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

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Key indicators

Single-crystal X-ray study
T = 293 K
Mean σ(C–C) = 0.005 Å
R factor = 0.058
wR factor = 0.110
Data-to-parameter ratio = 15.4

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

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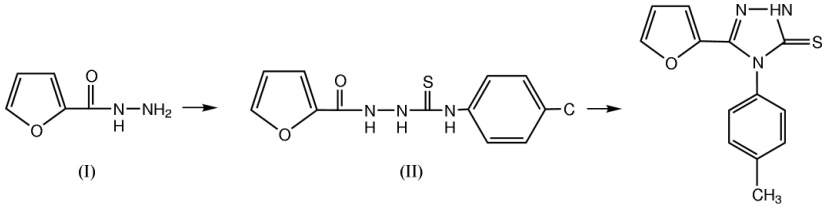
In the title molecule, $C_{13}H_{11}N_3OS$, the triazole plane forms dihedral angles of 3.8 (2) and 81.3 (2)° with the furan and *p*-tolyl ring planes, respectively. In the crystal structure, the molecules exist as centrosymmetric N—H···S hydrogen-bonded dimers, with an N···S distance of 3.312 (2) Å. The packing is further stabilized by C—H···O, C—H···N, C—H···π and π–π interactions.

Comment

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 activities (Kane *et al.*, 1988), the latter being usually 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 title compound, (III), has been newly synthesized by the reaction of *p*-tolyl isothiocynate and furan-2-carboxylic acid hydrazide, (I), through 1-(2-furoyl)-4-*p*-tolylthiosemicarbazide, (II) (see scheme). Base-catalysed intramolecular dehydrative cyclization of this intermediate furnished the thione (III) in good yield (79%) (Cansız *et al.*, 2003); its crystal structure is presented here.



(I) (II) (III)

The molecular structure of (III) is non-planar (Fig. 1). The triazole plane forms dihedral angles of 3.8 (2) and 81.3 (2)° with the furan and *p*-tolyl ring planes, respectively [C3—C4—C5—N3 = −5.3 (6)°, O1—C4—C5—N1 = −3.0 (4)°, C5—N3—C7—C12 = 79.3 (4)° and C6—N3—C7—C8 = 83.9 (4)°].

N—H···S, C—H···O and C—H···N intermolecular hydrogen bonds are observed in the crystal structure (Table 2 and Fig. 2). The N2—H2*A*···S1^{i} hydrogen bond links inversion-related molecules into dimers. The N···S distance [3.312 (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 (164°) 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*-

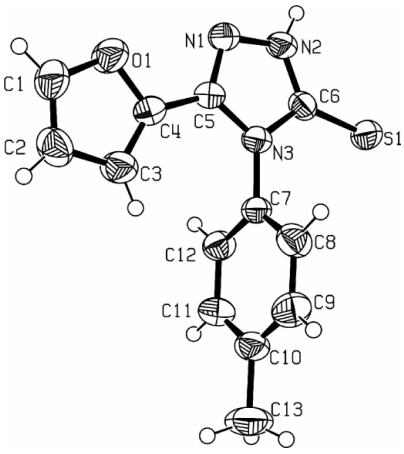


Figure 1
An *ORTEP*-3 (Farrugia, 1997) drawing of (III), with the atom-numbering scheme. Displacement ellipsoids for non-H atoms are drawn at the 50% probability level. H atoms are shown as spheres of arbitrary radii.

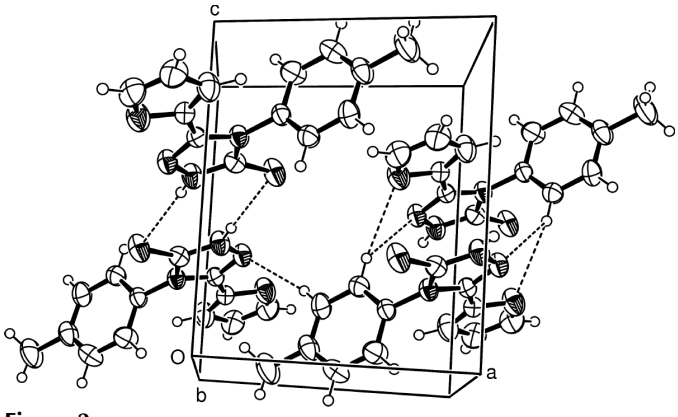


Figure 2
A packing diagram of (III), illustrating the hydrogen-bonding network (dashed lines).

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 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. The C12—H12···O1^{iii} and C12—H12···N1^{iii} weak interactions (Desiraju, 1996) constitute a pair of bifurcated hydrogen bonds [symmetry code: (iii) $-x, -y, 1-z$; Fig. 2].

A *PLATON* analysis (Spek, 1997) showed the presence of a weak π–π interaction between the furan ring and triazole ring of the inversion-related molecule at ($-x, -y, 1-z$) [centroid–centroid distance is 3.611 (2) Å]. Furthermore, C—H···π interactions involving the benzene ring are also observed in the crystal structure (Table 2).

Experimental

A mixture of furan-2-carboxylic acid hydrazide, (I) (0.01 mol), and *p*-tolyl isothiocynate (0.01 mol) in dry C_6H_6 was refluxed for 6 h. The solid material obtained on cooling was filtered off and recrystallized from methanol to yield 1-(2-furoyl)-4-*p*-tolylthiosemicarbazide, (II). A stirred mixture of compound (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 to obtain the title compound, (III). The precipitate was then crystallized from ethanol (yield 79%, m.p. 530–551 K). IR ν (cm^{-1}): 3351, 3285 (N—H), 2576 (SH), 1621 (C=N), 1250 (C—O—C), 1534, 1258, 1050, 951 (N—C=S, amide I, II, III and IV bands). ^{1}H NMR: δ 2.46 (*s*, 3H, CH_3), 5.94–6.36 (*m*, 3H, furan), 7.31–7.47 (*m*, 4H, Ar-H), 14.01 (*s*, 1H, SH, or NH). Calculated for $C_{13}H_{11}N_3OS$: C 60.68, H 4.31, N 16.33, S 12.46%; found: C 60.65, H 4.39, N 16.50, S 12.42%.

Crystal data

$C_{13}H_{11}N_3OS$	$Z = 2$
$M_r = 257.31$	$D_x = 1.332$ Mg m^{-3}
Triclinic, $P\overline{1}$	Mo $K\alpha$ radiation
$a = 8.5665$ (15) Å	Cell parameters from 7019 reflections
$b = 8.7759$ (16) Å	$\theta = 2.1$–27°
$c = 9.5372$ (17) Å	$\mu = 0.24$ mm^{-1}
$\alpha = 91.796$ (15)°	$T = 293$ (2) K
$\beta = 91.407$ (14)°	Prism, colorless
$\gamma = 116.386$ (12)°	0.31 × 0.20 × 0.07 mm
$V = 641.4$ (2) Å^3	

Data collection

Stoe IPDS-2 diffractometer	2518 independent reflections
ω scans	1539 reflections with $I > 2\sigma(I)$
Absorption correction: by integration (*X-RED*32; Stoe & Cie, 2002)	$R_{int} = 0.090$
	$\theta_{max} = 26.0^\circ$
$T_{min} = 0.937$, $T_{max} = 0.987$	$h = -10 \rightarrow 10$
8282 measured reflections	$k = -10 \rightarrow 10$
	$l = -11 \rightarrow 11$

Refinement

Refinement on F^2	H-atom parameters constrained
$R[F^2 > 2\sigma(F^2)] = 0.058$	$w = 1/[\sigma^2(F_o^2) + (0.0375P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.110$	$(\Delta/\sigma)_{max} = 0.020$
$S = 1.01$	$\Delta\rho_{max} = 0.21$ e Å^{-3}
2518 reflections	$\Delta\rho_{min} = -0.21$ e Å^{-3}
164 parameters	

Table 1
Selected geometric parameters (Å, °).

S1—C6	1.675 (3)	N3—C7	1.448 (3)
N1—C5	1.298 (3)	C5—N3	1.378 (4)
N2—C6	1.332 (4)	C6—N3	1.380 (3)
N2—N1	1.366 (3)		
C1—O1—C4	106.5 (2)	N1—C5—N3	111.0 (2)
C5—N1—N2	104.1 (2)	N1—C5—C4	123.6 (3)
C6—N2—N1	114.0 (2)	N3—C5—C4	125.5 (2)
C5—N3—C6	107.6 (2)	N2—C6—N3	103.2 (2)
C5—N3—C7	127.2 (2)	N2—C6—S1	129.2 (2)
C6—N3—C7	125.0 (2)	N3—C6—S1	127.6 (2)

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N2—H2*A*···S1^{i}	0.86	2.48	3.312 (2)	164
C11—H11···N1^{ii}	0.93	2.56	3.468 (4)	165
C12—H12···O1^{iii}	0.93	2.75	3.567 (4)	147
C12—H12···N1^{iii}	0.93	2.69	3.477 (4)	143
C1—H1···*CgP*^{iv}	0.93	2.85	3.663 (4)	146
C3—H3···*CgP*	0.93	2.96	3.706 (4)	138

Symmetry codes: (i) $-x, 1-y, 1-z$; (ii) $1+x, y, z$; (iii) $-x, -y, 1-z$; (iv) $x-1, y-1, z$. ; *CgP* is the centroid of the benzene ring.

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, respectively. The U_{iso}(H) values were set equal to $1.5U_{eq}$(O) for the hydroxy and ethane H atoms, and $1.2U_{eq}$(parent atom) for the other 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).

References

Allen, F. H., Bird, C. M., Rowland, R. S. & Raithby, P. R. (1997). *Acta Cryst.* B**53**, 680–695.

Cansız, A., Koparır, M. & Demirbağ, A. (2003). *Molecules*. Submitted.

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

Desiraju, G. R. (1996). *Acc. Chem. Res.* **29**, 441–449.

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

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

Jones, D. H., Slack, R., 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). JP 77-25028 (A01N 9/12); *Chem. Abstr.* (1977). **87**, 147054a.

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., Şekerci, 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, Sh. 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). *SHELXL*97. University of Göttingen, Germany.

Spek, A. L. (1997). *PLATON*. University of Utrecht, 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.