

4-(4-Chlorophenyl)-3-(furan-2-yl)-1H-1,2,4-triazole-5(4H)-thione

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Key indicators

Single-crystal X-ray study

$T = 100\text{ K}$

Mean $\sigma(\text{C}-\text{C}) = 0.003\text{ \AA}$

R factor = 0.033

wR factor = 0.098

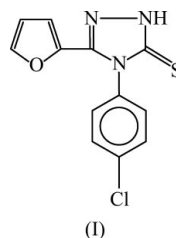
Data-to-parameter ratio = 20.0

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

The title molecule, $\text{C}_{12}\text{H}_8\text{ClN}_3\text{OS}$, is not planar. The benzene and furan rings make dihedral angles of $78.4(1)$ and $5.6(1)^\circ$ with the mean plane of the central triazole ring. The crystal structure is stabilized by $\text{N}-\text{H}\cdots\text{S}$, $\text{C}-\text{H}\cdots\text{Cl}$, $\text{C}-\text{H}\cdots\text{N}$, $\text{C}-\text{H}\cdots\pi$ and $\pi-\pi$ interactions.

Comment

Derivatives of 1,2,4-triazole are known to exhibit anti-inflammatory (Unangst *et al.*, 1992; Mullican *et al.*, 1993), antiviral, analgesic (Sughen & Yoloye, 1978), antimicrobial (Shams El-Dine & Hazzaa, 1974; Misato *et al.*, 1977; Cansız *et al.*, 2001), anticonvulsant (Stillings *et al.*, 1986) and anti-depressant activity (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 anti-depressant properties seem to be the best documented. In addition, some studies have been published on the electronic structures and thiol–thione tautomeric equilibrium of heterocyclic thione derivatives (Aydoğan *et al.*, 2002; Charistos *et al.*, 1994). The title compound, (I), has been newly synthesized by the reaction of 4-chlorophenyl isothiocyanate and furan-2-carboxylic acid hydrazide through the intermediate 1-(2-furoyl)-4-(4-chlorophenyl)thiosemicarbazide. We present here the crystal structure of (I).



A perspective view of (I), including the atomic numbering scheme, is shown in Fig. 1. In the structure of (I), the benzene and furan rings make dihedral angles of $78.4(1)$ and $5.6(1)^\circ$ with the mean plane of the central triazole ring, the dihedral angle between them being $78.7(1)^\circ$.

The $\text{C}-\text{N}$ bond distances lie in the range $1.346(2)$ – $1.384(2)\text{ \AA}$; these are markedly shorter than the normal $\text{C}-\text{N}$ single-bond distance (1.47 \AA ; Sasada, 1984) and longer than the $\text{C}=\text{N}$ double-bond distance (1.28 \AA ; Wang *et al.*, 1998).

The $\text{Csp}^2=\text{Csp}^2$ and Csp^2-O bond distances within the furan ring are normal and comparable with reported values (Öztürk *et al.*, 2004). The $\text{C}=\text{S}$ bond length of $1.677(2)\text{ \AA}$ is in agreement with the literature data (Allen *et al.*, 1987).

An intramolecular $\text{C}-\text{H}\cdots\pi$ interaction involving the benzene ring is observed in the molecular structure. In the

Received 10 February 2004

Accepted 17 February 2004

Online 20 February 2004

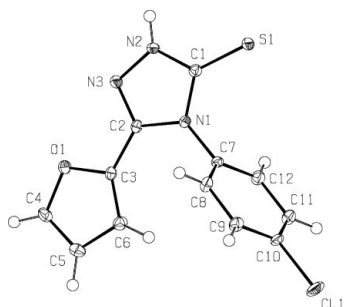


Figure 1
An ORTEP-3 drawing (Farrugia, 1997) of (I), with the atom-numbering scheme. Displacement ellipsoids for non-H atoms are drawn at the 50% probability level.

crystal structure, the molecules are linked by intermolecular N—H...S, C—H...Cl, C—H...N and C—H... π interactions, resulting in a network structure (Fig. 2); the details of these interactions are listed in Table 2. The crystal structure is further stabilized by the stacking interactions between the furan ring and symmetry-related triazole ring at $(2-x, 1-y, 2-z)$, with a centroid-centroid separation of 3.555 (2) Å.

Experimental

A stirred mixture of 1-(2-furoyl)-4-(4-chlorophenyl)thiosemicarbazide (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 ethanol (yield 72%, m.p. 547–548 K). IR $\nu(\text{cm}^{-1})$: 3351, 3288 (N—H), 1625 (C=N), 1250 (C—O—C), 1535, 1260, 1050, 950 (N—C=S, amide I, II, III and IV bands). ^1H NMR: δ 6.16–6.50 (*m*, 3H, furan), 7.45–7.78 (*m*, 4H, Ar—H), 13.98 (*s*, 1H, SH). Calculated for $\text{C}_{12}\text{H}_8\text{ClN}_3\text{OS}$: C 51.90, H 2.90, N 15.13, S 11.54%; found: C 51.88, H 2.99, N 15.15, S 11.49%.

Crystal data

$\text{C}_{12}\text{H}_8\text{ClN}_3\text{OS}$	$Z = 2$
$M_r = 277.73$	$D_x = 1.499 \text{ Mg m}^{-3}$
Triclinic, $P\bar{1}$	Mo $K\alpha$ radiation
$a = 8.524$ (5) Å	Cell parameters from 78 reflections
$b = 8.640$ (5) Å	$\theta = 6\text{--}20^\circ$
$c = 9.307$ (5) Å	$\mu = 0.47 \text{ mm}^{-1}$
$\alpha = 91.426$ (5)°	$T = 100 \text{ K}$
$\beta = 90.250$ (5)°	Prism, colorless
$\gamma = 116.059$ (5)°	$0.23 \times 0.15 \times 0.07 \text{ mm}$
$V = 615.5$ (6) Å ³	

Data collection

Bruker–Nonius KappaCCD diffractometer	3274 independent reflections
ω scans	2673 reflections with $I > 2\sigma(I)$
Absorption correction: multi-scan (SADABS; Sheldrick, 1996)	$R_{\text{int}} = 0.035$
$T_{\text{min}} = 0.900$, $T_{\text{max}} = 0.968$	$\theta_{\text{max}} = 29.0^\circ$
17300 measured reflections	$h = -11 \rightarrow 11$
	$k = -11 \rightarrow 11$
	$l = -12 \rightarrow 12$

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.053P)^2 + 0.1559P]$
$R[F^2 > 2\sigma(F^2)] = 0.033$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.098$	$(\Delta/\sigma)_{\text{max}} = 0.001$
$S = 1.16$	$\Delta\rho_{\text{max}} = 0.43 \text{ e \AA}^{-3}$
3274 reflections	$\Delta\rho_{\text{min}} = -0.34 \text{ e \AA}^{-3}$
164 parameters	Extinction correction: SHELXL97
H-atom parameters constrained	Extinction coefficient: 0.012 (4)

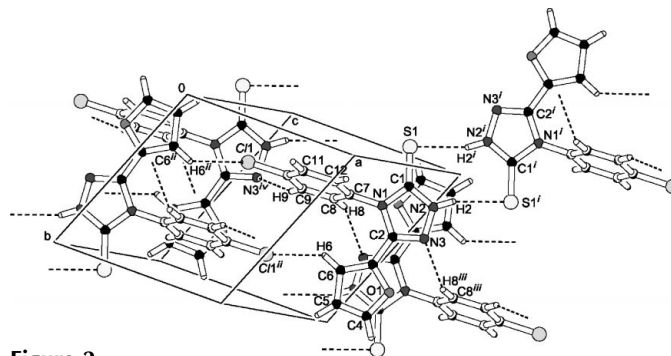


Figure 2
A view of hydrogen-bond contacts [symmetry codes: (i) $2-x, -y, 2-z$; (ii) $1-x, 1-y, 1-z$; (iii) $2-x, 1-y, 2-z$; (iv) $x-1, y, z$].

Table 1

Selected geometric parameters (Å, °).

Cl1—C10	1.747 (2)	N1—C2	1.384 (2)
S1—C1	1.6773 (19)	N1—C7	1.446 (2)
O1—C3	1.376 (2)	N2—N3	1.374 (2)
O1—C4	1.372 (2)	N2—C1	1.346 (2)
N1—C1	1.383 (2)	N3—C2	1.311 (2)
C3—O1—C4	106.04 (14)	N1—C2—C3	125.81 (15)
C1—N1—C2	107.65 (14)	N3—C2—C3	123.03 (15)
C1—N1—C7	124.81 (14)	O1—C3—C2	113.89 (14)
C2—N1—C7	127.24 (13)	O1—C3—C6	110.38 (14)
N3—N2—C1	113.82 (14)	O1—C4—C5	110.71 (14)
N2—N3—C2	103.93 (13)	N1—C7—C8	118.51 (14)
N1—C1—N2	103.43 (13)	N1—C7—C12	119.65 (15)
S1—C1—N1	127.51 (14)	Cl1—C10—C11	119.36 (13)
S1—C1—N2	129.05 (13)	Cl1—C10—C9	118.34 (14)
N1—C2—N3	111.16 (13)		

Table 2

Hydrogen-bonding geometry (Å, °).

$D\text{—}H\cdots A$	$D\text{—}H$	$H\cdots A$	$D\cdots A$	$D\text{—}H\cdots A$
N2—H2...S1 ⁱ	0.86	2.48	3.304 (2)	160
C6—H6...Cl1 ⁱⁱ	0.93	2.77	3.406 (3)	127
C8—H8...N3 ⁱⁱⁱ	0.93	2.56	3.368 (3)	146
C9—H9...N3 ^{iv}	0.93	2.42	3.302 (3)	158
C4—H4...Cg1 ^v	0.93	2.71	3.529 (3)	147
C6—H6...Cg1	0.93	2.99	3.729 (3)	138
Cl2—H12...Cg2 ^{vi}	0.93	3.09	3.733 (3)	128

Symmetry codes: (i) $2-x, -y, 2-z$; (ii) $1-x, 1-y, 1-z$; (iii) $2-x, 1-y, 2-z$; (iv) $x-1, y, z$; (v) $1+x, 1+y, z$; (vi) $2-x, 1-y, 1-z$. Cg1 and Cg2 denote the centroids of the benzene and furan rings, respectively.

All H atoms were positioned geometrically and treated as riding on their parent atoms, with C—H = 0.93 Å and N—H = 0.86 Å. The $U_{\text{iso}}(\text{H})$ values were set equal to $1.2U_{\text{eq}}(\text{parent})$.

Data collection: COLLECT (Nonius, 1999); cell refinement: EvalCCD (Duisenberg *et al.*, 2003); data reduction: EvalCCD; program(s) used to solve structure: SIR97 (Altomare *et al.*, 1999); program(s) used to refine structure: SHELXL97 (Sheldrick, 1997); molecular graphics: ORTEP-3 for Windows (Farrugia, 1997); software used to prepare material for publication: WinGX (Farrugia, 1999).

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