Acta Crystallographica Section E
Structure Reports Online
ISSN 1600-5368

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

Necmi Dege,[a]* Ahmet Çetin,[b] Ahmet Cansız,[b] Memet Şekerci,[b] Cavit Kazaz,[c] Muharrem Dinçer[a] and Orhan Büyükgüngör[a]

[a]Department of Physics, Arts and Sciences Faculty, Ondokuz Mayıs University, 55139 Samsun, Turkey, [b]Department of Chemistry, Arts and Sciences Faculty, Fırat University, 23119 Elazığ, Turkey, and [c]Department of Chemistry, Arts and Sciences Faculty, Atatürk University, 25240 Erzurum, Turkey

Correspondence e-mail: dege@omu.edu.tr

Key indicators

Single-crystal X-ray study
T = 296 K
Mean σ(C–C) = 0.004 Å
R factor = 0.043
wR factor = 0.109
Data-to-parameter ratio = 14.8

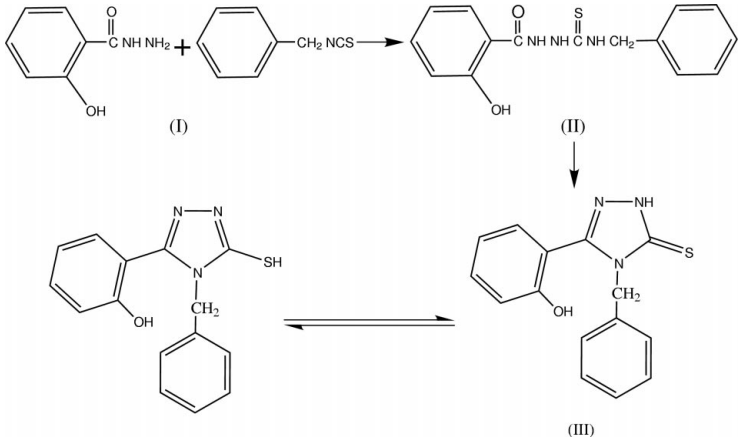
For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

Received 17 September 2004
Accepted 22 September 2004
Online 30 September 2004

In the title molecule, $C_{15}H_{13}N_3OS$, the triazole ring plane forms dihedral angles of 18.99 (7) and 89.35 (7)° with the hydroxyphenyl and benzyl substituent ring planes, respectively. In the crystal structure, the molecules exist as centrosymmetric N—H···S hydrogen-bonded dimers, with an N···S distance of 3.287 (2) Å.

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 *et al.*, 2004*a*,*b*; 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 *et al.*, 2004).



In the present study, the title compound, (III), was synthesized by the reaction of benzyl isothiocyanate and 2-salicylic hydrazide, (I), *via* 4-benzyl-1-(2-hydroxybenzoyl)-thiosemicarbazide, (II). Base-catalysed intramolecular dehydrative cyclization of this intermediate furnished the thione in good yield (86%). The reaction sequences depicted in the scheme were followed to obtain (III). Initially, the atomic

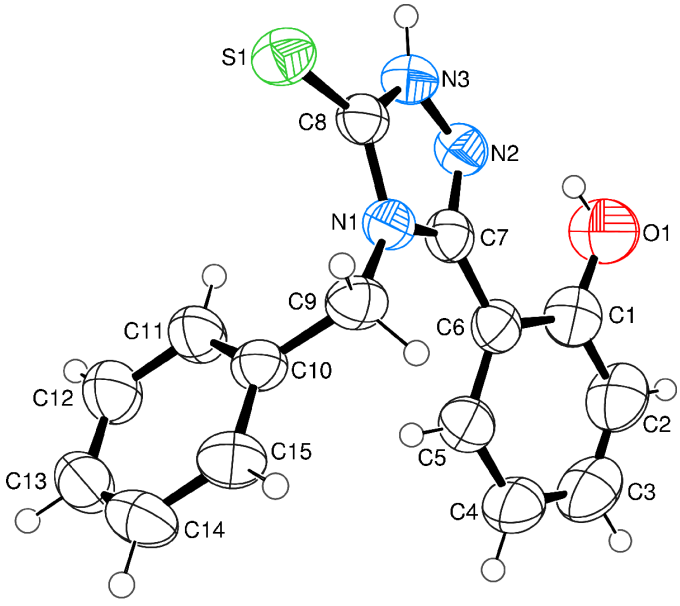


Figure 1
An *ORTEP*-3 (Farrugia, 1997) drawing of (III), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as spheres of arbitrary radii.

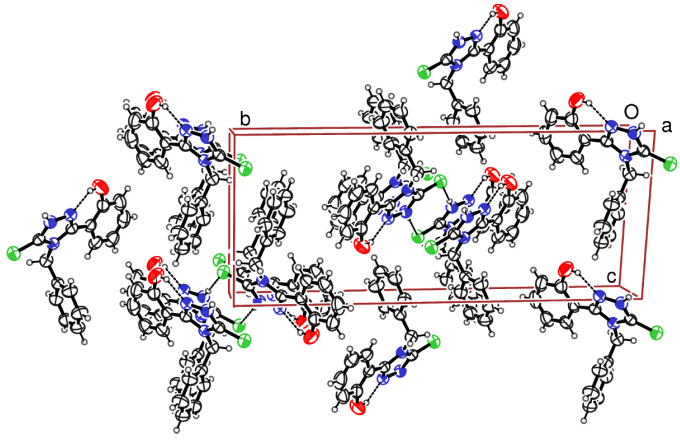


Figure 2
A packing diagram of (III), with the intra- and intermolecular hydrogen bonds indicated by dashed lines.

connectivity in (III) was elucidated from IR and ^{1}H NMR spectra.

The molecule of (III) is non-planar (Fig. 1). The triazole ring plane forms dihedral angles of 18.99 (7) and 89.35 (7)° with the hydroxyphenyl and benzyl substituent ring planes, respectively [C1—C6—C7—N2 = 17.1 (3)°, C5—C6—C7—N1 = 19.8 (3)°, C8—N1—C9—C10 = 98.6 (2)° and C7—N1—C9—C10 = −86.2 (3)°].

An intramolecular O—H···N hydrogen bond exists between the hydroxyphenyl group and the triazole N atom and N—H···S intermolecular hydrogen bonds are observed in the crystal structure (Table 2 and Fig. 2). An N3—H3···S1^{i} hydrogen bond links inversion-related molecules into dimers. The N···S distance [3.287 (2) Å] in this interaction is shorter than the mean value of 3.44 (1) Å reported for such hydrogen bonds by Allen *et al.* (1997); also, the N—H···S angle (175°) is wider than the mean angle of 158 (1)°. By comparing 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, Cansız, 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 the dimer formation shortens the N···S distances. The N···S distances in (III), (IV), (V), (VI) and (VII), which exist as centrosymmetric N—H···S hydrogen-bonded dimers, are 3.312 (2), 3.473 (1), 3.501 (2), 3.321 (3) and 3.304 (2) Å, respectively.

Experimental

Starting materials were obtained from Fluka or Aldrich. For the synthesis of (II), a mixture of (I) (0.01 mol) and benzyl isothiocyanate (0.01 mol) in absolute ethanol (100 ml) was refluxed for 8 h. The solid material obtained on cooling was filtered off, washed with diethyl ether, dried and crystallized from ethanol–dioxane (yield 84%; m.p. 487 K). IR (ν, cm^{-1}): 3425, 3300 (N—H, OH), 1672 (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 a methanol–dioxane mixture (yield 95%; m.p. 471–473 K). IR (ν, cm^{-1}): 3298 (OH), 2925–2752 (SH), 1628 (C═N). ^{1}H NMR (δ): 5.16 (*s*, 2H, N-CH$_2$), 6.79 (*t*, *J* = 7.32 Hz, 1H, H$_3$), 6.89 (*m*, 3H, H$_1$, H$_{5a}$, H$_{5b}$), 7.02 (*m*, 2H, H$_2$, H$_4$), 7.23 (*m*, 2H, H$_{6a}$, H$_{6b}$), 7.34 (*t*, *J* = 8.05 Hz, 1H, H$_7$), 10.40 (*s*, 1H, OH), 13.94 (*s*, 1H, SH).

Crystal data

$C_{15}H_{13}N_3OS$
M_r = 283.34
Monoclinic, $P2_1/n$
a = 5.7387 (5) Å
b = 23.842 (3) Å
c = 10.3045 (9) Å
β = 104.655 (7)°
V = 1364.0 (2) Å^3
Z = 4
D_x = 1.380 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 5446 reflections
θ = 1.7–26.0°
μ = 0.24 mm^{-1}
T = 296 K
Plate, colourless
0.74 × 0.43 × 0.05 mm

Data collection

Stoe IPDS-II diffractometer
ω scans
Absorption correction: by integration (*X-RED*32; Stoe & Cie, 2002)
T_{min} = 0.859, T_{max} = 0.988
7312 measured reflections
2673 independent reflections
1737 reflections with $I > 2\sigma(I)$
R_{int} = 0.078
θ_{max} = 26.1°
$h = -7 \rightarrow 7$
$k = -29 \rightarrow 29$
$l = -12 \rightarrow 12$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.044
$wR(F^2)$ = 0.109
S = 0.87
2673 reflections
181 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0654P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.001
$\Delta\rho_{max}$ = 0.16 e Å^{-3}
$\Delta\rho_{min}$ = −0.26 e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

S1—C8	1.673 (2)	N2—C7	1.308 (2)
O1—C1	1.355 (3)	N2—N3	1.368 (2)
N1—C8	1.379 (2)	N3—C8	1.334 (2)
N1—C7	1.385 (2)	C6—C7	1.458 (3)
N1—C9	1.461 (2)	C9—C10	1.500 (3)
C1—O1—H1	109.5	C5—C6—C7	123.2 (2)
C8—N1—C9	121.40 (16)	N2—C7—C6	122.33 (18)
C7—N1—C9	130.44 (16)	N3—C8—S1	129.07 (15)
O1—C1—C2	116.8 (2)	N1—C8—S1	127.13 (15)
O1—C1—C6	123.3 (2)	N1—C9—C10	114.47 (16)
C1—C6—C7	119.48 (19)		
C7—N2—N3—C8	−0.2 (2)	C9—N1—C8—S1	−3.9 (3)
O1—C1—C6—C7	−3.0 (3)	C8—N1—C9—C10	98.6 (2)
C9—N1—C7—C6	1.4 (3)	C7—N1—C9—C10	−86.2 (3)
C1—C6—C7—N2	17.1 (3)	N1—C9—C10—C11	−14.2 (3)
C5—C6—C7—N1	19.8 (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	2.43	3.287 (2)	175
O1—H1···N2	0.82	1.91	2.631 (3)	146

Symmetry code: (i) $3-x, -y, -z$.

All 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 (0.97 Å for methylene H atoms), respectively. The U_{iso}(H) values were set equal to $1.5U_{eq}$(O) for the hydroxyl and methylene H atoms, and to $1.2U_{eq}$(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, 2003); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

The authors acknowledge the Faculty of Arts and Sciences, Ondokuzmayıs University, Turkey, for the use of the Stoe IPDS-II diffractometer (purchased under grant F.279 of the University Research Fund). The financial support of the Firat University Research Fund (FUBAB) is gratefully acknowledged (project No. 798). AÇ is grateful to TÜBİTAK–BAYG for assistance in supporting the synthesis of (III).

References

Allen, F. H., Bird, C. M., Rowland, R. S. & Raithby, P. R. (1997). *Acta Cryst.* B**53**, 680–695.
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*a*). *Acta Cryst.* E**60**, o1340–o1342.
Genç, S., Dege, N., Çetin, A., Cansız, A., Şekerci, M. & Dinçer, M. (2004*b*). *Acta Cryst.* E**60**, o1580–o1582.
Genç, S., Dege, N., Yılmaz, I., Çukurovalı, A. & Dinçer, M. (2004). *Acta Cryst.* E**60**, e10.
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.
Öztürk, S., Akkurt, M., Cansız, A., Çetin, A., Sekerci, M. & Heinemann, F. W. (2004). *Acta Cryst.* E**60**, o322–o323.
Öztürk, S., Akkurt, M., Cansız, A., Koparır, M., Şekerci, M. & Heinemann, F. W. (2004). *Acta Cryst.* E**60**, o425–o427.
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.
Shanmuga Sundara Raj, S., Puviarasan, K., Velmurugan, D., Jayanthi, G. & Fun, H.-K. (1999). *Acta Cryst.* C**55**, 1318–1320.
Sheldrick, G. M. (1997). *SHELXS*97 and *SHELXL*97. University of Göttingen, Germany.
Spek, A. L. (2003). *J. Appl. Cryst.* **36**, 7–13.
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.