

Wei Wei, Qiong Wu, Tong-Yin Jin, Ya-Zhai Zhang, Zhao-Kun Xuan and Heng-Qiang Zhang*

Crystal structure of (Z)-4-[(p-tolylamino)(furan-2-yl)methylene]-3-phenyl-1-1-p-tolyl-1H-phenyl-1H-pyrazol-5(4H)-one, C₂₈H₂₃N₃O₂

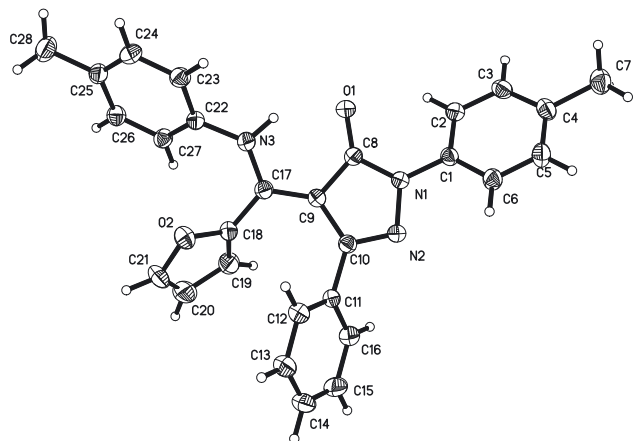


Table 1: Data collection and handling.

Crystal:	Yellow block
Size:	0.22 × 0.20 × 0.17 mm
Wavelength:	Mo K α radiation (0.71073 Å)
μ :	0.08 mm ⁻¹
Diffractometer, scan mode:	φ and ω
$\theta_{\max}$, completeness:	26.0°, >99%
$N(hkl)_{\text{measured}}$, $N(hkl)_{\text{unique}}$, R_{int} :	8538, 4388, 0.023
Criterion for I_{obs} , $N(hkl)_{\text{gt}}$:	$I_{\text{obs}} > 2 \sigma(I_{\text{obs}})$, 3024
$N(\text{param})_{\text{refined}}$:	304
Programs:	CrysAlis ^{PRO} [1], SHELX [2], WinGX/ORTEP [3], PLATON [4]

<https://doi.org/10.1515/ncrs-2022-0086>

Received February 22, 2022; accepted April 5, 2022;
published online April 15, 2022

Abstract

C₂₈H₂₃N₃O₂, triclinic, $P\bar{1}$ (no. 2), $a = 7.6590(7)$ Å, $b = 11.8598(12)$ Å, $c = 12.4954(14)$ Å, $\alpha = 92.027(9)^\circ$, $\beta = 99.837(9)^\circ$, $\gamma = 93.597(8)^\circ$, $V = 1114.9(2)$ Å³, $Z = 2$, $R_{\text{gt}}(F) = 0.0508$, $wR_{\text{ref}}(F^2) = 0.1317$, $T = 293(2)$ K.

CCDC no.: 2164536

The molecular structure is shown in the figure. Table 1 contains crystallographic data and Table 2 contains the list of the atoms including atomic coordinates and displacement parameters.

*Corresponding author: Heng-Qiang Zhang, Department of Chemistry, Hebei Normal University for Nationalities, Chengde 067000, People's Republic of China, E-mail: zhanghengqiang80@163.com. <https://orcid.org/0000-0001-7138-2905>

Wei Wei, Department of Architecture Engineering, Chengde Petroleum College, Chengde 067000, People's Republic of China

Qiong Wu, Tong-Yin Jin, Ya-Zhai Zhang and Zhao-Kun Xuan, Department of Chemistry, Hebei Normal University for Nationalities, Chengde 067000, People's Republic of China

Source of material

All reagents were obtained from commercial sources and used without further purification. A mixture of 40 mL 1-*p*-tolyl-3-phenyl-4-(2-furoyl)-5-pyrazolone (PTFPF) (20 mmol, 6.887 g), and 30 mL 4-aminotoluene (20 mmol, 2.143 g) was refluxed for 7 h, adding a few drops of glacial acetic acid as a catalyst. After cooled to the room temperature, the mixture was filtrated and the collected solid was washed with additional ethanol and dried in the air. Yellow block crystals were obtained by evaporation of an ethanol/dichloromethane (1:1) mixed solution for a few days.

Experimental details

The structure was solved by direct methods with the SHELXS-2018 program [2]. The H atoms bonded to N3 atoms were located in difference maps and refined freely. Other H atoms were placed in calculated positions, with C–H = 0.93 for phenyl and furyl, 0.96 for methyl H atoms, and refined as riding, with $U_{\text{iso}}(\text{H})$ values of 1.2 $U_{\text{eq}}(\text{C})$ for phenyl and furyl H, and 1.5 $U_{\text{eq}}(\text{C})$ for methyl H.

Comment

Acylpyrazolones are an interesting class of β -diketones, containing a pyrazole-bearing chelating arm. Thus,

Table 2: Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²).

Atom	x	y	z	<i>U</i> _{iso} */ <i>U</i> _{eq}
C1	0.0002 (2)	0.05579 (16)	0.64870 (16)	0.0396 (5)
C2	0.0382 (3)	−0.05326 (16)	0.62514 (16)	0.0447 (5)
H2	0.155547	−0.071278	0.629315	0.054*
C3	−0.0977 (3)	−0.13536 (17)	0.59544 (17)	0.0496 (5)
H3	−0.070840	−0.208723	0.579189	0.059*
C4	−0.2733 (3)	−0.11177 (18)	0.58910 (17)	0.0505 (5)
C5	−0.3083 (3)	−0.00191 (19)	0.61306 (19)	0.0549 (6)
H5	−0.425645	0.016003	0.609275	0.066*
C6	−0.1740 (3)	0.08212 (18)	0.64249 (17)	0.0493 (5)
H6	−0.200563	0.155729	0.657978	0.059*
C7	−0.4243 (3)	−0.2077 (2)	0.5567 (2)	0.0660 (7)
H7A	−0.535330	−0.180404	0.568312	0.099*
H7B	−0.398245	−0.271387	0.600587	0.099*
H7C	−0.432246	−0.230254	0.481427	0.099*
C8	0.3004 (2)	0.13005 (16)	0.74587 (16)	0.0405 (5)
C9	0.3843 (2)	0.24296 (15)	0.75952 (16)	0.0399 (5)
C10	0.2538 (2)	0.31304 (16)	0.70561 (16)	0.0393 (4)
C11	0.2539 (2)	0.43778 (16)	0.70690 (17)	0.0420 (5)
C12	0.2937 (3)	0.50002 (17)	0.80455 (19)	0.0517 (6)
H12	0.325973	0.463223	0.868709	0.062*
C13	0.2863 (3)	0.61552 (19)	0.8083 (2)	0.0634 (7)
H13	0.312007	0.656344	0.874636	0.076*
C14	0.2408 (3)	0.6705 (2)	0.7138 (3)	0.0692 (7)
H14	0.237282	0.748747	0.716074	0.083*
C15	0.2006 (3)	0.6107 (2)	0.6164 (2)	0.0697 (7)
H15	0.169524	0.648332	0.552622	0.084*
C16	0.2059 (3)	0.49392 (18)	0.6122 (2)	0.0556 (6)
H16	0.177273	0.453369	0.545721	0.067*
C17	0.5542 (2)	0.26726 (16)	0.81862 (16)	0.0403 (5)
C18	0.6509 (2)	0.37537 (17)	0.81142 (17)	0.0438 (5)
C19	0.6824 (3)	0.43177 (19)	0.7252 (2)	0.0602 (6)
H19	0.639546	0.411220	0.652537	0.072*
C20	0.7935 (3)	0.5286 (2)	0.7661 (3)	0.0821 (9)
H20	0.838439	0.584342	0.725700	0.099*
C21	0.8208 (3)	0.5243 (2)	0.8726 (3)	0.0812 (9)
H21	0.889878	0.578351	0.920001	0.097*
C22	0.8039 (2)	0.18327 (16)	0.93897 (16)	0.0398 (5)
C23	0.8263 (3)	0.12474 (17)	1.03329 (17)	0.0466 (5)
H23	0.727838	0.091969	1.057914	0.056*
C24	0.9940 (3)	0.11485 (18)	1.09091 (17)	0.0502 (5)
H24	1.007266	0.074783	1.154106	0.060*
C25	1.1426 (3)	0.16264 (17)	1.05749 (17)	0.0461 (5)
C26	1.1174 (3)	0.21994 (17)	0.96197 (17)	0.0461 (5)
H26	1.216048	0.252422	0.937359	0.055*
C27	0.9511 (2)	0.23034 (17)	0.90231 (16)	0.0442 (5)
H27	0.938016	0.268619	0.838045	0.053*
C28	1.3255 (3)	0.1524 (2)	1.1203 (2)	0.0706 (7)
H28A	1.405001	0.136832	1.070879	0.106*
H28B	1.322803	0.091891	1.169181	0.106*
H28C	1.365857	0.221994	1.161232	0.106*
H3A	0.556 (3)	0.121 (2)	0.8739 (19)	0.073(7)*
N1	0.1405 (2)	0.14062 (13)	0.67961 (13)	0.0410 (4)
N2	0.1102 (2)	0.25321 (13)	0.65883 (13)	0.0425 (4)
N3	0.6282 (2)	0.18772 (15)	0.88100 (15)	0.0471 (4)

Table 2: (continued)

Atom	x	y	z	<i>U</i> _{iso} */ <i>U</i> _{eq}
O1	0.35499 (17)	0.04123 (11)	0.78503 (12)	0.0513 (4)
O2	0.7348 (2)	0.43048 (13)	0.90490 (13)	0.0630 (5)

their metal complexes are used for the separation of elements with similar properties [5]. Alkaline-earth metal β-diketonate complexes also have recently provoked a growing interest as suitable precursors in the synthesis of high T_c superconducting films [6–8]. So far research has been restricted to those acylpyrazolones with aryl substituents at 4-positions [9]. Only a few studies have involved heterocyclic substituents at the 4-position [10–12]. In recent years, we have reported the Schiff bases derived from 4-heterocyclic acylpyrazolones and their complexes, which possess high antibacterial activation [13, 14]. Knowledge of the crystal structure of such 4-heterocyclic acylpyrazolones derivatives gives us not only sufficient information about nuclearity of the complex molecule, but is important in understanding the behavior of this compound in the vapor phase, and the mechanisms of sublimation and decomposition.

In the crystal, molecules (see the Figure) are linked via weak C–H···N and C–H···O hydrogen bonds. In the title crystal structure, the compound crystallized with a structural configuration in which the phenyl ring(C(1)–(6)) is twisted with a dihedral angle of 32.92(15)° with respect to a plane defined by the pyrazole ring(N(1)–C(8)). The pyrazole ring and the O(1)/C(8)/C(9)/C(17)/N(3) plane are nearly coplanar with the largest deviation of 0.074 Å (dihedral angle 7.16(14)°). The bond length of C(9)–C(17) (1.390(3) Å) between the usual C–C and C=C bonds indicates the delocalization of the electrons because of the addition of a proton to N(3). The atom O(1) of PTPFP moiety and the N(3) atom of the 4-aminotoluene group are on the same side of the C(9)–C(17) bond, which are available for the coordination with metals. A strong intramolecular N(3)–H(3A)···O(1) hydrogen bond is observed, leading to keto form. Other weak intramolecular bonds C(2)–H(2)···O(1) are also found, stabilizing the structure. All bond lengths and angles are normal and comparable with those found for related compounds [15–17].

Author contributions: All the authors have accepted responsibility for the entire content of this submitted manuscript and approved submission.

Research funding: This study was financially supported by Foundation of Hebei Education Department (No. ZD2020412).

Conflict of interest statement: The authors declare no conflicts of interest regarding this article.

References

1. Rigaku OD. *CrysAlis PRO*; Rigaku Oxford Diffraction Ltd: Yarnton, Oxfordshire, England, 2015.
2. Sheldrick G. M. Crystal structure refinement with SHELXL. *Acta Crystallogr.* 2015, *C71*, 3–8.
3. Farrugia L. J. WinGX and ORTEP for Windows: an update. *J. Appl. Crystallogr.* 2012, *45*, 849–854.
4. Spek A. L. Structure validation in chemical crystallography. *Acta Crystallogr.* 2009, *D65*, 148–155.
5. Nishihama S., Hirai T., Komasa I. Review of advanced liquid–liquid extraction systems for the separation of metal ions by a combination of conversion of the metal species with chemical reaction. *Ind. Eng. Chem. Res.* 2001, *40*, 3085–3091.
6. El-Gaby M. S., Atalla A. A., Gaber A. M., Al-Wahab K. A. Studies on aminopyrazoles: antibacterial activity of some novel pyrazol. *Farmaco* 2000, *55*, 596–602.
7. Timerbaev A. R., Rudnev A. V., Semenova O., Hartinger C. G., Keppler B. K. Comparative binding of antitumor indazolium [*trans*-tetrachlorobis(1*H*-indazole)ruthenate(III)] to serum transport proteins assayed by capillary zone electrophoresis. *Anal. Biochem.* 2005, *341*, 326–333.
8. Marchetti F., Pettinari R., Pettinari C. Recent advances in acylpyrazolone metal complexes and their potential applications. *Coord. Chem. Rev.* 2015, *303*, 1–31.
9. Marchetti F., Pettinari C., Pettinari R. Acylpyrazolone ligands: synthesis, structures, metal coordination chemistry and applications. *Coord. Chem. Rev.* 2005, *249*, 2909–2945.
10. Li J., Li J. Z., Zhang H. Q., Zhang Y., Li J. Q. Synthesis, characterization and crystal structure of a Ni(II) complex derived from heterocyclic acylpyrazolone. *J. Coord. Chem.* 2009, *62*, 2465–2471.
11. Li J. Q., Li J. Z., Zhang H. Q., Li J. Solvothermal syntheses and crystal structures of two 4-heterocyclic acylpyrazolone complexes. *Cryst. Res. Technol.* 2009, *44*, 669–674.
12. Sun R. X., Li J. Z., Zhang H. Q., Pang X. Z., Fu Y. S., Cui J. Z. Synthesis, crystal structure, characterization and DNA binding studies of novel copper (II) complex based on amino acid Schiff base. *Curr. Org. Chem.* 2012, *16*, 2868–2878.
13. Raman N., Selvaganapathy M. Pyrazolone incorporating amino acid metallointercalators as effective DNA targets: synthesis and in vitro biocidal evaluation. *Inorg. Chem. Commun.* 2013, *37*, 114–120.
14. Kiran R. S. Synthesis, spectroscopy and biological investigations of manganese(III) Schiff base complexes derived from heterocyclic β -diketone with various primary amine and 2,2-bipyridyl. *Spectrochim. Acta, Part A* 2011, *79*, 272–277.
15. Zhang H.-Q., Yang X., Wu Q., Chen H.-L. Crystal structure of (4*Z*)-4-[[[(2-chlorophenyl)amino](furan-2-yl)methylidene]-3-methyl-1-phenyl-4,5-dihydro-1*H*-pyrazol-5-one. *Acta Crystallogr.* 2015, *E71*, o177–o178.
16. Zhang H.-Q., Wu Q., Jin T.-Y., Li Y.-Y., Chen H.-L. Crystal structure of (Z)-2-(4-chlorophenyl)-4-(furan-2-yl(phenylamino)methylene)-5-methyl-2,4-dihydro-3*H*-pyrazol-3-one, $C_{21}H_{16}ClN_3O_2$. *Z. Kristallogr. N. Cryst. Struct.* 2018, *233*, 883–884.
17. Zhang B.-Q., Zhang L., Zhang H.-Q., Zhao C.-L., Chen B. Crystal structure of (Z)-4-(furan-2-yl(*p*-tolylamino)methylene)-3-methyl-1-*p*-tolyl-1*H*-pyrazol-5(4*H*)-one, $C_{23}H_{21}N_3O_2$. *Z. Kristallogr. N. Cryst. Struct.* 2016, *231*, 281–283.