# 3-Acetyl-4-benzoyl-2-methyl-5-phenyl-3,3a-dihydropyrazolo[2,3-c]-pyrimidine-7(6H)-thione

## Mehmet Akkurt *et al.*

**Electronic paper**

This paper is published electronically. It meets the data-validation criteria for publication in Acta Crystallographica Section C. The submission has been checked by a Section C Co-editor though the text in the 'Comments' section is the responsibility of the authors.

# 3-Acetyl-4-benzoyl-2-methyl-5-phenyl-3,3a-dihydropyrazolo[2,3-c]-pyrimidine-7(6H)-thione

**Mehmet Akkurt,[a]\* Sema Öztürk,[a] Hoong-Kun Fun,[b]
Zülbíye Önal[c] and Behzat Altural[c]**

[a]Department of Physics, Faculty of Arts and Sciences, Erciyes University, 38039 Kayseri, Turkey, [b]X-ray Crystallography Unit, School of Physics, Universiti Sains Malaysia, 11800 USM, Penang, Malaysia, and [c]Department of Chemistry, Faculty of Arts and Sciences, Erciyes University, 38039 Kayseri, Turkey
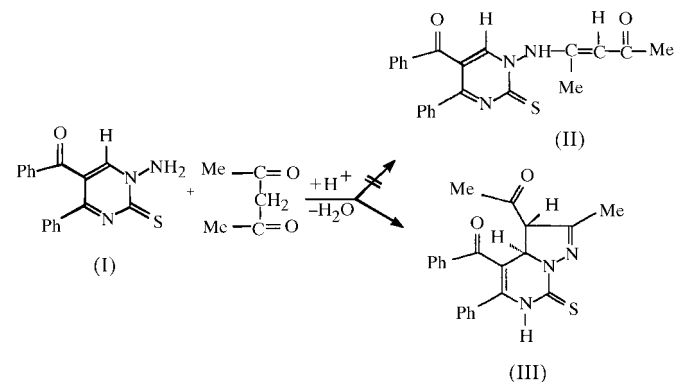Correspondence e-mail: akkurt@erciyes.edu.tr

The molecule of the title compound, $C_{22}H_{19}N_3O_2S$, is not planar. The dihedral angle between the two phenyl rings is 27.46 (7)° and in the dihydropyrazolopyrimidine ring the total puckering amplitude $Q_T$ is 0.526 (3) Å. The structure is stabilized by both intra- and intermolecular C—H···O interaction, and by an intermolecular N—H···S hydrogen bond.

## Comment

Dihydro derivatives of pyrazolo[1,5-*a*]pyrimidine have high physiological activity, the most important being cardiovascular activity (Tsuda *et al.*, 1986). The antitumor activity and the potential therapeutic applications of several pyrazolo[3,4-*d*]-ave also promped a more thorough investigation of these compounds (Youssif, 1997). This paper reports on the crystal structure of a substitution product of a fused pyrazole–pyri-

midine system, (III), interesting for its possible pharmacological activity.

In the pyrimidine ring, there are two local pseudo-mirrors, one running along N1···C20 and the other along the midpoints of the N2—C16 and C14—C15 bonds. The distance N1—C16 of 1.371 (3) Å is significantly shorter than N2—C20 of 1.481 (3) Å, because C16 is in an $sp^2$ hybridized state, while C20 is $sp^3$.

The C16=S1 [1.664 (2) Å] double-bond length of the pyrimidine ring is not significantly different to the C=S double-bond length [1.669 (3) Å] in 1-amino-5-benzoyl-4-phenyl-1*H*-pyrimidine-2-thione (Akkurt *et al.*, 1992). The angles N1—C16—S1 [121.2 (2)°] and N2—C16—S1 [126.1 (2)°] are almost equal, probably due to some attraction between S1 and H1*A* (S1···H1*A* = 2.72 Å) and some repulsion between S1 and N3 [S1···N3 = 3.080 (2) Å].

As the total puckering amplitude $Q_T$ (Cremer & Pople, 1975) of the pyrazole ring is 0.230 (3) Å, in the nine-membered dihydropyrazolopyrimidine ring with the C20 atom displaced 0.439 (3) Å from the plane of the other atoms, the puckering amplitude is 0.526 (3) Å. This amplitude appears sensitive to the type of substituents present in the related ring, since the corresponding amplitudes in 2-methyl-5,6,7-tri-phenyl-6,7-dihydropyrazolo[2,3-*a*]pyrimidine (Lindeman *et al.*, 1993) and in 7-acetyl-5-benzoyl-6-phenyl-8-methyl-4,7-di-hydropyrazolo[1,5-*c*]-1*H*-pyrimidine- 2-one (Çelik *et al.*, 2000) are 0.56 and 0.37 (3), respectively.

The C20—C14—C15—C1 and N2—C20—C14—C15 torsion angles are −168.4 (2) and −31.8 (3)°, respectively. The C1—C15—C14—C13 torsion angle of 2.2 (4)° possibly indicates π-conjugation involving the phenyl and benzoyl systems. It is interesting to note the relative orientations of the substituents attached to the pyrimidine ring. The dihedral angle between the two phenyl rings is 27.46 (7)°. The basic factor influencing the orientation of the two rings is inter-molecular interactions. The crystal structure is stabilized by the inter- and intramolecular hydrogen bonds.



## Experimental

1-Amino-5-benzoyl-4-phenyl-1*H*-pyrimidine-2-dione (0.2 g) was dissolved in acetylacetone (0.18 g; 1:30 mol) and *p*-toluene sulfonic acid (0.18 g) was added in this solution as a catalyst at room temperature. The mixture was heated in a furnace at 388 K for 45 min. After cooling, the precipitate was separated from acetylacetone by filtering and the oily residue was stirred with diethyl ether. The crude product so formed was crystallized from *n*-butanol. Yield: 60%; m.p.: 520 K; IR (KBr), cm$^{-1}$: 3600–3400 (N—H), 3200–3100 (aromatic C—CH), 3000 (CH₃), 1720 (C=O), 1600 (C=C and C=N), 1540–1400 (aromatic skeleton), 1220 (C=S), 780–680 (pyrimidine skeleton); ¹H NMR (DMSO) p.p.m.: 2.14–2.49 (*s*, 6 H, CH₃), 4.10–4.15 (*s*, 1 H, CH), 5.37–5.43 (*s*, 1 H, NH), 6.99–7.33 (*m*, 10 H, aromatic H) (Önal, 1997). Elemental analysis, $C_{22}H_{19}N_3O_2S$ requires: C 67.85, H 4.91, N 10.79, S 8.22%; found: C 67.73, H 4.77, N 10.41, S 8.15%.

*Crystal data*

$C_{22}H_{19}N_3O_2S$
$M_r = 389.46$
Monoclinic, $P2_1/c$
$a = 6.9505 (3)$ Å
$b = 21.8820 (8)$ Å
$c = 12.9619 (5)$ Å
$\beta = 100.239 (1)°$
$V = 1939.99 (13)$ Å$^3$
$Z = 4$

$D_x = 1.333$ Mg m$^{-3}$
Mo $K\alpha$ radiation
Cell parameters from 4312
  reflections
$\theta = 1.9–28.4°$
$\mu = 0.190$ mm$^{-1}$
$T = 293 (2)$ K
Needle, yellow
$0.38 \times 0.12 \times 0.08$ mm

*Data collection*

Siemens SMART CCD area-
  detector diffractometer
$\omega$ scans
Absorption correction: empirical
  (*SADABS*; Sheldrick, 1996)
  $T_{min} = 0.931$, $T_{max} = 0.985$
13 631 measured reflections
4769 independent reflections

2422 reflections with $I > 2\sigma(I)$
$R_{int} = 0.082$
$\theta_{max} = 28.43°$
$h = -9 \rightarrow 9$
$k = -28 \rightarrow 28$
$l = -8 \rightarrow 17$
Intensity decay: none

*Refinement*

Refinement on $F^2$
$R[F^2 > 2\sigma(F^2)] = 0.061$
$wR(F^2) = 0.152$
$S = 0.953$
4769 reflections
253 parameters

H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0609P)^2]$
  where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.23$ e Å$^{-3}$
$\Delta\rho_{min} = -0.28$ e Å$^{-3}$

**Table 1**
Selected geometric parameters (Å, °).

| | | | |
|---|---|---|---|
| S1—C16 | 1.664 (2) | N2—C20 | 1.481 (3) |
| N1—C16 | 1.371 (3) | N3—C17 | 1.281 (3) |
| N1—C15 | 1.388 (3) | O1—C13 | 1.228 (3) |
| N2—C16 | 1.333 (3) | O2—C21 | 1.197 (3) |
| N2—N3 | 1.394 (3) | | |
| C16—N1—C15 | 124.9 (2) | C14—C15—N1 | 119.7 (2) |
| C16—N2—N3 | 122.9 (2) | N2—C16—N1 | 112.6 (2) |
| C16—N2—C20 | 125.5 (2) | N2—C16—S1 | 126.1 (2) |
| N3—N2—C20 | 111.6 (2) | N1—C16—S1 | 121.2 (2) |
| C17—N3—N2 | 107.0 (2) | N3—C17—C19 | 114.4 (2) |

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

| $D-H\cdots A$ | $D-H$ | $H\cdots A$ | $D\cdots A$ | $D-H\cdots A$ |
|---|---|---|---|---|
| N1—H1A$\cdots$S1$^i$ | 0.86 | 2.72 | 3.565 (2) | 170 |
| C4—H4A$\cdots$O1$^{ii}$ | 0.93 | 2.44 | 3.245 (4) | 145 |
| C20—H20A$\cdots$O2 | 0.98 | 2.43 | 2.869 (3) | 107 |

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

Data collection: *SMART* (Siemens, 1996); cell refinement: *SAINT* (Siemens, 1996); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1990); program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993); software used to prepare material for publication: *PARST* (Nardelli, 1995).

**References**

Akkurt, M., Güldeste, A., Soylu, H., Altural, B. & Sarıpınar, E. (1992). *Acta Cryst.* C**48**, 315–317.
Çelik, İ., Akkurt, M., İde, S., Önal, Z. & Altural, B. (2000). *Z. Kristallogr.* **215**, 48–51.
Cremer, D. & Pople, J. A. (1975). *J. Am. Chem. Soc.* **97**, 1354–1358.
Lindeman, S. V., Struchkov, Yu. T., Shishkin, O. V., Desenko, S. M., Lipson, V. V. & Orlov, V. D. (1993). *Acta Cryst.* C**49**, 896–898.
Nardelli, M. (1995). *J. Appl. Cryst.* **28**, 659.
Önal, Z. (1997). PhD thesis, Erciyes University, Turkey.
Sheldrick, G. M. (1990). *Acta Cryst.* A**46**, 467–473.
Sheldrick, G. M. (1993). *SHELXL*93. University of Göttingen, Germany.
Sheldrick, G. M. (1996). *SADABS*. University of Göttingen, Germany.
Siemens (1996). *SMART* and *SAINT* (Version 4). Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.
Tsuda, N., Mishina, T., Obata, M., Inui, A. & Nakamura, T. (1986). Jpn Kokai Tokyo Koho, Jpn Patent 61/227 584 (Cl. C07D487/04).
Youssif, Ś. (1997). *Monatsh. Chem.* **128**, 493–501.