Acta Crystallographica Section C
Crystal Structure Communications
ISSN 0108-2701

6-Phenyl-3-(4-pyridyl)-1,2,4-triazolo-[3,4-*b*][1,3,4]thiadiazole

Muharrem Dinçer,[a] Namık Özdemir,[a]* Ahmet Çetin,[b] Ahmet Cansız[b] and Orhan Büyükgüngör[a]

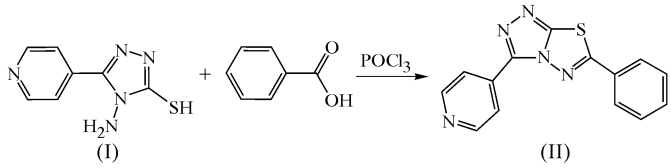
[a]Department of Physics, Faculty of Arts and Sciences, Ondokuz Mayıs University, 55139 Samsun, Turkey, and [b]Department of Chemistry, Faculty of Arts and Sciences, Fırat University, 23119 Elazığ, Turkey
Correspondence e-mail: namiko@omu.edu.tr

Received 15 August 2005
Accepted 10 October 2005
Online 27 October 2005

The title compound, $C_{14}H_9N_5S$, has been synthesized and characterized both spectroscopically and structurally. The triazolo–thiadiazole system, the pyridine ring and the phenyl ring are all planar. The plane of the triazolo–thiadiazole system forms dihedral angles of 1.53 (13) and 7.55 (12)° with the planes of the pyridine and phenyl rings, respectively. In the molecule, there are two intramolecular interactions of types C—H···N and C—H···S. Intermolecular C—H···N interactions involving a phenyl CH group and a triazole N atom lead to the formation of a one-dimensional chain. In the crystal structure, two types of π–π interactions affect the packing of the molecules. In addition, there are intermolecular non-bonded S···N contacts of 2.870 (2) Å, which may cause steric hindrance.

Comment

The prevalence of resistant infections has decreased the applicability of existing chemotherapeutic and chemopreventive antimicrobial agents and stimulated the search for new compounds. The 1,2,4-triazole nucleus and the nitrogen-bridged heterocycles derived from it have recently been incorporated into a variety of compounds with antibacterial (Holla & Kalluraya, 1988), antifungal (Prasad *et al.*, 1989) and antiparasitic (El-Dawy *et al.*, 1983) properties. In addition, it is well known that derivatives of 1,2,4-triazole exhibit anti-inflammatory (Unangst *et al.*, 1992; Mullican *et al.*, 1993), antiviral (Jones *et al.*, 1965), antimicrobial (Shams El-Dine & Hazzaa, 1974; Misato *et al.*, 1977; Koparır *et al.*, 2004) and antidepressant activities (Kane *et al.*, 1988), the last 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. Several thiadiazoles find important applications in the fields of medicine, agriculture and industry (Holla, Sarojini & Gonsalves, 1998). 4-Amino-5-(4-aryl/4-heteroaryl)-4*H*-1,2,4-triazole-3-thiols have been condensed with aromatic carboxylic acids to yield a series of 3,6-(4-aryl/4-heteroaryl)-1,2,4-triazolo[3,4-*b*][1,3,4]thiadiazoles. Phosphorous oxychloride is used as a cyclizing agent (Çetin, 2004; Holla, Gonsalves & Shenoy, 1998). In view of these important properties, the present single-crystal X-ray diffraction study of the title compound, (II), was carried out in order to investigate this bicyclic system and to confirm the assigned structure.



(I) (II)

In the present study, the new compound 6-phenyl-3-(4-pyridyl)-1,2,4-triazolo[3,4-*b*][1,3,4]thiadiazole, (II), was synthesized in 70% yield by the reaction of 4-amino-5-(4-pyridyl)-4*H*-1,2,4-triazole-3-thiol, (I), benzoic acid and phosphorous oxychloride. The reaction sequences depicted in the scheme were followed to obtain the new compound. The structure of this compound has been confirmed by IR, ^{1}H NMR and ^{13}C NMR spectroscopies.

Compound (II) (Fig. 1) consists of a fused triazolo–thiadiazole system, one pyridine ring and one phenyl ring. The four rings are almost coplanar. As expected, the 1,2,4-triazole and pyridine rings are planar, which can be attributed to a wide range of electron delocalization. The plane of the triazolo–thiadiazole system forms dihedral angles of 1.53 (13) and 7.55 (12)° with the planes of the pyridine and phenyl rings, respectively.

The N1═C1 and N2═C2 bond distances [average = 1.315 (2) Å] are in good agreement with those found for structures containing the 1,2,4-triazole ring (Özbey *et al.*, 2000; Bruno *et al.*, 2003). In (II), the presence of the pyridine ring in the 3-position of the triazole ring leads to an elongation of the N1—N2 bond length to 1.395 (2) Å. This bond is 1.371 (2) Å in 5-amino-3-trifluoromethyl-1*H*-1,2,4-triazole (Borbulevych *et al.*, 1998), in which an electron-withdrawing group is bound to the 3-position of the triazole ring. The thiadiazole moiety

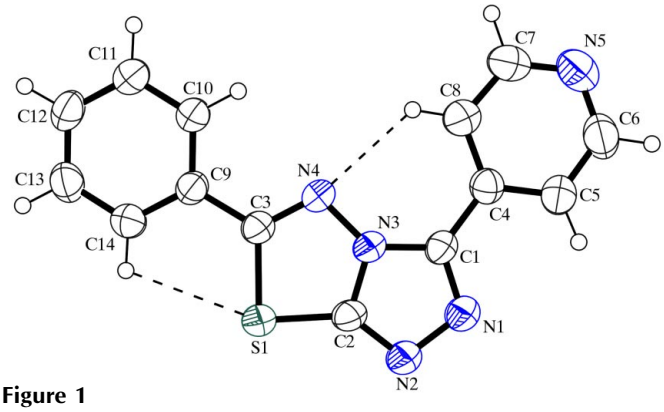


Figure 1
A view of the molecule of compound (II), showing the atomic numbering scheme. Displacement ellipsoids are drawn at the 50% probability level. Intramolecular non-bonded C—H···S and C—H···N contacts are represented by dashed lines.

 DOI: 10.1107/S0108270105032403

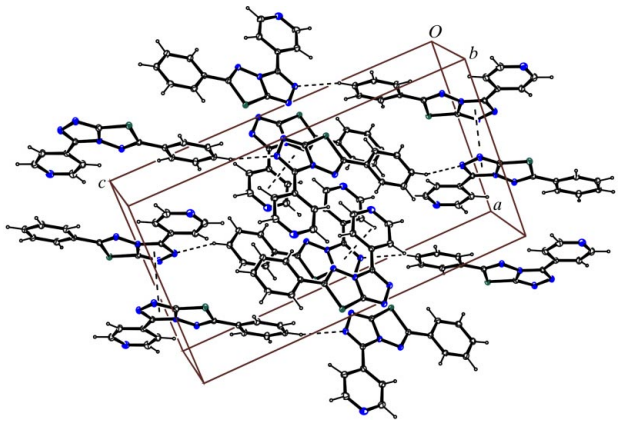


Figure 2
The crystal packing of (II), showing the intermolecular C—H···N and π–π interactions (dashed lines).

displays differences in the pairs of bonds S1—C2/S1—C3 and C2—N3/C3—N4, due to the fused 1,2,4-triazole ring and the two different groups attached to either side of the triazolo–thiadiazole system. The difference between the S1—C2 [1.724 (2) Å] and S1—C3 [1.7651 (17) Å] bond distances indicates that the resonance effect caused by the triazole ring is stronger than that caused by the thiadiazole ring. The bond distances and angles of the pyridine ring are comparable with those in the literature (Ni *et al.*, 2003).

In the molecular structure, an intramolecular C14—H14···S1 contact leads to the formation of a five-membered ring which is fused with the phenyl ring, while an intramolecular C8—H8···N4 contact leads to the formation of a six-membered ring which is fused with the pyridine ring (Fig. 1). Each of these rings is also fused with the triazolo–thiadiazole system. In the intramolecular C—H···N interaction, the C···N distance is 3.140 (2) Å, a little longer than those in the literature [3.032 (5) (Xiang *et al.*, 2004) and 3.063 (3) Å (Özbey *et al.*, 2000)].

In the crystal structure of (II), intermolecular C—H···N interactions lead to a one-dimensional polymer which extends almost along the *c* axis. In addition to these interactions, the crystal structure contains two π–π stacking interactions. The first of these is between the triazole ring and its symmetry-related partner at $(1-x, 1-y, -z)$, with a distance of 3.4594 (11) Å between the ring centroids and a perpendicular distance between the rings of 3.259 (2) Å. The second is between the triazole ring and the pyridine ring at $(x, -1+y, z)$, with a distance of 3.5029 (13) Å between the ring centroids and a perpendicular distance between the rings of 3.501 (2) Å. The hydrogen-bonding geometry is listed in Table 2. A short contact distance not listed in the tables, yet noteworthy, is S1···N2$(1-x, -y, -z)$ of 2.870 (2) Å, which may cause steric hindrance.

Experimental

To a mixture of 4-amino-5-(4-pyridyl)-4*H*-1,2,4-triazole-3-thiol, (I) (5 mmol, 0.965 g), and benzoic acid (1 mmol, 0.61 g), phosphorous oxychloride (27 mmol, 2.5 ml) was added and and the resulting mixture heated under reflux for 8 h in a water bath. The excess phosphorous oxychloride was then distilled off and the residue was poured onto crushed ice while stirring. The resulting solid was washed with dilute sodium bicarbonate solution and then recrystallized from dimethylformamide (yield 70%; m.p. 495–497 K). IR (ν, cm^{-1}): 3120–3060 (Ar CH), 1624–1580 (C═C, C═N), 680 (CH—S—CH); ^{1}H NMR (400 MHz, DMSO-d_6): δ 8.07 (*d*, J = 7.03 Hz, 2H, *o*-Ar CH), 7.62–7.69 (*m*, 3H, *m*, *p*-Ar CH), 8.24 (*dd*, J = 6.23 and 1.47 Hz, 2H, pyridine C—CH), 8.82 (*d*, J = 5.87 Hz, 2H, pyridine N—CH); ^{13}C NMR (100 MHz, DMSO-d_6): δ 168.36 (C5), 151.46 (C1), 144.39 (C4), 133.69 (C3), 133.07 (C2), 130.43 (C6), 130.20 (C9), 129.50 (C7), 128.08 (C8), 120.16 (C10).

Crystal data

$C_{14}H_9N_5S$
M_r = 279.32
Monoclinic, $P2_1/n$
a = 11.3331 (9) Å
b = 5.4092 (3) Å
c = 20.3509 (18) Å
β = 90.653 (7)°
V = 1247.49 (16) Å^3
Z = 4
D_x = 1.487 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 10973 reflections
θ = 1.8–27.2°
μ = 0.26 mm^{-1}
T = 296 K
Plate, pale yellow
0.80 × 0.36 × 0.03 mm

Data collection

Stoe IPDS-2 diffractometer
ω scans
Absorption correction: integration *X-RED32* (Stoe & Cie, 2002)
T_{min} = 0.868, T_{max} = 0.989
13221 measured reflections
2426 independent reflections
1642 reflections with $I > 2\sigma(I)$
R_{int} = 0.085
θ_{max} = 26.0°
$h = -13 \rightarrow 13$
$k = -6 \rightarrow 6$
$l = -25 \rightarrow 25$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.037
$wR(F^2)$ = 0.077
S = 1.02
2426 reflections
217 parameters
All H-atom parameters refined
$w = 1/[\sigma^2(F_o^2) + (0.0296P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.001
$\Delta\rho_{max}$ = 0.16 e Å^{-3}
$\Delta\rho_{min}$ = −0.21 e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

S1—C2	1.724 (2)	S1—C3	1.7651 (17)
C2—S1—C3	87.58 (9)	N3—C2—S1	109.62 (12)
N2—C2—S1	139.23 (15)		
N4—N3—C2—N2	179.62 (15)	N1—C1—C4—C8	−178.8 (2)
C1—N3—C2—S1	−179.33 (13)	N4—C3—C9—C14	174.4 (2)

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

D—H···A	D—H	H···A	D···A	D—H···A
C8—H8···N4	0.95 (2)	2.44 (2)	3.112 (3)	128 (2)
C14—H14···S1	0.97 (2)	2.73 (2)	3.140 (2)	106 (2)
C12—H12···N1^{i}	0.94 (2)	2.56 (2)	3.452 (3)	160 (2)

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

The H atoms were located in a difference map and refined isotropically [C—H = 0.94 (2)–1.02 (3) Å].

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 for Windows* (Farrugia, 1997); software used to prepare material for publication: *WinGX* (Farrugia, 1999) and *PLATON* (Spek, 2003).

AÇ is greateful to TUBİTAK–BAYG (the Scientific and Technical Research Council of Turkey – Directorate of Human Resources Development) for assistance in supporting the synthesis of (II). This study was supported financially by the Research Centre of Ondokuz Mayıs University (project No. F-366).

Supplementary data for this paper are available from the IUCr electronic archives (Reference: GZ1015). Services for accessing these data are described at the back of the journal.

References

Borbulevych, O. Ya., Shishkin, O. V., Desenko, S. M., Chernenko, V. N. & Orlov, V. D. (1998). *Acta Cryst.* C**54**, 442–444.
Bruno, G., Nicoló, F., Puntoriero, F., Giuffrida, G., Ricevuto, V. & Rosace, G. (2003). *Acta Cryst.* C**59**, o390–o391.
Çetin, A. (2004). PhD thesis, Firat University, Elazığ, Turkey.
El-Dawy, M. A., Omar, A. M. M. E., Ismail, A. M. & Hazzaa, A. A. B. (1983). *J. Pharm. Sci.* **72**, 45–50.
Farrugia, L. J. (1997). *J. Appl. Cryst.* **30**, 565.
Farrugia, L. J. (1999). *J. Appl. Cryst.* **32**, 837–838.
Holla, B. S., Gonsalves, R. & Shenoy, S. (1998). *Il Farmaco*, **53**, 574–578.
Holla, B. S. & Kalluraya, B. (1988). *Indian J. Chem. Sect. B*, **27**, 683–685.
Holla, B. S., Sarojini, B. K. & Gonsalves, R. (1998). *Il Farmaco*, **53**, 395–398.
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.
Koparır, M., Çetin, A. & Cansız, A. (2004). *Molecules*, **10**, 475–480.
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.
Ni, J., Li, Y.-Z., Qi, W.-B., Liu, Y.-J., Chen, H.-L. & Wang, Z.-L. (2003). *Acta Cryst.* C**59**, o470–472.
Özbey, S., Ulusoy, N. & Kendi, E. (2000). *Acta Cryst.* C**56**, 222–224.
Porsolt, R. D., Bertin, A. & Jalfre, M. (1977). *Arch. Int. Pharmacol.* **229**, 327–336.
Prasad, A. R., Ramalingam, T., Rao, A. B., Diwan, P. W. & Sattur, P. B. (1989). *Eur. J. Med. Chem.* **24**, 199–201.
Shams El-Dine, S. A. & Hazzaa, A. A. B. (1974). *Pharmazie*, **29**, 761–768.
Sheldrick, G. M. (1997). *SHELXS97* and *SHELXL97*. University of Göttingen, Germany.
Spek, A. L. (2003). *J. Appl. Cryst.* **36**, 7–13.
Stoe & Cie (2002). *X-AREA* (Version 1.18) and *X-RED32* (Version 1.04). Stoe & Cie, Darmstadt, Germany.
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.
Xiang, G.-Q., Zhang, L.-X., Zhang, A.-J., Cai, X.-Q. & Hu, M.-L. (2004). *Acta Cryst.* E**60**, o2249–o2251.