



HAL
open science

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

Smaail Radi, Said Tighadouini, Driss Eddike, Monique Tillard, Yahia N. Mabkhot

► To cite this version:

Smaail Radi, Said Tighadouini, Driss Eddike, Monique Tillard, Yahia N. Mabkhot. Crystal structure of (Z)-1-(1,5-dimethyl-1H-pyrazol-3-yl)-3-hydroxy-3-(p-toly)prop-2-en-1-one, C₁₅H₁₆N₂O₂. Zeitschrift für Kristallographie - New Crystal Structures, 2017, 232 (2), pp.209. 10.1515/ncrs-2016-0199 . hal-01491960

HAL Id: hal-01491960

<https://hal.science/hal-01491960>

Submitted on 6 Jul 2020

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

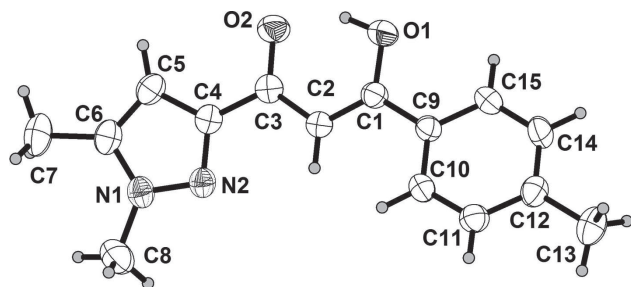
L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.



Distributed under a Creative Commons Attribution - NonCommercial - NoDerivatives 4.0 International License

Smaail Radi*, Said Tighadouini, Driss Eddike, Monique Tillard and Yahia N. Mabkhot*

Crystal structure of (Z)-1-(1,5-dimethyl-1*H*-pyrazol-3-yl)-3-hydroxy-3-(*p*-tolyl)prop-2-en-1-one, $C_{15}H_{16}N_2O_2$



DOI 10.1515/ncrs-2016-0199

Received July 17, 2016; accepted December 19, 2016; available online January 11, 2017

Abstract

$C_{15}H_{16}N_2O_2$, monoclinic, $P2_1/c$ (no. 14), $a = 10.8334(5)$ Å, $b = 11.7225(5)$ Å, $c = 12.6861(6)$ Å, $\beta = 123.417(5)^\circ$, $V = 1344.73(1)$ 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:	$0.62 \times 0.40 \times 0.36$ mm
Wavelength:	Mo $K\alpha$ radiation (0.71073 Å)
μ :	0.9 cm^{-1}
Diffractometer, scan mode:	Xcalibur Sapphire3, ω -scans
$2\theta_{\text{max}}$, completeness:	61° , >99%
$N(hkl)_{\text{measured}}$, $N(hkl)_{\text{unique}}$, R_{int} :	26340, 4099, 0.033
Criterion for I_{obs} , $N(hkl)_{\text{gt}}$:	$I_{\text{obs}} > 2\sigma(I_{\text{obs}})$, 3126
$N(\text{param})_{\text{refined}}$:	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 CH_2Cl_2 , 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 $1.5U_{\text{eq}}(\text{C})$ and the U_{iso} values of all other hydrogen atoms were set to $1.2U_{\text{eq}}$ 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

*Corresponding authors: Smaail Radi, LCAE, Faculté des Sciences, Université Mohamed I, 60000 Oujda, Morocco, e-mail: radi_smaail@yahoo.fr; and Yahia N. Mabkhot, Department of Chemistry, College of Science, King Saud University, P.O. Box 2455, Riyadh 1451, Saudi Arabia, e-mail: yahia@ksu.edu.sa

Said Tighadouini: LCAE, Department of Chemistry, Faculty of Sciences, Mohamed Premier University, Oujda 60000, Morocco
Driss Eddike: LCSMA, Faculté des Sciences, Université Mohamed I, 60000 Oujda, Morocco

Monique Tillard: Institut Charles Gerhardt, AIME, UMR CNRS 5253 CC15, Université de Montpellier II, Sciences et Techniques du Languedoc, 2 Place Eugène Bataillon, 34095 Montpellier Cédex 5, France

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.

Acknowledgements: The authors extend their appreciation to the PPR2-MESRSFC-CNRST-P10 project (Morocco) for supporting this work. Sincere appreciation was also extended to the Deanship of Scientific Research at King Saud University for supporting this Prolific Research group (PRG-1437-29).

References

- Hui, Y. Y.; Shu, H. M.; Hu, H. M.; Song, J.; Yao, H. L.; Yang, X. L.; Wu, Q. R.; Yang, M. L.; Xue, G. L.: Syntheses, structures and magnetic properties of tetranuclear and trinuclear nickel(II) complexes with β-diketone-functionalized pyridinecarboxylate ligand. *Inorg. Chim. Acta* **363** (2010) 3238–3243.
- McCleverty, J. A.; Meyer, T. J.: β-Diketones and related ligands. *Compr. Coord. Chem. II* (2004) 97–115.
- Aromi, G.; Gamez, P.; Reedijk, J.: Poly beta-diketones: Prime ligands to generate supramolecular metaloclusters. *Coord. Chem. Rev.* **252** (2008) 964–989.
- Vigato, P. A.; Peruzzo, V.; Tamburini, S.: The evolution of β-diketone or β-diketophenol ligands and related complexes. *Coord. Chem. Rev.* **253** (2009) 1099–1201.
- Jiménez-Cruz, F.; Mar, L. F.; Gutierrez, J. L. G.: Molecular structure and O–H···O hydrogen bond in 1-aryl-1,3-diketone malonates. *J. Mol. Struct.* **1034** (2013) 43–50.
- Gilli, G.; Belluci, F.; Ferreti, V.; Bertolasi, V.: Evidence for resonance-assisted hydrogen bonding from crystal-structure correlations on the enol form of the β-diketone fragment. *J. Am. Chem. Soc.* **111** (1989) 1023–1228.
- Bertolasi, V.; Gilli, P.; Ferreti, V.; Gilli, G.: Evidence for resonance-assisted hydrogen bonding. 2. Intercorrelation between crystal structure and spectroscopic parameters in eight intramolecularly hydrogen bonded 1,3-diaryl-1,3-propanedione enols. *J. Am. Chem. Soc.* **113** (1991) 4917–4925.
- Gilli, P.; Bertolasi, V.; Ferreti, V.; Gilli, G.: Evidence for resonance-assisted hydrogen bonding. 4. Covalent nature of the strong homonuclear hydrogen bond. Study of the O–H–O system by crystal structure correlation methods. *J. Am. Chem. Soc.* **116** (1994) 909–915.
- Radi, S.; Tighadouini, S.; Ben Hadda, T.; Akkurt, M.; Özdemir, N.; Sirajuddin, M.; Mabkhot, Y. N.: Crystal structure of (2Z)-3-hydroxy-1-(1,5-dimethyl-1H-pyrazol-3-yl)but-2-en-1-one. *Z. Kristallogr. NCS* **231** (2016) 617–618.
- Oxford Diffraction. CrysAlis CCD and CrysAlis RED. Version 171. Oxford Diffraction Ltd, Abingdon, Oxfordshire, England, (2004).
- Sheldrick, G. M.: A short history of SHELX. *Acta Crystallogr. A* **64** (2008) 112–122.
- Farrugia, L. J.: WinGX, ORTEP for Windows, an update. *J. Appl. Crystallogr.* **45** (2012) 849–854.