



## Molecular Structure, Vibrational Spectra, Theoretical NBO and HOMO-LUMO Analysis of Bi-Glycine Hydrobromide by DFT Method

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An organic non linear optical material of bi-glycine hydrobromide was successfully grown by slow evaporation method. The optimized molecular geometry, harmonic vibrational spectra, natural bond orbital (NBO) analysis, highest occupied molecular orbital and lowest unoccupied molecular orbital, milliken atomic charge, thermodynamic properties of zero-point vibrational energies, rotational constants, dipole moment, entropies were calculated for the title compound by density functional B3LYP method with 6.31 ++G(d,p) basis set using Gaussian 03 W program package on a intel core i3/1.6 GHz personal computer. We also recorded the FT-IR, FT Raman spectra of bi-glycine hydrobromide at room temperature.

**Keywords:** Vibrational spectra, DFT, Natural bond orbital analysis, HOMO-LUMO, Bi-glycine hydrobromide.

### INTRODUCTION

Bi-glycine hydrobromide (BGHB) and its derivatives play major role in the emerging photonic and optoelectronic technologies<sup>1-3</sup> and telecommunications, frequency mixing, electro-optic modulation, optical parameter oscillator, optical bistability<sup>4,5</sup>, medicine, photochemistry<sup>6</sup> and other applications. The investigation on the structure and fundamental vibrations of bi-glycine hydrobromide and its derivatives are still being carried out increasingly.

From the literature survey, which divulges that there is no *ab initio* and density functional wave number calculation of Bi-glycine hydrobromide to the best of our knowledge. In the present study, we were using DFT method for the calculation of the geometric parameter and vibrational spectra of Bi-glycine hydrobromide. Along with bond order analysis, natural bond orbital (NBO) analysis, highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) analysis, non-linear optical properties and thermodynamic properties of zero point vibrational energies, rotational constants, dipole moment and entropies were calculated for the title compound at B3LYP/6.31 ++G(d,p) level.

### EXPERIMENTAL

High purity glycine salt (E. Merck) and hydrobromic acid (E. Merck) were taken in the molar ratio 2:1 in deionized water

to synthesis bi-glycine hydrobromide salt. The saturated BGHB solution of pH value of 2 had been prepared using doubly recrystallized salt. The solution was filtered using sintered glass filter 1 micror porosity. The filtered solution was transferred into the petty disc and allowed to evaporate slowly at room temperature. Transparent and flawless crystals of size: 22 mm × 6 mm × 8 mm were obtained after 10 days.

The sample was prepared in slow evaporation method at room temperature. The FT-IR spectrum of the sample was recorded in the region near 4000-400 cm<sup>-1</sup> using a BRUKER IFS-66v FT IR Spectrometer at a resolution of 1 cm<sup>-1</sup> equipped with a MCT detector, a KBr beam splitter and glober source. The FT-Raman spectrum of bi-glycine hydrobromide is recorded on a BRUKER IFS-66v model interferometer equipped with FRA-106 FT Raman accessory in the 4000-100 cm<sup>-1</sup> stokes region using the 1064 nm line of Nd-YAG laser for excitation operating at 200 mw powers. The molecule bi-glycine hydrobromide was newly synthesized by Sampathkrishnan *et al.*<sup>18</sup>.

**Computational detail:** Whole calculation conducted were performed using density functional B3LYP method 6.31 ++G(d,p) basis set using Gaussian 03 W program package<sup>7</sup> on a intel core i3/1.6 Ghz personal computer for the title compound. The Geometric optimization and calculation of other parameters were carried out 6.31 ++G(d,p) basis set. In DFT method it is observed that all the stationary points are minima<sup>8</sup>. The vibrational frequency is assigned by means of

visual inspection using the Gauss view program. We have used NBO 3.1 program<sup>9</sup> in the Gaussian 03 W program package on a intel core i3/1.6 GHz personal computer. We have NBO calculation to under in intra molecular delocalization or hyper conjugation.

**Non-linear optical effect:** Non linear optical effects means, when it propagates through a material it changes the properties of the medium, such as the refractive index. In the recent year NLO materials play major role in the telecommunication, photonic, opto electronic technologies and optical computing<sup>10-12</sup>. Many organic NLO Materials composed of aromatic molecules that are substituted with  $\pi$  electron donors and acceptors which exhibit intermolecular charge transfer resulting in high SHG efficiency<sup>13</sup>.

The molecular structure of bi-glycine hydrobromide is shown in Fig. 1.

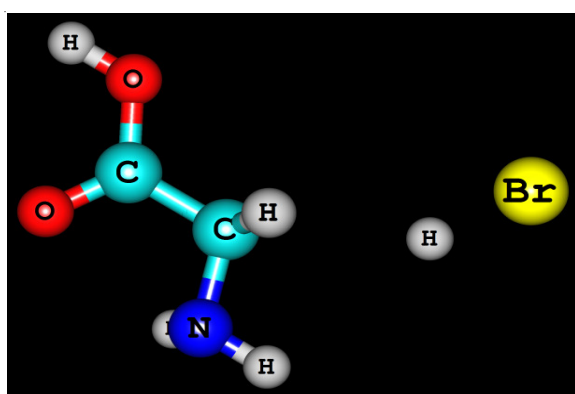


Fig. 1. Molecular structure of bi-glycine hydrobromide

The first hyperpolarizability ( $\beta_0$ ) of this novel molecular system and the related properties ( $\beta_0$ ,  $\alpha_0$ ) of bi-glycine hydrobromide are calculated by B3LYP method using 6.31 ++G(d,p) basis set, based on the finite-field approach. In the presence of electric field. The first hyper polarizability is a third-rank tensor that can be described by a  $3 \times 3 \times 3$  matrix. The 27 components of the 3D matrix can be reduced to 10 components due to the Klein man symmetry<sup>14,15</sup>. It can be given in the lower tetrahedral. The components of  $\beta$  are defined as the coefficients in the Taylor series expansion of the energy in the external electric field. When the external electric field is weak and homogenous, this expansion becomes.

$$E = E^0 - \mu_\alpha F_\alpha - 1/2 \alpha_{\alpha\beta} F_\alpha F_\beta - 1/6 \beta_{\alpha\beta\gamma} F_\alpha F_\beta F_\gamma + \dots$$

where  $E^0$  is the energy of the unperturbed molecules,  $F_\alpha$ , the field at the origin and  $\mu_\alpha$ ,  $\alpha_{\alpha\beta}$  and  $\beta_{\alpha\beta\gamma}$  are the components of dipole moment  $\mu$ , polarizability  $\alpha$ , mean polarizability  $\Delta\mu$  and the first hyperpolarizabilities  $\beta_0$  using the x, y, z components are defined as follows<sup>16,17</sup>.

$$\mu = \mu_x^2 + \mu_y^2 + \mu_z^2,$$

$$\alpha_0 = \frac{\alpha_{xx} + \alpha_{yy} + \alpha_{zz}}{3},$$

$$\Delta\alpha = 2^{1/2} \left[ (\alpha_{xx} - \alpha_{yy})^2 + (\alpha_{yy} - \alpha_{xx})^2 + 6\alpha_{xx}^2 \right]^{1/2},$$

$$\beta = (\beta_x^2 + \beta_y^2 + \beta_z^2)^{1/2},$$

$$\beta_x = \beta_{xxx} + \beta_{xyy} + \beta_{xzz},$$

$$\beta_y = \beta_{yyy} + \beta_{xyx} + \beta_{yzz},$$

$$\beta_z = \beta_{zzz} + \beta_{xxz} + \beta_{yzz}$$

Since the values of the polarizability ( $\alpha$ ) and first hyperpolarizability ( $\alpha$ ) di pole moment ( $\mu$ ) of Gaussian 03 output are reported in atomic units (a.u), the calculated values have been converted into electrostatic units (esu) ( $\alpha$ : 1 a.u =  $0.1482 \times 10^{-12}$  esu,  $\beta$ : 1 a.u =  $8.6393 \times 10^{-33}$  esu). The total molecular dipole moment and mean first hyperpolarizability of BGHB is 3.6186 Debye and  $1.12525 \times 10^{-30}$  esu respectively shown in Table-1. Total dipole moment of BGHB is approximately three times greater than that of urea. This is how non-linear properties of the molecule is confirmed.

TABLE-1  
CALCULATED ALL  $\beta$  COMPONENTS  
AND  $\beta_{tot}$  VALUE OF BI-GLYCINE HYDROBROMIDE

Parameters	B3LYP	Parameters	B3LYP
$\mu_x$	0.9191	$\beta_{xxx}$	97.0153
$\mu_y$	-0.7357	$\beta_{xxy}$	-47.733
$\mu_z$	1.3518	$\beta_{xyy}$	5.8408
$\mu$	3.2132	$\beta_{yyy}$	-12.4371
$\alpha_{xx}$	59.9763	$\beta_{xxz}$	10.1911
$\alpha_{xy}$	9.1025	$\beta_{xyz}$	-7.5744
$\alpha_{yy}$	46.1545	$\beta_{yyz}$	7.2344
$\alpha_{yz}$	-3.504	$\beta_{zzz}$	16.083
$\alpha_{zz}$	3.0188	$\beta_{yzz}$	-2.6536
$\alpha$ (esu)	$.077 \times 10^{-10}$	$\beta$ (esu)	$1.738 \times 10^{-30}$
$\Delta\alpha$ (esu)	$1.8104 \times 10^{-30}$	-	-

## RESULTS AND DISCUSSION

Sampathkrishnan *et al.*<sup>18</sup> determined the crystal structure of BGHB [(C<sub>2</sub>H<sub>5</sub>NO<sub>2</sub>)<sub>2</sub> Hbr] which is non-centro symmetric space group P2<sub>1</sub>2<sub>1</sub>2<sub>1</sub>, with the cell dimension a = 5.39 Å, b = 8.18 Å, c = 18.39 Å,  $\alpha = 90.18^\circ$ ,  $\beta = 89.88^\circ$ ,  $\gamma = 89.99^\circ$ ,  $V = 812.43$ . The optimized geometrical parameters (bond lengths and angles) by DFT, B3LYP with 6.311 ++G(d,p) as basis set are listed in Table-2. It is found that N<sub>2</sub>-H<sub>6</sub> bond length is very high and its corresponding value is 2.6402 Å. This clearly indicates that O<sub>5</sub>-H<sub>2</sub> occupy the low energy value. The next higher bond length value is 1.5132 Å. These values are found for N<sub>2</sub>-C<sub>3</sub>, H<sub>6</sub>-Br<sub>7</sub> and C<sub>1</sub>-O<sub>5</sub> and are 1.4228 Å, 1.4232 Å, 1.3595 Å, respectively. For the title compound the N-H group bond length is found at the range 2.6402-1.0022 (*i.e.*, N<sub>2</sub>-H<sub>6</sub>, N<sub>2</sub>-H<sub>8</sub>, N<sub>2</sub>-H<sub>9</sub> are 2.6402, 1.0021, 1.0022 Å respectively). It shows that the N-H bond occupies in the higher energy level. The least bond length value is 0.972. The bond lengths a value clearly indicates that this amino group are at the higher energy level.

For the title compound, the higher bond angle is found at C<sub>3</sub>-C<sub>1</sub>-O<sub>4</sub>, O<sub>4</sub>-C<sub>1</sub>-O<sub>5</sub>, C<sub>1</sub>-C<sub>3</sub>-N<sub>2</sub>, N<sub>2</sub>-C<sub>3</sub>-H<sub>10</sub>, H<sub>8</sub>-N<sub>2</sub>-H<sub>9</sub> and their corresponding values are 128.72°, 117.30°, 115.50°, 109.08° and 108.76° respectively. The least bond angle value is 106.69° and it is found at H<sub>6</sub>-N<sub>2</sub>-H<sub>8</sub>.

**Vibrational band assignments:** The maximum number of potentially active observable fundamental non-linear molecules, which contains N atoms, is equal to (3N-6) a part from

TABLE-2  
OPTIMIZED GEOMETRICAL PARAMETERS OF BGHB  
OBTAINED BY B3LYP/6-31 ++G(d,p) DENSITY  
FUNCTIONAL CALCULATIONS

Bond length	Value (Å)	Bond angle	Value (°)
C <sub>1</sub> -C <sub>3</sub>	1.5132	C <sub>3</sub> -C <sub>1</sub> -O <sub>4</sub>	128.7253
C <sub>1</sub> -O <sub>4</sub>	1.2346	C <sub>3</sub> -C <sub>1</sub> -O <sub>5</sub>	113.9657
C <sub>1</sub> -O <sub>5</sub>	1.3595	O <sub>4</sub> -C <sub>1</sub> -O <sub>5</sub>	117.3089
N <sub>2</sub> -C <sub>3</sub>	1.4338	C <sub>3</sub> -N <sub>2</sub> -H <sub>6</sub>	111.3589
N <sub>2</sub> -H <sub>6</sub>	2.6402	C <sub>3</sub> -N <sub>2</sub> -H <sub>8</sub>	111.258
N <sub>2</sub> -H <sub>8</sub>	1.0021	C <sub>3</sub> -N <sub>2</sub> -H <sub>9</sub>	111.226
N <sub>2</sub> -H <sub>9</sub>	1.0022	H <sub>6</sub> -N <sub>2</sub> -H <sub>8</sub>	106.6981
C <sub>3</sub> -H <sub>10</sub>	1.1281	H <sub>6</sub> -N <sub>2</sub> -H <sub>9</sub>	107.3429
C <sub>3</sub> -H <sub>11</sub>	1.1285	H <sub>8</sub> -N <sub>2</sub> -H <sub>9</sub>	108.7602
O <sub>5</sub> -H <sub>12</sub>	0.972	C <sub>1</sub> -C <sub>3</sub> -N <sub>2</sub>	115.5028
H <sub>6</sub> -Br <sub>7</sub>	1.4232	C <sub>1</sub> -C <sub>3</sub> -H <sub>10</sub>	107.5272
-	-	C <sub>1</sub> -C <sub>3</sub> -H <sub>11</sub>	107.3932
-	-	N <sub>2</sub> -C <sub>3</sub> -H <sub>10</sub>	109.0846
-	-	N <sub>2</sub> -C <sub>3</sub> -H <sub>11</sub>	109.1495
-	-	H <sub>10</sub> -C <sub>3</sub> -H <sub>11</sub>	107.9329
-	-	C <sub>1</sub> -O <sub>5</sub> -H <sub>12</sub>	109.7263
-	-	N <sub>2</sub> -H <sub>6</sub> -Br <sub>7</sub>	167.9443

three translational and three rotational degrees of freedom<sup>19,20</sup>. The intention of the vibrational analysis is to find vibrational modes connected with specific molecular structure of calculated compound. We have using density functional theory B3LYP level with the 6.311 ++G (d,p) basis set to calculated the vibration frequency of FT-IR, FT Raman spectra. The intricate information of vibration assignment of fundamental modes are shown in Table-3. The observed experimental FT-IR and FT-Raman spectra and simulated IR and Raman spectra at DFT B3LYP level with the 6.31 ++G(d,p) basis set are shown in Figs. 2 and 3.

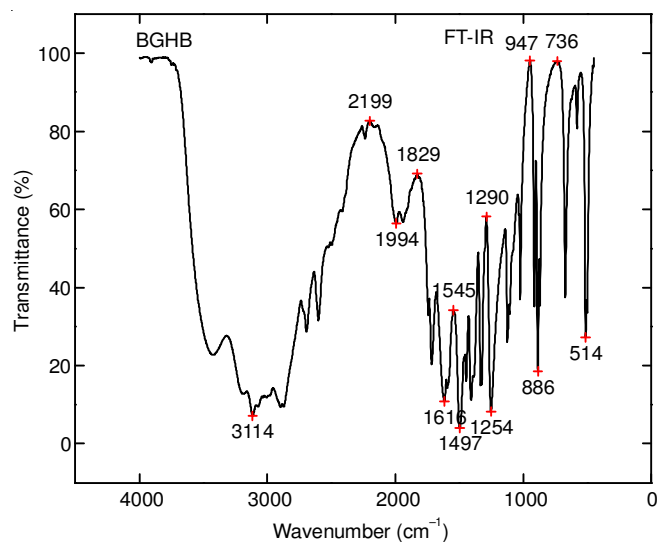


Fig. 2. Observed IR spectrum

**Amino group vibrations:** In associated aliphatic and alicyclic primary amines, the NH<sub>2</sub> antisymmetric stretching vibration occurs<sup>19,21</sup>. In dilute solution or in the vapour state, the  $\nu_{as}$  NH<sub>2</sub> appears<sup>22</sup>. Aliphatic and alicyclic primary amines in the associated state display  $\nu_{as}$  NH<sub>2</sub> in the region  $3290 \pm 30$  cm<sup>-1</sup> and at  $3350 \pm 40$  cm<sup>-1</sup> in a gas or in dilute solution. In the vibration spectra of copper complexes of L-asparagine and

TABLE-3  
OBSERVED AND CALCULATION VIBRATIONAL OF BGHB AT  
B3LYP METHOD WITH 6.311 ++G(d,p) AND BASIS SETS

Mode nos	Observed frequency (cm <sup>-1</sup> )		Frequency 6.311+G(d,p)	Assignment
	IR	Raman		
1	-	-	3597	H-N-H asymstr
1	-	3450	-	H-N-H asymstr
2	-	3400	3409	H-N-H asymstr
3	-	-	3323	H-N-H asymstr
3	3114	-	-	O-H Str
3	-	3027	-	H-C $\alpha$ -H str asym
3	-	3001	-	H-C $\alpha$ -H str asym
3	-	2984	-	H-C $\alpha$ -H str asym
3	-	2968	-	H-C $\alpha$ -H str asym
4	-	-	2799	H-C $\alpha$ -H str asym
5	-	-	2746	H-C $\alpha$ -H str asym
6	2199	-	2164	H-C $\alpha$ -H str asym
6	-	2000	-	H-C $\alpha$ -H str asym
6	1994	-	-	H-C $\alpha$ -H str asym
7	-	1713	1726	C=O
8	-	-	1602	H-N-H Sciss
8	-	1590	-	H-N-H Sciss
8	1545	-	-	H-N-H Sciss
8	1497	-	-	H-N-H Sciss
8	-	1490	-	H-N-H Sciss
9	-	1445	1444	OH Str
10	-	-	1412	OH Str
10	-	1407	-	OH Str
10	-	1324	-	H-C $\alpha$ -H Wagg
10	-	1298	-	H-C-H Twist
11	-	-	1294	H-C $\alpha$ -H Twist
11	1290	-	-	H-C $\alpha$ -H Wagg
12	-	-	1246	H-C $\alpha$ -H Wagg
12	1254	-	-	C(=O)O
13	-	-	1185	C $\alpha$ -C-O asym str
13	-	1121	-	H-N-H Twist
14	-	-	1100	C-N Amine
14	-	1101	-	C-N Amine
15	-	-	1070	C-Cstr
15	-	1030	-	C-Cstr
16	-	-	1015	C-Cstr
16	947	-	-	O-H-tor
16	886	-	-	H-C $\alpha$ -H-rock
16	-	884	-	H-C $\alpha$ -H-rock
16	-	870	-	H-C-H rock
17	-	-	840	C-O Str
18	-	-	798	H-N-H Wagg
18	736	-	-	C=O
19	-	-	623	C=O amide
20	-	-	597	C=O amide
20	514	-	-	H-C $\alpha$ -H rock
20	-	513	-	H-C $\alpha$ -H rock
21	-	-	511	C(=O)O
22	-	-	470	C(=O)O
23	-	-	455	C(=O)O
24	-	-	450	C(=O)O
25	-	-	351	C $\alpha$ -C-C sciss
25	-	342	-	C $\alpha$ -C-C sciss
26	-	-	265	N-H Tor
26	-	149	-	H-N-H rock
27	-	-	125	H-N-H rock
27	-	81	-	O=C-O twist
28	-	-	53	O=C-O twist
29	-	-	47	O=C-O twist
30	-	-	38	O=C-O twist

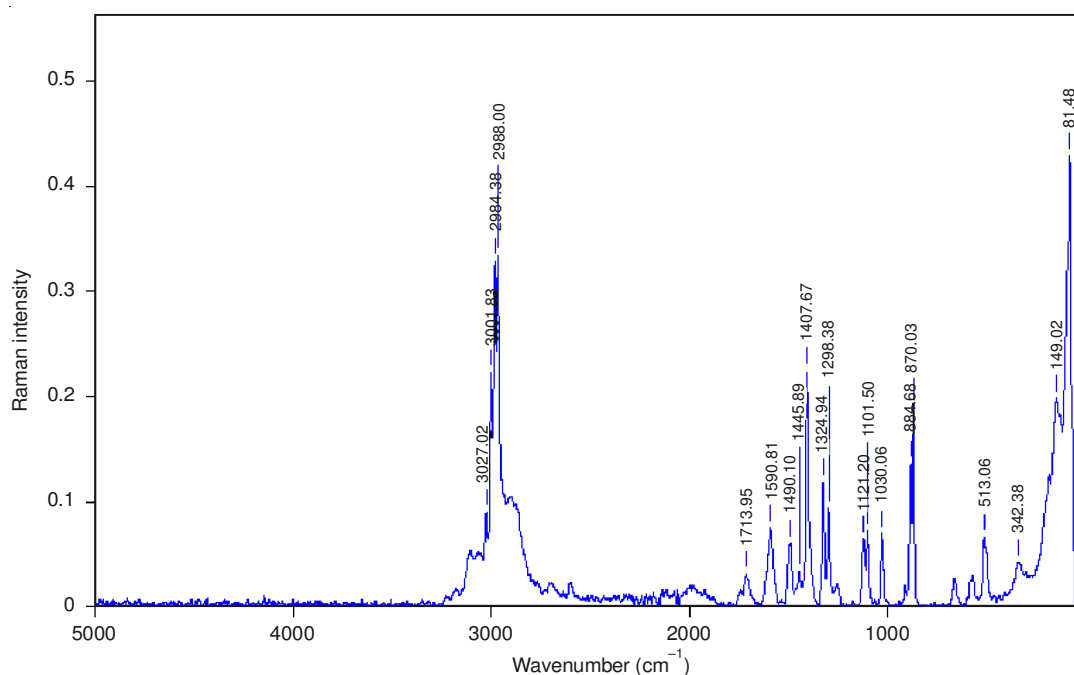


Fig. 3. Observed FTIR spectrum

L-glycine the  $\nu_{\text{as}} \text{NH}_2$  amino is reported at 3265, 3278  $\text{cm}^{-1}$  in the IR spectrum<sup>23</sup>. For this title compound we have observed  $\nu_{\text{as}} \text{NH}_2$  amino 3400  $\text{cm}^{-1}$  (Raman) and 3409, 3323  $\text{cm}^{-1}$  theoretically.

The  $\text{NH}_2$  scissoring vibration<sup>22</sup> give rise to a broad strong band in the region  $1600 \pm 50 \text{ cm}^{-1}$ . The title compound observed 1590  $\text{cm}^{-1}$  (Raman) 1602  $\text{cm}^{-1}$  theoretically. According to Roeges<sup>22</sup> the rocking, twisting  $\text{NH}_2$  mode is expected in the region  $1160 \pm 140 \text{ cm}^{-1}$ . The title compound reported  $\text{NH}_2$  twist (1121  $\text{cm}^{-1}$ ). The band 1298  $\text{cm}^{-1}$  (Raman), 1290  $\text{cm}^{-1}$  (IR), 1246  $\text{cm}^{-1}$  theoretically is assigned  $\omega/\tau \text{NH}_2$  for BGHB.

The primary amines show a characteristic very broad diffuse  $\omega \text{NH}_2$  band between 1000  $\text{cm}^{-1}$  and 700  $\text{cm}^{-1}$ , with a maximum absorption at  $840 \pm 55 \text{ cm}^{-1}$ . For the title compound 870  $\text{cm}^{-1}$  (Raman), 798  $\text{cm}^{-1}$  observed in theoretically. The  $\text{NH}_2$  torsion is expected in the region  $290 \pm 130 \text{ cm}^{-1}$  and in  $\alpha$ -saturated amines the region<sup>21,24</sup> is reduced to  $280 \pm 70 \text{ cm}^{-1}$ . Medium to weak absorption band in the unconjugated C-N linkage in primary, secondary and tertiary aliphatic amines<sup>25</sup>, appear in the region of 1250-1020  $\text{cm}^{-1}$ . The vibrations responsible for these bands involve C-N stretching coupled with the stretching of adjacent bonds in the molecule. Baran *et al.*<sup>23</sup> reported a value at around 1129  $\text{cm}^{-1}$  as C-N amino stretching frequency. For the title compound the band at 1101  $\text{cm}^{-1}$  (Raman) 1100  $\text{cm}^{-1}$  and 1070  $\text{cm}^{-1}$  (DFT) is assigned as  $\nu(\text{C-N})$  mode.

**COOH group vibrations:** The  $-\text{C}(=\text{O})\text{OH}$  group is best characterized by the OH stretch, the C=O stretch and the OH out-of-plane deformation and even by the C-O stretch and the OH in-plane deformation. The C=O stretching vibration in the spectra of carboxylic acid gives rise to strong band in the region  $1725 \pm 65 \text{ cm}^{-1}$ . In the present case 1713  $\text{cm}^{-1}$  (Raman) and 1726  $\text{cm}^{-1}$  (DFT) is observed as C=O carboxyl.

The OH in-plane deformation, coupled to the C-O stretching vibration is expected in the region  $1390 \pm 55 \text{ cm}^{-1}$ . For the title compound 1445  $\text{cm}^{-1}$  (Raman) 1407  $\text{cm}^{-1}$  (Raman), 1444  $\text{cm}^{-1}$

and 1412  $\text{cm}^{-1}$  (DFT) is observed. The C(=O)-O stretching vibration, coupled to the OH in-plane deformation, exhibits a moderate to strong band in the region  $1250 \pm 80 \text{ cm}^{-1}$ . The out-of-plane OH deformation<sup>26</sup> exhibits a moderate band in the region  $905 \pm 65 \text{ cm}^{-1}$ . For the title compound 947  $\text{cm}^{-1}$  (IR) is observed. The C=O in-plane deformation is weakly to moderately active in the region  $725 \pm 95 \text{ cm}^{-1}$ . The title compound 736  $\text{cm}^{-1}$  (IR) observed. Most carboxylic acids display C=O in the region  $595 \pm 85 \text{ cm}^{-1}$  which is in the vicinity of that of methyl and ethyl esters  $-\text{C}(=\text{O})\text{O}$  deformation or rock has a weak to moderate intensity and appears in the region  $445 \pm 120 \text{ cm}^{-1}$ . The band 947  $\text{cm}^{-1}$  (IR) is assigned as OH of carboxylic group. The deformation C=O bands are calculated to be at 736  $\text{cm}^{-1}$  (Raman) and 23  $\text{cm}^{-1}$ , 597  $\text{cm}^{-1}$  theoretically.

**CH<sub>2</sub> group vibrations:** The asymmetric stretch  $\nu_{\text{as}} \text{CH}_2$  symmetric stretch  $\nu_{\text{as}} \text{CH}_2$ , scissoring vibrations  $\text{CH}_2$  and wagging vibration  $\nu_{\text{as}} \text{CH}_2$  appear in the region  $3000 \pm 85 \text{ cm}^{-1}$ ,  $2965 \pm 30$ ,  $1455 \pm 55$  and  $1350 \pm 85 \text{ cm}^{-1}$  respectively<sup>22,27</sup>. Absorption arising from C-H stretching in alkenes occurs in the general region<sup>25</sup> of 3000-2840  $\text{cm}^{-1}$ . The position of the C-H stretch vibrations are among the stable in the spectrum, for the four  $\text{CH}_2$  groups, the asymmetric  $\text{CH}_2$  stretch bands at 3027, 3001, 2984, 2968  $\text{cm}^{-1}$  in the Raman spectrum. The in-plane deformations of  $\text{CH}_2$  bands are observed 1497  $\text{cm}^{-1}$  (IR), 1490  $\text{cm}^{-1}$  (Raman). The wagging mode of  $\omega \text{CH}_2$  group observed at 1324  $\text{cm}^{-1}$  in the Raman spectrum. The twisting mode  $\tau \text{CH}_2$  group are observed 1298  $\text{cm}^{-1}$  (Raman), 1290  $\text{cm}^{-1}$  (IR), 1294 and 1246  $\text{cm}^{-1}$  (DFT). The rocking modes<sup>22</sup>  $\rho \text{CH}_2$  is expected in the range  $895 \pm 85 \text{ cm}^{-1}$ , the band at 886  $\text{cm}^{-1}$  (IR), 884  $\text{cm}^{-1}$  (Raman), 870  $\text{cm}^{-1}$  (Raman) are assigned as  $\rho \text{CH}_2$  modes for the title compound. The torsional modes are seen in the low wave number range<sup>22</sup>.

**Other vibrations:** Baran *et al.*<sup>23</sup> reported the CC stretching bands in the range 1117-870  $\text{cm}^{-1}$  and CC bending modes below 400  $\text{cm}^{-1}$ . In this compound 1101  $\text{cm}^{-1}$ , 1030  $\text{cm}^{-1}$  (Raman)

and 1070 cm<sup>-1</sup>, 1051 cm<sup>-1</sup> (DFT) are observed. The bending modes δ CCC is calculated to be at 342 cm<sup>-1</sup> (Raman), 351 cm<sup>-1</sup> (DFT) are observed.

**NBO analysis:** NBO analysis provides the most accurate possible 'natural Lewis structure' picture of Φ, because all orbital detail are mathematically chosen to include the highest possible percentage of the electron density. A useful aspect of the NBO method is that it gives information about interaction in both filled and virtual orbital spaces that could enhance the analysis or intra and intermolecular interactions.

The second order Fock matrix was carried out to evaluate the donor-acceptor interactions in the NBO analysis<sup>28</sup>. The interactions result is a loss of occupancy from the localized NBO of the idealized Lewis structure into an empty non-Lewis orbital. For each donor (i) and acceptor (j), the stabilization energy E(2) associated with the delocalization i → j is estimated as

$$E(2) + \Delta E_{ij} = q_i \frac{F_{ij}^2}{\epsilon_j - \epsilon_i}$$

where q<sub>i</sub> is the donor orbital occupancy and are ε<sub>i</sub> and ε<sub>j</sub> diagonal elements and F(i, j) is the off diagonal NBO Fock matrix element.

Natural bond orbital analysis provides an efficient method for studying intra and intermolecular bonding and interaction among bonds and also provides a convenient basis for investigating charge transfer or conjugative interaction in molecular systems. Some electron donor orbital, acceptor orbital and the interacting stabilization energy resulted from the second order micro-disturbance theory<sup>29,30</sup>. The larger the E(2) value, the more intensive is the interaction between electron donors and electron acceptors, *i.e.* the more donating tendency from electron donors to electron acceptors and the greater the extent of conjugation of the whole system. Delocalization of electron density between occupied Lewis-type (bond or lone pair) NBO orbitals and formally unoccupied (antibond or Rydberg) non-Lewis NBO orbitals correspond to a stabilizing donor-acceptor interaction. NBO analysis has been performed on the molecule at the DFT/B3LYP/6.311 ++G(d,p) level in order to elucidate the intramolecular, rehybridization and delocalization of electron density within the molecule.

The intra-molecular interaction is formed by the orbital overlap between σ(C<sub>1</sub>-C<sub>3</sub>) and σ\*(C<sub>1</sub>-O<sub>4</sub>) which results into intramolecular charge transfer causing stabilization of the system. These interactions are observed as increase in electron density (ED) in C-C anti bonding orbital that weakens respective bonds<sup>31</sup>. The electron density of glycine HBr ring C<sub>3</sub>-C<sub>4</sub> is 1.94e. The most important interaction in the title compound having lone pair C<sub>1</sub> with anti-bonding O<sub>5</sub>-H<sub>12</sub> and C<sub>1</sub>-O<sub>5</sub>, results the stabilization of 0.83 and 0.51 kJ/mol, respectively. The most important interaction in the title compound having lone pair C<sub>3</sub> with anti-bonding C<sub>1</sub>-O<sub>5</sub> results the stabilization of 0.56 kJ/mol. The most important interaction in the title compound having lone pair N<sub>2</sub> with anti-bonding C<sub>3</sub>-H<sub>11</sub> and C<sub>1</sub>-C<sub>3</sub> results the stabilization of 7.72 and 1.36 kJ/mol, respectively. The most important interaction in the title compound having lone pair O<sub>4</sub> with anti-bonding C<sub>1</sub>-O<sub>5</sub> and C<sub>1</sub>-C<sub>3</sub> results the stabilization of 33.31 and 19.64 kJ/mol, respectively. The most

important interaction in the title compound having lone pair O<sub>5</sub> with anti-bonding C<sub>1</sub>-O<sub>4</sub> and C<sub>1</sub>-C<sub>3</sub> results the stabilization of 1.11 and 0.90 kJ/mol, respectively. The E<sup>(2)</sup> value is chemically significant and can be used as a measure of the intramolecular delocalization and these results are presented in Table-4.

TABLE -4  
SECOND-ORDER PERTURBATION THEORY ANALYSIS  
OF FOCK MATRIX IN NBO BASIS CORRESPONDING  
TO THE INTRAMOLECULAR OF BGHB

Donor NBO (i)	Acceptor NBO (j)	E <sup>(2)a</sup> (kJ/mol)	E(j)-E(i) <sup>b</sup> (a.u.)	F(i,j) <sup>c</sup> (a.u.)
σ(C <sub>1</sub> -C <sub>3</sub> )	σ*(C <sub>1</sub> -O <sub>4</sub> )	0.90	1.25	0.030
σ(C <sub>1</sub> -O <sub>4</sub> )	σ*(C <sub>1</sub> -C <sub>3</sub> )	1.27	1.48	0.039
σ(C <sub>1</sub> -O <sub>5</sub> )	σ*(N <sub>2</sub> -C <sub>3</sub> )	0.61	1.35	0.026
σ(N <sub>2</sub> -C <sub>3</sub> )	σ*(C <sub>1</sub> -C <sub>3</sub> )	0.54	1.12	0.022
σ(N <sub>2</sub> -H <sub>8</sub> )	σ*(C <sub>1</sub> -C <sub>3</sub> )	3.66	0.99	0.055
σ(N <sub>2</sub> -H <sub>9</sub> )	σ*(C <sub>3</sub> -H <sub>10</sub> )	3.04	1.01	0.050
σ(C <sub>3</sub> -H <sub>10</sub> )	σ*(C <sub>1</sub> -O <sub>4</sub> )	1.61	1.10	0.038
σ(O <sub>5</sub> -H <sub>12</sub> )	σ*(C <sub>1</sub> -C <sub>3</sub> )	4.07	1.16	0.062
LP2C <sub>1</sub>	σ*(O <sub>5</sub> -H <sub>12</sub> )	0.83	10.61	0.084
LP2C <sub>1</sub>	σ*(C <sub>1</sub> -O <sub>5</sub> )	0.51	10.55	0.67
LP2C <sub>3</sub>	σ*(C <sub>1</sub> -O <sub>5</sub> )	0.56	10.45	0.070
LP2N <sub>2</sub>	σ*(C <sub>3</sub> -H <sub>11</sub> )	7.72	0.67	0.064
LP2N <sub>2</sub>	σ*(C <sub>1</sub> -C <sub>3</sub> )	1.36	0.65	0.027
LP2O <sub>4</sub>	σ*(C <sub>1</sub> -O <sub>5</sub> )	33.31	0.60	0.128
LP2O <sub>4</sub>	σ*(C <sub>1</sub> -C <sub>3</sub> )	19.64	0.63	0.101
LP2O <sub>5</sub>	σ*(C <sub>1</sub> -O <sub>4</sub> )	8.19	1.11	0.085
LP2O <sub>5</sub>	σ*(C <sub>1</sub> -C <sub>3</sub> )	0.90	0.90	0.026

E<sup>(2)a</sup> means energy of hyperconjugative interaction; <sup>b</sup>Energy difference between donor and acceptor i and j NBO orbital; <sup>c</sup> F(i,j) is the Fock matrix element between i and j NBO orbitals

**HOMO and LUMO analysis:** The higher occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) are the main orbitals that take part in chemical stability<sup>32</sup>. The HOMO represents the ability to donate an electron LUMO as an electron acceptor represents the ability to obtain an electron<sup>33</sup>. The electron transition absorption corresponds to the transition from the ground to the first excited state and is mainly described by an electron excitation from the HOMO to the LUMO. HOMO and LUMO energies calculated by B3LYP/6.311 ++G(d,p) method as shown below. The plots of highest HOMO and LUMO are shown in Fig. 4.

HOMO energy (B3LYP) = -11.724 eV

LUMO energy (B3LYP) = 0.399 eV

HOMO-LUMO energy gap (B3LYP) = 12.123 eV

**Mulliken atomic charges:** Mulliken atomic charge calculation has an important role in the application of quantum chemical calculation to molecular system<sup>34</sup>. Because of atomic charges affect dipole moment, polarizability, electronic structure and more a lot of properties of molecular systems. The calculated Mulliken charge values are listed in Table-5. The charge values with 6-31 ++G(d,p) basis set due to polarization.

The charge of C<sub>3</sub> atom is 0.502 electrons for BGHB molecule. In amino group, the H<sub>5</sub> and H<sub>4</sub> atom accommodate less positive charge and become less acidic. These lead to C<sub>3</sub> and C<sub>4</sub> become high positive and become high acidic as compared to C<sub>2</sub>.

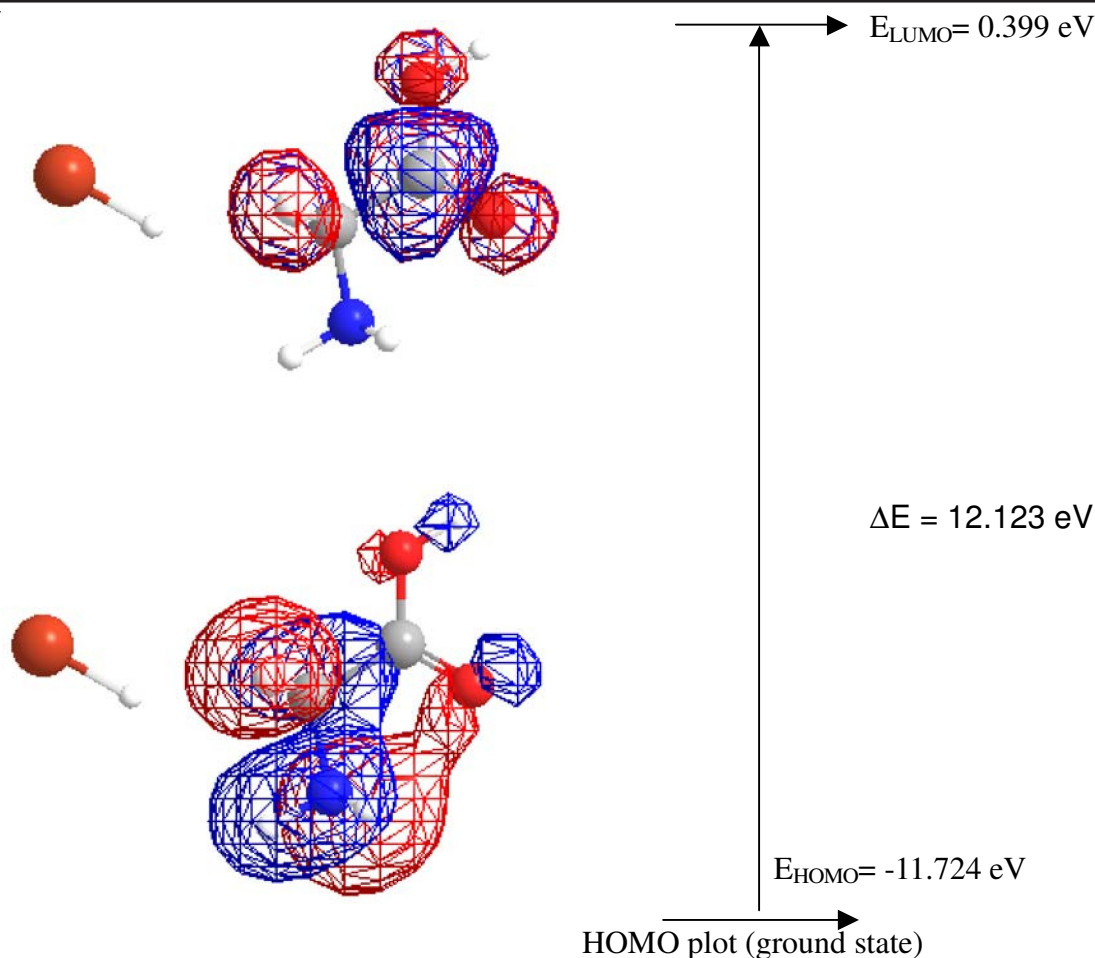


Fig. 4. Frontier molecular orbital (HOMO and LUMO) of Bi-glycine Hydrobromide. LUMO plot (first excited state)

TABLE-5  
ATOMIC CHARGE FOR OPTIMIZED GEOMETRY  
OF BGHB AT B3LYP/6.31++ G(d,p) LEVEL

Atom No	Atomic charge (e)	Atom No	Atomic charge (e)
C1	0.502	H4	0.187
N1	-0.632	H5	0.15
C2	-0.213	H6	0.401
O1	-0.378	C3	0.502
O2	-0.567	N2	-0.07
H1	0.088	C4	0.125
Br1	-0.1	O3	-0.378
H2	0.273	O4	-0.166
H3	0.288	Br2	-0.012

**Thermodynamic parameters:** Over and above the thermodynamic parameters of BGHB is present in Table-6 the basis of vibration analysis B3LYP/6.311 ++G(d,p) level at this scale factors have been recommended<sup>35</sup> for an accurate prophecy in determining the Zero-point vibrations energy (ZPVE), rotational constants, dipole moment and entropy  $S_{vib}(T)$ . The vibration in the ZPVE's appeared to be insignificant.

### Conclusion

The new organic NLO material from the amino acid family, *viz.* bi-glycine hydrobromide (BGHB) was grown by slow evaporation method. The crystal structure of BGHB is manifested using X-ray diffraction data. The FT-IR, FT-Raman spectra were recorded and detailed vibrational assignment

TABLE-6  
THEORETICALLY COMPUTED ENERGIES (a.u.), ZERO-POINT  
VIBRATIONAL ENERGIES (Kcal mol<sup>-1</sup>), ROTATIONAL  
CONSTANTS (GHz), ENTROPIES (cal mol<sup>-1</sup> K<sup>-1</sup>), DIPOLE  
MOMENT ( $\mu$ ) AND ROTATIONAL TEMPERATURE (K)

Thermo dynamical parameters	B3LYP6-31G ++(d,p) values
Total energy	-419.6749
Zero point energy (Joules/mol) (Kcal/Mpl)	245731.6 58.73127
Rotational Constants	4.30033 0.49354 0.44454
Zero-point correction (Hartree/Particle)	0.093594
Thermal correction to energy	0.100858
Thermal correction to enthalpy	0.101803
Thermal correction to Gibbs free energy	0.059111
Entropy	
Total	58.44
Translational	0.889
Rotational	0.889
Vibrational	56.662
Dipole moment	3.2132

using DFT method with 6.31 ++(d,p) basis set were presented for BGHB. The FT-IR and FT-Raman spectrum were theoretically and experimentally also correlated. Using theoretical spectrum, the bond angle and bond length were calculated. Dipole moment, mean polarizability and first order hyper

polarizability were determined with which the non-linear optical behaviour of the title molecule was investigated. HOMO LUMO orbital localization and NBO analysis also confirmed these NLO properties with the help of intermolecular charge transfer.

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