

# Glycolaldehyde dimer in the stable crystal phase has axial OH groups: Raman, infrared and X-ray data analysis



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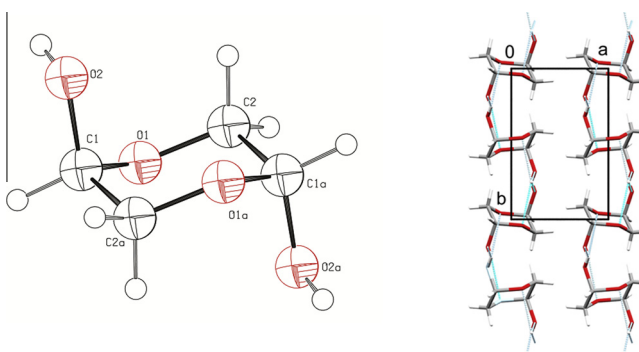
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## HIGHLIGHTS

- Glycolaldehyde dimer crystallizes in the monoclinic system, space group  $P2_1/c$ .
- Its hydroxyl groups are in the axial position.
- Raman and infrared spectra were reassigned.

## GRAPHICAL ABSTRACT



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## ABSTRACT

Although a small molecule and a simple 1,4-dioxane derivative, 2,5-dihydroxy-1,4-dioxane or glycolaldehyde dimer has a crystal structure that has eluded researchers so far, chief reason lying presumably in substance polymorphism. Here we report for the first time on the stable crystal structure of the glycolaldehyde dimer characterized by the X-ray powder diffraction method at room temperature. It crystallizes in the monoclinic system, space group  $P2_1/c$ , with unit cell parameters  $a = 5.9473(1)$  Å,  $b = 8.3997(1)$  Å,  $c = 5.61953(8)$  Å and  $\beta = 114.8814(9)^\circ$ . The glycolaldehyde dimer molecules are the *trans*-isomers with the electronegative hydroxyl groups in axial positions and molecules are arranged in hydrogen bonded layers parallel to (100). Each layer is stabilized by intermolecular medium strong O–H...O hydrogen bonds. The 1,4-dioxane ring of the molecule adopts a chair conformation.

Raman and infrared spectra were re-examined and assigned with the help of *ab initio* calculation followed by a normal modes analysis modes most sensitive to crystal packing were identified as the C–OH deformations which were assigned to the IR and Raman bands at 1239 and 1237  $\text{cm}^{-1}$ , respectively; the two O–C–O deformation modes, both associated with the Raman and IR bands at 561 and 535  $\text{cm}^{-1}$  and, the two OH torsion modes assigned to the IR bands at 630 and 604  $\text{cm}^{-1}$ .

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## 1. Introduction

Glycolaldehyde is the simplest sugar – related molecule containing both an aldehyde and a hydroxyl group,  $\text{CHOCH}_2\text{OH}$ . The fact that it is the first saccharide found in the interstellar space [1] and the role it plays in the energy metabolism in humans [2],

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has motivated microwave [3] and conformational studies [4–7], electron beam radiation experiments [8], as well as infrared spectroscopic studies of molecules isolated in noble gases [9] or para-hydrogen matrix [10]. In the solid state, pure glycolaldehyde exists in the form of a dimer [11,12]. Previous vibrational studies on solid glycolaldehyde were done by Michelsen and Klæboe [13] who compared infrared and Raman spectra of solid with the infrared spectrum of vapor, confirming centrosymmetric structure of the dimer as completely different from the monomer structure present in the vapor. Kobayashi et al. [14] succeeded in obtaining two crystalline forms  $\alpha$  and  $\beta$  of glycolaldehyde and compared their infrared and Raman spectra, including the far infrared region. They claimed that in the  $\alpha$  form the hydroxyl groups are placed in equatorial position on the 1,4-dioxane ring, while in the  $\beta$  form axial position of the OH groups was more probable. Mohaček-Grošev used low temperature Raman spectroscopy to probe the  $\alpha$  structure, and performed semi-empirical normal coordinate analysis of the dimer both with equatorial and with axial hydroxyl groups [15] in order to establish the dimer conformation. Doubling of the number of the phonon bands below 80 K indicated that the  $\alpha$  phase might be transformed into the third,  $\gamma$  phase. Her conclusion that a dimer with equatorial groups is present in the stable phase was based on the expectation of  $150\text{ cm}^{-1}$  Raman mode for an axial conformer, which was not observed.

Here we report on the crystal structure of 2,5-dihydroxy-1,4-dioxane (glycolaldehyde dimer) characterized by the X-ray powder diffraction method. Infrared and Raman spectra were re-examined and reassigned, this time using *ab initio* method of calculation, accompanied with potential energy distribution.

## 2. Experimental

Glycolaldehyde, purity greater than 98%, was purchased from Fluka and sealed in a capillary tube. Raman and infrared experiments were performed at room temperature as described in [15].

### 2.1. Powder diffraction

The powder diffraction data for glycolaldehyde dimer were collected on a laboratory PANalytical X'Pert Pro diffractometer in the capillary transmission geometry mode with focusing mirror and X'Celerator detector, using Cu K $\alpha$  radiation. The sample was contained in a 0.5 mm glass capillary. Patterns were collected from  $12^\circ$  to  $80^\circ$  ( $2\theta$ ) with a step size of  $0.0084^\circ$ . The total data collection time was 5 h and 40 min. The powder pattern was indexed on first 15 peaks by the DICVOL04 program [16] integrated into the HighScore Plus program [17]. The initial cell parameters were obtained with the figure of merit  $M(15) = 191$ . One peak at  $17.8^\circ$  ( $2\theta$ ) with the relative intensity of 1.2% remained unindexed, indicating a low level polymorphic or chemical impurity and was excluded from the unit cell refinement. The unit cell parameters were refined by the least squares fit implemented in the HighScore Plus program. The refined unit cell parameters are  $a = 5.9473(1)\text{ \AA}$ ,  $b = 8.3997(1)\text{ \AA}$ ,  $c = 5.61953(8)\text{ \AA}$  and  $\beta = 114.8814(9)^\circ$ . Space group search was made by trying the Le Bail full profile fitting [18] for all monoclinic space groups. The comparison of fitting residue values and goodness of fit suggested space group  $P2_1/c$  as the most probable one. The structure was solved in the space group  $P2_1/c$  by direct methods, using the EXPO2009 [19] program. Structure refinement was carried out by the Rietveld [20] refinement program implemented in the HighScore Plus. The peak profiles were refined by the Pseudo-Voigt profile function (modified by the asymmetry correction of Finger, Cox and Jephcoat [21]). The background was modeled by the Chebyshev-I function. The fractional atomic coordinates and isotropic thermal parameters

for all non-H atoms were refined without any constraints. The final fit of the model to the experimental data and a difference plot are given in Fig. S1. The residual of the final fit were:  $R_p = 0.052$  and  $R_{wp} = 0.074$ . The crystallographic data are summarized in Table 1.

## 3. Computational details

Vibrations were calculated with the Gaussian 03 program [22]. The geometry of the dimer was optimized by using the hybrid B3LYP functional with the 6-31++G(d,p) basis set. Practically all calculated normal modes except the  $441\text{ cm}^{-1}$  mode can be classified according to the group  $C_i$ , either as transforming according to  $A_g$  or  $A_u$  irreducible representation. Optimized geometrical parameters are listed and compared to the X-ray data in Table S1 of the Supplementary material. For the normal coordinate calculations, the BALGA program was used [23,24]. Definition of internal coordinates is given in Table S2, while local symmetry coordinates are listed in Table S3 of the Supplementary material. Finally, a detailed potential energy distribution is presented in Table S4.

## 4. Results and discussion

Glycolaldehyde in the melt is a rich mixture of monomers, open and closed dimers, some of which include hydroxyl groups simultaneously present in axial and equatorial position in the same molecule [25]. Therefore, determination of the relative stability of two glycolaldehyde dimer forms, one having two hydroxyl groups placed axially, and the other having two OH groups placed equatorially, is not possible in the way it was performed, e.g. in vibrational studies of bicyclopopyl [26] or cyclobutanol [27].

Observed Raman and infrared spectra of different glycolaldehyde phases were compared to those of dioxane and glyceraldehyde in previous vibrational studies [13–15]. Kobayashi et al. [14] were the first to report the existence of a second crystal phase of glycolaldehyde at room temperature and called it the  $\beta$  phase. Mohaček-Grošev studied low temperature Raman spectra and found spectral evidence of a new phase  $\gamma$  existing below 80 K, which is not present at room temperature [15]. Vibrational spectra of  $\alpha$  and  $\beta$  phase are rather similar, displaying differences in bands

**Table 1**  
Crystallographic data for glycolaldehyde dimer.

	Glycolaldehyde dimer
Chemical formula	C <sub>4</sub> H <sub>8</sub> O <sub>4</sub>
$M_r$	60.05
Powder color	White
Crystal system	Monoclinic
Space group	$P2_1/c$
<i>Unit cell parameters</i>	
$a$ (Å)	5.9473(1)
$b$ (Å)	8.3997(1)
$c$ (Å)	5.61953(8)
$\alpha$ (°)	90
$\beta$ (°)	114.8814(9)
$\gamma$ (°)	90
$V$ (Å <sup>3</sup> )	254.27
$Z$	2
$D_{\text{calc}}$ (g cm <sup>-3</sup> )	1.566
Temperature (K)	293
Wavelength (Å)	1.540598
$R_p$	0.052
$R_{wp}$	0.074
$R_{\text{exp}}$	0.028
Goodness of fit	6.95
Starting angle (°, $2\theta$ )	12
Final angle (°, $2\theta$ )	80
Step width (°, $2\theta$ )	0.0084
Time/scan	5 h 40 min

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