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3-(2-Hydroxyphenyl)-4-phenyl-1*H*-1,2,4-triazole-5(4*H*)-thione

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The title molecule, $C_{14}H_{11}N_3OS$, is non-planar. The phenyl and hydroxyphenyl rings form dihedral angles of 69.08 (9) and 24.57 (9)°, respectively, with the five-membered 2,4-dihydro-1,2,4-triazole ring. The molecules form centrosymmetric dimers through N—H$\cdots$S hydrogen bonds, with an N$\cdots$S distance of 3.279 (2) Å. In addition, the molecule contains one O—H$\cdots$N and one C—H$\cdots\pi$(phenyl) intramolecular interactions. The dimers are connected through weak intermolecular C—H$\cdots\pi$(hydroxyphenyl) interactions into chains in the **a** direction.

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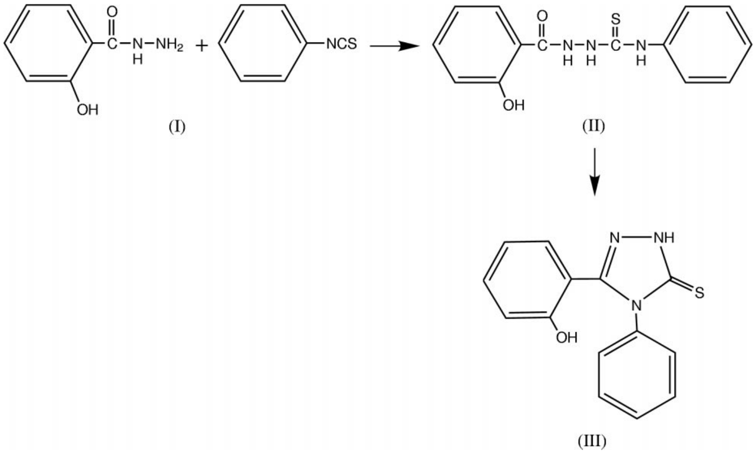
Key indicators

Single-crystal X-ray study
T = 293 K
Mean σ(C–C) = 0.002 Å
R factor = 0.038
wR factor = 0.094
Data-to-parameter ratio = 16.2

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

Comment

Derivatives of 1,2,4-triazole are known to exhibit anti-inflammatory (Mullican *et al.*, 1993; Unangst *et al.*, 1992), antiviral (Jones *et al.*, 1965), analgesic (Sughen & Yoloye, 1978), antimicrobial (Shams El-Dine & Hazzaa, 1974; Misato *et al.*, 1977; Cansız *et al.*, 2001), 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 most widely documented. Derivatives of 4,5-disubstituted 1,2,4-triazole are synthesized by intramolecular cyclization of 1,4 disubstituted thiosemicarbazides (Cansız *et al.*, 2004; Genç, Dege, Çetin *et al.*, 2004; Zamani *et al.*, 2003). Also, the electronic structures and thiol–thione tautomeric equilibrium of heterocyclic thione derivatives have been studied previously (Aydogan *et al.*, 2002; Charistos *et al.*, 1994; Dege *et al.*, 2004; Genç, Dege, Yılmaz *et al.*, 2004).



In the present study, the title compound, (III), was synthesized by the reaction of phenyl isothiocyanate and salicylic hydrazide, (I), *via* 1-(2-hydroxybenzoyl)-4-phenyl-

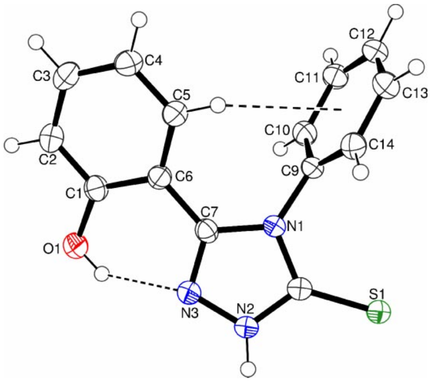


Figure 1
An *ORTEP*-3 (Farrugia, 1997) drawing of (III), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as spheres of arbitrary radii.

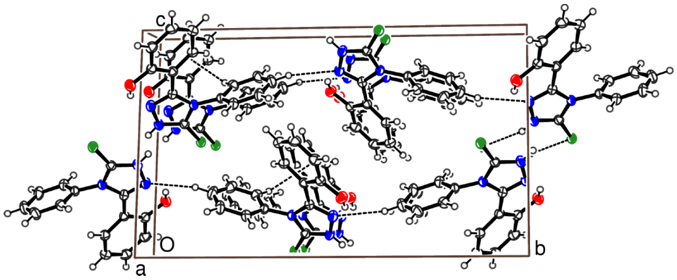


Figure 2
A packing diagram for (III), with the intermolecular hydrogen bonds shown as dashed lines.

thiosemicarbazide, (II). Base-catalysed intramolecular dehydrative cyclization of this intermediate furnished the thione in good yield (75%). The reaction sequences depicted in the scheme were followed to obtain (III). Initially, the atomic connectivity in (III) was elucidated from IR and ^{1}H NMR spectra.

The molecular structure of (III) is non-planar (Fig. 1). The phenyl and hydroxyphenyl rings form dihedral angles of 69.08 (9) and 24.57 (9)°, respectively, with the five-membered 2,4-dihydro-1,2,4-triazole ring. The dihedral angle between the phenyl and hydroxyphenyl rings is 64.19 (9)°.

An intramolecular O—H···N hydrogen bond [O···N = 2.693 (2) Å and O—H···N = 145°] exists between the hydroxyphenyl group and the triazole N atom, resulting in a nearly planar six-membered ring in the central part of the molecule. An intramolecular C5—H5···π interaction involving the phenyl ring is also observed in the molecular structure (Fig. 1). Two types of intermolecular hydrogen bonds, N—H···S and C—H···N, are observed in the crystal structure (Fig. 2 and Table 2). The molecules are linked to form centrosymmetrically related N—H···S hydrogen-bonded dimers. The molecules translated by a unit along the *a* axis are linked by a C14—H14···π interaction involving the hydroxyphenyl ring.

Experimental

Starting materials were obtained from Fluka or Aldrich. For the synthesis of 1-(2-hydroxybenzoyl)-4-phenylthiosemicarbazide, (II), a mixture of (I) (0.01 mol) and phenyl isothiocynate (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 60%; m.p. 473–475 K). IR (ν, cm^{-1}): 3482, 3317 (N—H), 1660 (C═O), 1257 (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 75%; m.p. 573–574 K). IR (ν, cm^{-1}): 3330, 3260 (N—H), 1620 (C═N), 1535, 1260, 1050, 950 (N—C═S, amide I, II, III and IV bands); ^{1}H NMR (δ): 6.82–7.34 (*m*, 9H, Ar-H), 10.10 (*s*, 1H, OH), 13.95 (*s*, 1H, SH).

Crystal data

$C_{14}H_{11}N_3OS$
$M_r = 269.32$
Monoclinic, $P2_1/c$
$a = 5.7333$ (4) Å
$b = 19.1695$ (16) Å
$c = 11.6547$ (8) Å
$\beta = 103.441$ (6)°
$V = 1245.82$ (16) Å^3
$Z = 4$
$D_x = 1.436$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 26084 reflections
$\theta = 1.8$–27.7°
$\mu = 0.25$ mm^{-1}
$T = 293$ (2) K
Rod, colourless
0.76 × 0.33 × 0.09 mm

Data collection

Stoe *IPDS*-2 diffractometer
ω scans
Absorption correction: by integration (*X-RED*32; Stoe & Cie, 2002)
$T_{\min} = 0.889$, $T_{\max} = 0.981$
16413 measured reflections
2800 independent reflections
2202 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.061$
$\theta_{\max} = 27.4°$
$h = -7 \rightarrow 7$
$k = -24 \rightarrow 24$
$l = -14 \rightarrow 14$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.038$
$wR(F^2) = 0.094$
$S = 1.06$
2800 reflections
173 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0489P)^2 + 0.1859P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} < 0.001$
$\Delta\rho_{\max} = 0.18$ e Å^{-3}
$\Delta\rho_{\min} = -0.30$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

C8—S1	1.6757 (17)	N2—C8	1.340 (2)
O1—C1	1.359 (2)	N2—N3	1.367 (2)
N1—C8	1.377 (2)	N3—C7	1.311 (2)
N1—C7	1.385 (2)	C6—C7	1.458 (2)
N1—C9	1.442 (2)		
C7—N1—C9	127.03 (14)	N1—C7—C6	127.50 (15)
O1—C1—C6	124.05 (16)	N2—C8—S1	127.96 (13)
C5—C6—C7	122.47 (15)	N1—C8—S1	128.36 (12)
N3—C7—C6	122.71 (15)		
N2—N3—C7—C6	−178.68 (14)	C7—N1—C9—C10	−65.6 (2)
C8—N1—C9—C14	−72.3 (2)		

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

D—H···A	D—H	H···A	D···A	D—H···A
O1—H1···N3	0.82	1.98	2.693 (2)	145
N2—H2N···S1$^{\rm i}$	0.86	2.46	3.279 (2)	159
C12—H12···N3$^{\rm ii}$	0.93	2.59	3.502 (2)	165
C5—H5···Cg1	0.93	2.83	3.551 (2)	135
C14—H14···Cg2$^{\rm iii}$	0.93	2.71	3.546 (2)	150

Symmetry codes: (i) $-x, 1-y, -z$; (ii) $1-x, y-\frac{1}{2}, \frac{1}{2}-z$; (iii) $x-1, y, z$. Cg1 and Cg2 denote the centroids of the phenyl ring and hydroxyphenyl ring, respectively.

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The hydroxyl H atom was located in a difference map. H atoms were placed in geometrically idealized positions and allowed to ride on their parent atoms, with O—H, N—H and C—H distances of 0.82, 0.86 and 0.93 Å, respectively. The $U_{\rm iso}$(H) values were set equal to $1.5U_{\rm eq}$(O) for the hydroxyl H atom, and $1.2U_{\rm eq}$(parent atom) for the remaining H atoms.

Data collection: *X-AREA* (Stoe & Cie, 2002); cell refinement: *X-AREA*; data reduction: *X-RED*32 (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) and *PLATON* (Spek, 1997); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

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References

Aydogan, F., Turgut, Z., Olcay, N. & Erdem, S. S. (2002). *Turk. J. Chem.* **26**, 159–169.

Cansız, A., Koparır, M. & Demirdağ, A. (2004). *Molecules*, **9**, 204–212.

Cansız, A., Servi, S., Koparır, M., Altıntaş, M. & Dığrak, M. J. (2001). *J. Chem. Soc. Pak.* **23**, 237–239.

Charistos, D. D., Vagenes, G. V., Tzavellas, L. C., Tsoleridis, C. A. & Rodios, N. A. (1994). *J. Heterocycl. Chem.* **31**, 1593–1598.

Dege, N., Andac, O., Cansız, A., Çetin, A., Şekerci, M. & Dinçer, M. (2004). *Acta Cryst.* E**60**, o1405–o1407.

Farrugia, L. J. (1997). *J. Appl. Cryst.* **30**, 565.

Farrugia, L. J. (1999). *J. Appl. Cryst.* **32**, 837–838.

Genç, S., Dege, N., Çetin, A., Cansız, A., Şekerci, M. & Dinçer, M. (2004). *Acta Cryst.* E**60**, o1340–o1342.

Genç, S., Dege, N., Yılmaz, I., Çukurovalı, A. & Dinçer, M. (2004). *Acta Cryst.* E**60**, o889–o891.

Jones, D. H., Slack, R., Squires, S. & Wooldridge, K. R. H. (1965). *J. Med. Chem.* **8**, 676–680.

Kane, J. M., Dudley, M. W., Sorensen, S. M. & Miller, F. P. (1988). *J. Med. Chem.* **31**, 1253–1258.

Misato, T., Ko, K., Honma, Y., Konno, K. & Taniyama, E. (1977). *Chem. Abstr.* **87**, 147054a. [JP 77-25028(A01N 9/12)]

Mullican, M. D., Wilson, M. W., Connor, D. T., Kostlan, C. R., Schrier, D. J. & Dyer, R. D. (1993). *J. Med. Chem.* **36**, 1090–1099.

Porsolt, R. D., Bertin, A. & Jalfre, M. (1977). *Arch. Int. Pharmacol.* **229**, 327–336.

Shams El-Dine, S. A. & Hazzaa, A. A. B. (1974). *Pharmazie*, **29**, 761–768.

Sheldrick, G. M.(1997). *SHELXS*97 and *SHELXL*97. University of Göttingen, Germany.

Spek, A. L. (1997). *PLATON*97. Utrecht University, The Netherlands.

Stillings, M. R., Welbourn, A. P. & Walter, D. S. (1986). *J. Med. Chem.* **29**, 2280–2284.

Stoe & Cie (2002). *X-AREA* (Version 1.18) and *X-RED*32 (Version 1.04). Stoe & Cie, Darmstadt, Germany.

Sughen, J. K. & Yoloye, T. (1978). *Pharm. Acta Helv.* **58**, 64–68.

Unangst, P. C., Shurum, G. P., Connor, D. T., Dyer, R. D. & Schrier, D. J. (1992). *J. Med. Chem.* **35**, 3691–3698.

Vamvakides, A. (1990). *Pharm. Fr.* **48**, 154–159.

Zamani, K., Faghihi, K., Sangi, M. R. & Zolgharnein, J. (2003). *Turk. J. Chem.* **27**, 119–125.

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