

4-Phenyl-3-(pyridin-4-yl)-1*H*-1,2,4-triazole-5(4*H*)-thioneSema Öztürk Yıldırım,^a Mehmet Akkurt,^{a*} Ahmet Çetin,^b Ahmet Cansız,^b Memet Şekerci^b and Canan Kazak^c^aDepartment of Physics, Faculty of Arts and Sciences, Erciyes University, 38039 Kayseri, Turkey, ^bDepartment of Chemistry, Faculty of Arts and Sciences, Firat University, 23119 Elazığ, Turkey, and ^cDepartment of Physics, Faculty of Arts and Sciences, Ondokuz Mayıs University, 55139 Samsun, Turkey

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Key indicators

Single-crystal X-ray study
T = 296 K
Mean $\sigma(\text{C}-\text{C}) = 0.002 \text{ \AA}$
R factor = 0.031
wR factor = 0.076
Data-to-parameter ratio = 16.7For details of how these key indicators were automatically derived from the article, see <http://journals.iucr.org/e>.

In the title compound, $\text{C}_{13}\text{H}_{10}\text{N}_4\text{S}$, the almost ideally planar triazole ring forms dihedral angles of $58.5 (1)^\circ$ and $36.9 (1)^\circ$ with the phenyl and pyridine planes, respectively. The planes of the phenyl and pyridyl substituents form a dihedral angle of $58.5 (1)^\circ$ with each other. The crystal packing is stabilized by intermolecular $\text{N}-\text{H}\cdots\text{N}$ hydrogen bonds.

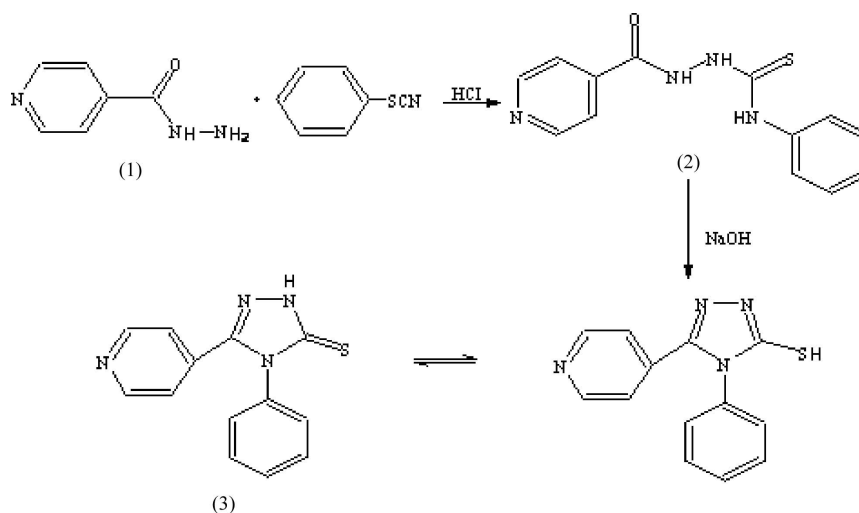
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Comment

Among the pharmacological profiles of 1,2,4-triazoles, their antimicrobial, anticonvulsant and antidepressant properties seem to be the best documented. Derivatives of 4,5-disubstituted 1,2,4-triazole are known, synthesized by intramolecular cyclization of 1,4-disubstituted thiosemicarbazides (Zamani *et al.*, 2003; Cansız *et al.*, 2004). In addition, there are some studies on the electronic structures and thiol–thione tautomeric equilibria of heterocyclic thione derivatives (Aydoğan *et al.*, 2002; Charistos *et al.*, 1994). We present here the structure of a new 1,2,4-triazole derivative, namely 4-phenyl-3-(pyridin-4-yl)-1*H*-1,2,4-triazole-5(4*H*)-thione, (3) (Fig. 1).



The $\text{C1}=\text{S1}$ bond length [$1.6619 (14) \text{ \AA}$] compares with $1.6773 (19) \text{ \AA}$ in 4-(4-chlorophenyl)-3-(furan-2-yl)-1*H*-1,2,4-triazole-5(4*H*)-thione (Öztürk *et al.*, 2004*a*) and $1.668 (5) \text{ \AA}$ in 4-amino-3-(1,2,3,4,5-pentahydroxypentyl)-1*H*-1,2,4-triazole-5(4*H*)-thione (Zhang *et al.*, 2004). In the triazole ring, the $\text{N2}=\text{C2}$ bond [$1.2974 (17) \text{ \AA}$] shows double-bond character (Table 1). In the crystal structure, all bond lengths and angles are comparable with those observed in related structures (Öztürk *et al.*, 2004*a,b*). The triazole ring is planar within 0.002 \AA . Its plane forms dihedral angles of $58.5 (1)^\circ$ and

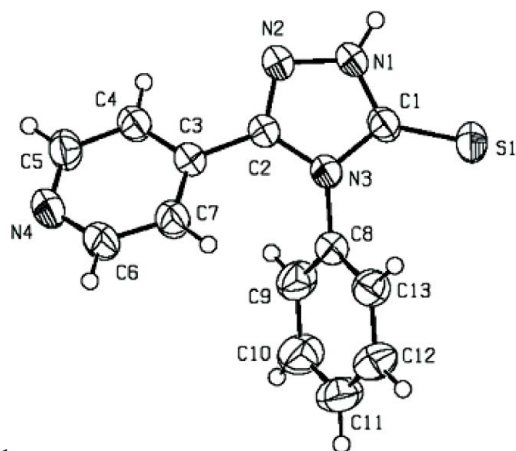


Figure 1
View of (3), showing 50% probability displacement ellipsoids and the atom-numbering scheme.

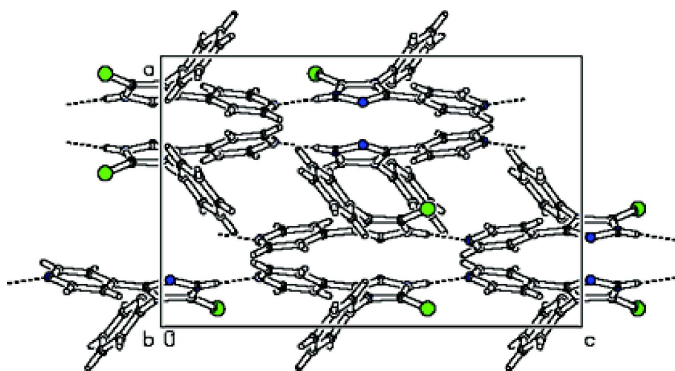


Figure 2
Packing diagram of the title compound, viewed down the *b* axis. Hydrogen bonds are shown as dashed lines.

36.9 (1)° with the mean planes of the phenyl and pyridine rings, respectively. The dihedral angle between the least-squares planes of the phenyl and pyridine rings happens to be identical with the triazole/phenyl dihedral angle [58.5 (1)°]. N1—H1...N4 hydrogen bonds link molecules of (3) into infinite chains extending along the *c* axis of the unit cell (Fig. 2 and Table 2).

Experimental

For the synthesis of 2-isonicotinoyl-*N*-phenylhydrazinecarbothioamide (see scheme), (2), a mixture of isonicotinohydrazide [(1); 0.01 mol, 1.37 g] and phenyl isothiocyanate (0.01 mol, 1.35 g, 1.196 ml) in absolute ethanol (100 ml) was refluxed for 8 h. The solid material obtained on cooling was filtered off, washed with diethyl ether (250 ml), dried and crystallized from acetone (yield 85%; m.p. 467–469 K). IR ν (KBr, cm⁻¹): 3425, 3295 (N—H), 1666 (C=O), 1264 (C=S). ¹H NMR δ : 8.90–7.10 (*m*, 9H, Ar-H), 9.87–9.91 (*d*, 2H, NH), 10.80–10.91 (*s*, 1H, NH), 13.95 (*s*, 1H, SH or NH exchanged; DMSO-*d*₆).

For the synthesis of 4-phenyl-3-(pyridin-4-yl)-1*H*-1,2,4-triazole-5(4*H*)-thione, (3), a stirred mixture of (2) (1 mmol, 2.72 g) and sodium hydroxide (40 mg, 1 mmol, as a 2 *N* solution) was refluxed for 6 h. After cooling, the solution was acidified to pH 4 with 5 *M* hydrochloric acid and the precipitate was filtered off. The precipitate was then crystallized from a mixture of ethanol–dioxane (yield 90%;

m.p. 570–571 K). IR ν (KBr, cm⁻¹): 2678 (SH), 1614 (C=N), 1535, 1260, 1050, 950 (N—C=S, amide I, II, III and IV bands); ¹H NMR δ : 8.56–7.20 (*m*, 9H, Ar-H), 13.95 (*s*, 1H, SH or NH).

Crystal data

C₁₃H₁₀N₄S
M_r = 254.32
 Orthorhombic, *Pbcn*
a = 11.2958 (6) Å
b = 12.7480 (8) Å
c = 17.5607 (8) Å
V = 2528.7 (2) Å³
Z = 8
D_x = 1.336 Mg m⁻³

Mo K α radiation
 Cell parameters from 2731 reflections
 θ = 1.6–27.2°
 μ = 0.24 mm⁻¹
T = 296 K
 Prism, yellow
 0.50 × 0.42 × 0.15 mm

Data collection

Stoe IPDS-II diffractometer
 ω scans
 Absorption correction: by integration (*X-RED32*; Stoe & Cie, 2002)
T_{min} = 0.915, *T_{max}* = 0.947
 23863 measured reflections

2731 independent reflections
 1779 reflections with *I* > 2 σ (*I*)
R_{int} = 0.067
 θ_{\max} = 27.2°
h = -14 → 14
k = -16 → 16
l = -22 → 22

Refinement

Refinement on *F*²
R[*F*² > 2 σ (*F*²)] = 0.031
wR(*F*²) = 0.076
S = 0.90
 2731 reflections
 164 parameters
 H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0422P)^2]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} = 0.001$
 $\Delta\rho_{\max} = 0.16 \text{ e \AA}^{-3}$
 $\Delta\rho_{\min} = -0.16 \text{ e \AA}^{-3}$
 Extinction correction: *SHELXL97*
 Extinction coefficient: 0.0087 (8)

Table 1

Selected geometric parameters (Å, °).

S1—C1	1.6619 (14)	N3—C2	1.3785 (17)
N1—N2	1.3700 (15)	N3—C8	1.4387 (17)
N1—C1	1.3379 (18)	N4—C5	1.334 (2)
N2—C2	1.2974 (17)	N4—C6	1.328 (2)
N3—C1	1.3836 (16)		
N2—N1—C1	114.12 (10)	S1—C1—N1	127.97 (10)
N1—N2—C2	103.82 (11)	N3—C2—C3	126.03 (11)
C1—N3—C2	107.46 (11)	N2—C2—N3	111.54 (11)
C1—N3—C8	124.82 (11)	N2—C2—C3	122.43 (12)
C2—N3—C8	127.18 (11)	N4—C5—C4	123.24 (14)
C5—N4—C6	117.12 (13)	N4—C6—C7	123.53 (14)
S1—C1—N3	128.91 (11)	N3—C8—C9	118.93 (12)
N1—C1—N3	103.07 (11)	N3—C8—C13	119.72 (13)
C1—N3—C8—C9	-116.69 (16)	N3—C2—C3—C7	36.9 (2)
N2—C2—C3—C7	-141.88 (16)		

Table 2

Hydrogen-bonding geometry (Å, °).

<i>D</i> —H... <i>A</i>	<i>D</i> —H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> —H... <i>A</i>
N1—H1...N4 ⁱ	0.86	1.97	2.8305 (16)	179

Symmetry code: (i) *x*, -*y*, $\frac{1}{2}$ + *z*.

All H atoms were positioned geometrically (C—H = 0.93 Å and N—H = 0.86 Å) and included in the refinement in the riding-model approximation, with *U_{iso}*(H) = 1.2*U_{eq}* of the carrier atom.

Data collection: *X-AREA* (Stoe & Cie, 2002); cell refinement: *X-AREA*; data reduction: *X-RED32* (Stoe & Cie, 2002); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular

graphics: *ORTEP-3* (Farrugia, 1997); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

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