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

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Key indicators

Single-crystal X-ray study
T = 296 K
Mean σ(C–C) = 0.003 Å
R factor = 0.038
wR factor = 0.110
Data-to-parameter ratio = 12.4

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

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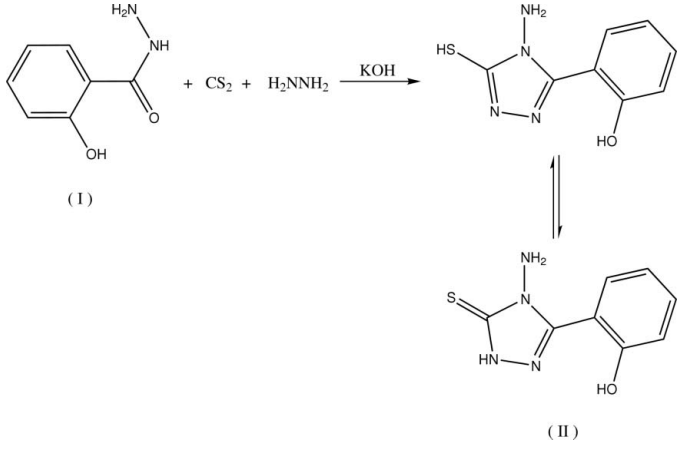
In the title compound, $C_8H_8N_4OS$, the planar triazole ring is effectively coplanar with the benzene ring, which facilitates the formation of three intramolecular interactions N—H···S (leading to a thione tautomer in the solid state), O—H···N and C—H···N. Intermolecular N—H···S interactions lead to the formation of dimers, which are, in turn, linked to each other by N—H···O hydrogen bonds.

Comment

1,2,4-Triazole ring systems are typical planar six-π-electron partially aromatic systems, and are used, along with their derivatives, as starting materials for the synthesis of many heterocycles (Desenko, 1995). Substituted 1,2,4-triazoles have also been actively studied as bridging ligands coordinating through their vicinal N atoms and some have special structures with interesting magnetic properties (Vos *et al.*, 1983; Albada *et al.*, 1984; Vreugdenhil *et al.*, 1987; Kahn & Martinez, 1998). Studies also indicate that the 1,2,4-triazole system is associated with anticorrosion (Al-Kharafi *et al.*, 1986) and anti-inflammatory action (Gupta & Bhargava, 1978), and other pharmacological activities, by exhibiting antiviral, anti-asthmatic, diuretic, analgesic, antimicrobial, antidepressant and antifungal effects (Jones *et al.*, 1965; Bennur *et al.*, 1976; Webb & Parsons, 1977; Sughen & Yoloye, 1978; Heubach *et al.*, 1980; Kane *et al.*, 1988; Massa *et al.*, 1992; Mohamed *et al.*, 1993; Cansiz *et al.*, 2001). Furthermore, nitro derivatives of 1,2,4-triazole are of interest as highly energetic compounds (Pevzner, 1997). In addition, there are some studies on electronic structures and the thiol–thione tautomeric equilibrium of heterocyclic thione derivatives (Koparır *et al.*, 2005). As part of our ongoing study of the relationship between the molecular and crystal structures of triazole derivatives, the crystal structure determination of the title compound, (II), has been undertaken and the results are presented here.



(I)

(II)

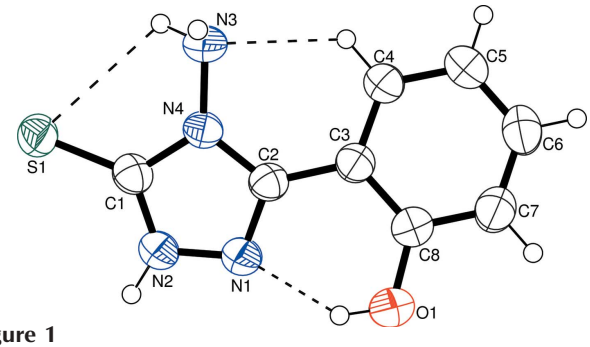


Figure 1
The molecular structure of (II), showing the atomic numbering scheme. Displacement ellipsoids are drawn at the 50% probability level. The intramolecular N—H···S, O—H···N and C—H···N hydrogen bonds are represented by dashed lines.

Previously, we have reported the structure of the closely related compound 4-ethyl-5-(2-hydroxyphenyl)-2*H*-1,2,4-triazole-3(4*H*)-thione, (III) (Dege *et al.*, 2005). The main aim of the present investigation was to study the differences between the structures of (II) and (III).

In the present study, (II) was synthesized by the reaction of 2-hydroxybenzohydrazide, (I), and a solution of KOH in absolute ethanol solution. The resulting 2-(2-hydroxyphenyl)dithiocarbazate was cyclized with hydrazine to give the triazole in good yield.

The conformation of (II), together with the atom-numbering scheme and the intramolecular hydrogen bonding, is shown in Fig. 1. The crystallographic analysis demonstrates that compound (II) exists as the thione illustrated on the lower right-hand side of the scheme rather than the thiol shown above it. The 1,2,4-triazole ring is planar, with a maximum deviation of 0.0074 (9) Å for atom N4. The dihedral angle between this plane and that through the benzene ring is 10.95 (12)°. This value indicates that the molecule is almost planar. When the bond lengths and angles of the triazole ring in (II) (Table 1) are compared with those in (III) (Dege *et al.*, 2005), it is noted that there are no significant differences.

The observed conformation allows for three intramolecular N—H···S, O—H···N and C—H···N interactions, as detailed in Fig. 1 and Table 2. Each of these interactions leads to the formation of a ring, the first being five-membered and the others being six-membered.

In the crystal structure, two intermolecular hydrogen-bonding interactions are also observed (Table 2). In a fashion similar to that found in the structure of (III) (Dege *et al.*, 2005), centrosymmetric dimers are formed *via* N—H···S hydrogen bonds, generating an $R_2^2(8)$ ring highlighted in Fig. 2. The dimers are connected to each other *via* intermolecular N—H···O hydrogen bonds.

Experimental

To a solution of KOH (0.015 mol, 8.40 g) and 2-hydroxybenzhydrazide (0.01 mol, 1.52 g) in absolute ethanol (100 ml) was added CS_2 (0.015 mol, 0.91 ml). This mixture was diluted with absolute ethanol (50 ml) and shaken for 14 h. It was then diluted with dry diethyl ether (200 ml) and vacuum-dried at 343 K. A suspension of the potassium salts, 98% hydrazine hydrate (0.03 mol, 15 ml) and water (2 ml) was refluxed with stirring for 1 h. The color of the reaction mixture turned green, H_2S was evolved and a homogeneous solution resulted. Dilution with cold water (100 ml) and acidification with concentrated HCl precipitated a white solid. The product was filtered, washed with 3 × 10 ml portions of cold water and recrystallized from ethanol solution to analytical purity. Yield 80%; m.p. 489–491 K.

Crystal data

$C_8H_8N_4OS$
M_r = 208.24
Monoclinic, $P2_1/a$
a = 12.0231 (19) Å
b = 5.7685 (8) Å
c = 14.434 (2) Å
β = 114.393 (11)°
V = 911.7 (2) Å^3
Z = 4
D_x = 1.517 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 5061 reflections
θ = 1.6–27.2°
μ = 0.33 mm^{-1}
T = 296 K
Prism, pale yellow
0.68 × 0.48 × 0.37 mm

Data collection

Stoe IPDS-II diffractometer
ω scans
Absorption correction: none
5961 measured reflections
1979 independent reflections
1620 reflections with $I > 2\sigma(I)$
R_{int} = 0.053
θ_{max} = 27.1°
$h = -15 \rightarrow 15$
$k = -6 \rightarrow 7$
$l = -18 \rightarrow 18$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.038
$wR(F^2)$ = 0.110
S = 1.02
1979 reflections
159 parameters
All H-atom parameters refined
$w = 1/[\sigma^2(F_o^2) + (0.0684P)^2 + 0.0697P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.001
$\Delta\rho_{max}$ = 0.21 e Å^{-3}
$\Delta\rho_{min}$ = −0.19 e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

S1—C1	1.6773 (18)	N3—N4	1.399 (2)
O1—C8	1.357 (2)	N4—C1	1.367 (2)
N1—N2	1.366 (2)	N4—C2	1.375 (2)
N1—C2	1.309 (2)	C2—C3	1.457 (2)
N2—C1	1.329 (2)		
N2—N1—C2	105.47 (14)	N2—C1—N4	103.55 (14)
N1—N2—C1	112.96 (14)	N1—C2—N4	108.86 (14)
N3—N4—C1	123.64 (14)	N1—C2—C3	122.39 (15)
N3—N4—C2	127.14 (14)	N4—C2—C3	128.74 (15)
C1—N4—C2	109.14 (13)	O1—C8—C3	123.75 (16)
S1—C1—N2	130.49 (13)	O1—C8—C7	116.39 (16)
S1—C1—N4	125.91 (13)		
N1—C2—C3—C4	169.24 (16)	N4—C2—C3—C8	168.64 (15)

Table 2
Hydrogen-bond geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
O1—H1···N1	0.86 (3)	1.89 (3)	2.611 (2)	140 (2)
C4—H4···N3	0.97 (2)	2.35 (2)	3.013 (3)	125 (2)
N3—H3*A*···S1	0.91 (3)	2.73 (4)	3.1319 (18)	108 (3)
N2—H2···S1^{i}	0.90 (2)	2.34 (2)	3.2400 (16)	174 (2)
N3—H3*B*···O1^{ii}	0.88 (4)	2.37 (4)	3.083 (2)	138 (3)

Symmetry codes: (i) $-x+2, -y+1, -z+1$; (ii) $x-\frac{1}{2}, -y+\frac{5}{2}, z$.

The H atoms were located in a difference map and refined isotropically [C—H = 0.91 (2)–0.97 (2) Å].

Data collection: *X-AREA* (Stoe & Cie, 2002); cell refinement: *X-AREA*; data reduction: *X-RED32* (Stoe & Cie, 2002); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 1997); software used to prepare material for publication: *WinGX* (Farrugia, 1999) and *PLATON* (Spek, 2003).

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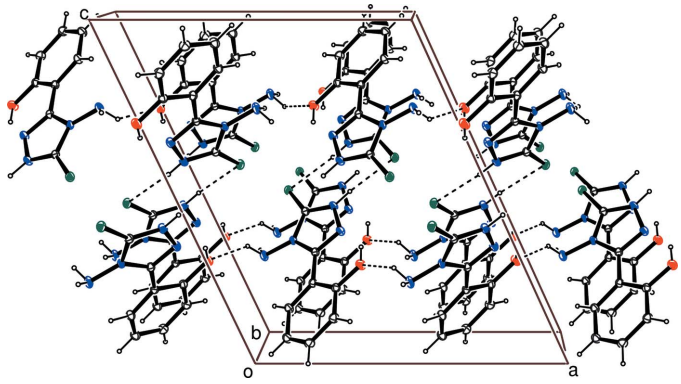

Figure 2
A projection of the crystal structure of (II) along the *b* axis. Dashed lines show the N—H···S and N—H···O interactions.

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