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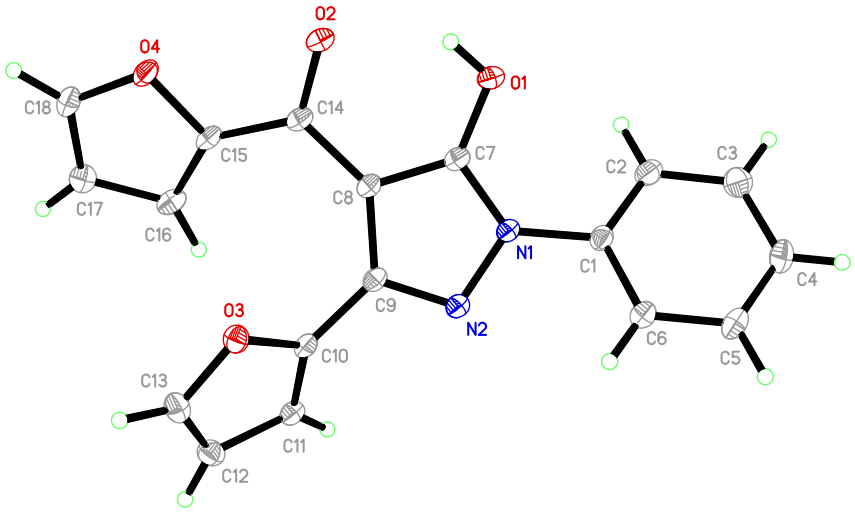
Crystal structure of 1-phenyl-4-(2-furoyl)-3-furyl-1*H*-pyrazol-5-ol, $C_{18}H_{12}N_2O_4$



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Abstract

$C_{18}H_{12}N_2O_4$, monoclinic, $P2_1/c$ (no. 14), a = 12.3075(7) Å, b = 6.5075(3) Å, c = 18.4929(9) Å, β = 92.883(4)°, V = 1,479.24(13) Å^3, Z = 4, $R_{gt}(F)$ = 0.0394, $wR_{ref}(F^2)$ = 0.1047, T = 173 K.

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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.

Table 1: Data collection and handling.

Crystal:	Yellow block
Size:	0.20 × 0.18 × 0.14 mm
Wavelength:	Mo *K*α radiation (0.71073 Å)
μ:	0.10 mm^{-1}
Diffractometer, scan mode:	Xcalibur
θ_{max}, completeness:	29.5°, >99 %
$N(hkl)_{measured}$, $N(hkl)_{unique}$, R_{int}:	7,418, 4,090, 0.015
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\sigma(I_{obs})$, 2,837
$N(param)_{refined}$:	218
Programs:	CrysAlis^{PRO},[1] SHELX,[2] WinGX/ORTEP,[3] PLATON[4]

1 Source of material

All reagents were obtained from commercial sources and used without further purification. 3-Furyl-1-phenyl-5-pyrazolone was synthesized according to the method proposed by Jensen[5] (yield 74 %; m.p. 443–446 K). 3-Furyl-1-phenyl-5-pyrazolone (5 g) was dissolved in dioxane (100 mL) by warming and $Ca(OH)_2$ (2.5 g), added. 2–Furoyl chloride (2.5 mL) was next added, drop by drop, with stirring within 5 min. After refluxing gently for 2.0 h, the orange mixture was cooled and poured with stirring into chilled 2 M HCI (500 mL). A handful of ice-salt mixture was added and vigorous stirring continued for another 30 min, after which the reaction mixture was kept in a refrigerator until crystallisation occurred. Filtration of the product gave 64 % yield of yellow crystals at room temperature.

2 Experimental details

The hydroxyl H atom was located in a difference Fourier map and refined as riding, with O–H distance restraint of

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

Atom	x	y	z	U_{iso}*/U_{eq}
C1	0.74737 (10)	1.4148 (2)	−0.03539 (7)	0.0249 (3)
C2	0.66390 (12)	1.4450 (3)	−0.08737 (8)	0.0400 (4)
H2	0.605734	1.353898	−0.091807	0.048*
C3	0.66909 (14)	1.6144 (3)	−0.13267 (10)	0.0527 (5)
H3	0.612963	1.638359	−0.167206	0.063*
C4	0.75635 (14)	1.7478 (3)	−0.12723 (10)	0.0455 (4)
H4	0.759177	1.860032	−0.158227	0.055*
C5	0.83921 (13)	1.7142 (2)	−0.07570 (8)	0.0350 (3)
H5	0.898100	1.803775	−0.072108	0.042*
C6	0.83535 (11)	1.5479 (2)	−0.02928 (7)	0.0271 (3)
H6	0.891143	1.525683	0.005642	0.032*
C7	0.66056 (10)	1.1521 (2)	0.04267 (7)	0.0238 (3)
C8	0.70039 (10)	0.9980 (2)	0.08921 (7)	0.0224 (3)
C9	0.81556 (10)	1.01751 (19)	0.08651 (6)	0.0214 (3)
C10	0.90238 (10)	0.9096 (2)	0.12706 (6)	0.0225 (3)
C11	0.99640 (10)	0.8229 (2)	0.10836 (7)	0.0257 (3)
H11	1.024065	0.820996	0.062479	0.031*
C12	1.04515 (11)	0.7347 (2)	0.17273 (8)	0.0305 (3)
H12	1.110545	0.663068	0.177037	0.037*
C13	0.97795 (12)	0.7756 (2)	0.22587 (8)	0.0306 (3)
H13	0.989956	0.734793	0.273807	0.037*
C14	0.62371 (10)	0.8749 (2)	0.12749 (7)	0.0239 (3)
C15	0.65419 (10)	0.6816 (2)	0.16273 (7)	0.0236 (3)
C16	0.73856 (11)	0.5489 (2)	0.15891 (7)	0.0276 (3)
H16	0.799325	0.564610	0.131501	0.033*
C17	0.71611 (11)	0.3811 (2)	0.20487 (7)	0.0291 (3)
H17	0.759361	0.265740	0.213655	0.035*
C18	0.62024 (12)	0.4218 (2)	0.23314 (7)	0.0310 (3)
H18	0.586169	0.336796	0.265475	0.037*
N1	0.74548 (8)	1.24335 (17)	0.01265 (6)	0.0233 (2)
N2	0.84299 (8)	1.16415 (17)	0.04122 (6)	0.0237 (2)
O1	0.55899 (7)	1.21224 (17)	0.02916 (5)	0.0331 (2)
H1	0.519017	1.151816	0.056254	0.050*
O2	0.52740 (7)	0.93535 (16)	0.12850 (5)	0.0325 (2)
O3	0.88939 (8)	0.88527 (14)	0.20005 (5)	0.0264 (2)
O4	0.57950 (8)	0.60421 (15)	0.20818 (5)	0.0305 (2)

0.82(1) Å and with U_{iso}(H) = 1.5U_{eq}(O). Other H atoms were placed in calculated positions, with C–H = 0.93 for phenyl and furan, and refined as riding, with U_{iso}(H) = 1.2U_{eq}(C) for phenyl H and furan H.

3 Comment

4–Acylpyrazolones are both very interesting class of β-diketones and compounds, which are widely used as solvent extractions of metal ions, laser working materials and NMR shift-reagents.[6–8] Metal complexes with these ligands are utilized in analytical chemistry, catalytic performance, biological activity and enhanced luminescence.[9] Alkaline-earth metal β-diketonate complexes also have recently provoked a growing interest as suitable precursors in the synthesis of high Tc superconducting films.[10,11] Although there have been numerous reports on acylpyrazolones, only a few 4-heterocyclic acylpyrazolone compounds have been reported so far.[12,13] Moreover, research has been restricted to those acylpyrazolones with alkyl or aryl substituents at the 3- and 4-positions. Only a few studies have involved heterocyclic substituents at the 3- and 4-positions.[14] Knowledge of the crystal structure of 3-furyl-4-(2-furoyl)-pyrazolone give us not only information about nuclearity of this molecule, but is important in understanding the behaviour of this compounds. In this paper we present the synthesis and structural characterization of the title compound with electronic-donating substituent is reported hereby.

The structure of the title compound is shown in Figure. The bond lengths and angles are within normal ranges.[15] The phenyl ring is slightly twisted by 30.00(5)° with respect to the pyrazolone ring. Atom O1 has a partial anionic character, as shown by the shortening of the formal single bond C7–O1 [1.3217(15) Å]. The intermolecular O1–H1···O2 hydrogen bond results in the formation of a dimer with an $R^2_2(12)$ graph-set motif.[16] It is apparent that the C14=O2 and C8=C7 distances correspond to well defined double bonds. The clear presence of the hydroxyl H atom in the difference Fourier synthesis and the absence of any residual electronic density in the vicinity of O1 confirm that title compound crystallizes as a pure hydroxyl tautomer and that no desmotropism is present.[17]

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

References

1. Rigaku, O. D. *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. Jensen, B. S. The Synthesis of 1-Phenyl-3-Methyhl-4-Acyl-Pyrazolones-5. *Acta Chem. Scand.* **1959**, *13*, 1668–1670.
6. Marchetti, F.; Pettinari, C.; Di Nicola, C.; Tombesi, A.; Pettinari, R. Coordination Chemistry of Pyrazolone-Based Ligands and Applications of Their Metal Complexes. *Coord. Chem. Rev.* **2019**, *401*, 213069.
7. Wang, X. H.; Jia, D. Z.; Liang, Y. J.; Yan, S. L.; Ding, Y.; Chen, L. M.; Shi, Z.; Zeng, M. S.; Liu, G. F.; Fu, L. W. Lgf–YL-9 Induces Apoptosis in Human Epidermoid Carcinoma KB Cells and Multidrug Resistant KBv200 Cells via Reactive Oxygen Species-Independent Mitochondrial Pathway. *Cancer Lett.* **2007**, *249*, 256–270.
8. Li, J.-Z.; Li, Y. G.; Yu, W.-J. Synthesis, Characterization and Bioactivity of Complexes of Rare Earth with Bis–Schiff Base from Furoylpyrazolone. *J. Rare Earths* **2000**, *18*, 233–236.
9. Rahman, M.; Siddiqui, A. Pyrazoline Derivatives: A Worthy Insight Into the Recent Advances and Potential Pharmacological Activities. *Int. J. Pharm. Pharmaceut. Sci.* **2010**, *2*, 165–175.
10. Mukherjee, R. Coordination Chemistry with Pyrazole-Based Chelating Ligands: Molecular Structural Aspects. *Coord. Chem. Rev.* **2000**, *203*, 151–158.
11. Marchetti, F.; Pettinari, C.; Pettinari, R. Acylpyrazolone Ligands: Synthesis, Structures, Metal Coordination Chemistry and Applications. *Coord. Chem. Rev.* **2005**, *249*, 2909–2945.
12. Wu, Q.; Huang, Z.-Y.; Liu, Y.-X.; Zhang, H.-Q.; Jin, T.-Y.; Xue, Y.-N.; Liu, C. Crystal Structure of 1-(*p*-Tolylphenyl)-4-(2-Furoyl)-3-Methyl -1*H*-Pyrazol-5-ol, $C_{16}H_{14}N_2O_3$. *Z. Kristallogr. N. Cryst. Struct.* **2024**, *239*, 327–329.
13. Wu, Q.; Zhang, W.-Y.; Zhang, Z.-M.; Zhang, H.-Q.; Jin, T.-Y. Crystal Structure of 1-(4-Chlorophenyl)-4-(2-Furoyl)-3-Phenyl-1*H*-Pyrazol-5- ol, $C_{20}H_{13}ClN_2O$. *Z. Kristallogr. N. Cryst. Struct.* **2024**, *239*, 565–567.
14. Li, J.-Z.; Zhang, H.-Q.; Li, H.-X.; Che, P.-Z.; Wang, T.-C. 1-(4–Chlorophenyl)-4-(2-Furoyl)-3-(2-Furyl)-1*H*-Pyrazol-5-ol. *Acta Crystallogr.* **2007**, *E63*, o1289–o1290.
15. Allen, F. H.; Kennard, O.; Watson, D. G.; Brammer, L.; Orpen, A. G.; Taylor, R. *J. Chem. Soc., Perkin Trans.* **1987**, *2*, 1–19.
16. Etter, M. C.; MacDonald, J. C.; Bernstein, J. Graph-set Analysis of Hydrogen-Bond Patterns in Organic Crystals. *Acta Crystallogr.* **1990**, *B46*, 256–262.
17. Foces-Foces, C.; Fontenas, C.; Elguero, J.; Sobrados, I. *An. Quim. Int. Ed.* **1997**, *93*, 219–224.