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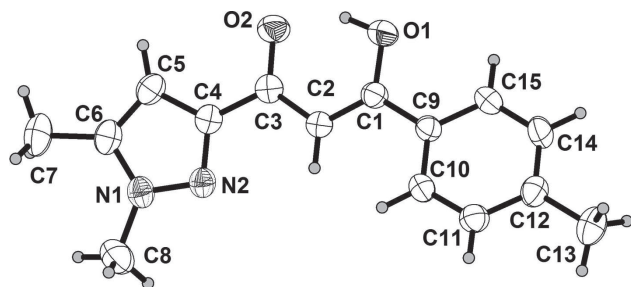
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Crystal structure of (Z)-1-(1,5-dimethyl-1*H*-pyrazol-3-yl)-3-hydroxy-3-(*p*-tolyl)prop-2-en-1-one, C₁₅H₁₆N₂O₂



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Abstract

C₁₅H₁₆N₂O₂, monoclinic, *P*₂/*c* (no. 14), *a* = 10.8334(5) Å, *b* = 11.7225(5) Å, *c* = 12.6861(6) Å, β = 123.417(5)°, *V* = 1344.73(1) Å³, *Z* = 4, *R*_{gt}(*F*) = 0.0607, *wR*_{ref}(*F*²) = 0.1662, *T* = 297 K.

CCDC no.: 1486977

The asymmetric unit of the title crystal structure is shown in the figure. Tables 1 and 2 contain details of the measurement method and a list of the atoms including atomic coordinates and displacement parameters.

Source of material

A suspension of metallic sodium (0.4 g; 17.39 mmol) in anhydrous toluene was mixed with ethyl-1,5-dimethyl-1-

Table 1: Data collection and handling.

Crystal:	Colourless bipyramid
Size:	0.62 × 0.40 × 0.36 mm
Wavelength:	Mo Kα radiation (0.71073 Å)
μ:	0.9 cm ⁻¹
Diffractometer, scan mode:	Xcalibur Sapphire3, ω-scans
2θ _{max} , completeness:	61°, >99%
<i>N</i> (<i>hkl</i>) _{measured} , <i>N</i> (<i>hkl</i>) _{unique} , <i>R</i> _{int} :	26340, 4099, 0.033
Criterion for <i>I</i> _{obs} , <i>N</i> (<i>hkl</i>) _{gt} :	<i>I</i> _{obs} > 2 σ(<i>I</i> _{obs}), 3126
<i>N</i> (<i>param</i>) _{refined} :	183
Programs:	CrysAlis [10], SHELX [11], ORTEP [12]

H-pyrazole-3-carboxylate (2.5 g; 14.86 mmol). Then 1-*p*-tolylethanone (1.99 g; 14.86 mmol) was added at 0 °C. The resulting mixture was stirred at room temperature for 7 days. The precipitate formed was filtered, washed and neutralized in water to pH = 5.5 using acetic acid. After extraction with CH₂Cl₂, the organic layer was dried over anhydrous sodium sulfate and concentrated in vacuo. Adding some milliliter of hexane, the product precipitated. Crystals of the title compound were obtained by slow evaporation. Yield: 32%, M.p. 132 – 134 °C.

Experimental details

All hydrogen atoms were inserted at calculated positions using a riding model. The *U*_{iso} values of the hydrogen atoms of methyl groups were set to 1.5*U*_{eq}(C) and the *U*_{iso} values of all other hydrogen atoms were set to 1.2*U*_{eq} of their parent atoms.

Discussion

β-Ketoenol-functionalized heterocycles, as one of the classical chelating ligands, play a significant role in coordination chemistry for over a century [1, 2], several of these ligands have been reviewed [3, 4]. Complex formation of such systems with transition metals have additional features, including unusual optical, magnetic, photoactive, catalytic and electrochemical properties. The intramolecular H-bond found in these systems, in which two oxygen atoms are interconnected through the hydrogen atom by a conjugated single and double bonds, has been discussed in numerous studies

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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	0.01862(15)	0.59334(12)	0.27258(13)	0.0379(3)
C2	0.13551(15)	0.65792(12)	0.36266(12)	0.0400(3)
H2	0.1752	0.7141	0.3379	0.048*
C3	0.19615(15)	0.63988(12)	0.49272(13)	0.0394(3)
C4	0.31447(15)	0.71328(12)	0.58847(12)	0.0382(3)
C5	0.36337(16)	0.72292(13)	0.71587(13)	0.0444(3)
H5	0.3301	0.6817	0.7582	0.053*
C6	0.46982(16)	0.80513(13)	0.76494(13)	0.0458(4)
C7	0.5583(2)	0.85593(19)	0.89453(15)	0.0688(5)
H7A	0.6611	0.8384	0.9328	0.103*
H7B	0.5256	0.8248	0.9451	0.103*
H7C	0.5451	0.9372	0.8888	0.103*
C8	0.5767(2)	0.92746(17)	0.67085(18)	0.0693(5)
H8A	0.6134	0.9038	0.6206	0.104*
H8B	0.6583	0.9399	0.7563	0.104*
H8C	0.5216	0.9970	0.6372	0.104*
C9	−0.05302(14)	0.60795(12)	0.13556(12)	0.0370(3)
C10	−0.03874(16)	0.70784(12)	0.08385(13)	0.0418(3)
H10	0.0150	0.7688	0.1362	0.050*
C11	−0.10414(16)	0.71668(13)	−0.04498(14)	0.0452(3)
H11	−0.0955	0.7845	−0.0785	0.054*
C12	−0.18248(15)	0.62654(14)	−0.12545(13)	0.0440(3)
C13	−0.2483(2)	0.63514(17)	−0.26531(15)	0.0617(5)
H13A	−0.2318	0.5650	−0.2949	0.093*
H13B	−0.2023	0.6968	−0.2812	0.093*
H13C	−0.3526	0.6491	−0.3089	0.093*
C14	−0.19649(17)	0.52778(14)	−0.07330(14)	0.0497(4)
H14	−0.2486	0.4664	−0.1257	0.060*
C15	−0.13500(17)	0.51835(13)	0.05445(14)	0.0462(3)
H15	−0.1482	0.4517	0.0869	0.055*
N1	0.48166(13)	0.83981(11)	0.66866(11)	0.0447(3)
N2	0.38682(13)	0.78578(10)	0.55933(10)	0.0413(3)
O1	−0.03848(13)	0.51164(9)	0.30417(10)	0.0535(3)
H1	0.0160	0.5110	0.3930	0.080*
O2	0.14793(13)	0.56258(10)	0.53075(10)	0.0522(3)

[5–8]. Crystals of β-ketoenols consist of packings of the enol tautomers stabilized by a strong intramolecular H-bond; that is, the H–O···H tautomerization and their interconversion.

The crystal structure of the title compound shows the formation of an intramolecular (O1–H···O2) interaction balancing the intra-electrostatic forces. The two oxygen atoms O1, O2 are separated by a distance of 2.5104(6) Å. Furthermore, the N1–N2 distance (1.3454(6) Å) is in good agreement with the lengths of bonds reported for analogous compounds [9]. N1, N2, C4, C5, and C6 atoms are in the same plane with a r.m.s. deviation of 0.0038 Å. The torsion angle O2–C3–C4–N2 of 170.12(6)° indicates that the pyrazolyl moiety undergoes slight inclination with respect to the plane discussed before. The torsion angle O1–C1–C9–C10 of 160.84(7)° indicates

that the plane of phenyl ring undergoes a greater inclination relative to plane of the central moiety.

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