Acta Crystallographica Section E
Structure Reports Online
ISSN 1600-5368

3-Phenyl-5-(2-thienyl)-2-pyrazoline-1-thioamide

Şamil Işık,[a] Yavuz Köysal,[a]* Zuhal Özdemir[b] and A. Altan Bilgin[c]

[a]Department of Physics, Faculty of Arts and Sciences, Ondokuz Mayıs University, Kurupelit, 55139 Samsun, Turkey, [b]Department of Pharmaceutical Chemistry, Faculty of Pharmacy, Hacettepe University, 06100 Sıhhiye, Ankara, Turkey, and [c]Department of Pharmacology, Faculty of Pharmacy, Hacettepe University, 06100 Sıhhiye, Ankara, Turkey

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

Key indicators

Single-crystal X-ray study
T = 296 K
Mean σ(C–C) = 0.003 Å
R factor = 0.032
wR factor = 0.076
Data-to-parameter ratio = 15.1

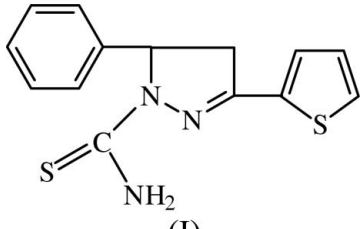
For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

Received 16 December 2005
Accepted 3 January 2006
Online 7 January 2006

In the crystal structure of the title compound, $C_{14}H_{13}N_3S_2$, the planar phenyl and thiophene rings are bridged by a pyrazoline ring. The phenyl group is almost perpendicular to the pyrazoline ring. The pyrazoline ring adopts an envelope conformation, and the two N atoms are involved in an intramolecular N—H···N(pyrazoline) and an intermolecular N—H···S hydrogen bond. The average C—N bond length is 1.385 (4) Å. The crystal structure is stabilized by intra- and intermolecular hydrogen bonds and C—H···π stacking interactions.

Comment

Pyrazoles are an important class of biologically active compounds. It is well known that pyrazoline derivatives have hypoglycaemic, antibacterial, antifungal, antihelmintic, local anaesthetic and sedative activities. Parmar *et al.* (1974) and Soni *et al.* (1978) demonstrated that 1,3,5-triphenyl-2-pyrazolines possess monoamine oxidase (MAO) inhibitory and anticonvulsant activities. In previous studies, we synthesized several pyrazolines, tested them for their antidepressant activities and found that 1-thiocarbamoyl-3,5-diphenyl-2-pyrazolines (Bilgin *et al.*, 1993) and their condensed analogues, 1-*N*-substituted thiocarbamoyl-3-phenyl-5-thienyl-2-pyrazolines (Gökhan *et al.*, 2003), have significant antidepressant activity. On the other hand, the stereochemistry of biologically active compounds plays an important role as far as drug-receptor interactions are concerned (Foye, 1989). In the ^{1}H NMR spectra of these compounds, atoms H2*A* and H2*B* were observed as a doublet at δ = 3.08–3.35 (J_{ab} = 16.80–18.49 Hz). The N-bound H atoms were not seen in the spectrum because of deuterium exchange. The N-bound H atoms of the thiocarbamoyl group were seen at 8.38–10.12 p.p.m., while the aromatic H atoms were seen at 5.90–7.95 p.p.m., as expected. The H atoms of the heteroaromatic rings were also observed at the expected positions. The crystal structure determination of the title compound, (I), was carried out in order to elucidate its molecular conformation.



(I)

The molecular structure of compound (I) is illustrated in Fig. 1. The five-membered pyrazoline ring has an envelope

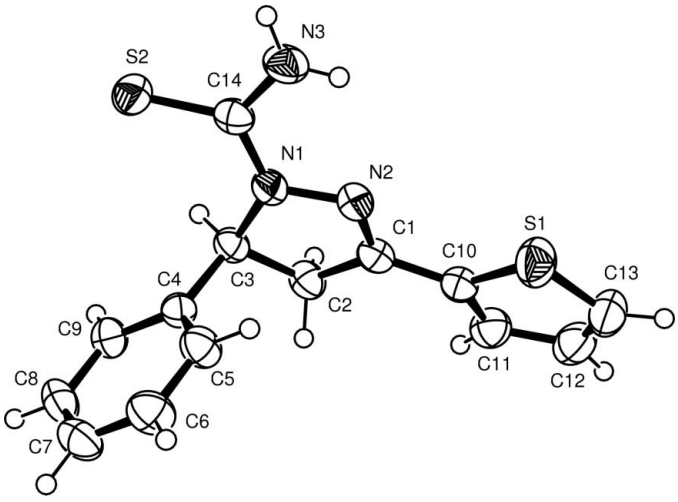


Figure 1
The molecular structure of compound (I), showing the atom-numbering scheme and displacement ellipsoids drawn at the 50% probability level.

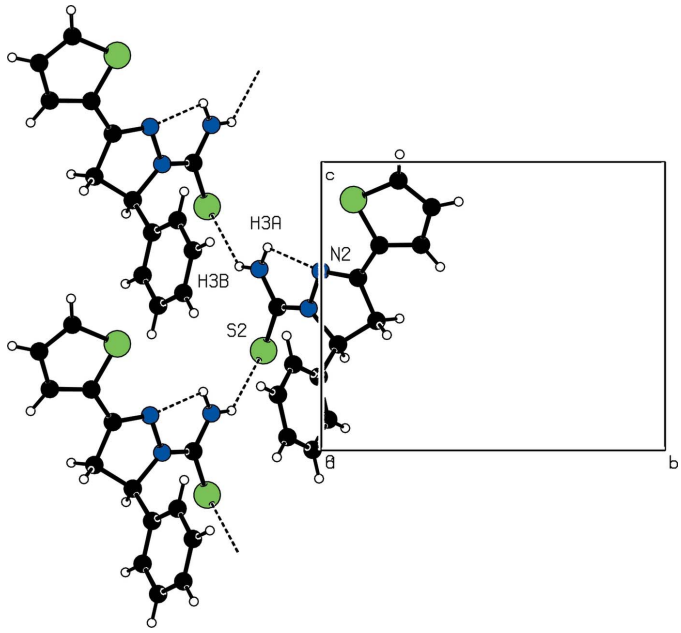


Figure 2
The crystal packing of compound (I), viewed along the *a* axis. The N—H···S and N—H···N hydrogen bonds are shown as dashed lines (further details are given in Table 1).

conformation with atom C3 forming the flap. Atoms N1, N2, C1 and C2 are coplanar, with a maximum deviation of 0.0145 (19)° from this plane for atom C1 [the puckering parameters (Cremer & Pople, 1975) are q_2 = 0.17 (19) Å and φ = 136.1 (7)°]. The bond lengths and angles in the five-membered ring are in agreement with expected values (Allen, 2002).

It has been reported (Krishna *et al.*, 1999) that the N—N bond length in the pyrazoline ring varies over a wide range, from 1.234 (8) to 1.385 (4) Å. In compound (I), the N1—N2 distance is even longer, 1.394 (2) Å, and it is thought that the length depends on the substituents bonded to atom N1.

The bond lengths and angles of the thiocarbamoyl group are comparable with those of a related compound, *O*-(2-*tert*-butyl-6-dimethylthiocarbamoyl-4-methylphenyl)*N*,*N*-diethylthiocarbamate (Castillo *et al.*, 2003). The thiocarbamoyl S2═C14 and pyrazoline N2═C1 bonds are well defined double bonds. The N—C—S bond angle around the C atoms of the thiocarbamoyl group is 121.59 (13)°. The phenyl group occupies a pseudo-axial position and, as a result, is approximately perpendicular to the mean plane of the pyrazoline ring. The torsion angles also show that the phenyl ring and thiocarbamoyl groups are linked to the pyrazoline ring system in axial and equatorial positions, respectively.

The crystal packing of compound (I) is illustrated in Fig. 2, and details concerning the hydrogen bonding are given in Table 1. For the NH_2 group of the carbamoyl group, one of the H atoms forms an intramolecular hydrogen bond with atom N2 of the pyrazoline group [graph set *S*(5); Bernstein *et al.*, 1995]. The other H atom forms an intermolecular hydrogen bond with the thienyl atom, S2, of a symmetry-related molecule [N3—H3*B*···S2^{i}, with graph set *C*(4); symmetry code: (i) $x, -y-\frac{1}{2}, z+\frac{1}{2}$]. The latter interaction leads to the formation of a one-dimensional chain extending in the *c* direction. In the crystal structure the thienyl ring systems align in an anti-parallel manner. There are also C—H···π stacking interactions between C2—H2*A*···*Cg*1^{ii}, where *Cg*1 is plane S1/C10/C11/C12/C13, distance H···*Cg* is 2.88 Å and angle *X*—H···*Cg* is 168° [symmetry code: (ii) $x, \frac{1}{2}-y, -\frac{1}{2}+z$].

Experimental

1-Thiocarbamoyl-3-phenyl-5-heteroaryl-2-pyrazolines were obtained by heating (8 h) thiosemicarbazide (0.012 mol) with the appropriate chalcone (0.01 mol) and sodium hydroxide (0.025 mol in 5 ml water) in ethanol (50 ml). The mixture was poured into ice–water and the crude product that separated out was filtered and crystallized from chloroform–ethanol (1:1). Yield 50%; m.p. 459–460 K. UV (nm): 235, 318.5; IR data (cm^{-1}): 1562 (C═N), 1445 (C^4—H), 1091 (C^5—N^1), 695 (C^5—H), 1353 (C═S), 3442, 3282 (N—H).

Crystal data

$C_{14}H_{13}N_3S_2$
M_r = 287.39
Monoclinic, $P2_1/c$
a = 13.9658 (14) Å
b = 10.7595 (11) Å
c = 9.621 (3) Å
β = 110.128 (13)°
V = 1357.4 (5) Å^3
Z = 4
D_x = 1.406 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 19876 reflections
θ = 2.5–28.0°
μ = 0.38 mm^{-1}
T = 296 (2) K
Prism, brown
0.44 × 0.30 × 0.04 mm

Data collection

Stoe IPDS-2 diffractometer
ω scans
Absorption correction: integration (*X-RED32*; Stoe & Cie, 2002)
T_{min} = 0.822, T_{max} = 0.978
18270 measured reflections
2659 independent reflections
2040 reflections with $I > 2\sigma(I)$
R_{int} = 0.055
θ_{max} = 26.0°
$h = -17 \rightarrow 17$
$k = -13 \rightarrow 13$
$l = -11 \rightarrow 11$

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0403P)^2 + 0.0583P]$ where $P = (F_o^2 + 2F_c^2)/3$
$R[F^2 > 2\sigma(F^2)] = 0.032$	$(\Delta/\sigma)_{max} < 0.001$
$wR(F^2) = 0.076$	$\Delta\rho_{max} = 0.15$ e Å^{-3}
$S = 1.02$	$\Delta\rho_{min} = -0.17$ e Å^{-3}
2659 reflections	
176 parameters	
H atoms treated by a mixture of independent and constrained refinement	

Table 1
Hydrogen-bond geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
N3—H3B···S2^{i}	0.86	2.76	3.464 (2)	140
N3—H3A···N2	0.86	2.26	2.627 (2)	106

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

Atom H3 was located in a difference Fourier map and refined isotropically [C3—H3 = 0.968 (16) Å]. The remaining H atoms were included in calculated positions and refined using a riding model, with C—$H_{aromatic}$ distances of 0.93 Å, C—$H_{methylene}$ distances of 0.97 Å, N—H distances of 0.86 Å and U_{iso}(H) = 1.2U_{eq}(parent C or N 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: *ORTEPIII* (Burnett & Johnson, 1996); software used to prepare material for publication: *WinGX* (Farrugia, 1999) and *PARST* (Nardelli, 1995).

References

Allen, F. H. (2002). *Acta Cryst.* B**58**, 380–388.
Bernstein, J., Davies, R. E., Shimoni, L. & Chang, N.-L. (1995). *Angew. Chem. Int. Ed. Engl.* **34**, 1555–1573.
Bilgin, A. A., Palaska, E. & Sunal, R. (1993). *Arzneim.-Forsch. Drug Res.* **43**, 1041–1044.
Burnett, M. N. & Johnson, C. K. (1996). *ORTEPIII*. Report ORNL-6895. Oak Ridge National Laboratory, Tennessee, USA.
Castillo, I., Flores-Figuerro, A. & Ortega, S. H. (2003). *Acta Cryst.* C**59**, o577–o579.
Cremer, D. & Pople, J. A. (1975). *J. Am. Chem. Soc.* **97**, 1354–1358.
Farrugia, L. J. (1999). *J. Appl. Cryst.* **32**, 837–838.
Foye, W. O. (1989). In *Principles of Medicinal Chemistry*. Philadelphia: Lea & Febiger.
Gökhan, N., Yeşilada, A., Uçar, G., Erol, K. & Bilgin, A. A. (2003). *Arch. Pharm. Med. Chem.* **336**, 362–371.
Krishna, R., Velmurugan, D., Murugesan, R., Sunderaman, M. S. & Raghunathan, R. (1999). *Acta Cryst.* C**55**, 1676–1677.
Nardelli, M. (1995). *J. Appl. Cryst.* **28**, 659.
Parmar, S. S., Pandey, B. R., Dwivedi, C. & Harbison, R. D. (1974). *J. Pharm. Sci.* **63**, 1152–1155.
Sheldrick, G. M. (1997). *SHELXS97* and *SHELXL97*. University of Göttingen, Germany.
Soni, N., Pande, K., Kalsi, R., Gupta, T. K., Parmar, S. S. & Barthwal, J. P. (1978). *Res. Commun. Chem. Pathol. Pharmacol.* **56**, 129–132.
Stoe & Cie (2002). *X-AREA* (Version 1.18) and *X-RED32* (Version 1.04). Stoe & Cie, Darmstadt, Germany.