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4-(5-Bromo-2-hydroxybenzylideneamino)-3-methyl-1*H*-1,2,4-triazole-5(4*H*)-thione

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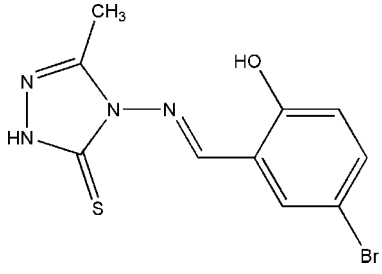
Key indicators: single-crystal X-ray study; T = 293 K; mean σ(C–C) = 0.006 Å; R factor = 0.040; wR factor = 0.111; data-to-parameter ratio = 15.9.

In the title compound, $C_{10}H_9BrN_4OS$, the triazole ring forms a dihedral angle of 72.05 (14)° with the benzene ring. The conformation of the molecule is stabilized by intramolecular O—H···N hydrogen bonding. The crystal packing is determined by intermolecular N—H···S interactions, a short Br···S contact of 3.4464 (13) Å and π–π stacking of the triazole rings and of the benzene rings (centroid–centroid distances of 3.4109 and 3.569 Å, respectively).

Related literature

For related literature, see: Allen *et al.* (1987); Awad *et al.* (1991); Eweiss *et al.* (1986); Ji *et al.* (2002); Mohan (1983); Xu *et al.* (2002).



Experimental

Crystal data

$C_{10}H_9BrN_4OS$
M_r = 313.18
Triclinic, $P\overline{1}$
a = 6.9780 (8) Å
b = 7.1529 (8) Å
c = 12.3119 (14) Å
α = 83.561 (2)°
β = 88.820 (2)°
γ = 79.987 (2)°
V = 601.35 (12) Å^3
Z = 2
Mo $K\alpha$ radiation
μ = 3.58 mm^{-1}
T = 293 (2) K
0.30 × 0.28 × 0.26 mm

Data collection

Bruker SMART CCD diffractometer
Absorption correction: multi-scan (Blessing; 1995)
T_{min} = 0.404, T_{max} = 0.519
(expected range = 0.307–0.394)
4340 measured reflections
2560 independent reflections
1977 reflections with $I > 2\sigma(I)$
R_{int} = 0.038

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.040
$wR(F^2)$ = 0.111
S = 1.10
2560 reflections
161 parameters
2 restraints
H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$ = 0.42 e Å^{-3}
$\Delta\rho_{min}$ = −0.59 e Å^{-3}

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

D—H···A	D—H	H···A	D···A	D—H···A
N2—H2···S1^{i}	0.862 (19)	2.44 (2)	3.295 (3)	173 (5)
O1—H1···N4	0.821 (19)	1.97 (4)	2.676 (4)	144 (5)
O1—H1···N1^{ii}	0.821 (19)	2.69 (5)	3.178 (5)	120 (5)

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

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: *SHELXTL* (Bruker, 2001); software used to prepare material for publication: *SHELXTL*.

We thank Xianggao Meng for assistance with refinement of the crystal structure.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: GK2112).

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4-(5-Bromo-2-hydroxybenzylideneamino)-3-methyl-1*H*-1,2,4-triazole-5(4*H*)-thione

Min Wang, Minna Cao, Bo Hu, CuiXia Cheng and XueGang Song

S1. Comment

Recently, compounds containing 1*H*-1,2,4-triazole group have attracted much interest because compounds containing this ring system are well known as efficient fungicides in pesticides and they exhibit good plant-growth regulatory activity for a wide variety of crops (Xu *et al.*, 2002). In addition, amine- and thione-substituted triazoles have been studied as anti-inflamatory and antimicrobial agents (Eweiss *et al.*, 1986; Awad *et al.*, 1991). In a search for new triazole compounds with better biological activity, the title compound, (I), was synthesized and we report here its crystal structure.

The molecule of (I) exists in the thione tautomeric form, with the S==C distance of 1.681 (4) Å, which indicates a substantial double-bond character (Allen *et al.*, 1987). The dihedral angle between the thione-substituted triazole ring and the benzene ring is 72.05 (14)°. The crystal packing is determined by intermolecular N–H···S interaction (Table 1), short Br···S contact of 3.4464 (13) Å and π-π stacking of the triazole rings (centroid-to-centrod distance of 3.410 Å) and π-π stacking of the benzene rings (centroid-to-centrod distance of 3.569 Å).

S2. Experimental

4-Amino-5-methyl-1,2,4-triazole-3-thione (0.02 mol in 15 ml e thanol), synthesized according to a reported method (Mohan, 1983), was added to a solution of 5-bromosalicylaldehyde (0.02 mol in 20 ml). Then several drops of concentrated sulfuric acid were added to the solution, which was then refluxed for 1 h. The mixture was filtered and crystallized from ethanol to afford the title compound (I). Yellow plates of (I) were obtained by recrystallization from ethanol at room temperature.

S3. Refinement

The N– and O-bound H atoms were located in difference maps and refined with distance restraints [N–H = 0.86 (2) Å, O–H = 0.82 (2) Å] and the constraints for U_{iso}(H) = 1.5U_{eq}(N, O).

The C-bound H atoms were geometrically placed in idealized positions [C–H = 0.96 Å (methyl), 0.96 Å (aromatic), 0.96 Å (methine)]. Isotropic displacement parameters of H atoms were: U_{iso}(H)=1.5U_{eq}(C, methyl), U_{iso}(H) = 1.2U_{eq}(C, aromatic and methine).

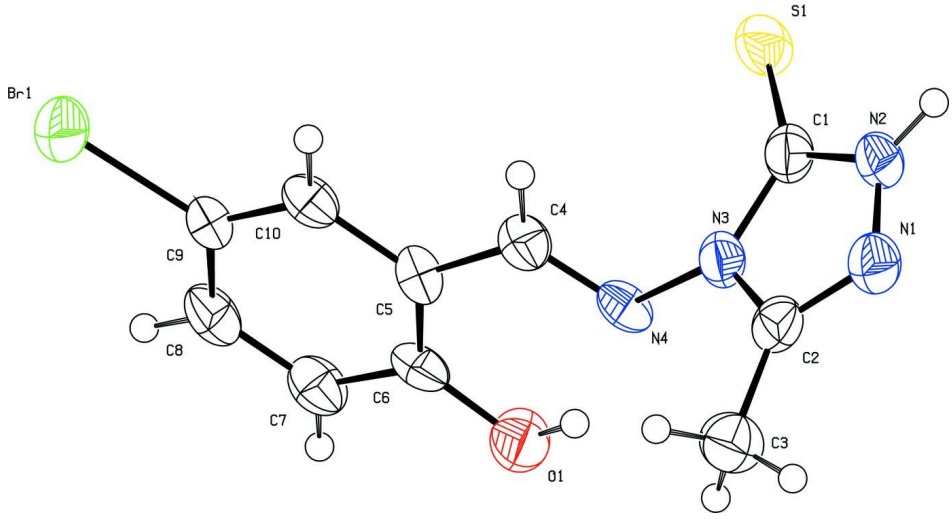

Figure 1

View of the molecular structure of (I), showing 50% probability displacement ellipsoids for the non-hydrogen atoms.

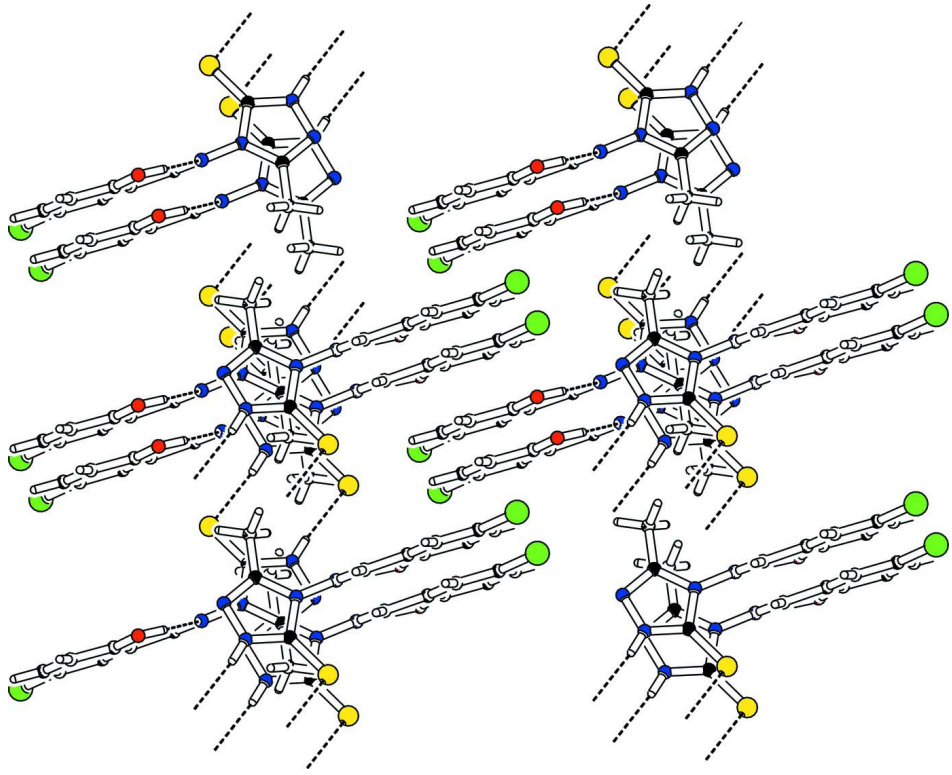

Figure 2

Part of the crystal structure of (I) showing the formation of the two-dimensional network. Hydrogen bonds are shown as dashed lines.

4-(5-Bromo-2-hydroxylbenzylideneamino)-3-methyl-1*H*-1,2,4-triazole-5(4*H*)-thione

Crystal data

$C_{10}H_9BrN_4OS$
$M_r = 313.18$
Triclinic, $P\overline{1}$
Hall symbol: -P 1
$a = 6.9780\ (8)$ Å
$b = 7.1529\ (8)$ Å
$c = 12.3119\ (14)$ Å
$\alpha = 83.561\ (2)°$
$\beta = 88.820\ (2)°$
$\gamma = 79.987\ (2)°$
$V = 601.35\ (12)$ Å^3
$Z = 2$
$F(000) = 312$
$D_x = 1.730$ Mg m^{-3}
Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Cell parameters from 1728 reflections
$\theta = 2.9–26.2°$
$\mu = 3.58$ mm^{-1}
$T = 293$ K
Plate, yellow
0.30 × 0.28 × 0.26 mm

Data collection

Bruker SMART CCD diffractometer
Radiation source: fine-focus sealed tube
Graphite monochromator
ω scans
Absorption correction: multi-scan (Blessing; 1995)
$T_{min} = 0.404$, $T_{max} = 0.519$
4340 measured reflections
2560 independent reflections
1977 reflections with $I > 2\sigma(I)$
$R_{int} = 0.038$
$\theta_{max} = 27.0°$, $\theta_{min} = 1.7°$
$h = -8\rightarrow8$
$k = -9\rightarrow8$
$l = -13\rightarrow15$

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.040$
$wR(F^2) = 0.111$
$S = 1.10$
2560 reflections
161 parameters
2 restraints
Primary atom site location: structure-invariant direct methods
Secondary atom site location: difference Fourier map
Hydrogen site location: inferred from neighbouring sites
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0416P)^2 + 0.455P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.42$ e Å^{-3}
$\Delta\rho_{min} = -0.59$ e Å^{-3}

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 (Å^2)

	x	*y*	*z*	U_{iso}*/U_{eq}
Br1	0.79546 (7)	0.36351 (7)	0.64076 (4)	0.05088 (18)
C1	0.2803 (6)	0.3219 (6)	0.0688 (3)	0.0386 (9)
C2	0.5585 (6)	0.2362 (6)	−0.0218 (3)	0.0383 (9)

C3	0.7615 (6)	0.1524 (7)	−0.0409 (4)	0.0500 (11)
H3A	0.7832	0.1481	−0.1178	0.075*
H3B	0.7886	0.0253	−0.0038	0.075*
H3C	0.8457	0.2290	−0.0134	0.075*
C4	0.5834 (6)	0.2340 (6)	0.2504 (3)	0.0387 (9)
H4	0.5514	0.3663	0.2371	0.046*
C5	0.6609 (5)	0.1469 (6)	0.3552 (3)	0.0350 (9)
C6	0.6983 (5)	−0.0480 (6)	0.3857 (3)	0.0377 (9)
C7	0.7585 (6)	−0.1188 (6)	0.4911 (3)	0.0415 (10)
H7	0.7807	−0.2500	0.5114	0.050*
C8	0.7855 (6)	0.0030 (6)	0.5659 (3)	0.0422 (10)
H8	0.8259	−0.0456	0.6365	0.051*
C9	0.7521 (5)	0.2008 (6)	0.5355 (3)	0.0356 (9)
C10	0.6892 (6)	0.2752 (6)	0.4322 (3)	0.0384 (9)
H10	0.6654	0.4065	0.4126	0.046*
N1	0.4330 (5)	0.3251 (5)	−0.0963 (3)	0.0419 (8)
N2	0.2652 (5)	0.3746 (5)	−0.0387 (3)	0.0372 (8)
N3	0.4714 (5)	0.2332 (4)	0.0799 (3)	0.0355 (8)
N4	0.5586 (5)	0.1292 (5)	0.1755 (3)	0.0398 (8)
O1	0.6727 (5)	−0.1790 (4)	0.3183 (3)	0.0500 (8)
S1	0.10932 (16)	0.35060 (17)	0.16652 (9)	0.0457 (3)
H2	0.161 (5)	0.440 (6)	−0.069 (4)	0.069*
H1	0.640 (8)	−0.123 (7)	0.258 (2)	0.069*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Br1	0.0587 (3)	0.0552 (3)	0.0373 (3)	−0.0031 (2)	−0.0109 (2)	−0.0079 (2)
C1	0.044 (2)	0.037 (2)	0.035 (2)	−0.0072 (18)	−0.0095 (18)	−0.0040 (18)
C2	0.043 (2)	0.033 (2)	0.041 (2)	−0.0098 (18)	−0.0050 (18)	−0.0098 (18)
C3	0.047 (3)	0.047 (3)	0.055 (3)	−0.004 (2)	−0.003 (2)	−0.005 (2)
C4	0.038 (2)	0.040 (2)	0.036 (2)	−0.0030 (18)	−0.0052 (17)	−0.0012 (18)
C5	0.0302 (19)	0.041 (2)	0.034 (2)	−0.0083 (17)	−0.0078 (16)	0.0013 (18)
C6	0.0279 (19)	0.033 (2)	0.047 (2)	0.0047 (16)	−0.0057 (17)	0.0024 (19)
C7	0.039 (2)	0.036 (2)	0.045 (2)	−0.0042 (18)	−0.0069 (19)	0.0075 (19)
C8	0.035 (2)	0.050 (3)	0.036 (2)	−0.0016 (19)	−0.0069 (17)	0.010 (2)
C9	0.0286 (19)	0.040 (2)	0.038 (2)	−0.0015 (16)	−0.0091 (16)	−0.0059 (18)
C10	0.038 (2)	0.033 (2)	0.039 (2)	0.0024 (17)	−0.0083 (18)	0.0067 (18)
N1	0.046 (2)	0.046 (2)	0.0337 (18)	−0.0062 (17)	−0.0059 (16)	−0.0034 (16)
N2	0.0391 (19)	0.0380 (19)	0.0325 (18)	−0.0021 (15)	−0.0100 (15)	−0.0007 (15)
N3	0.0396 (18)	0.0323 (18)	0.0345 (18)	−0.0054 (15)	−0.0119 (14)	−0.0024 (14)
N4	0.0440 (19)	0.0285 (17)	0.0389 (19)	0.0097 (14)	−0.0155 (15)	0.0086 (15)
O1	0.062 (2)	0.0376 (17)	0.0481 (19)	−0.0034 (15)	−0.0136 (16)	−0.0005 (15)
S1	0.0458 (6)	0.0541 (7)	0.0325 (6)	0.0015 (5)	−0.0055 (4)	0.0006 (5)

Geometric parameters (Å, º)

Br1—C9	1.898 (4)	C5—C10	1.431 (5)
C1—N2	1.336 (5)	C6—O1	1.356 (5)
C1—N3	1.375 (5)	C6—C7	1.385 (6)
C1—S1	1.681 (4)	C7—C8	1.373 (6)
C2—N1	1.312 (5)	C7—H7	0.9300
C2—N3	1.381 (5)	C8—C9	1.402 (6)
C2—C3	1.463 (6)	C8—H8	0.9300
C3—H3A	0.9600	C9—C10	1.372 (5)
C3—H3B	0.9600	C10—H10	0.9300
C3—H3C	0.9600	N1—N2	1.370 (5)
C4—N4	1.285 (5)	N2—H2	0.862 (19)
C4—C5	1.440 (5)	N3—N4	1.409 (4)
C4—H4	0.9300	O1—H1	0.821 (19)
C5—C6	1.383 (5)		
N2—C1—N3	102.6 (3)	C8—C7—C6	120.5 (4)
N2—C1—S1	129.2 (3)	C8—C7—H7	119.7
N3—C1—S1	128.2 (3)	C6—C7—H7	119.7
N1—C2—N3	109.8 (4)	C7—C8—C9	119.9 (4)
N1—C2—C3	126.3 (4)	C7—C8—H8	120.1
N3—C2—C3	123.9 (4)	C9—C8—H8	120.1
C2—C3—H3A	109.5	C10—C9—C8	120.8 (4)
C2—C3—H3B	109.5	C10—C9—Br1	120.7 (3)
H3A—C3—H3B	109.5	C8—C9—Br1	118.4 (3)
C2—C3—H3C	109.5	C9—C10—C5	118.8 (4)
H3A—C3—H3C	109.5	C9—C10—H10	120.6
H3B—C3—H3C	109.5	C5—C10—H10	120.6
N4—C4—C5	120.0 (4)	C2—N1—N2	104.2 (3)
N4—C4—H4	120.0	C1—N2—N1	114.4 (3)
C5—C4—H4	120.0	C1—N2—H2	123 (3)
C6—C5—C10	119.7 (4)	N1—N2—H2	122 (3)
C6—C5—C4	124.2 (4)	C1—N3—C2	109.0 (3)
C10—C5—C4	116.0 (4)	C1—N3—N4	126.2 (3)
O1—C6—C5	123.4 (4)	C2—N3—N4	124.1 (3)
O1—C6—C7	116.3 (4)	C4—N4—N3	113.7 (3)
C5—C6—C7	120.3 (4)	C6—O1—H1	109 (4)
N4—C4—C5—C6	−5.4 (6)	C3—C2—N1—N2	179.5 (4)
N4—C4—C5—C10	178.1 (4)	N3—C1—N2—N1	0.2 (4)
C10—C5—C6—O1	179.1 (3)	S1—C1—N2—N1	−178.5 (3)
C4—C5—C6—O1	2.6 (6)	C2—N1—N2—C1	0.5 (4)
C10—C5—C6—C7	1.5 (6)	N2—C1—N3—C2	−0.7 (4)
C4—C5—C6—C7	−174.9 (4)	S1—C1—N3—C2	178.0 (3)
O1—C6—C7—C8	−179.0 (4)	N2—C1—N3—N4	−171.4 (3)
C5—C6—C7—C8	−1.3 (6)	S1—C1—N3—N4	7.3 (6)
C6—C7—C8—C9	0.0 (6)	N1—C2—N3—C1	1.1 (4)

C7—C8—C9—C10	1.2 (6)	C3—C2—N3—C1	−179.3 (4)
C7—C8—C9—Br1	−179.0 (3)	N1—C2—N3—N4	172.1 (3)
C8—C9—C10—C5	−0.9 (6)	C3—C2—N3—N4	−8.4 (6)
Br1—C9—C10—C5	179.2 (3)	C5—C4—N4—N3	176.5 (3)
C6—C5—C10—C9	−0.4 (6)	C1—N3—N4—C4	−71.7 (5)
C4—C5—C10—C9	176.3 (3)	C2—N3—N4—C4	118.9 (4)
N3—C2—N1—N2	−0.9 (4)		

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N2—H2···S1^{i}	0.86 (2)	2.44 (2)	3.295 (3)	173 (5)
O1—H1···N4	0.82 (2)	1.97 (4)	2.676 (4)	144 (5)
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