

Structural Analysis of Γ -Glycine Crystal Grown using the Aqueous Solution of α -Glycine and Guanidine Hydrochloride

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Abstract: Gamma-glycine (γ -glycine) crystals were grown by slow evaporation method using the commercially available α glycine and guanidine hydrochloride (1:1 molar ratio) in the solvent of water. The crystals have been harvested after a growth period of 35 days. The grown crystal was subjected to single crystal X-ray diffraction method to solve the complete crystal structure. The obtained compound is observed to be crystallizing in hexagonal structure with the space group $P3_2$. The crystal data were collected using BRUKER AXS KAPPA APEX II CCD X ray diffractometer. The structure was solved by direct methods and refined on F^2 Full matrix least squares procedures to the final R_1 of 0.0263 using SHELXL.

Key words: Gamma-glycine; single crystal; solution growth; XRD; crystal structure.

Introduction

Extensive studies have been made on the synthesis and crystal growth of nonlinear optical materials over the past decade because of their potential applications in the field of telecommunications, optical signal processing and optical switching. Optical nonlinearity of the crystals with O-H bond has been studied¹. Crystallization of a molecule into a non-centrosymmetric structure can be achieved either by attaching to it a suitable substituent which cause a crystal structure. Among the organic crystals for NLO applications, amino acids display special features of interest such as molecular chirality which secures acentric crystallographic structure, wide transparency in the visible and UV range, zwitterionic nature of the molecule which favours the hardness of the crystal etc^{2,3}. In solid state, amino acid contains the donor and acceptor groups, which provide the ground state charge asymmetry of the molecule, required for second order nonlinearity. These enhanced properties of amino acids are due to the presence of a proton donor carboxylic acid (COOH) group and the proton acceptor amino (NH_2) group. Due to this dipolar nature, amino acids have physical properties which make them ideal candidates for NLO applications. Hydrogen bonds have also been used in the possible generation of non-centrosymmetric structures, which is a prerequisite for an effective NLO crystal⁴⁻⁶.

Glycine is the simplest amino acid and it can exist in zwitterionic form. Unlike other amino acids, it has no centre of chirality and is optically inactive. While glycine can exist as a neutral molecule in the gas phase, it exists as a zwitterion in solution and in the solid state. Certain chemical compounds show the ability to crystallize into more than one structural form with different physical properties, known as polymorphs. Under different conditions, glycine crystallizes in three kinds of polymorphs with different relative stabilities, α , β and

γ which exhibits different characteristics. The α -form consists of hydrogen bonded double layers of molecules, which are packed by Van der Waal's forces. The least stable form β is monotropically related to the other two polymorphs. It is always obtained from a water–alcohol mixed solvent and can transform rapidly to the α form in the presence of water or upon heating. Both α - and β -forms crystallize in centrosymmetric space group $P2_1/c$ ruling out the possibility of optical second harmonic generation. But γ -glycine crystallizes in a non-centrosymmetric space group $P3_2$ making it a potential candidate for piezoelectric and NLO applications⁷⁻⁹. In the γ -glycine, there exists a dipolar ion in which carboxyl group is present as a carboxylate ion and amino group is present as ammonium ion. Due to this dipolar nature, glycine has high melting point. In addition to this, the presence of chromophores namely amino group and carboxyl group which makes the γ -glycine crystal transparent in the UV–visibel region. Narayan Bhat¹⁰ carried out a detailed study on the growth of γ -glycine crystals from aqueous solutions of glycine with (i) sodium chloride, (ii) sodium hydroxide, (iii) sodium fluoride, (iv) sodium nitrate and (v) sodium acetate and analyzed the effect of these solvents on the various physical characteristics of glycine. The present study reports the growth and structural characterization of γ -glycine crystals grown from aqueous solution of glycine in the presence of guanidine hydrochloride for the first time. In this paper, the complete crystal structure of gamma-glycine with the space group $P3_2$ was analysed and the results are discussed.

Experimental

All chemical reagents were used as obtained commercially without purification. A mixture of glycine and guanidine hydrochloride of 1:1 molar ratio was dissolved in de-ionised water and was stirred at 50 °C then the solution was filtered in room temperature (30 °C). Colourless transparent crystals of the title compound were formed by slow evaporation technique after four weeks. A preliminary study of the powder SHG was made with laser beam of wave length 1064 nm of beam Q switched Nd:YAG laser confirms the NLO property of the title compound. Three dimensional intensity data were collected on a Bruker4 SMART KAPPA APEX II CCD diffractometer using graphite monochromatized MoK α radiation ($\lambda = 0.71073 \text{ \AA}$). The structure was solved by direct methods and refined on F^2 by full-matrix least-squares procedures using the SHELXL programs. All the non-hydrogen atoms were refined using isotropic and later anisotropic thermal parameters. The refinement based on F^2 to an R value of 0.0257. The hydrogen atoms were included in the structure factor calculation at idealized positions by using a riding model, but not refined. Images were created with the ORTEP-36.

Results and Discussion

The obtained single crystal XRD data for the grown gamma-glycine crystal are given in the table 1. The grown crystal is observed to be crystallizing in hexagonal structure with the space group $P3_2$ and the number of molecules per unit cell of gamma-glycine crystal is 3. The molecular structure of the title compound drawn at the 50% probability level and the molecular structure of the title compound as viewed down the crystallographic axis are given in the figures 1 and 2. The molecular packing of gamma-glycine crystal is shown in the figure 3. The crystal packing of the title compound forming inversion dimers viewed about b-axis is presented in the figure 4.



Fig.1:Molecular structure of gamma-glycine crystal with anisotropic displacement ellipsoids drawn at the 50% probability level

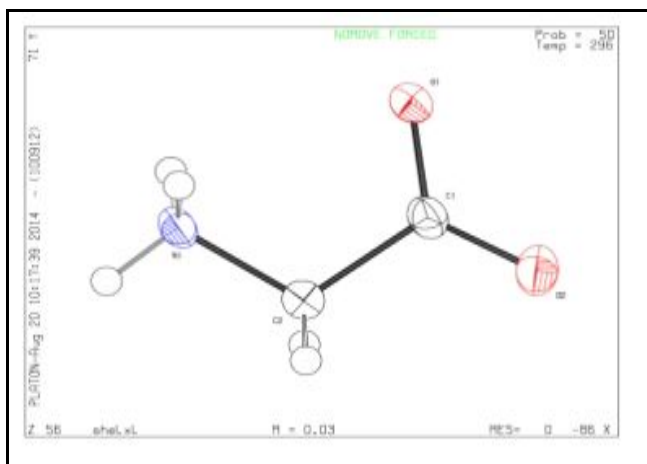


Fig.2: Molecular structure of the title compound as viewed down the crystallographic axis.

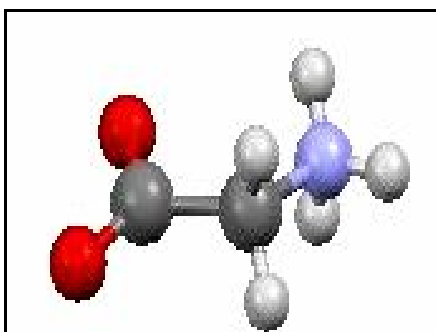


Fig.3: Molecular packing of the grown gamma-glycine crystal

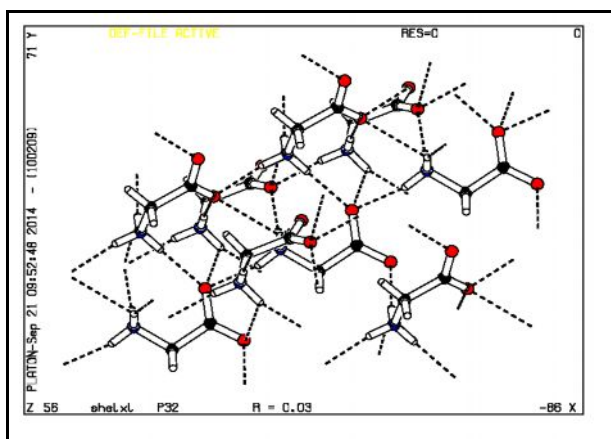


Fig. 4: The crystal packing of the title compound forming inversion dimers

The bond lengths between N(1) and H(2N) is $0.87(2)^\circ$. Similarly O(1) and C(1) is $1.2519(16)^\circ$. The another atom of O(2) and C(1) having $1.2406(18)^\circ$. The torsion angles between O(2)-C(1)-C(2)-N(1) is $166.96(13)^\circ$ and the angle between O(1)-C(1)-C(2)-N(1) is of $-15.32(17)^\circ$. The packing of the crystal is stabilized by intra and intermolecular C—H...O hydrogen bonds. It also features C—H...N an intramolecular hydrogen bond. The obtained hydrogen bonds for gamma-glycine crystal and the coordinates are provided in the table 2. The atomic coordinates and equivalent isotropic displacement parameters for gamma-glycine crystal are given in the table 3. Here in the table 3, $U(eq)$ is defined as one third of the trace of the orthogonalized U_{ij} tensor. The bond lengths [Å] and the corresponding angles [deg.] are provided in the table 4 and the anisotropic displacement parameters are given in the table 5. The anisotropic displacement factor exponent takes in the form of $-2 \pi^2 [h^2 a^{*2} U_{11} + \dots + 2 h k a^* b^* U_{12}]$. The obtained hydrogen coordinates and isotropic displacement parameters are provided in the table 6.

Table 1: Single crystal XRD data for gamma-glycine crystal.

Identification code	SHELXL
Empirical formula	C ₂ H ₅ N O ₂
Formula weight	75.07
Temperature	296(2) K
Wavelength	0.71073 Å
Crystal system, space group	Hexagonal, P3 ₂
Unit cell dimensions	a = 7.011(2) Å, alpha = 90 deg. b = 7.011(2) Å beta = 90 deg. c = 5.469(2) Å, gamma = 120 deg.
Volume	232.83(14) Å ³
Z, Calculated density	3, 1.606 Mg/m ³
Absorption coefficient	0.143 mm ⁻¹
F(000)	120
Crystal size	0.35 x 0.30 x 0.30 mm ³
Theta range for data collection	3.36 to 28.24 deg.
Limiting indices	-9<=h<=8, -8<=k<=9, -7<=l<=4
Reflections collected / unique	1435 / 610 [R(int) = 0.0241]
Completeness to theta = 28.24	99.7 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.9585 and 0.9518
Refinement method	Full-matrix least-squares on F ²
Data / restraints / parameters	610 / 1 / 59
Goodness-of-fit on F ²	0.806
Final R indices [I>2sigma(I)]	R1 = 0.0257, wR2 = 0.0670
R indices (all data)	R1 = 0.0263, wR2 = 0.0677
Absolute structure parameter	-0.1(14)
Extinction coefficient	0.46(4)
Largest diff. peak and hole	0.264 and -0.157 e. Å ⁻³

Table 2: Hydrogen bonds for gamma-glycine crystal

D-H	d(D-H)	d(H..A)	<DHA	d(D..A)	A
N1-H2N	0.875	2.101	175.24	2.973	O1 [-x+y-1, -x+1, z+1/3]
N1-H1N	0.909	1.905	166.01	2.796	O1 [x, y, z+1]
N1-H3N	0.938	1.908	157.26	2.796	O2 [-x+y, -x+1, z+1/3]

Table 3: Atomic coordinates (x 10⁴) and equivalent isotropic displacement parameters (Å² x 10³).

	x	y	z	U(eq)
N(1)	295(2)	7830(2)	5518(2)	20(1)
O(1)	119(2)	7786(2)	626(2)	25(1)
O(2)	-7(2)	4570(2)	303(2)	35(1)
C(1)	3(2)	6079(2)	1496(3)	20(1)
C(2)	-238(3)	5774(2)	4252(3)	25(1)

Table 4: Bond lengths [Å] and angles [deg.]

N(1)-C(2)	1.4693(18)
N(1)-H(2N)	0.87(2)
N(1)-H(1N)	0.91(2)
N(1)-H(3N)	0.938(19)
O(1)-C(1)	1.2519(16)
O(2)-C(1)	1.2406(18)
C(1)-C(2)	1.520(2)
C(2)-H(2A)	0.9700
C(2)-H(2B)	0.9700
C(2)-N(1)-H(2N)	112.4(13)
C(2)-N(1)-H(1N)	108.8(11)
H(2N)-N(1)-H(1N)	111.8(17)
C(2)-N(1)-H(3N)	107.5(11)
H(2N)-N(1)-H(3N)	107.5(17)
H(1N)-N(1)-H(3N)	108.6(17)
O(2)-C(1)-O(1)	125.85(14)
O(2)-C(1)-C(2)	116.64(11)
O(1)-C(1)-C(2)	117.47(12)
N(1)-C(2)-C(1)	111.92(11)
N(1)-C(2)-H(2A)	109.2
C(1)-C(2)-H(2A)	109.2
N(1)-C(2)-H(2B)	109.2
C(1)-C(2)-H(2B)	109.2
H(2A)-C(2)-H(2B)	107.9

Table 5: Anisotropic displacement parameters ($\text{\AA}^2 \times 10^3$)

	U11	U22	U33	U23	U13	U12
N(1)	26(1)	25(1)	13(1)	1(1)	0(1)	14(1)
O(1)	37(1)	25(1)	16(1)	1(1)	-3(1)	19(1)
O(2)	58(1)	36(1)	22(1)	-7(1)	-6(1)	33(1)
C(1)	22(1)	25(1)	16(1)	-1(1)	-3(1)	13(1)
C(2)	38(1)	21(1)	18(1)	1(1)	1(1)	15(1)

Table 6: Hydrogen coordinates ($\times 10^4$) and isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for the gamma-glycine crystal.

	x	y	z	U(eq)
H(2A)	-1739	4658	4639	30
H(2B)	731	5257	4835	30
H(2N)	-550(30)	8360(30)	5050(40)	29(5)
H(1N)	210(30)	7590(30)	7160(40)	26(5)
H(3N)	1750(30)	8880(30)	5120(40)	28(4)

Conclusions

Single crystals of gamma-glycine were grown by slow evaporation method using the aqueous solutions of guanidine hydrochloride for the first time. The complete crystal structure of the grown gamma-glycine was solved by single crystal XRD studies. The structure of the grown gamma-glycine crystal is elucidated as hexagonal structure with the space group $P3_2$. The NLO property of the grown gamma-glycine sample was checked by Kurtz powder technique.

Supplementary Material

Crystallographic data for the structure reported in this paper have been deposited at the Cambridge Crystallographic Data Centre (CCDC) and the allocated deposition number is **CCDC 1025258** for the title compound and can be obtained free of charge on application to CCDC 12 Union Road, Cambridge CB2 1EZ, UK (Fax: 44(1223)336-033; E-mail: deposit@ccdc.cam.ac.uk).

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