_{int} = 0.060
T = 273(2) K	θ_{max} = 26.0º
φ and ω scan	θ_{min} = 2.7º
Absorption correction: multi-scan (SADABS; Bruker, 2001)	*h* = −9→9
T_{min} = 0.950, T_{max} = 0.973	*k* = −16→17
4402 measured reflections	*l* = −8→18

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
$wR(F^2)$ = 0.169	$w = 1/[\sigma^2(F_o^2) + (0.0857P)^2 + 0.3739P]$ where $P = (F_o^2 + 2F_c^2)/3$
S = 1.01	$(\Delta/\sigma)_{max}$ = 0.048
1626 reflections	$\Delta\rho_{max}$ = 0.29 e Å^{-3}
118 parameters	$\Delta\rho_{min}$ = −0.28 e Å^{-3}
Primary atom site location: structure-invariant direct methods	Extinction correction: none

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}
S1	0.11589 (13)	0.51429 (7)	0.38748 (7)	0.0572 (4)
N5	0.2341 (3)	0.73058 (19)	0.24951 (19)	0.0425 (8)
C6	0.2889 (4)	0.6629 (2)	0.2010 (2)	0.0362 (8)
N3	0.2571 (3)	0.57925 (19)	0.2400 (2)	0.0414 (7)
C3	0.3732 (4)	0.6799 (2)	0.1189 (2)	0.0366 (8)
N1	0.5323 (3)	0.7249 (2)	−0.0353 (2)	0.0468 (8)
N4	0.1676 (3)	0.68743 (19)	0.31970 (19)	0.0401 (7)
H4B	0.1229	0.7172	0.3624	0.048*
C7	0.1781 (4)	0.5945 (2)	0.3160 (2)	0.0409 (9)
C1	0.5178 (5)	0.7863 (3)	0.0293 (3)	0.0551 (11)
H1A	0.5630	0.8462	0.0219	0.066*
N2	0.2980 (4)	0.49002 (19)	0.2082 (2)	0.0579 (10)
H2B	0.2642	0.4458	0.2463	0.087*
H2C	0.2407	0.4820	0.1550	0.087*
C4	0.3874 (5)	0.6154 (3)	0.0534 (3)	0.0564 (11)
H4A	0.3438	0.5550	0.0596	0.068*
C5	0.4670 (5)	0.6408 (3)	−0.0219 (3)	0.0591 (11)
H5A	0.4753	0.5959	−0.0663	0.071*
C2	0.4414 (4)	0.7675 (3)	0.1055 (2)	0.0493 (10)
H2A	0.4350	0.8138	0.1488	0.059*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
S1	0.0686 (7)	0.0505 (6)	0.0540 (7)	0.0022 (5)	0.0170 (6)	0.0140 (5)
N5	0.0460 (16)	0.0430 (16)	0.0394 (18)	−0.0043 (12)	0.0104 (15)	−0.0002 (13)
C6	0.0297 (16)	0.0445 (19)	0.034 (2)	−0.0018 (13)	0.0000 (15)	0.0030 (16)
N3	0.0415 (15)	0.0405 (16)	0.0433 (18)	0.0031 (11)	0.0118 (14)	0.0008 (13)
C3	0.0259 (15)	0.0485 (19)	0.035 (2)	0.0043 (13)	0.0030 (15)	0.0050 (16)
N1	0.0402 (15)	0.062 (2)	0.0383 (19)	0.0031 (14)	0.0070 (14)	0.0012 (16)
N4	0.0420 (15)	0.0470 (17)	0.0324 (17)	−0.0008 (12)	0.0111 (14)	0.0011 (13)
C7	0.0330 (16)	0.043 (2)	0.047 (2)	0.0027 (14)	0.0053 (17)	0.0025 (16)
C1	0.064 (2)	0.048 (2)	0.055 (3)	−0.0077 (17)	0.018 (2)	0.002 (2)
N2	0.076 (2)	0.0413 (17)	0.060 (2)	0.0057 (15)	0.0273 (19)	−0.0025 (16)
C4	0.070 (2)	0.047 (2)	0.053 (3)	−0.0123 (18)	0.018 (2)	−0.005 (2)
C5	0.077 (3)	0.059 (3)	0.043 (2)	−0.002 (2)	0.021 (2)	−0.0063 (19)
C2	0.061 (2)	0.046 (2)	0.042 (2)	0.0017 (17)	0.0151 (19)	−0.0012 (17)

Geometric parameters (Å, °)

S1—C7	1.659 (4)	N4—C7	1.325 (4)
N5—C6	1.295 (4)	N4—H4B	0.8600
N5—N4	1.350 (4)	C1—C2	1.349 (5)
C6—N3	1.356 (4)	C1—H1A	0.9300
C6—C3	1.452 (4)	N2—H2B	0.9000
N3—C7	1.347 (4)	N2—H2C	0.8999
N3—N2	1.399 (4)	C4—C5	1.371 (5)
C3—C4	1.355 (5)	C4—H4A	0.9300
C3—C2	1.372 (5)	C5—H5A	0.9300
N1—C5	1.319 (5)	C2—H2A	0.9300
N1—C1	1.317 (5)		
C6—N5—N4	104.9 (3)	N3—C7—S1	127.2 (3)
N5—C6—N3	109.5 (3)	N1—C1—C2	124.0 (3)
N5—C6—C3	122.4 (3)	N1—C1—H1A	118.0
N3—C6—C3	128.1 (3)	C2—C1—H1A	118.0
C7—N3—C6	109.3 (3)	N3—N2—H2B	109.6
C7—N3—N2	124.1 (3)	N3—N2—H2C	108.1
C6—N3—N2	126.6 (3)	H2B—N2—H2C	109.5
C4—C3—C2	117.3 (3)	C3—C4—C5	119.0 (4)
C4—C3—C6	124.6 (3)	C3—C4—H4A	120.5
C2—C3—C6	118.1 (3)	C5—C4—H4A	120.5
C5—N1—C1	115.9 (3)	N1—C5—C4	124.1 (4)
C7—N4—N5	113.1 (3)	N1—C5—H5A	118.0
C7—N4—H4B	123.4	C4—C5—H5A	118.0
N5—N4—H4B	123.4	C1—C2—C3	119.7 (3)
N4—C7—N3	103.2 (3)	C1—C2—H2A	120.1
N4—C7—S1	129.6 (3)	C3—C2—H2A	120.1

Hydrogen-bond geometry (Å, °)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N4—H4B···N1^{i}	0.86	1.91	2.772 (4)	175

Symmetry codes: (i) *x*−1/2, −*y*+3/2, *z*+1/2.

Fig. 1