

3-Methylsulfanyl-5-phenyl-4H-1,2,4-triazol-4-amine–water (6/1)

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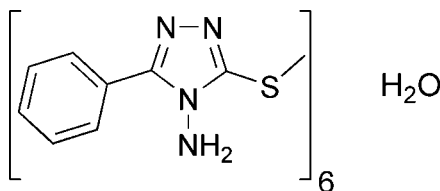
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Key indicators: single-crystal X-ray study; $T = 298$ K; mean $\sigma(\text{C}-\text{C}) = 0.007$ Å; disorder in solvent or counterion; R factor = 0.073; wR factor = 0.204; data-to-parameter ratio = 14.7.

In the title compound, $6\text{C}_9\text{H}_{10}\text{N}_4\text{S}\cdot\text{H}_2\text{O}$, the dihedral angle between the five-membered triazole ring and the phenyl ring is $44.33(16)^\circ$. The solvent water molecule is disordered about a special position with $\bar{3}$ symmetry and its occupancy cannot be greater than 0.1667. The crystal structure is stabilized by intermolecular $\text{N}-\text{H}\cdots\text{N}$ and $\text{C}-\text{H}\cdots\text{N}$ hydrogen bonds.

Related literature

For general background to 1,2,4-triazoles, see: Feng *et al.* (1992); Hui *et al.* (2000); Prasad *et al.* (1989); Mohan *et al.* (1987) For related structures, see: Xiang *et al.* (2004); Jin *et al.* (2004)



Experimental

Crystal data

$6\text{C}_9\text{H}_{10}\text{N}_4\text{S}\cdot\text{H}_2\text{O}$
 $M_r = 1255.73$

Hexagonal, $R\bar{3}$
 $a = 23.0266(15)$ Å

$c = 10.5190(9)$ Å
 $V = 4830.2(6)$ Å³
 $Z = 3$
Mo $K\alpha$ radiation

$\mu = 0.27$ mm⁻¹
 $T = 298$ K
 $0.32 \times 0.23 \times 0.15$ mm

Data collection

Bruker SMART CCD area-detector diffractometer
Absorption correction: multi-scan (*SADABS*; Bruker, 2002)
 $T_{\min} = 0.918$, $T_{\max} = 0.960$
8946 measured reflections
2011 independent reflections
1647 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.047$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.073$
 $wR(F^2) = 0.204$
 $S = 0.99$
2011 reflections
137 parameters
H-atom parameters constrained
 $\Delta\rho_{\max} = 0.70$ e Å⁻³
 $\Delta\rho_{\min} = -0.27$ e Å⁻³

Table 1

Hydrogen-bond geometry (Å, °).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
$\text{N4}-\text{H4A}\cdots\text{N1}^{\text{i}}$	0.86	2.30	3.127 (4)	162
$\text{N4}-\text{H4B}\cdots\text{N2}^{\text{ii}}$	0.86	2.21	3.060 (4)	172
$\text{C5}-\text{H5}\cdots\text{N1}^{\text{i}}$	0.93	2.60	3.507 (6)	167

Symmetry codes: (i) $y, -x + y + 1, -z + 1$; (ii) $-y + \frac{5}{3}, x - y + \frac{1}{3}, z + \frac{1}{3}$.

Data collection: *SMART* (Bruker, 2002); cell refinement: *SAINT* (Bruker, 2002); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *SHELXTL* (Sheldrick, 2008); software used to prepare material for publication: *SHELXTL*.

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: SJ2552).

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supplementary materials

Acta Cryst. (2009). E65, o676 [doi:10.1107/S1600536808041056]

3-Methylsulfanyl-5-phenyl-4*H*-1,2,4-triazol-4-amine-water (6/1)

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Comment

A literature survey reveals that 1,2,4-triazoles are good intermediates in the synthesis of some fused heterocycles which exhibit various biological properties, including antimicrobial (Feng *et al.*, 1992), antibacterial and antifungal (Hui *et al.*, 2000), anti-inflammatory (Prasad *et al.*, 1989) and diuretic (Mohan & Anjaneyulu, 1987) activities.

The molecule of (I), Fig. 1, contains a five-membered triazole ring A(N1,N2,C3,N3,C2) with a benzene ring substituent B(C1—C6). The two rings are each essentially planar, with average deviations from planarity of 0.003 (1) and 0.004 (1) Å, respectively. The dihedral angle between the thiadiazole ring and the benzene ring is 44.33 (16)°.

The water molecule is disordered about a threefold inversion axis such that the asymmetric unit comprises one C₉H₁₀N₄S molecule and a water molecule with occupancy *ca* 0.167

The C—N bond lengths in the molecule lie in the range 1.302 (5)–1.364 (4) Å. These are longer than a typical double C=N bond [*ca* 1.269 (2) Å] (Xiang *et al.*, 2004), but shorter than a C—N single bond [*ca* 1.443 (4) Å] (Jin *et al.*, 2004), indicating a degree of electron delocalization in the triazole ring.

The crystal packing in (I), Fig. 2, is stabilized by intermolecular and intramolecular N—H···N and C—H···N hydrogen bonds, Table 1.

Experimental

4-Amino-5-phenyl-2,4-dihydro[1,2,4]triazole-3-thione(0.96 g 5.0 mmol), methyl iodide(1.07 g 7.5 mmol) and sodium hydroxide(0.28 g 7.0 mmol) were dissolved in stirred dichloromethane (30 ml)and left for 2 h at room temperature. The resulting solid was filtered off and recrystallized from ethanol to give the title compound in 73% yield. Crystals suitable for X-ray analysis were obtained by slow evaporation of a ethanol solution at room temperature (m.p. 425–426 K).

Refinement

H atoms bound to N and O atoms were found in difference Fourier maps and their distances restrained to N—H = 0.86 (2)Å and O—H = 0.85 (2)Å with $U_{\text{iso}} = 1.2U_{\text{eq}}$ (parent atom), respectively. All other H atoms were positioned geometrically and allowed to ride on their parent atoms at distances of $C_{\text{sp}^2}\text{—H} = 0.93$ Å with $U_{\text{iso}} = 1.2 U_{\text{eq}}$ (parent atom), C(methyl)-H = 0.96 Å with $U_{\text{iso}} = 1.5 U_{\text{eq}}$ (parent atom).

Figures

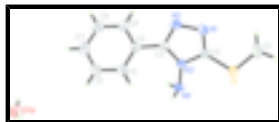


Fig. 1. The formula unit of (I) with atom numbering, showing displacement ellipsoids at the 50% probability level.

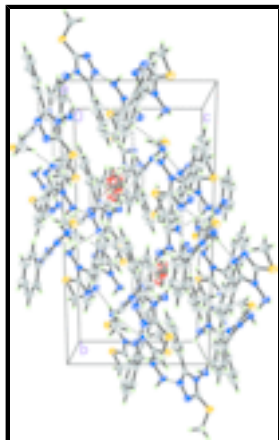


Fig. 2. Part of the crystal structure, showing the infinite hydrogen-bonding network of (I) running along the *a* axis. Hydrogen bonds are indicated by dashed lines.

3-Methylsulfanyl-5-phenyl-4*H*-1,2,4-triazol-4-amine–water (6/1)

Crystal data

$6\text{C}_9\text{H}_{10}\text{N}_4\text{S}\cdot\text{H}_2\text{O}$

$M_r = 1255.73$

Hexagonal, $R\bar{3}$

Hall symbol: $-R\ 3$

$a = 23.0266\ (15)\ \text{\AA}$

$b = 23.0266\ (15)\ \text{\AA}$

$c = 10.5190\ (9)\ \text{\AA}$

$\alpha = 90^\circ$

$\beta = 90^\circ$

$\gamma = 120^\circ$

$V = 4830.2\ (6)\ \text{\AA}^3$

$Z = 3$

$F_{000} = 2004$

$D_x = 1.314\ \text{Mg m}^{-3}$

Mo $K\alpha$ radiation

$\lambda = 0.71073\ \text{\AA}$

Cell parameters from 2375 reflections

$\theta = 2.2\text{--}23.0^\circ$

$\mu = 0.27\ \text{mm}^{-1}$

$T = 298\ \text{K}$

Prism, colorless

$0.32 \times 0.23 \times 0.15\ \text{mm}$

Data collection

Bruker SMART CCD area-detector
diffractometer

Radiation source: fine-focus sealed tube

Monochromator: graphite

$T = 298\ \text{K}$

φ and ω scans

Absorption correction: multi-scan
(SADABS; Bruker, 2002)

$T_{\min} = 0.918$, $T_{\max} = 0.960$

2011 independent reflections

1647 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.047$

$\theta_{\text{max}} = 25.5^\circ$

$\theta_{\text{min}} = 1.8^\circ$

$h = -27 \rightarrow 27$

$k = -27 \rightarrow 20$

8946 measured reflections

$l = -10 \rightarrow 12$

Refinement

Refinement on F^2

Secondary atom site location: difference Fourier map

Least-squares matrix: full

Hydrogen site location: inferred from neighbouring sites

$R[F^2 > 2\sigma(F^2)] = 0.073$

H-atom parameters constrained

$wR(F^2) = 0.204$

$$w = 1/[\sigma^2(F_o^2) + (0.1049P)^2 + 19.9182P]$$

where $P = (F_o^2 + 2F_c^2)/3$

$S = 0.99$

$(\Delta/\sigma)_{\max} < 0.001$

2011 reflections

$\Delta\rho_{\max} = 0.70 \text{ e } \text{\AA}^{-3}$

137 parameters

$\Delta\rho_{\min} = -0.27 \text{ e } \text{\AA}^{-3}$

Primary atom site location: structure-invariant direct methods

Extinction correction: none

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.

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

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$	Occ. (<1)
S1	1.03285 (6)	0.89151 (5)	0.71331 (11)	0.0608 (4)	
O1W	0.645 (2)	0.348 (3)	0.356 (2)	0.095 (12)	0.166667
H1W	0.6667	0.3333	0.3967	0.142*	0.50
H2W	0.6439	0.3779	0.3102	0.142*	0.166667
N1	1.08197 (15)	0.83742 (16)	0.5409 (3)	0.0520 (8)	
N2	1.05881 (15)	0.77523 (16)	0.4828 (3)	0.0501 (8)	
N3	0.98055 (13)	0.76822 (14)	0.6086 (3)	0.0381 (7)	
N4	0.92266 (14)	0.74747 (15)	0.6827 (3)	0.0457 (8)	
H4A	0.8918	0.7438	0.6318	0.055*	
H4B	0.9136	0.7090	0.7124	0.055*	
C1	1.1062 (3)	0.9644 (2)	0.6516 (5)	0.0809 (15)	
H1A	1.1442	0.9579	0.6578	0.121*	
H1B	1.1146	1.0031	0.7001	0.121*	
H1C	1.0989	0.9709	0.5642	0.121*	
C2	1.03399 (18)	0.83096 (18)	0.6157 (3)	0.0433 (9)	
C3	0.99830 (17)	0.73476 (18)	0.5243 (3)	0.0410 (8)	
C4	0.95704 (18)	0.66410 (18)	0.4868 (3)	0.0427 (8)	

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C5	0.8903 (2)	0.6366 (2)	0.4557 (4)	0.0555 (10)
H5	0.8695	0.6622	0.4626	0.067*
C6	0.8543 (2)	0.5711 (2)	0.4142 (5)	0.0726 (13)
H6	0.8092	0.5526	0.3935	0.087*
C7	0.8845 (3)	0.5333 (2)	0.4034 (5)	0.0783 (14)
H7	0.8600	0.4892	0.3746	0.094*
C8	0.9510 (3)	0.5600 (2)	0.4349 (5)	0.0689 (13)
H8	0.9714	0.5341	0.4276	0.083*
C9	0.9874 (2)	0.6252 (2)	0.4773 (4)	0.0524 (10)
H9	1.0322	0.6431	0.4996	0.063*

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
S1	0.0603 (7)	0.0493 (6)	0.0676 (7)	0.0236 (5)	0.0099 (5)	-0.0071 (5)
O1W	0.050 (15)	0.09 (3)	0.100 (18)	0.001 (10)	0.041 (12)	-0.015 (14)
N1	0.0389 (17)	0.0496 (19)	0.060 (2)	0.0166 (15)	0.0097 (15)	0.0029 (15)
N2	0.0428 (18)	0.0512 (19)	0.0565 (19)	0.0236 (15)	0.0112 (14)	0.0018 (15)
N3	0.0322 (14)	0.0406 (16)	0.0436 (16)	0.0197 (13)	0.0060 (12)	0.0054 (12)
N4	0.0378 (16)	0.0474 (17)	0.0534 (19)	0.0225 (14)	0.0097 (13)	0.0090 (14)
C1	0.079 (3)	0.044 (2)	0.095 (4)	0.012 (2)	0.013 (3)	-0.005 (2)
C2	0.0404 (19)	0.0412 (19)	0.048 (2)	0.0203 (16)	0.0030 (16)	0.0040 (15)
C3	0.0404 (19)	0.045 (2)	0.0417 (19)	0.0245 (16)	0.0027 (15)	0.0037 (15)
C4	0.048 (2)	0.045 (2)	0.0392 (19)	0.0258 (17)	0.0067 (15)	0.0056 (15)
C5	0.050 (2)	0.053 (2)	0.069 (3)	0.029 (2)	-0.0036 (19)	-0.005 (2)
C6	0.056 (3)	0.057 (3)	0.100 (4)	0.025 (2)	-0.012 (2)	-0.012 (3)
C7	0.080 (3)	0.048 (3)	0.102 (4)	0.028 (2)	0.000 (3)	-0.014 (2)
C8	0.081 (3)	0.060 (3)	0.081 (3)	0.047 (3)	0.010 (3)	0.001 (2)
C9	0.055 (2)	0.056 (2)	0.054 (2)	0.033 (2)	0.0063 (18)	0.0038 (18)

Geometric parameters (\AA , $^\circ$)

S1—C2	1.743 (4)	N4—H4B	0.8600
S1—C1	1.804 (5)	C1—H1A	0.9600
O1W—O1W ⁱ	0.88 (3)	C1—H1B	0.9600
O1W—O1W ⁱⁱ	0.88 (3)	C1—H1C	0.9600
O1W—O1W ⁱⁱⁱ	1.28 (4)	C3—C4	1.470 (5)
O1W—O1W ^{iv}	1.28 (4)	C4—C5	1.378 (5)
O1W—O1W ^v	1.55 (4)	C4—C9	1.388 (5)
O1W—H1W	0.8501	C5—C6	1.379 (6)
O1W—H2W	0.8500	C5—H5	0.9300
N1—C2	1.302 (5)	C6—C7	1.365 (7)
N1—N2	1.395 (5)	C6—H6	0.9300
N2—C3	1.305 (5)	C7—C8	1.375 (7)
N3—C2	1.352 (5)	C7—H7	0.9300
N3—C3	1.364 (4)	C8—C9	1.377 (6)
N3—N4	1.406 (4)	C8—H8	0.9300
N4—H4A	0.8601	C9—H9	0.9300

C2—S1—C1	98.7 (2)	S1—C1—H1C	109.5
O1W ⁱ —O1W—O1W ⁱⁱ	93 (4)	H1A—C1—H1C	109.5
O1W ⁱ —O1W—O1W ⁱⁱⁱ	89.994 (4)	H1B—C1—H1C	109.5
O1W ⁱⁱ —O1W—O1W ^{iv}	89.995 (9)	N1—C2—N3	110.8 (3)
O1W ⁱⁱⁱ —O1W—O1W ^v	60.000 (8)	N1—C2—S1	128.0 (3)
O1W ⁱ —O1W—O1W ^v	55.4 (9)	N3—C2—S1	121.2 (3)
O1W ⁱⁱ —O1W—O1W ^v	55.4 (9)	N2—C3—N3	109.2 (3)
O1W ⁱ —O1W—H1W	85.0	N2—C3—C4	124.7 (3)
O1W ⁱⁱ —O1W—H1W	85.0	N3—C3—C4	126.1 (3)
O1W ^v —O1W—H1W	48.2	C5—C4—C9	119.5 (4)
O1W ⁱ —O1W—H2W	67.8	C5—C4—C3	121.8 (3)
O1W ⁱⁱ —O1W—H2W	108.1	C9—C4—C3	118.6 (3)
O1W ⁱⁱⁱ —O1W—H2W	144.8	C4—C5—C6	119.9 (4)
O1W ^{iv} —O1W—H2W	110.0	C4—C5—H5	120.0
O1W ^v —O1W—H2W	117.3	C6—C5—H5	120.0
H1W—O1W—H2W	149.9	C7—C6—C5	120.4 (4)
C2—N1—N2	106.3 (3)	C7—C6—H6	119.8
C3—N2—N1	108.1 (3)	C5—C6—H6	119.8
C2—N3—C3	105.6 (3)	C6—C7—C8	120.1 (4)
C2—N3—N4	122.3 (3)	C6—C7—H7	119.9
C3—N3—N4	132.0 (3)	C8—C7—H7	119.9
N3—N4—H4A	106.6	C7—C8—C9	120.1 (4)
N3—N4—H4B	104.5	C7—C8—H8	120.0
H4A—N4—H4B	111.3	C9—C8—H8	120.0
S1—C1—H1A	109.5	C8—C9—C4	119.9 (4)
S1—C1—H1B	109.5	C8—C9—H9	120.1
H1A—C1—H1B	109.5	C4—C9—H9	120.1
C2—N1—N2—C3	0.4 (4)	N4—N3—C3—C4	1.5 (6)
N2—N1—C2—N3	-0.6 (4)	N2—C3—C4—C5	-135.3 (4)
N2—N1—C2—S1	-179.7 (3)	N3—C3—C4—C5	45.9 (5)
C3—N3—C2—N1	0.6 (4)	N2—C3—C4—C9	41.9 (5)
N4—N3—C2—N1	178.1 (3)	N3—C3—C4—C9	-137.0 (4)
C3—N3—C2—S1	179.7 (2)	C9—C4—C5—C6	-0.7 (6)
N4—N3—C2—S1	-2.7 (5)	C3—C4—C5—C6	176.4 (4)
C1—S1—C2—N1	11.9 (4)	C4—C5—C6—C7	-0.2 (7)
C1—S1—C2—N3	-167.1 (3)	C5—C6—C7—C8	0.6 (8)
N1—N2—C3—N3	-0.1 (4)	C6—C7—C8—C9	-0.1 (8)
N1—N2—C3—C4	-179.1 (3)	C7—C8—C9—C4	-0.8 (7)
C2—N3—C3—N2	-0.3 (4)	C5—C4—C9—C8	1.2 (6)
N4—N3—C3—N2	-177.5 (3)	C3—C4—C9—C8	-176.0 (4)
C2—N3—C3—C4	178.7 (3)		

Symmetry codes: (i) $y+1/3, -x+y+2/3, -z+2/3$; (ii) $x-y+1/3, x-1/3, -z+2/3$; (iii) $-y+1, x-y, z$; (iv) $-x+y+1, -x+1, z$; (v) $-x+4/3, -y+2/3, -z+2/3$.

supplementary materials

Hydrogen-bond geometry (Å, °)

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
$N4-H4A\cdots N1^{vi}$	0.86	2.30	3.127 (4)	162
$N4-H4B\cdots N2^{vii}$	0.86	2.21	3.060 (4)	172
$C5-H5\cdots N1^{vi}$	0.93	2.60	3.507 (6)	167

Symmetry codes: (vi) $y, -x+y+1, -z+1$; (vii) $-y+5/3, x-y+1/3, z+1/3$.

Fig. 1

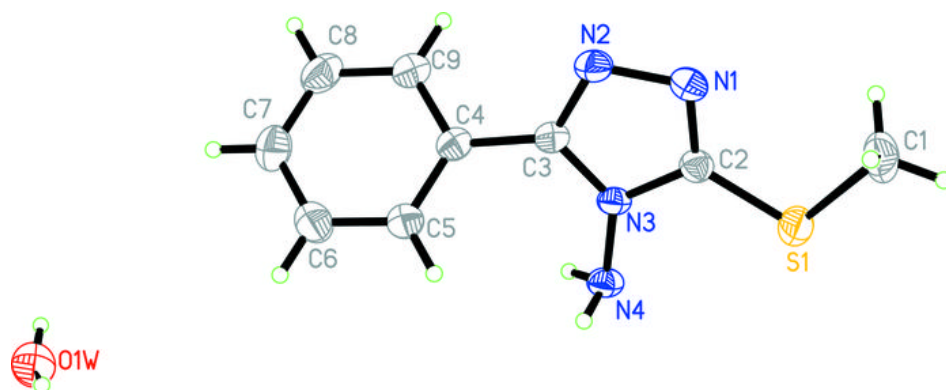


Fig. 2

