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

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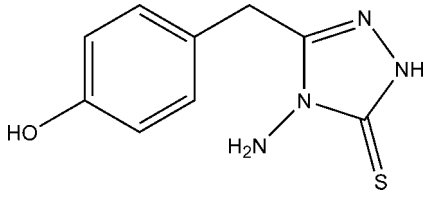
Key indicators: single-crystal X-ray study; T = 173 K; mean σ(C–C) = 0.004 Å; R factor = 0.041; wR factor = 0.102; data-to-parameter ratio = 13.1.

In the title compound, $C_9H_{10}N_4OS$, the dihedral angle between the benzene and 1*H*-1,2,4-triazole-5(4*H*)-thione rings is 67.51 (16)°. In the crystal, molecules are liked *via* N—H···O hydrogen bonds, forming chains along the *c*-axis direction. The chains are linked *via* O—H···S hydrogen bonds, forming corrugated layers lying parallel to the *bc* plane. The layers are linked *via* N—H···N and N—H···S hydrogen bonds, forming a three-dimensional network.

Related literature

For biological properties of 1,2,4-triazole derivatives, see: Holla *et al.* (2001, 2006); Mullican *et al.* (1993); Jones *et al.* (1965); Shams El-Dine *et al.* (1974); Misato *et al.* (1977); Kane *et al.* (1988). For related structures, see: Puviarasan *et al.* (1999); Chen *et al.* (2007); Karczmarzyk *et al.* (2012); Gao *et al.* (2011).



Experimental

Crystal data

$C_9H_{10}N_4OS$
M_r = 222.27
Triclinic, $P\overline{1}$
a = 4.2117 (5) Å
b = 6.1891 (7) Å
c = 10.0641 (11) Å
α = 100.590 (9)°
β = 94.916 (9)°
γ = 104.589 (10)°
V = 247.14 (5) Å^3
Z = 1
Mo $K\alpha$ radiation
μ = 0.31 mm^{-1}
T = 173 K
0.34 × 0.30 × 0.24 mm

Data collection

Agilent Gemini EOS diffractometer
Absorption correction: multi-scan (*CrysAlis PRO* and *CrysAlis RED*; Agilent, 2012).
T_{min} = 0.941, T_{max} = 1.000
2555 measured reflections
1897 independent reflections
1826 reflections with $I > 2\sigma(I)$
R_{int} = 0.035

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.041
$wR(F^2)$ = 0.102
S = 1.10
1897 reflections
145 parameters
3 restraints
H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$ = 0.29 e Å^{-3}
$\Delta\rho_{min}$ = −0.27 e Å^{-3}
Absolute structure: Flack (1983), 265 Friedel pairs (15% coverage)
Absolute structure parameter: −0.02 (9)

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

D—H···A	D—H	H···A	D···A	D—H···A
N2—H2···O1^{i}	0.88	1.97	2.840 (3)	170
O1—H1···S1^{ii}	0.95 (5)	2.27 (5)	3.180 (2)	159 (4)
N4—H4*A*···S1^{iii}	0.86	2.74	3.435 (3)	138
N4—H4*B*···N1^{iv}	0.91 (3)	2.32 (3)	3.149 (4)	153 (3)

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

Data collection: *CrysAlis PRO* (Agilent, 2012); cell refinement: *CrysAlis PRO*; data reduction: *CrysAlis RED* (Agilent, 2012); program(s) used to solve structure: *SUPERFLIP* (Palatinus & Chapuis, 2007); program(s) used to refine structure: *SHELXL2012* (Sheldrick, 2008); molecular graphics: *OLEX2* (Dolomanov *et al.*, 2009); software used to prepare material for publication: *OLEX2*.

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: SU2674).

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supporting information

Acta Cryst. (2014). E**70**, o48–o49 [https://doi.org/10.1107/S1600536813033370]

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

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S1. Comment

The chemistry of triazoles has received considerable attention in recent years because of their versatility in the synthesis of many other heterocyclic compounds. 1,2,4-Triazole derivatives are well known for their different biological activities, therefore various 1,2,4-triazole derivatives and their N-bridged heterocyclic analogs have been extensively studied (Holla *et al.*, 2001,2006). The derivatives of 1,2,4-triazole are known to exhibit anti-inflammatory (Mullican *et al.*, 1993), antiviral (Jones *et al.*, 1965), antimicrobial (Shams El-Dine *et al.*, 1974; Misato *et al.*, 1977) and antidepressant activity (Kane *et al.*, 1988). Hence synthesis of the corresponding heterocyclic compounds could be of interest from the viewpoint of chemical reactivity and biological activity.

The crystal structures of some related triazoles have been reported: 5-(2-Chlorophenyl)-4-phenyl-3,4-dihydro-2*H*-1,2,4-triazole-3-thione (Puviarasan *et al.*, 1999); 4-Amino-5-(2-ethoxyphenyl)-2,4-dihydro- 2*H*-1,2,4-triazole-3-thione-triphenylphosphine oxide (Chen *et al.*, 2007); Ethyl2-(3-methyl-5-sulfanylidene-4,5-dihydro- 1*H*-1,2,4-triazol-4-yl)acetate (Karczmarzyk *et al.*, 2012); 3-(4-Amino-3-phenyl-5-sulfanylidene-4,5-dihydro-1*H*-1,2,4-triazol-1- yl)-3-(2-chlorophenyl)-1-phenylpropan-1-one (Gao *et al.*, 2011). The present work describes the synthesis and crystal structure of the title compound.

In the title compound, Fig. 1, the dihedral angle between the benzene ring (C2-C7) and the 1*H*-1,2,4-triazole-5(4*H*)-thione ring (N1/N2/C9/N3/C8) is 67.51 (16) °.

In the crystal, a single N2—H2···O1 hydrogen bond and additional weak O1—H1···S1, N4—H4A···S1 and N4—H4B···N1 hydrogen bonds are observed (Table 1 and Fig. 2). These interactions link the molecules into one-dimensional chains extending along each of the three axes forming a three-dimensional supramolecular framework.

S2. Experimental

The synthesis of the title compound is described in Fig. 3. A well triturated mixture of 4-hydroxyphenylacetic acid (0.755 g, 0.005 mol) and thiocarbohydrazide (0.53 g, 0.005 mol) was fused in a round bottom flask for one hour on an oil bath at 413 K. It was cooled to room temperature and washed with sodium bicarbonate (5%) solution to remove unreacted acid and again washed with water. The dried compound was recrystallized from methanol yielding colourless block-like crystals (M.p. 475-477 K).

S3. Refinement

The OH and NH_2 H atoms (H1, and H4A/H4B, respectively) were located in a difference Fourier map and freely refined. The remaining H atoms were placed in calculated positions and refined using the riding model approximation: N-H = 0.88 Å, C-H = 0.95 and 0.99 Å for CH and CH_2 H atoms, respectively, with $U_{iso}(H) = 1.2U_{eq}(N,C)$.

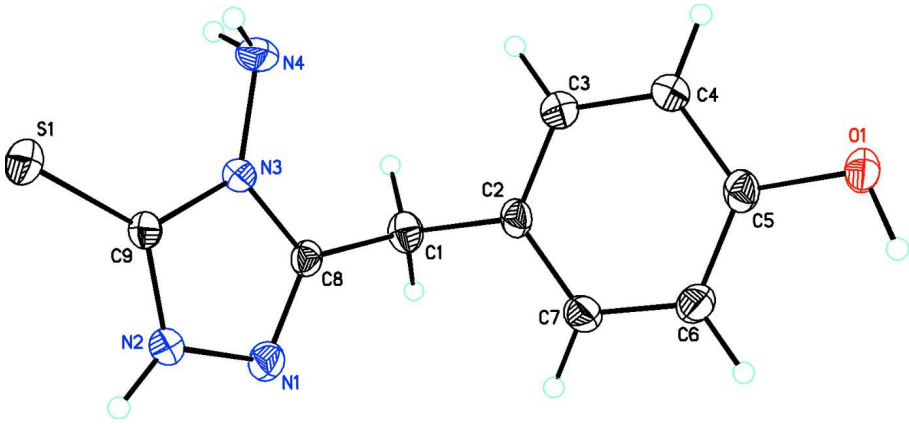

Figure 1

A view of the molecular structure of the title molecule, with atom labelling. The displacement ellipsoids are drawn at the 50% probability level.

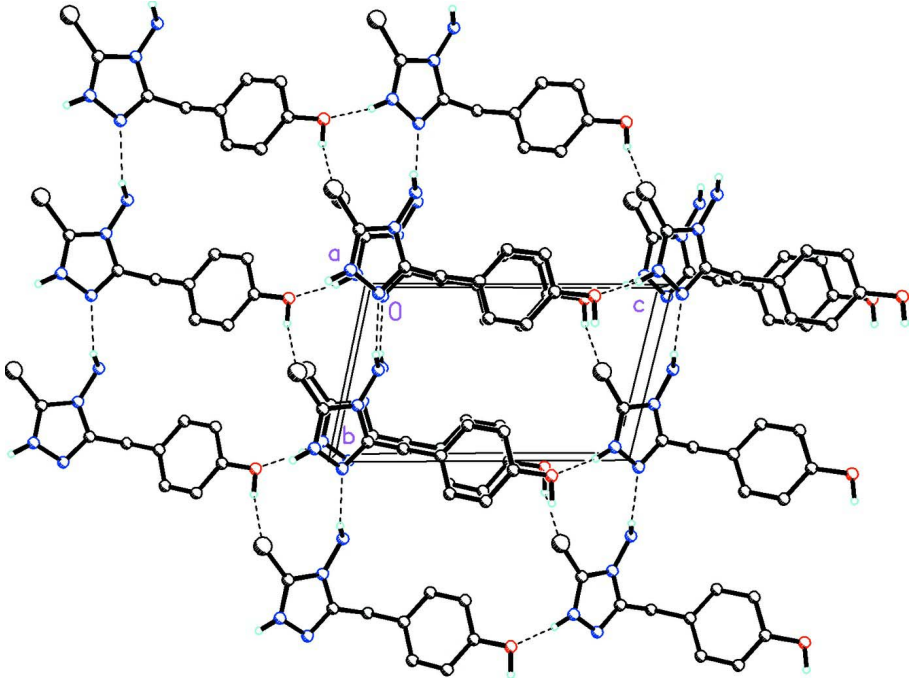

Figure 2

A view along the a axis of the crystal packing of the title compound. The hydrogen bonds are shown as dashed lines; see Table 1 for details; H atoms not involved in hydrogen bonding have been omitted for clarity.

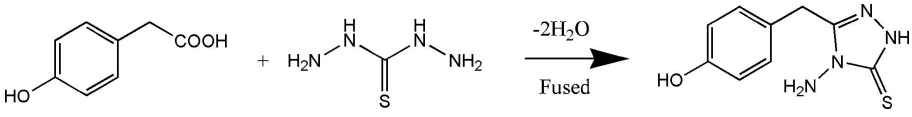

Figure 3

Synthesis of the title compound.

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

Crystal data

$C_9H_{10}N_4OS$
$M_r = 222.27$
Triclinic, $P\overline{1}$
$a = 4.2117$ (5) Å
$b = 6.1891$ (7) Å
$c = 10.0641$ (11) Å
$\alpha = 100.590$ (9)°
$\beta = 94.916$ (9)°
$\gamma = 104.589$ (10)°
$V = 247.14$ (5) Å^3
$Z = 1$
$F(000) = 116$
$D_x = 1.493$ Mg m^{-3}
Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Cell parameters from 1329 reflections
$\theta = 3.5$–$32.8°$
$\mu = 0.31$ mm^{-1}
$T = 173$ K
Block, colourless
0.34 × 0.30 × 0.24 mm

Data collection

Agilent Gemini EOS diffractometer
Radiation source: Enhance (Mo) X-ray Source
Detector resolution: 16.0416 pixels mm^{-1}
ω scans
Absorption correction: multi-scan (*CrysAlis PRO* and *CrysAlis RED*; Agilent, 2012).
$T_{min} = 0.941$, $T_{max} = 1.000$
2555 measured reflections
1897 independent reflections
1826 reflections with $I > 2\sigma(I)$
$R_{int} = 0.035$
$\theta_{max} = 32.9°$, $\theta_{min} = 3.5°$
$h = -6 \rightarrow 6$
$k = -8 \rightarrow 9$
$l = -14 \rightarrow 12$

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.041$
$wR(F^2) = 0.102$
$S = 1.10$
1897 reflections
145 parameters
3 restraints
Primary atom site location: structure-invariant direct methods
Hydrogen site location: mixed
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0512P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.29$ e Å^{-3}
$\Delta\rho_{min} = -0.27$ e Å^{-3}
Absolute structure: Flack (1983), 265 Friedel pairs (15% coverage)
Absolute structure parameter: −0.02 (9)

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}
S1	0.98393 (10)	0.49047 (8)	−0.16110 (7)	0.02134 (16)
O1	1.3407 (6)	1.0709 (3)	0.7411 (2)	0.0248 (4)
N1	0.8426 (6)	1.0486 (4)	0.0472 (3)	0.0217 (5)
N2	0.9604 (6)	0.9245 (4)	−0.0560 (2)	0.0205 (5)
H2	1.0738	0.9862	−0.1156	0.025*
N3	0.7176 (5)	0.6844 (3)	0.0529 (2)	0.0164 (4)

N4	0.5720 (6)	0.4828 (4)	0.0952 (3)	0.0227 (5)
H4A	0.3813	0.4158	0.0464	0.027*
C1	0.5336 (7)	0.9471 (5)	0.2357 (3)	0.0211 (5)
H1A	0.3342	0.8192	0.2314	0.025*
H1B	0.4603	1.0871	0.2357	0.025*
C2	0.7593 (7)	0.9795 (4)	0.3678 (3)	0.0187 (5)
C3	0.7404 (8)	0.8033 (5)	0.4367 (3)	0.0238 (6)
H3	0.5876	0.6587	0.3991	0.029*
C4	0.9400 (8)	0.8336 (5)	0.5596 (3)	0.0248 (6)
H4	0.9254	0.7104	0.6049	0.030*
C5	1.1611 (7)	1.0458 (5)	0.6157 (3)	0.0200 (5)
C6	1.1905 (7)	1.2236 (5)	0.5479 (3)	0.0229 (6)
H6	1.3466	1.3672	0.5849	0.027*
C7	0.9885 (8)	1.1898 (5)	0.4243 (3)	0.0219 (5)
H7	1.0071	1.3119	0.3779	0.026*
C8	0.6955 (6)	0.8986 (4)	0.1125 (3)	0.0167 (5)
C9	0.8850 (6)	0.7017 (4)	−0.0565 (3)	0.0168 (5)
H1	1.500 (12)	1.216 (7)	0.758 (5)	0.038 (11)*
H4B	0.713 (8)	0.395 (5)	0.079 (3)	0.009 (7)*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
S1	0.0238 (3)	0.0209 (3)	0.0187 (3)	0.0076 (2)	0.0035 (2)	0.0003 (2)
O1	0.0279 (10)	0.0253 (10)	0.0156 (10)	−0.0007 (8)	−0.0003 (8)	0.0027 (8)
N1	0.0283 (12)	0.0185 (10)	0.0187 (11)	0.0085 (9)	0.0033 (9)	0.0020 (8)
N2	0.0267 (12)	0.0182 (10)	0.0158 (11)	0.0041 (9)	0.0051 (9)	0.0039 (8)
N3	0.0182 (10)	0.0157 (9)	0.0148 (10)	0.0033 (8)	0.0018 (8)	0.0041 (8)
N4	0.0253 (11)	0.0180 (10)	0.0247 (13)	0.0021 (9)	0.0074 (10)	0.0079 (9)
C1	0.0215 (11)	0.0252 (12)	0.0185 (13)	0.0102 (10)	0.0038 (10)	0.0038 (10)
C2	0.0221 (11)	0.0212 (11)	0.0132 (12)	0.0070 (9)	0.0053 (9)	0.0017 (9)
C3	0.0278 (13)	0.0204 (11)	0.0203 (13)	0.0018 (10)	0.0023 (11)	0.0043 (10)
C4	0.0322 (14)	0.0202 (12)	0.0194 (13)	0.0012 (10)	0.0023 (11)	0.0061 (10)
C5	0.0215 (12)	0.0234 (12)	0.0145 (11)	0.0059 (10)	0.0058 (10)	0.0016 (9)
C6	0.0253 (13)	0.0194 (11)	0.0199 (13)	0.0007 (10)	0.0050 (11)	0.0008 (10)
C7	0.0289 (13)	0.0193 (11)	0.0187 (13)	0.0067 (10)	0.0067 (11)	0.0051 (9)
C8	0.0185 (11)	0.0173 (11)	0.0138 (11)	0.0059 (9)	−0.0013 (9)	0.0020 (9)
C9	0.0182 (11)	0.0173 (10)	0.0135 (11)	0.0034 (9)	0.0002 (9)	0.0026 (9)

Geometric parameters (Å, º)

S1—C9	1.683 (3)	C1—H1B	0.9900
O1—C5	1.376 (4)	C1—C2	1.517 (4)
O1—H1	0.95 (4)	C1—C8	1.484 (4)
N1—N2	1.379 (3)	C2—C3	1.385 (4)
N1—C8	1.297 (4)	C2—C7	1.396 (4)
N2—H2	0.8800	C3—H3	0.9500
N2—C9	1.334 (3)	C3—C4	1.389 (4)

N3—N4	1.403 (3)	C4—H4	0.9500
N3—C8	1.380 (3)	C4—C5	1.390 (4)
N3—C9	1.364 (3)	C5—C6	1.384 (4)
N4—H4A	0.8645	C6—H6	0.9500
N4—H4B	0.91 (3)	C6—C7	1.395 (4)
C1—H1A	0.9900	C7—H7	0.9500

C5—O1—H1	106 (3)	C2—C3—C4	121.4 (3)
C8—N1—N2	104.5 (2)	C4—C3—H3	119.3
N1—N2—H2	123.4	C3—C4—H4	120.3
C9—N2—N1	113.2 (2)	C3—C4—C5	119.4 (3)
C9—N2—H2	123.4	C5—C4—H4	120.3
C8—N3—N4	124.5 (2)	O1—C5—C4	117.3 (3)
C9—N3—N4	126.6 (2)	O1—C5—C6	122.3 (2)
C9—N3—C8	108.8 (2)	C6—C5—C4	120.4 (3)
N3—N4—H4A	109.6	C5—C6—H6	120.4
N3—N4—H4B	104 (2)	C5—C6—C7	119.3 (3)
H4A—N4—H4B	109.9	C7—C6—H6	120.4
H1A—C1—H1B	107.8	C2—C7—H7	119.4
C2—C1—H1A	109.0	C6—C7—C2	121.1 (3)
C2—C1—H1B	109.0	C6—C7—H7	119.4
C8—C1—H1A	109.0	N1—C8—N3	110.1 (2)
C8—C1—H1B	109.0	N1—C8—C1	125.8 (2)
C8—C1—C2	113.0 (2)	N3—C8—C1	124.2 (2)
C3—C2—C1	121.1 (2)	N2—C9—S1	129.2 (2)
C3—C2—C7	118.3 (3)	N2—C9—N3	103.4 (2)
C7—C2—C1	120.6 (2)	N3—C9—S1	127.36 (19)
C2—C3—H3	119.3		

O1—C5—C6—C7	−176.7 (3)	C3—C2—C7—C6	−0.9 (4)
N1—N2—C9—S1	−178.7 (2)	C3—C4—C5—O1	176.6 (3)
N1—N2—C9—N3	−1.2 (3)	C3—C4—C5—C6	−2.1 (5)
N2—N1—C8—N3	−0.1 (3)	C4—C5—C6—C7	1.9 (4)
N2—N1—C8—C1	178.4 (3)	C5—C6—C7—C2	−0.4 (4)
N4—N3—C8—N1	−177.2 (3)	C7—C2—C3—C4	0.7 (4)
N4—N3—C8—C1	4.3 (4)	C8—N1—N2—C9	0.8 (3)
N4—N3—C9—S1	−4.9 (4)	C8—N3—C9—S1	178.64 (19)
N4—N3—C9—N2	177.5 (3)	C8—N3—C9—N2	1.1 (3)
C1—C2—C3—C4	−178.2 (3)	C8—C1—C2—C3	−98.8 (3)
C1—C2—C7—C6	178.1 (3)	C8—C1—C2—C7	82.2 (3)
C2—C1—C8—N1	−94.8 (3)	C9—N3—C8—N1	−0.7 (3)
C2—C1—C8—N3	83.5 (3)	C9—N3—C8—C1	−179.1 (2)
C2—C3—C4—C5	0.7 (5)		

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N2—H2···O1^{i}	0.88	1.97	2.840 (3)	170

O1—H1···S1^{ii}	0.95 (5)	2.27 (5)	3.180 (2)	159 (4)
N4—H4*A*···S1^{iii}	0.86	2.74	3.435 (3)	138
N4—H4*B*···N1^{iv}	0.91 (3)	2.32 (3)	3.149 (4)	153 (3)

Symmetry codes: (i) *x*, *y*, *z*−1; (ii) *x*+1, *y*+1, *z*+1; (iii) *x*−1, *y*, *z*; (iv) *x*, *y*−1, *z*.