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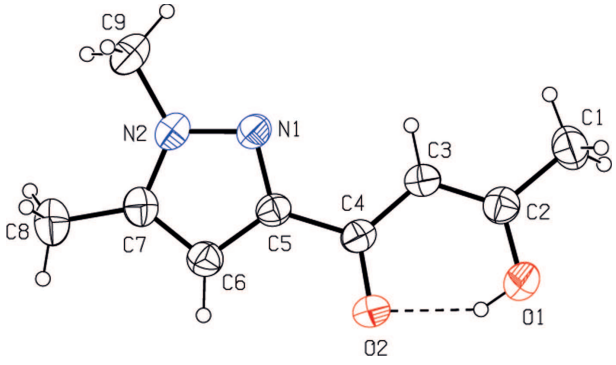
Crystal structure of (*Z*)-1-(1,5-dimethyl-1*H*-pyrazol-3-yl)-3-hydroxybut-2-en-1-one $C_9H_{12}N_2O_2$



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Abstract

$C_9H_{12}N_2O_2$, triclinic, $P\bar{1}$ (no. 2), $a = 6.6954(7)$ Å, $b = 7.6325(8)$ Å, $c = 9.8928(11)$ Å, $\alpha = 95.908(9)°$, $\beta = 92.810(9)°$, $\gamma = 108.360(8)°$. $V = 475.49(9)$ Å^3, $Z = 2$, $R_{gt}(F) = 0.0606$, $wR_{ref}(F^2) = 0.1549$, $T = 296(2)$ K.

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The figure shows the asymmetric unit of the title structure. Tables 1–3 contain details of the methods used and a list of the atoms including atomic coordinates and displacement parameters.

Table 1: Data collection and handling.

Crystal:	Colourless, plate, size 0.040×0.317×0.540 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	0.91 cm^{-1}
Diffractometer, scan mode:	STOE IPDS 2, ω scans
$2\theta_{max}$:	57.92°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	9019, 2509
$N(param)_{refined}$:	122
Programs:	X-Area [9], SHELX [10]

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

Atom	Site	*x*	*y*	*z*	U_{iso}
H(1)	2*i*	0.2341	0.3611	−0.0394	0.118
H(1A)	2*i*	−0.2924	0.2720	−0.0314	0.124
H(1B)	2*i*	−0.3091	0.1033	0.0503	0.124
H(1C)	2*i*	−0.2598	0.0912	−0.1030	0.124
H(3)	2*i*	−0.0147	0.1783	0.2125	0.072
H(6)	2*i*	0.7137	0.3781	0.3140	0.073
H(8A)	2*i*	0.7951	0.3856	0.66740	0.124
H(8B)	2*i*	0.9125	0.3245	0.5472	0.124
H(8C)	2*i*	0.7607	0.1740	0.6244	0.124
H(9A)	2*i*	0.3381	0.2624	0.7143	0.124
H(9B)	2*i*	0.3913	0.0773	0.6824	0.124
H(9C)	2*i*	0.1696	0.0870	0.6323	0.124

Source of material

A solution of ethyl 1,5-dimethyl-1*H*-pyrazole-3-carboxylate (12 mmol) in THF (25 mL) was added to a suspension of sodium (22 mmol) in THF (50 mL), and then acetone (1.2 g; 20.6 mmol) was added at 273 K. The resulting mixture was stirred at 273 K for 48 h and the formed residue was filtered, washed with THF, and neutralized with acetic acid to pH 5 after being dissolved in water. The organic layer was extracted with CH_2Cl_2, dried and concentrated in vacuum. The resulting mixture was chromatographed on silica using CH_2Cl_2 as eluant to give the target product. Crystals suitable for X-ray diffraction analysis were obtained by slow evaporated of methanol from the mixture; yield: 37%; M.p. 356–357 K.

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Table 3: Fractional coordinates and atomic displacement parameters (Å^2).

Atom	Site	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
O(1)	2*i*	0.1092(2)	0.3321(2)	−0.0671(1)	0.0770(9)	0.107(1)	0.0560(8)	0.0321(9)	0.0070(7)	0.0188(8)
O(2)	2*i*	0.4218(2)	0.3925(2)	0.1072(1)	0.0608(8)	0.104(1)	0.0670(8)	0.0196(7)	0.0154(6)	0.0352(8)
N(1)	2*i*	0.2620(2)	0.2152(2)	0.4169(2)	0.0632(9)	0.062(1)	0.0519(8)	0.0202(7)	0.0068(7)	0.0125(7)
N(2)	2*i*	0.3994(3)	0.2154(2)	0.5212(2)	0.075(1)	0.0603(9)	0.0505(8)	0.0259(8)	0.0061(7)	0.0105(7)
C(1)	2*i*	−0.2376(3)	0.1722(4)	−0.0188(2)	0.067(1)	0.101(2)	0.078(1)	0.027(1)	−0.008(1)	0.001(1)
C(2)	2*i*	−0.0075(3)	0.2498(3)	0.0239(2)	0.067(1)	0.065(1)	0.059(1)	0.0266(9)	0.0081(9)	0.0044(9)
C(3)	2*i*	0.0754(3)	0.2360(3)	0.1501(2)	0.057(1)	0.067(1)	0.058(1)	0.0182(8)	0.0123(8)	0.0139(8)
C(4)	2*i*	0.2944(3)	0.3072(2)	0.1873(2)	0.061(1)	0.057(1)	0.0525(9)	0.0234(8)	0.0118(8)	0.0117(8)
C(5)	2*i*	0.3857(3)	0.2848(2)	0.3202(2)	0.0573(9)	0.051(1)	0.0533(9)	0.0199(7)	0.0103(7)	0.0093(7)
C(6)	2*i*	0.5988(3)	0.3282(3)	0.3632(2)	0.059(1)	0.065(1)	0.062(1)	0.0230(9)	0.0089(8)	0.0101(9)
C(7)	2*i*	0.6036(3)	0.2820(3)	0.4932(2)	0.065(1)	0.058(1)	0.063(1)	0.0272(9)	−0.0002(8)	0.0027(8)
C(8)	2*i*	0.7841(4)	0.2925(4)	0.5918(2)	0.084(1)	0.093(2)	0.076(1)	0.038(1)	−0.012(1)	0.005(1)
C(9)	2*i*	0.3176(4)	0.1554(4)	0.6484(2)	0.103(2)	0.095(2)	0.056(1)	0.035(1)	0.012(1)	0.022(1)

Experimental details

The hydroxyl H atom and H atoms bonded to C atoms were positioned geometrically and were refined using a riding model with $U_{iso}(H) = 1.5U_{eq}(O)$ for hydroxyl and $U_{iso}(H) = 1.2U_{eq}(C)$ for the others.

Discussion

A new generation of highly promising inhibitors bearing β-keto-enol functionality has emerged. Their versatile utility in medicinal chemistry is firmly established including anti-HIV [1, 2], antitumor [3–5], anti-influenza [6], antioxidant [7], and anti-inflammatory [8] activities. In this study we coupled ethyl pyrazole carboxylate with acetone to produce the title compound in acceptable yield.

The crystal structure is quite interesting and displays the formation of an intramolecular OH—O hydrogen bond (see the figure). The structure leads to two independent N1, O2 and O1, O2-bidentate units having two different geometries with a very attractive evidence for even semi-combination probably existing between them, leading to a bis-bidentate N1, O2, O1-unit. However, both are held together by means of intra-electrostatic forces and van der Waals interactions. The oxygen atoms O1, O2 are separated by a distance of 2.538 Å. This distance is always found in the case of antibacterial pharmacophore site. Hence, this compound constitutes a promising anti-HIV agent. The whole molecule is almost planar, with an rms deviation of 0.002 Å for all non-hydrogen atoms. In the crystal, π-π stacking interactions [centroid-centroid distance = 3.5901(12) Å] between the pyrazole rings stabilize the molecular packing.

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