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A New 4-oxo-4-phenylbutanoic Acid Polymorph

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Abstract: A new Z = 8, Z' = 2 polymoroph of 4-oxo-4-phenylbutanoic (β-benzoylpropionic) acid, $C_{10}H_{10}O_3$, was obtained. The previously published two polymorphs with CCDC codes VERMAG and VERMAG01 crystallize with Z = 4, Z' = 1 in monoclinic space groups $P2_1/c$ [a = 15.071(10), b = 5.435(9), c = 16.058(10), β = 129.57(10)°] and $P2_1/n$ [a = 12.728(6), b = 5.200(3), c = 14.426(6), β = 111.33(3)°], respectively. Reported herein polymorph crystallizes in monoclinic space group $P2_1/c$ and has significant larger cell volume of 1754.51 Å^3 [a = 15.2673(6), b = 5.2028(2), c = 22.3063(8), β = 98.0217(7)°]. Structurally, new polymoroph differs from two known other slightly (RMSD of about 0.112-0.183 Å). All polymorphs contain dimers of molecules bounded by intermolecular hydrogen bonds leaving carbonyl groups at position 4 unaffected.

Keywords: 4-oxo-4-phenylbutanoic acid; β-benzoylpropionic acid; new polymoroph; hydrogen bonds

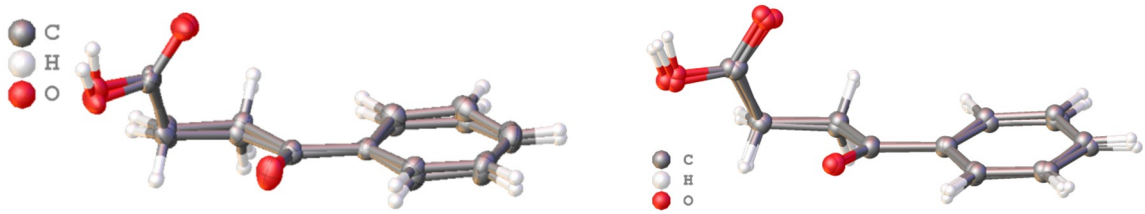
1. Introduction

In early nineties of the XX century there were published two works with the description of two different polymorphs of 4-oxo-4-phenylbutanoic acid, which were deposited in CCDC with codes VERMAG and VERMAG01, respectively [1,2]. The crystal of the first one, VERMAG, was obtained from methanol, while the second modification was synthesized in benzene. Both polymorphs crystallizes in monoclinic space groups, $P2_1/c$ (VERMAG) and the non-standard space group $P2_1/n$ (VERMAG01), and have similar parameters of the crystal lattice.

Today, scientists pay great attention to crystals with $Z' \geq 2$. Reported here new polymorph of 4-oxo-4-phenylbutanoic acid crystallizes also in $P2_1/c$ space group, but the parameters of crystal lattice differ from published before crystals significantly.

2. Results

Structurally, reported here polymorphic modification of 4-oxo-4-phenylbutanoic acid differs from deposited in CCDC with codes VERMAG and VERMAG01 crystals very slightly (RMSD of about 0.112-0.183 Å). The asymmetrical unit of reported crystal contains four pairs of crystallographically independent molecules (Z = 8, Z' = 2) with RMSD of 0.241 Å (with inversion) (Figure 1a). Interesting the fact that, according to the RMSD values, two crystallographically independent molecules in reported here crystal differ each other more significantly than the molecules from all known polymorphs (Figure 1b).



(**a**) (**b**)

Figure 1. Overlay diagrams of: (**a**) Two crystallogrtaphically indepent molecules in new polymorph (this study), RMSD of 0.241 Å (with inversion); (**b**) Three molecules from studied crystal, VERMAG and, VERMAG01 crystals, RMSD in 0.112-0.183 Å range.

All polymorphs contain dimers of molecules bounded by intermolecular hydrogen bonds between carboxyl groups. No interactions observed with oxygen atom of carbonyl group at position 4. The summarized H-bonds data for all considering crystals given in Table 1. It can be seen that the H…O distances in our crystal differ only by 0.036 Å, while the differences between this structure and VERMAG as well as VERMAG01 significantly more, and are 0.179 and 0.108 Å, correspondingly. Remarkable, that the H…O distance of studied crystal of 4-oxo-4-phenylbutanoic acid lies in between VERMAG and VERMAG01. The D…A distances of two molecules in studied crystal as well as in VERMAG01 polymorph are very similar (about 2.65 Å), in contrast with the VERMAG where this distance is about 0.1 Å longer.

Table 1. Hydrogen bonds for all known 4-oxo-4-phenylbutanoic acid polymorphs.

Polymorph	D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
This study	O(2)-H(2)...O(1)$^{\#1}$	0.880(19)	1.778(19)	2.6560(11)	175.2(18)
This study	O(2A)-H(2O)...O(1A)$^{\#2}$	0.920(19)	1.742(19)	2.6550(12)	171.3(17)
VERMAG	O(2)-H(2a)…O(3)$^{\#3}$	0.820(1)	1.939(2)	2.755(3)	173.200(8)
VERMAG01	O(3)-H(10)…O(2)$^{\#4}$	0.999(3)	1.652(3)	2.650(4)	176.56(19)

Symmetry transformations used to generate equivalent atoms: #1: −x+1, −y, −z+1; #2: −x, −y, −z; #3: x, 1+y, z; #4: x, 1+y, z.

Main differences of three polymorphs are in the crystal packing (Figure 2a–c). Briefly, the crystal package of VERMAG with the volume cell of 1013.91 Å^3 is the least dense of all crystals, while the reported polymorph have the most dense packing with the volume cell of 1754.51 Å^3 and two sets of molecules in comparison to early known modifications.

3. Discussion

The reported monoclinic crystal of 4-oxo-4-phenylbutanoic acid belongs to the space group $P2_1/c$ and has significant larger cell volume. Selladurai *et al.* reported their structure (VERMAG) as a monoclinic crystal of the space group $P2_1/c$ with an β angle of 129.57(10)°, while Thompson *et al.* refine their structure (VERMAG01) in the space group $P2_1/n$ with the less-obtuse β angle of 111.33(3)°. To the best of our knowledge, more accurate results can be achieved when use $P2_1/c$ for angles of less than 120°. So, our structure was refine in the space group $P2_1/c$ with more sharp β angle of 98.0217(7)°.

Surprisingly was the fact that, structurally, two crystallographically independent molecules in reported crystal differ each other more than the molecules from all known polymorphs. This can be explained by significant flexibility of the alkyl units of the acid.

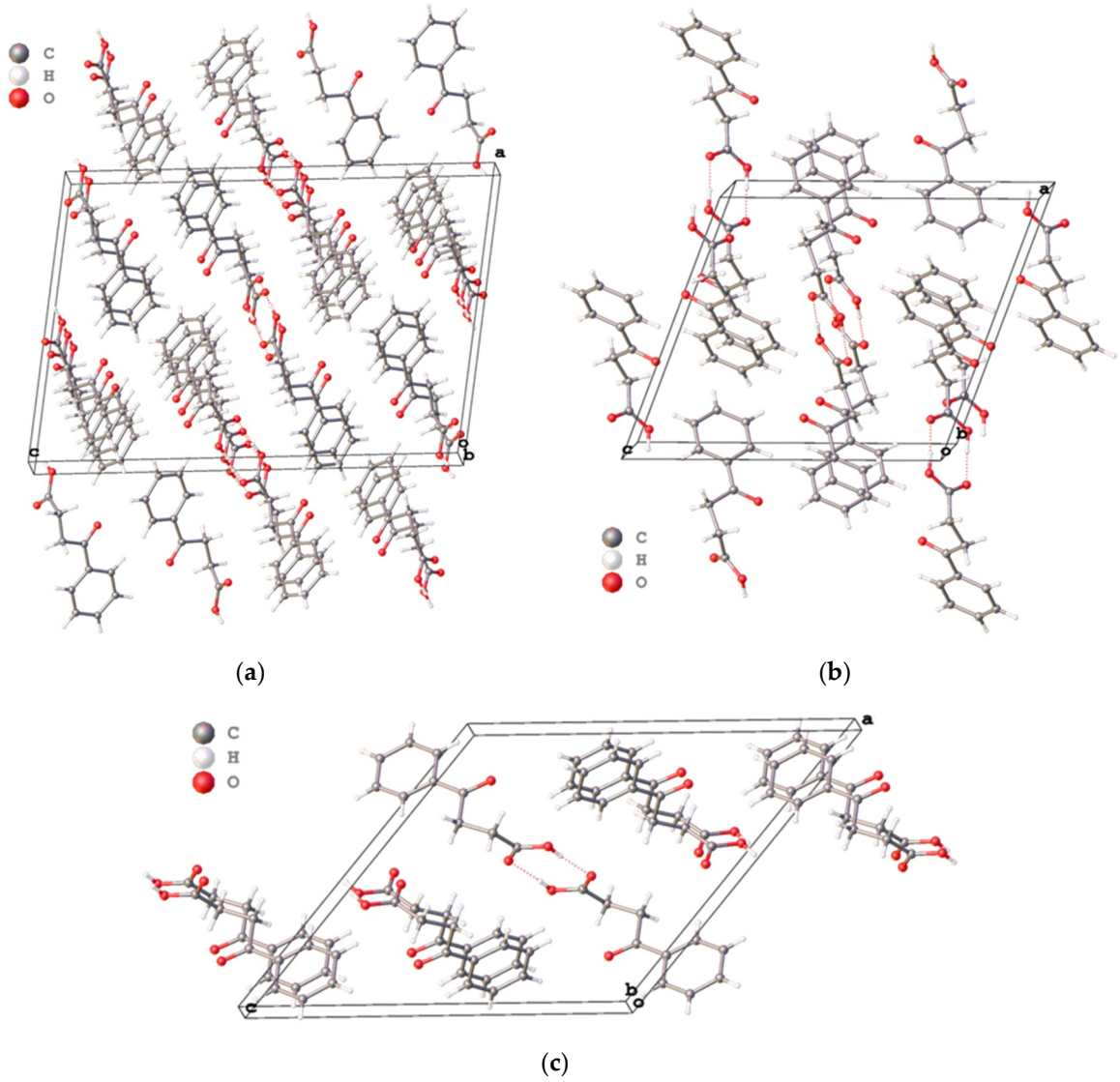


Figure 2. Packing diagrams of known polymorhs of 4-oxo-4-phenylbutanoic acid: (**a**) New polymorph (this study); (**b**) VERMAG01; (**c**) VERMAG.

Considering all three known at the day crystals of 4-oxo-4-phenylbutanoic acid, our polymorph has the most dense package. In all crystals molecules of the acid are formed dimers using carboxyl groups wich is in harmony with the common data for all carboxylic acids. The parameters of intermolecular hydrogen bonds of our crystal lies between corresponding values of known polymorhs and looks ordinary.

4. Materials and Methods

4-Oxo-4-phenylbutanoic acid was synthesized by Friedel-Crafts condensation from succinic anhydride and benzene with anhydrous $AlCl_3$ catalysis, recrystallized from water and dried under vaccuo. M.p. 112-114 °C. The single crystal for Xray study was obtained from benzene by slow evaporation.

Xray diffraction was performed on an automatic three-circle diffractometer *Bruker SMART Apex II* (graphite monochromator, λ(MoKα) = 0.71073 Å, ω scan) at 120 K. Integration of intensities was carried out using the procedure built into the software complex SAINT [3]. Semi-empirical corrections for absorption and for systematic errors are based on the intensity of equivalent

reflections in the program SADABS [4]. The structure was solved by a direct method and was refined by full-matrix least-squares versus F^2_{hkl} with anisotropic displacement parameters for all non-hydrogen atoms. The hydrogen atoms of the OH groups were found from the difference Fourier series and refined in the isotropic approximation. The other hydrogen atoms were placed in the calculated positions and were refined geometrically by using a riding model with U_{iso}(H) = 1.2 U_{iso}(C) and U_{iso}(H) = 1.5 U_{iso}(C) for methyl and other groups. Solving and refinement were carried out using the SHELX software package version 2016/6 [5]. The overlays and packing diagrams as well as parameters of non-covalent interactions were obtained using Olex2 software [6].

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Author Contributions: E.L. and E.K. carried out the synthesis of reported compound and obtained the single crystal, V.G. took part in the spectral characterization of synthesized compound, drafted the manuscript, prepared final version of the manuscript, assisted technically, A.Ye. designed and supervised all experiments, and manuscript drafting. All authors read and approved the final version of the manuscript.

Conflicts of Interest: The authors declare no conflict of interest.

Abbreviations

The following abbreviations are used in this manuscript:

MDPI: Multidisciplinary Digital Publishing Institute
DOAJ: Directory of open access journals
CCDC: The Cambridge Crystallographic Data Centre
RFBR: Russian Foundation for Basic Research

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