A.S. Safavora, Ivan Brito*, Jonathan Cisterna, Alejandro Cárdenas, E.Z. Huseynov, A.N. Khalilov, F.N. Naghiyev, R.K. Askerov and A.M. Maharramov

Crystal structure of ethyl (Z)-(4-oxo-4-phenylbut-2-en-2-yl)glycinate, $C_{14}H_{17}NO_3$

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Abstract

$C_{14}H_{17}NO_3$, monoclinic, $P2_1/n$ (no. 14), $a = 11.1445(7)$ Å, $b = 8.5442(5)$ Å, $c = 14.2503(8)$ Å, $\beta = 97.5684(11)^\circ$, $V = 1345.10(14)$ Å³, $Z = 4$, $R_{gt}(F) = 0.0668$, $wR_{ref}(F^2) = 0.1680$, $T = 296(2)$ 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.

*Corresponding author: Ivan Brito, Departamento de Quimica, Universidad de Antofagasta, Avda. Universidad de Antofagasta 02800, Campus Coloso Antofagasta-Chile, Antofagasta 1240000, Chile, e-mail: ivan.brito@uantof.cl

A.S. Safavora, E.Z. Huseynov, F.N. Naghiyev, R.K. Askerov and A.M. Maharramov: Department of Organic Chemistry, Baku State University, Z. Khalilov str. 23, AZ 1148 Baku, Azerbaijan

Jonathan Cisterna: Departamento de Quimica, Universidad de Antofagasta, Avda. Universidad de Antofagasta 02800, Campus Coloso Antofagasta-Chile, Antofagasta 1240000, Chile

Alejandro Cárdenas: Departamento de Fisica, Universidad de Antofagasta, Avda. Universidad de Antofagasta 02800, Campus Coloso Antofagasta-Chile, Antofagasta 1240000, Chile

A.N. Khalilov: Department of Organic Chemistry, Baku State University, Z. Khalilov str. 23, AZ 1148 Baku, Azerbaijan; and Department of Physics and Chemistry, "Composite Materials" Scientific Research Center, Azerbaijan State Economic University (UNEC), H.Aliyev str.135, Az 1063 Baku, Azerbaijan

Table 1: Data collection and handling.

Crystal:	Colourless prism
Size:	$0.24 \times 0.18 \times 0.13$ mm
Wavelength:	Mo $K\alpha$ radiation (0.71073 Å)
μ :	0.09 mm^{-1}
Diffractometer, scan mode:	Bruker APEX-II, φ and ω
$\theta_{\max}$, completeness:	29.0° , >99%
$N(hkl)_{\text{measured}}$, $N(hkl)_{\text{unique}}$, R_{int} :	13813, 3565, 0.038
Criterion for I_{obs} , $N(hkl)_{\text{gt}}$:	$I_{\text{obs}} > 2 \sigma(I_{\text{obs}})$, 1730
$N(\text{param})_{\text{refined}}$:	167
Programs:	Bruker [1], SHELX [2, 3], Olex2 [4]

Source of material

The title compound was obtained by the refluxing of benzoylacetone (1 mmol) with ethyl glycinate hydrochloride (10 mmol) in dimethylformamide similar to reported procedure [5]. Then the reaction mixture cooled down to room temperature and the solvent is removed *in vacuo*. The obtained residue was extracted with hot benzene. Then extract was evaporated *in vacuo*. In the solution of this residue in hexane were precipitated pale yellow crystals. The yield of ethyl (Z)-(4-oxo-4-phenylbut-2-en-2-yl)glycinate is 30%. Mp 76–77 °C.

Analysis: ¹H NMR (300 MHz, DMSO-*d*₆), δ [ppm], m.h.: 1.21 (t, 3H, CH₃, $^3J_{\text{H-H}} = 14.1$); 2.03 (s, 3H, CH₃); 4.17 (k, 2H, CH₂O, $^3J_{\text{H-H}} = 14.1$); 4.26 (d, 2H, CH₂, $^3J_{\text{H-H}} = 14.1$), 5.84 (s, 1H, CH=); 7.42–7.87 (m, 5H, 5Ar-H), 11.29 (s, 1H, NH).

¹³C NMR spektr (DMSO-*d*₆), δ [ppm], m.h.: 14.45 (CH₃), 19.57 (CH₃), 44.82 (CH₂N), 61.46 (CH₂O), 92.31 (CH=), 127.12 (2CH_{arom}), 128.71 (2CH_{arom}), 131.12 (CH_{arom}), 140.25 (C_{ar}), 165.38 (=C_{quat}), 170.09 (COO), 186.80 (C=O).

Experimental details

H atoms were located in the difference Fourier map, but refined with fixed individual displacement parameters, using a riding model with C–H distances of 0.93 Å (for aromatic rings), and C–H distances 0.97, 0.96 Å for methylene and methyl groups, with $U(\text{H})$ values of $1.2U_{\text{eq}}(\text{C}_{\text{Ar}}$ and CH₂) and $1.5U_{\text{eq}}(\text{C})$ (for CH₃). H atom attached at N atom was located in the difference Fourier map and refined freely.

Table 2: Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²).

Atom	x	y	z	$U_{\text{iso}}^*/U_{\text{eq}}$
O1	0.35424(13)	0.82838(19)	0.03049(11)	0.0801(5)
O2	0.32991(15)	0.5933(2)	−0.19795(12)	0.0944(6)
O3	0.46085(12)	0.46699(18)	−0.27700(10)	0.0784(5)
N1	0.51204(17)	0.6762(2)	−0.05831(13)	0.0646(5)
H1	0.434(2)	0.714(3)	−0.0578(15)	0.094(8)*
C1	0.41392(18)	0.9664(2)	0.17216(14)	0.0587(5)
C2	0.29745(18)	1.0247(2)	0.17100(16)	0.0667(6)
H2A	0.2395	1.0025	0.1196	0.080*
C3	0.2656(2)	1.1145(3)	0.24395(17)	0.0753(6)
H3A	0.1873	1.1538	0.2407	0.090*
C4	0.3480(2)	1.1461(3)	0.32082(18)	0.0838(7)
H4A	0.3260	1.2045	0.3709	0.101*
C5	0.4636(2)	1.0906(3)	0.32349(18)	0.0971(8)
H5A	0.5202	1.1120	0.3759	0.116*
C6	0.4977(2)	1.0036(3)	0.24977(16)	0.0825(7)
H6A	0.5773	0.9698	0.2522	0.099*
C7	0.44096(18)	0.8651(2)	0.09176(14)	0.0597(5)
C8	0.55970(18)	0.8114(2)	0.08697(16)	0.0647(6)
H8A	0.6199	0.8396	0.1355	0.078*
C9	0.59186(18)	0.7199(2)	0.01505(16)	0.0632(5)
C10	0.54114(18)	0.5848(3)	−0.13721(15)	0.0686(6)
H10A	0.5779	0.4868	−0.1142	0.082*
H10B	0.5994	0.6412	−0.1693	0.082*
C11	0.4303(2)	0.5515(3)	−0.20582(16)	0.0686(6)
C12	0.3654(2)	0.4148(3)	−0.34928(18)	0.0911(8)
H12A	0.3215	0.5038	−0.3789	0.109*
H12B	0.3088	0.3481	−0.3218	0.109*
C13	0.4247(3)	0.3268(4)	−0.41968(19)	0.1191(11)
H13A	0.3644	0.2899	−0.4691	0.179*
H13B	0.4804	0.3942	−0.4463	0.179*
H13C	0.4677	0.2393	−0.3894	0.179*
C14	0.7197(2)	0.6639(3)	0.01698(18)	0.0862(7)
H14A	0.7680	0.7028	0.0728	0.129*
H14B	0.7211	0.5516	0.0174	0.129*
H14C	0.7517	0.7016	−0.0381	0.129*

Comment

Enaminones or enamine of β -dicarbonyl compounds are versatile building blocks in organic synthesis in pharmaceutical development [6–8]. Therefore, the synthesis of this class of compounds has a great point of interest. In presence of several catalysts the condensation of the amines with the β -dicarbonyl compounds has been employed as a useful synthetic procedure to synthesis enaminones [9]. Shuntaro Mataka and co-workers [5] reported about convenient synthesis of pyrrole derivatives by the reaction of 1,3-diketones with ethyl glycinate hydrochloride in boiling dimethylformamide. Herein we report about identification of intermediate product, i.e. enamine, in the synthesis of corresponding pyrroles by applying the same procedure.

The title compound corresponds to an enaminone *Z* isomer in the solid state. All the distances and angles are normal [10, 11]. The molecular structure is basically planar (RMSD 0.05 Å). This conformation is reinforced by two intramolecular hydrogen bonds between two carbonyl groups and –NH fragment with distances 1.903 and 2.406 Å, with O1 and O2, respectively as consequence of *Z* conformation. Besides an intermolecular hydrogen bond between C13–H···O1 with a distance of 2.500 Å, generating a centrosymmetric packing in the crystal structure ($1/2-X, 1/2+Y, 1/2-Z$), along to [010] direction.

In order to verify and observe weak interactions, Hirshfeld surface analysis was conducted to verify the contributions of the different intermolecular interactions. This analysis was used to investigate the presence of hydrogen bonds and intermolecular interactions in the crystal structure. The Hirshfeld surface analysis [12] was generated by CrystalExplorer 17.5 [13] and comprised d_{norm} surface plots and 2D (two-dimensional) fingerprint plots [14]. The plots of the Hirshfeld surface confirms the presence of the non-covalent interaction, observed in the crystal structure, with contributions of interatomic contacts to the Hirshfeld surface O···H 20.0%; O···C 1.50%; H···N 0.60% and H···C (π –H) 17.9%, including reciprocal contacts.

The weak intermolecular interactions are mainly constituted by O···H, H···C, where the reciprocal contact for O···H, with $d_e + d_i \sim 2.5$ Å and H···C with $d_e + d_i \sim 3.5$ Å. This is due a H··· π weak interaction between –CH₃ moiety of ethyl fragment and the delocalized π orbitals over phenyl ring. Moreover, a minor contribution of O···C and H···N very weak intermolecular interaction with $d_e + d_i \sim 3.8$ Å and $d_e + d_i \sim 3.0$ Å, respectively, generating a pseudo-dimeric species in the crystal packing.

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