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6-Methyl-7*H*-1,2,4-triazolo[4,3-*b*][1,2,4]triazepin-8(9*H*)-thione

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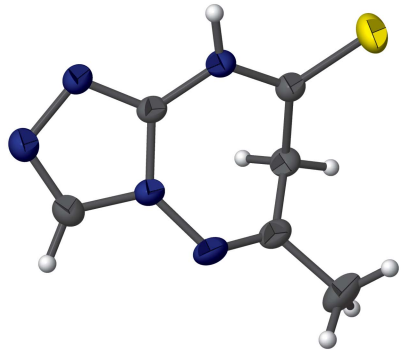
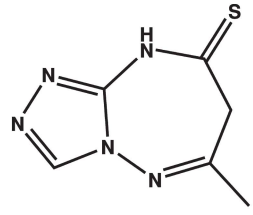
Structural data: full structural data are available from iucrdata.iucr.org

In the molecule of the title compound, $C_6H_7N_5S$, the triazole ring is planar, while the triazepine ring displays a boat conformation. The dihedral angle between the mean plane through the triazole and triazepine rings is 18.48 (8)°. In the crystal, molecules are linked into centrosymmetric dimers by N—H···N hydrogen bonds *via* eight-membered $\{\cdots HNCN\}_2$ synthons. Supramolecular layers in the *ab* plane are sustained by C—H···N and π–π interactions [inter-centroid separation between triazole rings = 3.2880 (16) Å]. Connections along the *c* axis occur between S atoms [S···S = 3.5972 (16) Å].

3D view



Chemical scheme



Structure description

Triazolotriazepine derivatives have been used as potent inhibitors of bone resorption (Chikazu *et al.*, 2000). They also exhibit anti-fungal activity (Gupta *et al.*, 2011). In view of the potential biological activity of fused azepines (Dabholkar & More, 2004; Sewell & Hawking, 1950; Acheson & Taylor, 1956) and as part of our interest in the synthesis of new heterocyclic systems containing triazole rings and triazepine (Essassi *et al.*, 1976, 1977; Gupta, 2007), the title compound was synthesized and its crystal structure determined.

The molecule of the title compound is built up from two fused rings linked to a methyl group and a thione-sulfur atom as shown in Fig. 1. The mean plane through the triazepine ring makes a dihedral angle of 18.48 (8)° with the triazole ring. The triazepine ring adopts a boat conformation as indicated by the total puckering amplitude Q_T = 0.7882 (15) Å and spherical polar angles $\theta2$ = 71.71 (10)° with $\varphi2$ = 22.27 (11)° and $\varphi3$ = 122.3 (3)° (calculated using *PARST*; Nardelli, 1983).

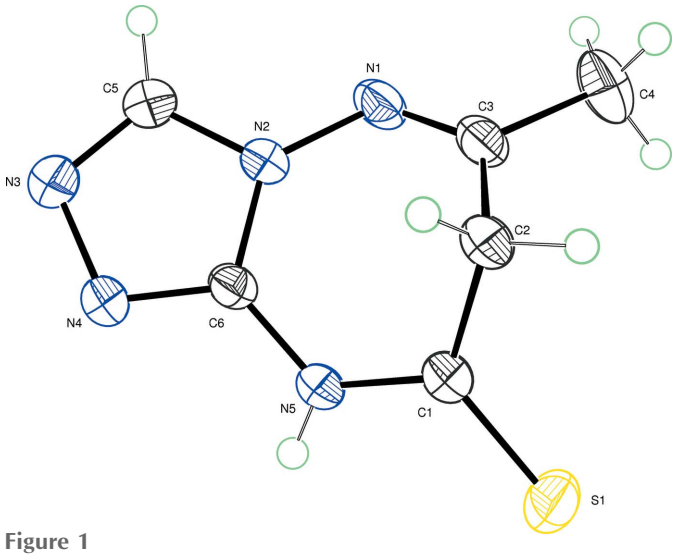


Figure 1
Plot of the molecule of the title compound showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 50% probability level.

In the crystal, the molecules are linked into supramolecular layers in the *ab* plane by N5—H5*N*···N4, C2—H2*A*···N3 and C5—H5···N1 hydrogen bonds, Table 1, in addition to π–π interactions between triazole rings, Fig. 2. Connections along the *c* axis occur between sulfur atoms [S···S = 3.5972 (16) Å]

Synthesis and crystallization

To a solution of 6-methyl-7*H*-[1,2,4]triazolo[4,3-*b*][1,2,4]tria-][1,2,4]triazepin-8(9*H*)-one (2 g, 12 mmol) and phosphore pentasulfide (2.7 g, 15 mmol) was added a small amount of sodium bicarbonate. The reaction mixture was heated at gentle reflux for 4 h then evaporated to dryness. The residue was taken up in boiling water (20 ml) and the precipitate that formed by cooling was filtered. The purified product was crystallized from ethanol to give colourless crystals in a yield of 65%.

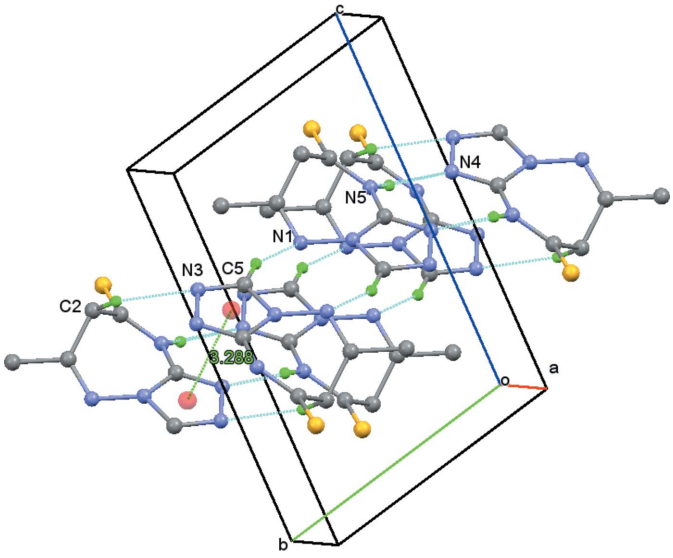


Figure 2
Plot showing molecules linked by N—H···N and C–H···N hydrogen bonds, in addition to π–π interactions.

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N5—H5*N*···N4^{i}	0.86	2.01	2.8530 (18)	167
C2—H2*A*···N3^{ii}	0.97	2.56	3.487 (2)	161
C5—H5···N1^{iii}	0.93	2.58	3.442 (2)	155

Symmetry codes: (i) $-x+1, -y, -z+1$; (ii) $-x, -y, -z+1$; (iii) $-x, -y+1, -z+1$.

Table 2
Experimental details.

Crystal data	
Chemical formula	$C_6H_7N_5S$
M_r	181.23
Crystal system, space group	Triclinic, $P\overline{1}$
Temperature (K)	296
a, *b*, *c* (Å)	6.238 (2), 7.234 (3), 10.887 (4)
α, β, γ (°)	103.331 (15), 92.329 (16), 113.846 (15)
V (Å^3)	432.3 (3)
Z	2
Radiation type	Mo *K*α
μ (mm^{-1})	0.33
Crystal size (mm)	0.35 × 0.30 × 0.26
Data collection	
Diffractometer	Bruker X8 APEX
Absorption correction	Multi-scan (*SADABS*; Krause *et al.*, 2015)
T_{min}, T_{max}	0.644, 0.747
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	10195, 2287, 2038
R_{int}	0.032
(sin $\theta/\lambda)_{max}$ (Å^{-1})	0.694
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, *S*	0.039, 0.119, 1.07
No. of reflections	2287
No. of parameters	110
H-atom treatment	H-atom parameters constrained
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.47, −0.38

Computer programs: *APEX2* and *SAINT* (Bruker, 2009), *SHELXT2014* (Sheldrick, 2015*a*), *SHELXL2014* (Sheldrick, 2015*b*), *ORTEPIII* (Burnett & Johnson, 1996), *ORTEP-3 for Windows* (Farrugia, 2012), *Mercury* (Macrae *et al.*, 2008) and *publCIF* (Westrip, 2010).

Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2.

Acknowledgements

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full crystallographic data

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Crystal data

$C_6H_7N_5S$
M_r = 181.23
Triclinic, $P\overline{1}$
a = 6.238 (2) Å
b = 7.234 (3) Å
c = 10.887 (4) Å
α = 103.331 (15)°
β = 92.329 (16)°
γ = 113.846 (15)°
V = 432.3 (3) Å^3
Z = 2
$F(000)$ = 188
D_x = 1.392 Mg m^{-3}
Mo $K\alpha$ radiation, λ = 0.71073 Å
Cell parameters from 2287 reflections
θ = 3.2–29.6°
μ = 0.33 mm^{-1}
T = 296 K
Block, colourless
0.35 × 0.30 × 0.26 mm

Data collection

Bruker X8 APEX diffractometer
Radiation source: fine-focus sealed tube
Graphite monochromator
φ and ω scans
Absorption correction: multi-scan (SADABS; Krause *et al.*, 2015)
T_{min} = 0.644, T_{max} = 0.747
10195 measured reflections
2287 independent reflections
2038 reflections with $I > 2\sigma(I)$
R_{int} = 0.032
θ_{max} = 29.6°, θ_{min} = 3.2°
h = −8→8
k = −10→10
l = −14→15

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.039
$wR(F^2)$ = 0.119
S = 1.07
2287 reflections
110 parameters
0 restraints
Hydrogen site location: mixed
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0613P)^2 + 0.1769P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.47 e Å^{-3}
$\Delta\rho_{min}$ = −0.38 e Å^{-3}

Special details

Geometry. All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²)

	x	*y*	*z*	U_{iso}*/U_{eq}
C1	0.5444 (3)	0.3425 (2)	0.76025 (13)	0.0284 (3)
C2	0.3456 (3)	0.4034 (2)	0.79409 (13)	0.0306 (3)
H2A	0.1951	0.2807	0.7656	0.037*
H2B	0.3627	0.4553	0.8861	0.037*
C3	0.3466 (3)	0.5699 (2)	0.73291 (14)	0.0318 (3)
C4	0.4105 (4)	0.7857 (3)	0.81648 (19)	0.0507 (5)
H4A	0.5692	0.8425	0.8607	0.076*
H4B	0.3025	0.7790	0.8775	0.076*
H4C	0.4007	0.8741	0.7650	0.076*
C5	0.1097 (3)	0.2566 (2)	0.41943 (15)	0.0344 (3)
H5	0.0219	0.3170	0.3869	0.041*
C6	0.3465 (2)	0.2043 (2)	0.54244 (13)	0.0253 (3)
N1	0.2954 (2)	0.54000 (18)	0.61292 (13)	0.0324 (3)
N2	0.2479 (2)	0.33992 (17)	0.53619 (11)	0.0275 (2)
N3	0.1165 (2)	0.0823 (2)	0.35948 (12)	0.0345 (3)
N4	0.2688 (2)	0.04725 (18)	0.43825 (11)	0.0295 (3)
N5	0.5193 (2)	0.23657 (19)	0.63695 (11)	0.0290 (3)
H5N	0.6036	0.1688	0.6148	0.035*
S1	0.77311 (8)	0.39546 (8)	0.86328 (4)	0.04839 (17)

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C1	0.0301 (7)	0.0290 (6)	0.0273 (6)	0.0153 (5)	0.0046 (5)	0.0045 (5)
C2	0.0326 (7)	0.0352 (7)	0.0271 (6)	0.0192 (6)	0.0079 (5)	0.0045 (5)
C3	0.0310 (7)	0.0285 (6)	0.0360 (7)	0.0160 (5)	0.0074 (6)	0.0020 (5)
C4	0.0658 (12)	0.0320 (8)	0.0477 (10)	0.0219 (8)	0.0097 (9)	−0.0037 (7)
C5	0.0345 (7)	0.0372 (7)	0.0336 (7)	0.0197 (6)	−0.0010 (6)	0.0059 (6)
C6	0.0259 (6)	0.0253 (6)	0.0271 (6)	0.0140 (5)	0.0056 (5)	0.0051 (5)
N1	0.0369 (6)	0.0246 (5)	0.0380 (7)	0.0176 (5)	0.0062 (5)	0.0042 (4)
N2	0.0292 (6)	0.0257 (5)	0.0294 (6)	0.0155 (4)	0.0027 (4)	0.0041 (4)
N3	0.0334 (6)	0.0378 (6)	0.0308 (6)	0.0178 (5)	−0.0017 (5)	0.0024 (5)
N4	0.0314 (6)	0.0287 (5)	0.0280 (6)	0.0158 (5)	0.0022 (4)	0.0017 (4)
N5	0.0317 (6)	0.0332 (6)	0.0261 (5)	0.0212 (5)	0.0029 (4)	0.0015 (4)
S1	0.0423 (3)	0.0695 (3)	0.0326 (2)	0.0328 (2)	−0.00534 (17)	−0.00263 (19)

Geometric parameters (Å, º)

C1—N5	1.3509 (18)	C4—H4C	0.9600
C1—C2	1.5072 (19)	C5—N3	1.298 (2)
C1—S1	1.6343 (16)	C5—N2	1.3636 (19)
C2—C3	1.503 (2)	C5—H5	0.9300
C2—H2A	0.9700	C6—N4	1.3144 (17)
C2—H2B	0.9700	C6—N2	1.3647 (17)
C3—N1	1.279 (2)	C6—N5	1.3675 (18)

C3—C4	1.495 (2)	N1—N2	1.3986 (16)
C4—H4A	0.9600	N3—N4	1.3898 (18)
C4—H4B	0.9600	N5—H5N	0.8599
N5—C1—C2	114.93 (12)	H4B—C4—H4C	109.5
N5—C1—S1	121.53 (11)	N3—C5—N2	111.33 (13)
C2—C1—S1	123.54 (10)	N3—C5—H5	124.3
C3—C2—C1	111.00 (12)	N2—C5—H5	124.3
C3—C2—H2A	109.4	N4—C6—N2	110.24 (12)
C1—C2—H2A	109.4	N4—C6—N5	124.33 (12)
C3—C2—H2B	109.4	N2—C6—N5	125.12 (12)
C1—C2—H2B	109.4	C3—N1—N2	115.92 (12)
H2A—C2—H2B	108.0	C5—N2—C6	104.35 (11)
N1—C3—C4	117.00 (15)	C5—N2—N1	122.64 (12)
N1—C3—C2	124.37 (12)	C6—N2—N1	132.08 (12)
C4—C3—C2	118.62 (15)	C5—N3—N4	106.88 (12)
C3—C4—H4A	109.5	C6—N4—N3	107.19 (12)
C3—C4—H4B	109.5	C1—N5—C6	125.05 (12)
H4A—C4—H4B	109.5	C1—N5—H5N	120.1
C3—C4—H4C	109.5	C6—N5—H5N	114.4
H4A—C4—H4C	109.5		

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N5—H5*N*···N4^{i}	0.86	2.01	2.8530 (18)	167
C2—H2*A*···N3^{ii}	0.97	2.56	3.487 (2)	161
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