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4-Ethyl-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 = 293 K
Mean σ(C–C) = 0.002 Å
R factor = 0.031
wR factor = 0.086
Data-to-parameter ratio = 15.6

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

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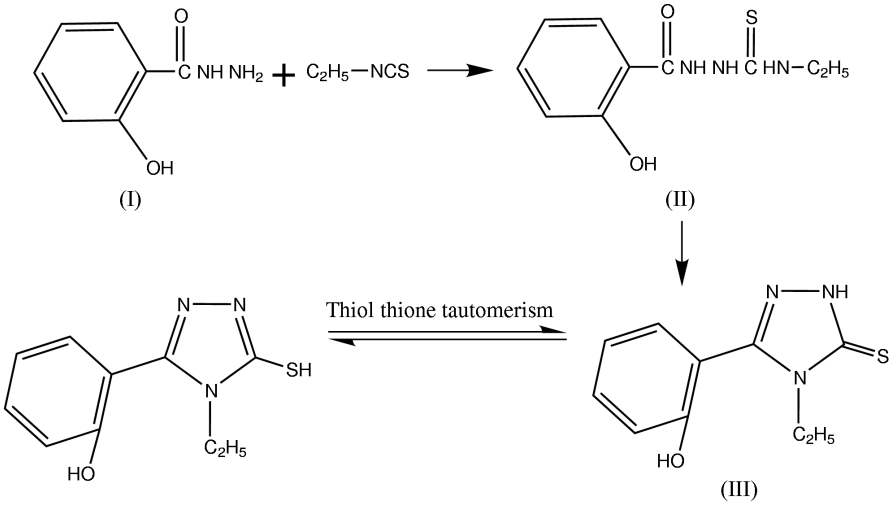
In the title compound, $C_{10}H_{11}N_3OS$, an intramolecular C—H···S hydrogen bond is observed, which leads to a thione tautomer in the solid state. The benzene ring forms a dihedral angle of 85.33 (6)° with the triazole ring. There are intermolecular N—H···S and O—H···N hydrogen bonds and C—H···π interactions.

Comment

1,2,4-Triazoles are very useful ligands in coordination chemistry. Derivatives of 1,2,4-triazole are known to exhibit anti-inflammatory (Unangst *et al.*, 1992; Mullican *et al.*, 1993), antiviral (Jones *et al.*, 1965), analgesic (Sughen & Yoloye, 1978), antimicrobial (Shams El-Dine & Hazzaa, 1974; Misato *et al.*, 1977; Cansız *et al.*, 2004), anticonvulsant (Stillings *et al.*, 1986) and antidepressant activity (Kane *et al.*, 1988), the last usually being explored by the forced swim test (Porsolt *et al.*, 1977; Vamvakides, 1990). Among the pharmacological profiles of 1,2,4-triazoles, their antimicrobial, anticonvulsant and antidepressant properties seem to be the best documented. The derivatives of 4,5-disubstituted 1,2,4-triazole are known to be synthesized by intramolecular cyclization of 1,4-disubstitued thiosemicarbazides (Zamani *et al.*, 2003; Cansız *et al.*, 2004). Furthermore, the electronic structures and thiol–thione tautomeric equilibrium of heterocyclic thione derivatives have been studied (Aydoğan *et al.*, 2002; Charıstos *et al.*, 1994; Dege *et al.*, 2004; Genç, Dege, Yılmaz *et al.*, 2004).



In the present study, the title compound, (III), has been synthesized by the reaction of ethyl isothiocyanate and salicylic hydrazide, (I), through 1-(2-hydroxybenzoyl)-4-ethyl thiosemicarbazide, (II). Base-catalysed intramolecular dehydrative cyclization of this intermediate furnished the thione in

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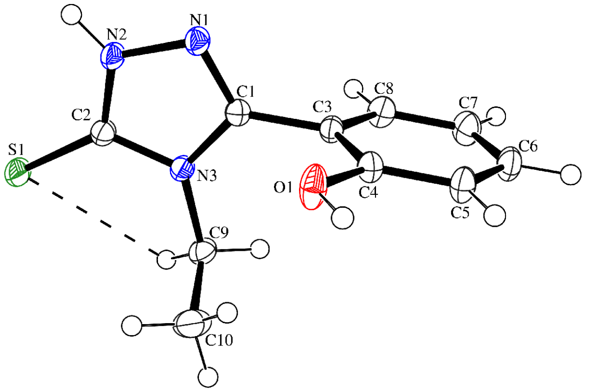

Figure 1
An *ORTEP*-3 (Farrugia, 1997) plot of (III), with displacement ellipsoids shown at the 50% probability level. The dashed line indicates the C—H···S interaction.

good yield (80–95%). As a continuation of our investigation of the structures of 1,2,4-triazole compounds, we describe here the structure of (III).

The conformation of (III), together with the atom-numbering scheme, is shown in Fig. 1. The dihedral angle between the benzene and triazole rings is 85.33 (6)°, indicating that these two rings are almost orthogonal to each other. Similarly, the plane of the ethyl moiety (N3/C9/C10) is twisted by 89.71 (8)° out of the mean plane of the triazole ring. There is one weak intramolecular C—H···S interaction (Fig. 1), forming a five-membered ring fused with the triazole ring. Intermolecular N2—H2···S1^{ii} hydrogen bonding (Table 2) results in the formation of a dimeric structure (Fig. 2).

Intermolecular O—H···N and C—H···π interactions (Table 2) link the molecules into an infinite two-dimensional network (*Cg*1 in Table 2 is the centroid of the triazole ring). Intermolecular weak π–π stacking interactions between the benzene ring and its symmetry-related partner at $(1 - x, -y, -z)$ are also observed along the *b* axis, with a distance of 3.906 (2) Å between the ring centroids and a perpendicular distance between the rings of 3.556 (2) Å.

Previously, we have reported the closely related compound 3-(2-hydroxyphenyl)-4-phenyl-*H*-1,2,4-triazole-5(4*H*)-thione, (VIII) (Genç, Dege, Çetin *et al.*, 2004), which differs only in the 4-position (ethyl *versus* phenyl). When the bond lengths and angles of the triazole rings in (III) and (VIII) are compared, it is seen that the values are very close to each other. However, the C1—C3 bond length of 1.4731 (14) Å in (III) is significantly longer than the corresponding value in (VIII), 1.458 (2) Å. This difference may be due to a shortening of the C1—C3 bond length in (VIII) caused by O—H···N and C—H···π intramolecular interactions.

By comparison of the N—H···S hydrogen bonding in *N*-benzoyl-*N*′-methyl-*N*′-phenylthiourea, (IV), *N*-benzoyl-*N*′-(3,4-dimethylphenyl)thiourea, (V) (Shanmuga Sundara Raj *et al.*, 1999), 5-(furan-2-yl)-1,3,4-oxadiazole-2(3*H*)-thione, (VI) (Öztürk, Akkurt, Cansiz, Çetin *et al.*, 2004), and 4-(4-chlorophenyl)-3-(furan-2-yl)-1*H*-1,2,4-triazole-5(4*H*)-thione, (VII) (Öztürk, Akkurt, Cansız, Koparır *et al.*, 2004), it can be seen that dimer formation shortens the intermolecular N···S distances. The N···S distances in (III)–(VII) are 3.2789 (10), 3.473 (1), 3.501 (2), 3.321 (3) and 3.304 (2) Å, respectively.

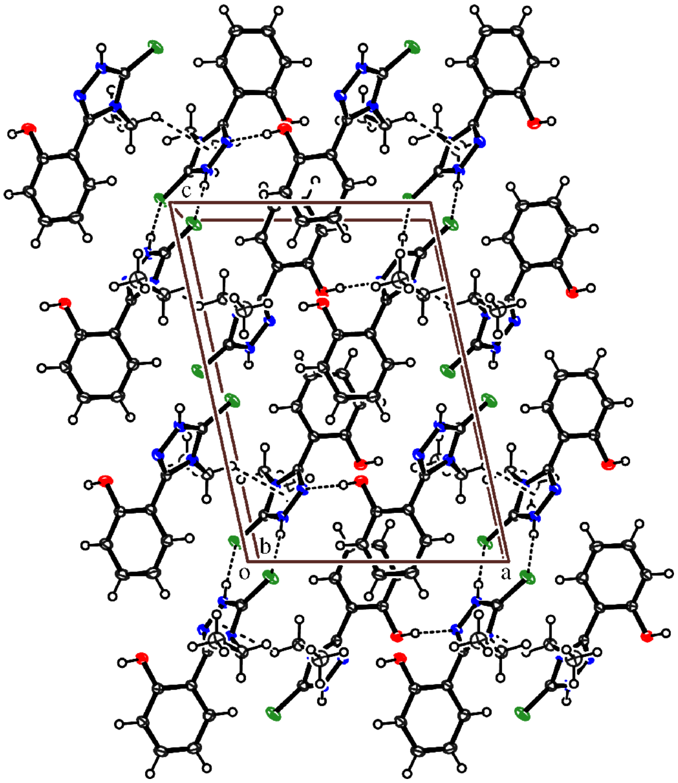

Figure 2
A projection of the crystal structure of (III) along the *b* axis. Dashed lines show O—H···N, N—H···S and C—H···π interactions.

Experimental

For the synthesis of 1(2-hydroxybenzoyl)-4-ethyl thiosemicarbazide, (II), a mixture of (I) (0.01 mol) and ethyl isothiocyanate (0.01 mol) in absolute ethanol was refluxed for 8 h. The solid material obtained on cooling was filtered, washed with diethyl ether, dried and crystallized from ethanol–dioxane (yield 65%, m.p. 489–491 K). IR (ν, cm^{-1}): 3495, 3317 (N—H, OH), 1668 (C═O), 1262 (C═S). For the synthesis of (III), a stirred mixture of (II) (1 mmol) and sodium hydroxide (40 mg, 1 mmol, as a 2 *N* solution) was refluxed for 4 h. After cooling, the solution was acidified with hydrochloric acid and the precipitate was filtered off. The precipitate was then crystallized from an ethanol–dioxane mixture (yield 85%, m.p. 527–531 K). IR (ν, cm^{-1}): 3390, 3216(N—H, OH), 1622 (C═N), 1535, 1260, 1050, 950 (N—C═S, amide I, II, III and IV bands); ^{1}H NMR: δ 1.1 (*d*, 3H, CH$_3$), 2.4 (*t*, 2H, CH$_2$), 7.82–7.14 (*m*, 5H, Ar-H), 10.00 (*s*, 1H, OH), 13.95 (*s*, 1H, SH).

Crystal data

$C_{10}H_{11}N_3OS$
$M_r = 221.28$
Monoclinic, $P2_1/c$
$a = 9.7879$ (8) Å
$b = 7.9071$ (5) Å
$c = 13.8045$ (10) Å
$\beta = 102.266$ (6)°
$V = 1043.99$ (13) Å^3
$Z = 4$
$D_x = 1.408$ Mg m^{-3}
Mo *Kα* radiation
Cell parameters from 9263 reflections
$\theta = 2.1$–29.4°
$\mu = 0.29$ mm^{-1}
$T = 293$ (2) K
Prism, colorless
0.60 × 0.49 × 0.40 mm

Data collection

Stoe IPDS-II diffractometer
ω scans
Absorption correction: by integration (*X-RED*; Stoe & Cie, 2002)
$T_{\min} = 0.869$, $T_{\max} = 0.935$
9857 measured reflections
2825 independent reflections
2440 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.028$
$\theta_{\max} = 29.3°$
$h = -13 \rightarrow 13$
$k = -10 \rightarrow 10$
$l = -18 \rightarrow 18$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.031$
$wR(F^2) = 0.086$
$S = 1.01$
2825 reflections
181 parameters
All H-atom parameters refined
$w = 1/[\sigma^2(F_o^2) + (0.0513P)^2 + 0.2483P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = 0.002$
$\Delta\rho_{\max} = 0.31$ e Å^{-3}
$\Delta\rho_{\min} = -0.26$ e Å^{-3}
Extinction correction: *SHELXL*97
Extinction coefficient: 0.043 (3)

Table 1
Selected geometric parameters (Å, °).

N1—C1	1.3076 (13)	N3—C2	1.3688 (13)
N1—N2	1.3737 (13)	N3—C1	1.3705 (13)
N2—C2	1.3376 (14)	N3—C9	1.4694 (13)
C1—N1—N2	104.20 (9)	N1—C1—N3	110.71 (9)
C2—N2—N1	113.06 (9)	N2—C2—N3	103.81 (9)
C2—N3—C1	108.20 (8)		
N3—C1—C3—C8	83.54 (13)	C1—N3—C9—C10	88.49 (13)

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

D—H···A	D—H	H···A	D···A	D—H···A
C9—H9B···S1	1.00 (2)	2.86 (2)	3.2383 (12)	104 (1)
O1—H1···N1$^{\rm i}$	0.85 (2)	1.98 (2)	2.8227 (12)	175 (2)
N2—H2···S1$^{\rm ii}$	0.90 (2)	2.38 (2)	3.2789 (10)	174 (2)
C9—H9B···$Cg1^{\rm iii}$	1.00 (2)	2.76 (2)	3.4652 (13)	128 (1)

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

H atoms were located in difference maps and refined isotropically. The O—H, N—H and C—H bond distances are 0.850 (19) Å, 0.901 (18) Å and 0.951 (18)–1.001 (17) Å, respectively.

Data collection: *X-AREA* (Stoe & Cie, 2002); cell refinement: *X-AREA*; data reduction: *X-RED* (Stoe & Cie, 2002); program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (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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