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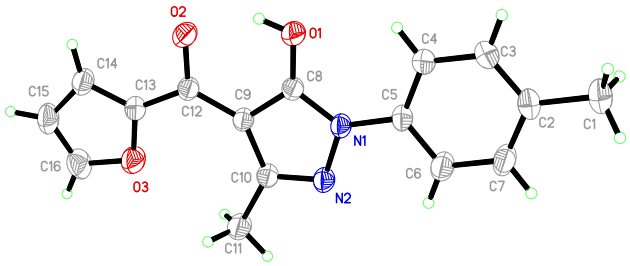
Crystal structure of 1-(*p*-tolylphenyl)-4-(2-furoyl)-3-methyl-1*H*-pyrazol-5-ol, $C_{16}H_{14}N_2O_3$



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Abstract

$C_{16}H_{14}N_2O_3$, monoclinic, $P2_1/n$ (no. 14), a = 4.9621(10) Å, b = 11.828(2) Å, c = 23.727(5) Å, β = 94.527(4)°, V = 1388.2(5) Å^3, Z = 4, $R_{gt}(F)$ = 0.0551, $wR_{ref}(F^2)$ = 0.1847, T = 296(2) K.

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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:	0.22 × 0.20 × 0.18 mm
Wavelength:	Mo *K*α radiation (0.71073 Å)
μ:	0.10 mm^{-1}
Diffractometer, scan mode:	Xcalibur, eos, gemini
θ_{max}, completeness:	27.5°, >99 %
$N(hkl)_{measured}$, $N(hkl)_{unique}$, R_{int}:	8692, 3201, 0.046
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\sigma(I_{obs})$, 1724
$N(param)_{refined}$:	193
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-methyl-1-p-tolyl-5-pyrazolone was synthesized according to the method proposed by Jensen (1959) (yield 78.6 %; m.p. 402–403 K). 3–methyl-1-p-tolyl-5-pyrazolone (5 g) was dissolved in dioxane (100 mL) by warming and $Ca(OH)_2$ (3 g), added. 2-Furoyl chloride (5 mL) was next added, drop by drop, with stirring within 3 min. After refluxing gently for 1 h, the orange mixture was cooled and poured with stirring into chilled 2 M HCl (450 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 76 % yield of light 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 0.82(1) A° and with U_{iso}(H) = 1.5 U_{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) = 1.2 U_{eq}(C) for phenyl H and 1.5 U_{eq}(C) for methyl H.

3 Comment

The 4-heterocyclic acylpyrazolones are an interesting class of β-diketones, containing a pyrazole-bearing chelating arm [5]. Such 4-heterocyclic acylpyrazolones derivatives were found to be useful as NMR shift-reagents [6], and it is also important in understanding the behavior of these compounds in the vapor phase, the mechanisms of pharmacological activities and physiological activities [7]. Moreover, they can coordinate

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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	−0.0413 (6)	0.3034 (3)	−0.07808 (11)	0.0708 (8)
H1A	−0.212469	0.301138	−0.061867	0.106*
H1B	−0.037049	0.246108	−0.106673	0.106*
H1C	−0.016884	0.376295	−0.094681	0.106*
C2	0.1817 (5)	0.2823 (2)	−0.03271 (10)	0.0560 (7)
C3	0.2785 (6)	0.3672 (2)	0.00323 (12)	0.0670 (8)
H3	0.204320	0.439193	−0.001124	0.080*
C4	0.4822 (5)	0.3490 (2)	0.04558 (11)	0.0631 (8)
H4	0.538539	0.407544	0.069891	0.076*
C5	0.6009 (5)	0.2442 (2)	0.05161 (10)	0.0470 (6)
C6	0.5079 (6)	0.1575 (2)	0.01628 (12)	0.0709 (9)
H6	0.584543	0.085883	0.020315	0.085*
C7	0.3006 (6)	0.1770 (2)	−0.02513 (12)	0.0731 (9)
H7	0.239611	0.117661	−0.048499	0.088*
C8	0.9559 (5)	0.2950 (2)	0.12885 (9)	0.0454 (6)
C9	1.1584 (5)	0.23178 (18)	0.16073 (9)	0.0445 (6)
C10	1.1187 (5)	0.11829 (19)	0.14008 (10)	0.0471 (6)
C11	1.2731 (6)	0.0123 (2)	0.15447 (12)	0.0664 (8)
H11A	1.194115	−0.049335	0.132633	0.100*
H11B	1.266723	−0.003782	0.194003	0.100*
H11C	1.457789	0.021925	0.146025	0.100*
C12	1.3334 (4)	0.2926 (2)	0.20037(9)	0.0468 (6)
C13	1.5466 (5)	0.2486 (2)	0.23858 (10)	0.0482 (6)
C14	1.7204 (5)	0.3037 (2)	0.27496 (11)	0.0638 (8)
H14	1.726344	0.381412	0.280863	0.077*
C15	1.8910 (6)	0.2236 (3)	0.30243 (12)	0.0710 (8)
H15	2.031200	0.237518	0.329922	0.085*
C16	1.8144 (6)	0.1248 (3)	0.28179 (13)	0.0757 (9)
H16	1.894076	0.056166	0.292658	0.091*
N1	0.8136 (4)	0.22280 (15)	0.09398 (8)	0.0465 (5)
N2	0.9161 (4)	0.11290 (16)	0.10102 (8)	0.0511 (5)
O1	0.9127 (4)	0.40260 (14)	0.13126 (8)	0.0627 (5)
H1	1.022698	0.431283	0.154615	0.094*
O2	1.3003 (4)	0.40023 (15)	0.20366 (8)	0.0675 (6)
O3	1.6004 (4)	0.13670 (16)	0.24193 (8)	0.0725 (6)

with metal to generate complexes [8, 9]. Although there have been numerous reports on acylpyrazolones, few 4-hetero cyclic acylpyrazolone compounds have been reported so far [10, 11].

The structure of the title compound is shown in figure. The p-tolylphenyl ring is slightly twisted by 6.23(6)° with respect to the pyrazolone ring, whereas the furyl rings make dihedral angles of 4.40(5)° with the pyrazolone. Atom O1 has a partial anionic character, as shown by the lengthening of the C8=O1 bond [1.293(3) Å] and this atom acts as hydrogen-bond acceptor. The intermolecular O1–H1···O2 hydrogen bond results in the formation of a dimer with an $R^2_2(12)$ graph-set motif [12]. It is apparent that the C12=O2 and C9=C12 distances correspond to double bonds. The conjugation effects also cause the pyrazolone and C2–C7 benzene ring to be nearly coplanar, with a mean deviation from the overall plane of 0.002 Å. Atoms O1, C8, C9, C12 and O2 are essentially coplanar, the largest deviation from the mean plane being 0.009 Å for C12. 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 the title compound crystallizes as a pure hydroxyl tautomer and that no desmotropism is present [13]. All geometric parameters are in the expected ranges [14].

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