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5-(2-Hydroxyphenyl)-4-(*p*-tolyl)-2,4-dihydro-1,2,4-triazole-3-thione

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Key indicators

Single-crystal X-ray study
T = 150 K
Mean σ(C–C) = 0.004 Å
R factor = 0.054
wR factor = 0.148
Data-to-parameter ratio = 13.8

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

In the structure of the title compound, $C_{15}H_{13}N_3OS$, the molecules form centrosymmetric dimers through strong N—H···S hydrogen bonds, with an N···S distance of 3.271 (3) Å. In addition, the molecule contains one O—H···N intramolecular hydrogen bond. The dimers are connected through weak intermolecular C—H···S hydrogen bonds into chains in the *c* direction, with a C···S distance of 3.742 (3) Å.

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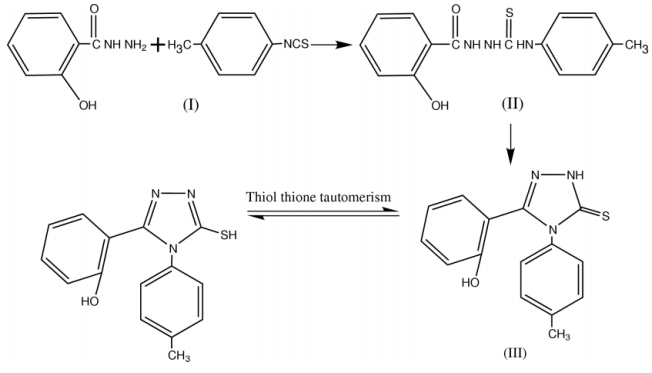
Comment

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.*, 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 usually synthesized by intramolecular cyclization of 1,4-disubstituted 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 previously (Aydogan *et al.*, 2002; Charıstos *et al.*, 1994; Genç *et al.*, 2004).

In the present study, the title compound, (III), was synthesized by the reaction of *p*-tolyl isothiocyanate and salicylic hydrazide, (I), *via* 1-(2-hydroxybenzoyl)-4-(*p*-tolyl)-thiosemicarbazide, (II). Base-catalysed intramolecular dehydrative cyclization of this intermediate furnished the thione in good yield (80%). The reaction sequences depicted in the scheme were followed to obtain (III). Initially, the structure of (III) was evaluated from IR and ^{1}H NMR spectra.



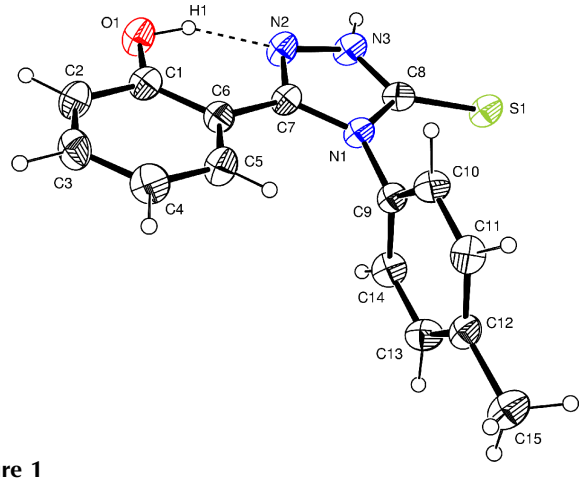


Figure 1
A view of the structure of (III), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radii. The intramolecular hydrogen bond is shown as a dashed line.

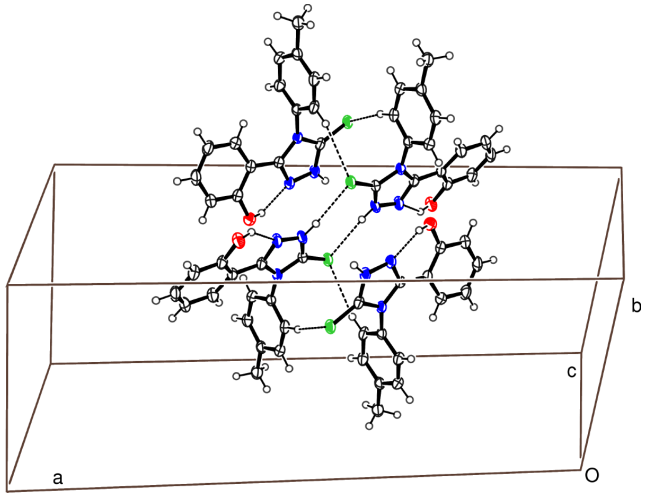


Figure 2
A partial packing diagram for (III), with the intermolecular hydrogen bonding shown as dashed lines.

The molecular structure of (III) is non-planar and is shown in Fig. 1. Two types of intermolecular hydrogen bonds, N—H···S and C—H···S, and one intramolecular interaction, O—H···N, are observed in the structure (Fig. 2 and Table 2). One intermolecular interaction involves atom N3 acting as donor to the symmetry-related atom S1^{i} [symmetry code: (i) $-x$, $1-y$, $-z$], forming centrosymmetric dimers. In another intermolecular interaction, atom C14 acts as donor to the symmetry-related atom S1^{ii} [symmetry code: (ii) $-x$, y, $-z-\frac{1}{2}$], forming weak hydrogen-bonded chains in the c direction. An intramolecular O—H···N hydrogen bond [O—H 0.82 Å, H···N 1.88 (3) Å and O—H···N 141.6 (2)°] exists between the hydroxyphenyl group and the triazole N atom.

The dihedral angle between the five-membered 2,4-dihydro-1,2,4-triazole ring and the hydroxyphenyl group is 10.18 (1)°. The *p*-tolyl moiety is almost perpendicular to both the 2,4-dihydro-1,2,4-triazole group and the hydroxyphenyl group, with dihedral angles of 84.42 (1) and 85.54 (1)°, respectively. The orientation of the substitutents with respect to the 1,2,4-triazole ring is defined by the torsion angles C1—C6—C7—N2 [9.2 (4)°], N2—N3—C8—S1 [−177.1 (2)°], C8—N1—C9—C10 [95.0 (3)°] and C10—C11—C12—C15 [177.8 (3)°].

Experimental

Starting materials were obtained from Fluka and Aldrich. For the synthesis of 1-(2-hydroxybenzoyl)-4-(*p*-tolyl)thiosemicarbazide (II), a mixture of salicylic hydrazide, (I) (0.01 mol), and *p*-tolyl 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 75%; m.p. 488–489 K). IR (KBr, ν, cm^{-1}): 3405, 3300 (N—H, OH), 1663 (C═O), 1254 (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. The precipitate was then crystallized from an ethanol–dioxane mixture (yield 90%; m.p. 566–368 K). IR (KBr, ν, cm^{-1}): 3390, 3240 (N—H, OH), 1622 (C═N), 1540, 1265, 1050, 955 (N—C═S, amide I, II, III and IV bands); ^{1}H NMR (DMSO-d_6, δ, p.p.m.): 2.1 (3H, CH_3-Ar) 6.92–7.64 (*m*, 8H, Ar-H), 10.02 (*s*, 1H, OH), 13.95 (*s*, 1H, SH).

Crystal data

$C_{15}H_{13}N_3OS$	D_x = 1.410 Mg m^{-3}
M_r = 283.34	Mo $K\alpha$ radiation
Monoclinic, $C2/c$	Cell parameters from 10 560 reflections
a = 26.524 (3) Å	θ = 1.6–27.2°
b = 11.3288 (18) Å	μ = 0.24 mm^{-1}
c = 9.2310 (11) Å	T = 150 K
β = 104.643 (9)°	Plate, colourless
V = 2683.7 (6) Å^3	0.38 × 0.26 × 0.08 mm
Z = 8	

Data collection

Stoe IPDS 2 diffractometer	2636 independent reflections
ω scans	1775 reflections with $I > 2\sigma(I)$
Absorption correction: by integration (*X-RED*32; Stoe & Cie, 2002)	R_{int} = 0.143
	θ_{max} = 26.0°
T_{min} = 0.919, T_{max} = 0.978	$h = -32 \rightarrow 32$
9354 measured reflections	$k = -13 \rightarrow 13$
	$l = -11 \rightarrow 11$

Refinement

Refinement on F^2	H-atom parameters constrained
$R[F^2 > 2\sigma(F^2)]$ = 0.054	$w = 1/[\sigma^2(F_o^2) + (0.0749P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2)$ = 0.148	$(\Delta/\sigma)_{max}$ = 0.001
S = 0.98	$\Delta\rho_{max}$ = 0.41 e Å^{-3}
2636 reflections	$\Delta\rho_{min}$ = −0.60 e Å^{-3}
191 parameters	

Table 1
Selected geometric parameters (Å, °).

S1—C8	1.671 (3)	C6—C7	1.464 (4)
O1—C1	1.353 (3)	C12—C15	1.507 (4)
N1—C9	1.445 (3)		
C8—N1—C9	121.8 (2)	N3—C8—S1	128.4 (2)
O1—C1—C6	123.4 (2)	C11—C12—C15	122.0 (3)
N2—C7—C6	121.4 (2)		
O1—C1—C2—C3	−177.9 (3)	N2—N3—C8—S1	−177.9 (2)
O1—C1—C6—C5	177.6 (3)	C8—N1—C9—C10	95.0 (3)
O1—C1—C6—C7	−1.2 (4)	C10—C11—C12—C15	177.8 (3)
C1—C6—C7—N2	9.2 (4)	C15—C12—C13—C14	−178.7 (3)
C1—C6—C7—N1	−170.7 (3)		

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

D—H···A	D—H	H···A	D···A	D—H···A
N3—H3···S1^{i}	0.86	2.41	3.271 (3)	174
C14—H14···S1^{ii}	0.93	2.83	3.742 (3)	168
O1—H1···N2	0.82	1.88	2.574 (3)	142

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

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 [0.96 Å for methyl H], respectively. The U_{iso}(H) values were set equal to $1.5U_{eq}$(O,C) for the hydroxyl and methyl H atoms, and $1.2U_{eq}$(parent atom) for the remaining H atoms. The reflections were very weak, due to the very thin nature of the plate crystal, and hence the R_{int} value (0.143) was higher than normal.

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. (2001). *J. Chem. Soc. Pak.* **23**, 237–239.
Charıstos, D. D., Vagenes, G. V., Tzavellas, L. C., Tsoleridis, C. A. & Rodios, N. A. (1994). *J. Heterocycl. Chem.* **31**, 1593–1598.
Farrugia, L. J. (1997). *J. Appl. Cryst.* **30**, 565.
Farrugia, L. J. (1999). *J. Appl. Cryst.* **32**, 837–838.
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*. University of Utrecht, The Netherlands.
Stillings, M. R., Welbourn, A. & 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. & Zolgharneın, J. (2003). *Turk. J. Chem.* **27**, 119–125.