Single crystal X-ray diffraction, Hirshfeld surface analysis and DFT studies of Bis(L-Serinium) oxalate dihydrate (BLSOD)

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Abstract. Bis(L-serinium) oxalate dihydrate (BLSOD) crystals synthesized and structure derived from single crystal x-ray diffraction analysis and compared with early reported BLSOD. Compared to the reported structure the present structure has two new C-H…O hydrogen bonding. The hydrogen bonding interactions of O•••H (69.6%), H•••H (24%), C•••H (2.7%), C•••O (1.6%) and O•••O (2.1%), are derived from the Hirshfeld surface analysis. The grown crystals characterized by Fourier Transform Infrared (FTIR) and Ultraviolet (UV) spectrum. The optimized structure, HOMO-LUMO, NBO and NLO properties of BLSOD were calculated and compared with early reported BLSOD structure using B3LYP method with 6-31G basis set as provided with Gaussian 5.0 software. The DFT theoretical calculation indicates the new change in the bonding interaction improved the NLO property compared to early reported structure of BLSOD. This may be due to the change in the molecular orientation.

1. Introduction

L-serine has a comparable framework crystal structure with a similar side chain CH₂OH to those of L-alanine, DL-alanine, L-cysteine. This side chain associated with the production of strong intermolecular O-H…O hydrogen bonds [1,2,3]. The crystal structure of L-serine monohydrate at ambient pressure consists of H-bonded layers of zwitterionic serine molecules connected to hydrate molecules through H-bonds. In this case, the hydrate molecules act as donors to oxygen atoms on carboxylate and alcohol groups in separate layers [4]. In the year 2013 the crystal structure of Bis (L-serinium) oxalate dihydrate: polymorph II reported [5] and the structure refined with anisotropic displacement parameters for all non H atoms, due to the charged moieties, the structure classified as a molecular salt. Intermolecular C—H…O, O—H…O and N+—H…O hydrogen bonds connects the components of the structure. The L-serinium cations and oxalate anions build a network of channels in [100] direction, packed with the hydrate molecules of crystallization. Our aim to report the change in the hydrogen bonding in the crystal packing of Bis (L-serinium) oxalate dehydrate (BLSOD) using Hirsfeld surface analysis and reporting the comparative density functional theory DFT details between newly synthesized crystal and early reported crystal structure of Bis (L-serinium) oxalate dihydrate.
2. Materials and methods

The crystal synthesized by the procedure reported in the early reported work [5] and the grown crystal shown in fig 1. Single-crystal X-ray diffraction data for the BLSOD crystal collected from Bruker AXS Kappa APEX II CCD Diffractometer using Mo Kα radiation (λ = 0.71073 Å, θmax = 28.2⁰) at 296 K. By direct method, the single crystal X-ray data and the structure were solved and refined over full-matrix least-squares method on F² using the CRYSTALS software version 14.61 crystallographic software package [6, 7]. The data were corrected for absorption using the multi-scan technique [8]. FTIR spectrum was recorded using Perkin – Elmer FTIR spectrophotometer over the range of 400 cm⁻¹ – 4000 cm⁻¹ at room temperature. The UV absorbance spectrum of the BLSOD crystal in the region of 200 - 1100 nm measured using Perkin Elmer- Lambda 35 UV spectrometer.

The crystal structure of BLSOD derived from single X-ray data and the early reported structure were compared with the optimized structure computed by using the B3LYP method with 6-31G basis set as provided with Gaussian 5.0 software [9]. The calculated molecular geometries of the title compound have been compared with the experimental data. Likewise, the Mulliken atomic charges, molecular electrostatic potential analysis (MEP) and the Frontier Molecular Orbital (FMO) analysis of the title compound were also investigated by theoretical calculations.

Figure 1. The title compound BLSOD grown crystal

3. Results and discussion

3.1 Single crystal X-ray diffraction analysis

Serine is a α-amino acid; it has indispensable applications in the field of biology such as Protein biosynthesis. Beside serine, there are different complexes of amino acids that exhibit nonlinear optical (NLO) properties. When they coordinated with an H-atom donor (such as dicarboxylic acids), it can appear as a cation (Serinium ion), with a net positive charge on the amino and a carboxyl group. Oxalic acid is the basic dicarboxylic acid, and it can exist in the form of oxalate, semioxalate or oxalic acid. The single-crystal X-ray diffraction structure of bis (L-serinium) oxalate dihydrate was reported [5], which data collected at 90K (-183.15⁰C).
This room temperature X-ray study showed the presence of short bonds and the absence of strong hydrogen bonds. This encourages us to perform X-ray diffraction on BLSOD crystals to investigate the possibility of any phase transitions due to the hydrogen disorder in these crystals. In the case of very short hydrogen bonds (2.52–2.58 Å), the H-bond could be asymmetric (the H atom is closer to one of the O atoms) or symmetric (the H atom is exactly in the center) or on either side of the bond center dynamically disordered over two positions.

X-ray studies and theoretical calculations were also performed to obtain a complete picture of the bonding in the BLSOD crystal structure.

Our analysis differs from earlier work [5] due to the following reason. The guessed inputs of hydrogen bond information result in intensity variation of reflection. This will have different kl values in hkl assignments. Additionally small difference in lattice parameter can also lead to different intensity distribution and assignment of hkl.

The asymmetric unit consists of two L-serine molecule in the cationic form with a positively charged amino group, one oxalate molecule in anionic form and two hydrate molecule. The oxalic acid molecule occurs as a doubly charged oxalate anion and two L-serinium molecules lie across an inversion center in the crystal with respect to oxalate molecule (Fig. 2 present work). In the packed crystal structure, an oxalate ion interacts with two L-serinium ions (Fig. 3 present work).

Table 2 shows the H-bond parameters measured in the present complex. The amine NH group of L-serinium forms a very strong H-bond (2.361Å) with an O atom of the doubly ionized oxalate molecule. It can also be seen that this hydrogen bond is asymmetric, i.e. the H atom is closer to the L-serinium ion. The two amino H atoms (H1 and H2) of L-serinium make a three-centered or bifurcated hydrogen bond (Table 2).

The amino H atoms of one of the L-serinium makes one hydrogen bond with the hydroxyl O15 atom of hydrate molecule and two hydrogen bonds to the carbonyl O4 atom of the oxalate molecule. Likewise, the amino H atom of another L-serinium makes one hydrogen bond with the hydroxyl O13 atom of hydrate molecule and two hydrogen bonds to the carbonyl O1 and O5 atom of the oxalate anion. In turn each O atom of the oxalate anion turns into an acceptor of four H-bonds. Therefore, the protonated L-serine molecules are connected by N-H...O hydrogen bonds and form a three dimensional network along all three principal axes, as given in Fig. 3.

The hydroxyl O6 and O7 atoms of one of the L-serinium form two H-bonds with the carbonyl O3 and O1 atom of the oxalate anion. The other hydroxyl O2 and O8 atoms of L-serinium form two H-bonds with the carbonyl O5 and O3 atom of the oxalate anion; these bonds fall in the normal category of O-H...O interactions.

In addition, C-H...O bonds also have been noticed for both C-H atoms of the L-serinium ion.
Figure 2.
I Molecular structure of the BLSOD (Early reported work) in a axis
II Molecular structure of the BLSOD (Present work) in a axis

Figure 3.
I Crystal packing of the Bis BLSOD (Early reported work) in a axis
II Crystal packing of the BLSOD (Present work) in a axis

A comparative single crystal X-ray diffraction data with earlier reported structure [5] tabulated in table 1. Hydrogen bonding interactions of the present work shown in table 2.

Table 1. Crystal data of title compound

| BLSOD (Early reported work) | BLSOD (Present work) |
|----------------------------|----------------------|
| 2C₃H₆NO₃⁺·C₂O₄²⁻·2H₂O     | C₄H₂₀N₂O₁₂           |
| \( M_r = 336.26 \)          | \( M_r = 336.25 \)    |
| Monoclinic, \( P2_1 \)      | Monoclinic, \( P2_1 \) |
| \( a = 5.1524 \ (2) \ \text{Å} \) | \( a = 5.1840 \ (7) \ \text{Å} \) |
| \( b = 11.1467 \ (4) \ \text{Å} \) | \( b = 11.1972 \ (19) \ \text{Å} \) |
| \( c = 12.4478 \ (5) \ \text{Å} \) | \( c = 12.535 \ (2) \ \text{Å} \) |
| \( \beta = 99.967 \ (4)° \) | \( \beta = 100.659 \ (7)° \) |
$V = 704.12 \pm (5) \, \text{Å}^3$

$Z = 2$

$F_{000} = 356$

$D_\chi = 1.586 \, \text{Mg m}^{-3}$

Mo $K\alpha$ radiation

$\lambda = 0.71073 \, \text{Å}$

Cell parameters from 8206 reflections

$\theta = 1.7^{\circ} - 26.4^{\circ}$

$\mu = 0.15 \, \text{mm}^{-1}$

$T = 90 (2) \, \text{K} (-183.15^{\circ}C)$

Needle, colourless

$0.28 \times 0.10 \times 0.08 \, \text{mm}$

Data collection

Agilent Xcalibur Opal diffractometer

Monochromator: graphite

$T = 90(2) \, \text{K}$

$\omega$ scans

Absorption correction: multi-scan

[SCALE3 ABSPACK (Blessing, 1995) and CrysAlis PRO (Agilent, 2012)]

$T_{\text{min}} = 0.980$, $T_{\text{max}} = 1.000$

17202 measured reflections

2876 independent reflections

$R_{\text{int}} = 0.030$

$\theta_{\text{max}} = 26.4^{\circ}$

$\theta_{\text{min}} = 1.7^{\circ}$

$h = -6$ $6$

$k = -13$ $13$

$l = -15$ $15$

Refinement

Refinement on $F^2$

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.032$

$wR(F^2) = 0.065$

$S = 1.01$

2876 reflections

217 parameters

5 restraints

Primary atom site location:---

Hydrogen site location:---

H atoms treated by a mixture of independent and constrained refinement

$w = 1/[(\sigma^2(F^2) + (0.0288P)^2)]$

$P = (F_o^2 + 2F_c^2)/3$

Refinement on $F^2$

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.035$

$wR(F^2) = 0.077$

$S = 0.92$

1813 reflections

110 parameters

27 restraints

Primary atom site location: Other

Hydrogen site location: difference Fourier map

H atoms treated by a mixture of independent and constrained refinement

Method = Modified Sheldrick $w = 1/[(\sigma^2(F^2) + (0.0632P)^2)]$

$P = (F_o^2 + 2F_c^2)/3$
where \( P = (\max(F_o^2,0) + 2F_c^2)/3 \)

\[ (\Delta/\sigma)_{\text{max}} < 0.001 \]
\[ \Delta \rho_{\text{max}} = 0.17 \text{ e Å}^{-3} \]
\[ \Delta \rho_{\text{min}} = -0.17 \text{ e Å}^{-3} \]

Extinction correction: none

Extinction correction: n/a

### Table 2. Hydrogen-bond geometry (Å, °)

| D—H···A        | D—H  | H···A | D···A  | D—H···A |
|----------------|------|------|-------|--------|
| C18—H181···O10\( ^i \) | 1.00 | 2.52 | 3.431 (3) | 152 (1) |
| C20—H201···O11\( ^ii \) | 0.97 | 2.58 | 3.360 (3) | 137 (1) |
| N9—H93···O4\( ^iii \) | 0.903 | 2.142 | 3.036 (3) | 170 (2) |
| N9—H92···O13\( ^iv \) | 0.917 | 1.917 | 2.827 (3) | 171.6 (19) |
| N12—H122···O15\( ^v \) | 0.876 | 1.983 | 2.851 (3) | 170 (2) |
| N12—H123···O1\( ^v \) | 0.910 | 1.961 | 2.794 (3) | 151 (2) |
| N12—H123···O5\( ^v \) | 0.910 | 2.361 | 3.052 (3) | 133 (2) |
| N12—H121···O5\( ^vi \) | 0.900 | 2.006 | 2.822 (3) | 150 (2) |
| N9—H91···O4\( ^iv \) | 0.907 | 2.045 | 2.945 (3) | 171.4 (19) |
| O15—H152···O2\( ^vii \) | 0.818 | 1.972 | 2.774 (3) | 166 (4) |
| O13—H132···O8\( ^viii \) | 0.835 | 1.931 | 2.746 (3) | 165 (4) |
| O15—H151···O13\( ^vii \) | 0.822 | 2.104 | 2.924 (3) | 176 (4) |
| O13—H131···O15\( ^vii \) | 0.813 | 2.136 | 2.938 (3) | 169 (4) |
| O6—H61···O3\( ^i \) | 0.838 | 1.715 | 2.546 (3) | 171 (3) |
| O7—H71···O1 | 0.855 | 1.660 | 2.514 (3) | 178 (3) |
| O7—H71···C16 | 0.855 | 2.503 | 3.279 (3) | 151 (3) |
| O2—H21···O5\( ^v \) | 0.839 | 2.008 | 2.822 (3) | 163 (3) |
| O8—H81···O3\( ^iii \) | 0.829 | 1.984 | 2.796 (3) | 166 (3) |

Symmetry codes: (i) \( x-1, y, z \); (ii) \( x+1, y, z \); (iii) \( -x+3, y-1/2, -z+1 \); (iv) \( -x+2, y-1/2, -z+1 \); (v) \( -x+1, y+1/2, -z \); (vi) \( -x+2, y+1/2, -z \); (vii) \( x+1, y-1, z \); (viii) \( x-1, y+1, z \); (ix) \( x, y+1, z \).

### 3.2 Hirshfeld surface analysis

The Hirshfeld surface analysis explores the intermolecular interactions of BLSOD crystal by crystal explorer 3.1 software. Figure 4 shows Hirshfeld surfaces map for BLSOD crystal with the shape index property. The complete fingerprint plot for BLSOD crystal and the contribution of all types of interaction shown in this figure 4. The red contacts indicate the inter molecular interactions with distances closer than the sum of the Van der Waals radii, at the same time as white shows contacts near the Van der Waals separation, and blue depicts longer contacts [10,11].
Figure 4. (I a) Hirshfeld surfaces of BLSOD (Early reported work) mapped with dnorm, shape index and curvedness.

(II a) Hirshfeld surfaces of BLSOD (Present work) mapped with dnorm, shape index and curvedness.

(I b) Two-dimensional fingerprint plots of the intermolecular contacts of BLSOD (Early reported work) resolved into (i)O···H/H···O, (ii)H···H, (iii)C···H/ H···C, (iv)O···O, (v)C···O/O···C respectively.

(II b) Full Two-dimensional fingerprint plots of the intermolecular contacts of resolved into (i)O···H/H···O, (ii)H···H, (iii)C···H/ H···C, (iv)O···O, (v)C···O/O···C respectively.

The deep red colour indicates hydrogen-bonding contact existence of a CH•••O H-bond (between H2O1 and O11). The other colour spots are detected due to the presence of other close contacts, such as C•••H, C•••O, O•••H, O...O and H•••H. The fingerprint plots of BLSOD dominated by O•••H (69.6%) and H•••H (24%) contacts. The surplus area of the fingerprint plot is occupied by C•••H (2.7%), C•••O (1.6%) and O•••O (2.1%) contact regions. The contribution from C•••H contacts (2.7%) results in a symmetrical pair of wings as shown in fig 4 (II a) and (II b). In the present work, H•••O contacts, H-bond interactions, exist as two sharp symmetric spikes in the two dimensional fingerprint plot. The presence of these long spikes is feature of strong hydrogen bonds.

From the 3 (I a) and (II a) each opposite side of central molecule oxalic acid has a set of L-serinium cation and hydrate molecules. In this structure with respect to oxalic acid L-serinium and hydrate molecules are arranged in an inversion centre in the present work of BLSOD. But in the early reported structure of BLSOD the two hydrate molecules are focused on one side of the oxalic acid molecule. These changes may be due to the nucleation formation during the experimental process.

3.3 FTIR spectrum analysis

Fourier Transform Infrared spectroscopy (FT-IR) is one of the most reliable tools for identification of functional groups in organic, inorganic and polymeric materials. Figure 5 shows the FTIR spectrum of BLSOD (present work) crystal. The band at 3421 cm⁻¹ is assigned to NH₃+ asymmetric stretching vibration in the IR spectrum. Medium bands discovered at 2953 cm⁻¹ and 2316 cm⁻¹ respectively, can be assigned to the CH stretching vibration mode. The CH bending
vibration is identified at 1247 cm$^{-1}$. The carboxyl group is generally identified by C–O stretching at 1732 cm$^{-1}$ to 1625 cm$^{-1}$ in the FT-IR spectrum.

Figure 5, FTIR spectrum of BLSOD (present work)

3.4 UV-Vis spectrum analysis

The UV absorbance spectrum of BLSOD crystal in the region of 200-1100 nm measured using Perkin Elmer- Lambda 35 Ultraviolet spectrophotometer. The absorbance spectrum of BLSOD (present work) crystal shown in Fig.6. The lower cutoff wavelength of BLSOD crystals is found to be 224 nm. There is a group strong absorption between the wavelengths of 224 to 332nm, thereafter no absorption till 1100nm. The broad transmission range in the whole visible region and non-centro symmetric nature, exhibiting non-linear properties of the crystal and it is a very favorable property in the applications of optoelectronics. The cutoff wavelength of pure L-serine is 208 nm. The transition at 224 nm may be as a reason of $\pi-\pi^*$ transition of the crystal.

In semiconductors, the absorption coefficient near the fundamental edge depends on the energy of the photon and is expressed by Tauc’s equation given by

$$(\alpha h\nu) = B(h\nu - E_g)^m,$$

Where $B$ is the absorption coefficient, $E_g$ is the optical band gap energy, $h$ is Planck’s constant, $\nu$ is the frequency of incident photon, and $m$ is an index which based on the electronic transition. The value of $m$ is $\frac{1}{2}$ for allowed direct transition and 2 for indirect transition. Optical transitions of the BLSOD under study are direct one. In figure 6, the Tauc’s plot of the optical absorption spectrum measured from the UV spectrum at room temperature for the BLSOD crystal. Thus the calculated band gap of the title compound is 5.03 eV.

For nondoped C60 which perform as an organic semiconductor since its energy band gap 4.6eV. The value of energy band gap increased positively when it is doped with metal oxides [12]. Thus BLSOD crystal has completely organic elements with energy band gap 5.03 eV. Based on the
literature review, we conclude that BLSOD will act as a potential candidate of organic semiconductor, which can be taken into consideration for electronic application.

Figure 6. UV-Vis spectrum and Tauc plot of BLSOD (present work)

3.5 Computational details

The optimized geometry and the arrangements of atom numbering of BLSOD crystal are shown in Figure 7. The optimized bond length, bond angle and the dihedral angle for the geometry of BLSOD calculated on the 6-31G basis set by using Gaussian03 program package. The most optimized parameters of this compound are calculated by both experimental and theoretical (6-31G) methods. The C5–C6 bond distance of oxalic acid in BLSOD is found to have a higher value (1.5497 Å), the bond angle O2-C6-O4 in oxalic acid are found to have a higher value as 126.2801 Å, and the H21-O7-C12-H15 dihedral angle of L-Serine is found to have the highest value (179 Å) on both experimental and theoretical methods.

Figure 7. Molecular geometry of BLSOD (Present work)
3.6 Molecular electrostatic potential

Molecular electrostatic potential (MEP) at a point in the field around a molecule provides detailed information about the net electrostatic effect generated at that point through total charge distribution (electron + proton) [13]. In addition, the MEP surface is used to forecast the reactivity of various chemical systems in both electrophilic and nucleophilic reactions and to study biological epidemic strategies and hydrogen bond interactions [14, 15]. The different values of the electrostatic potential at the surface are indicated by different colors; red represents the area with the most electronegative electrostatic potential, blue represents the area with the most positive electrostatic potential and green represents the area with the zero potential. The electrostatic potential rise in the order red < orange < yellow < green < blue [16].

![Fig.8 Comparison of Molecular Electrostatic Potential for BLSOD early reported and present work](image)

From fig 8 there are so much of red and yellow region, taking place in the BLSOD crysal (present work). It shows that much amount of hydrogen bond existing in the present work than early reported structure [5]. Especially the deep red region represents hydrogen-bond contacts. For example, a deep red region indicated the existence of a CH\(\cdots\)O H-bond in the BLSOD crystal (O9 and O25 atoms). The uniform charge distributions on the L-Serinium moiety protect the symmetry of the entire molecule.

3.7 Mullikan Atomic Charges

Mulliken atomic charge [17] calculation has a major role in the application quantum chemical calculations (QCC) of the molecular system. Atomic charge influences dipole moment, polarizability, electronic structure and other molecular properties of the system. The calculated Mulliken charge (e) values of BLSOD are compared with earlier reported work in Fig 9.

![Figure 9. Comparative Mullikan atomic charges of BLSOD early reported and present work](image)
Figure 9 shows that the atoms involved in the C-H…O H-bond has increased in the magnitude, such as O9, C11, O25 and C26 of BLSOD while compared to the earlier reported work [5].

3.8 Frontier Molecular Orbital’s Analysis

Molecular orbital contributes understanding into the nature of reactivity and some structural and physical properties of molecules. In Frontier Molecular Orbital’s analysis, red and green colour indicates the positive and negative phase respectively. The plots affirm that the region of HOMO disperse over the entire molecule of BLSOD while in the case of LUMO it disperse over the molecules of oxalic acid pre-eminently. The calculated energy gap value between HOMO and LUMO clarifies the extreme charge transfer interface within the molecule shown in figure 10. The frontier orbital energy gap (LUMO-HOMO) is calculated for BLSOD crystal by 6-31G method, is found to be 0.5038 a.u. It shows the decrease in energy gap when compared to early reported work [5] (0.5187 a.u.). Table 3 shows the HOMO, LUMO and energy gaps of BLSOD and early reported work [5] calculated by the 6-31G method. The energy gap decreases with conductivity increasing in the title compound.

![Figure 10 Comparative HOMO-LUMO of BLSOD early reported and present work](image)

Table 3. Comparative HOMO-LUMO values of BLSOD early reported and present work

| Molecular Orbitals   | Energy $E_H$ [a.u.] | Molecular orbitals | Energy $E_L$ [a.u.] | Energy gap $\Delta E = E_H - E_L$ [a.u.] | Eg from tauc plot (Experimental) [a.u.] |
|----------------------|---------------------|--------------------|---------------------|---------------------------------------|--------------------------------------|
| BLSOD (Early reported work) |                     |                    |                     |                                       |                                      |
| HOMO                 | -0.38860            | LUMO               | 0.13010             | 0.25850                               | --                                   |
| BLSOD (Present work) |                     |                    |                     |                                       |                                      |
| HOMO                 | -0.36659            | LUMO               | 0.13721             | 0.22938                               | 0.18485                              |
3.9 Non-linear optical property

It is notable that the higher values of dipole moments, molecular polarizability, and hyperpolarizability are significant for more dynamic NLO properties. The polarizability and hyperpolarizability are measured in atomic units (a.u), the calculated values have been converted into electrostatic units (esu) (for $\alpha$; 1 a.u = 0.1482 × 10^-24 esu, for $\beta$; 1 a.u = 8.6393 × 10^-33 esu). The measured value of dipole moment ($\mu$) was found to be 8.8321 Debye. The largest value of dipole moment ($\mu$) is realized for BLSOD crystal is equal to 1.2733 Debye of B3LYP. The anisotropy of the polarizability of the compound is 1.1913 x10^-23 esu. The magnitude of the molecular hyperpolarizability $\beta$, is one of significant key factors in the NLO system. The calculated first hyperpolarizability value ($\beta$) of the molecule is equal to 6.5415 x 10^-30esu are tabulated in table 4. The dipole moment and first hyperpolarizability of the present work is approximately 5.77821 and 6.0707 times than those of urea ($\alpha$ and $\beta$ of urea are 1.5285 Debye and 343.272 x 10^-33 esu obtained by HF/6-311G(d,p) method). For the BLSOD earlier reported work, the dipole moment and first hyperpolarizability is approximately 6.0707 and 5.34824 times than those of urea.

| Table 4. Comparative NLO property of BLSOD and early reported BLSOD |
|--------------------------|--------------------------|--------------------------|
| Parameters | Early Reported Work BLSOD | Present Work BLSOD | Parameters | Early Reported Work BLSOD | Present Work BLSOD |
| $\mu_x$ | -0.4355 | -8.7176 | $\beta_{xxx}$ | -165.2920 | -650.8901 |
| $\mu_y$ | -9.2410 | 0.6219 | $\beta_{yy}$ | -43.3044 | 7.8119 |
| $\mu_z$ | -7.1812 | 1.2733 | $\beta_{zz}$ | 3.4913 | 20.2752 |
| $\mu$ | 9.2791 | 8.8321 | $\beta_{xy}$ | 31.3140 | -23.7288 |
| $\alpha_{xx}$ | -122.6472 | 36.7238 | $\beta_{xy}$ | -120.7698 | -154.1335 |
| $\alpha_{yy}$ | -138.9810 | -144.2353 | $\beta_{xx}$ | -109.054 | 139.0590 |
| $\alpha_{zz}$ | -120.5658 | -133.0340 | $\beta_{xz}$ | 38.6433 | -55.9004 |
| $\alpha_{xy}$ | -1.9165 | 6.2884 | $\beta_{yz}$ | -25.6365 | 31.1183 |
| $\alpha_{yz}$ | -9.8266 | -18.8553 | $\beta_{zy}$ | -0.5967 | 2.4190 |
| $\alpha_{xz}$ | 4.3295 | 3.7809 | $\beta_{xz}$ | 18.6267 | 88.8663 |
| $\alpha_{tot}$(esu) | 1.8880 x 10^-23 | 1.1913 x 10^-23 | $\beta_{tot}$(esu) | 1.8359 x 10^-30 | 6.5415 x 10^-30 |

3.10 Natural Bond Orbital analysis analysis

In Natural Bond Orbital (NBO) analysis, all orbital values are mathematically picked to incorporate the highest possible percentage of the electron density. Interaction between both occupied and virtual orbital spaces effectively clarified explained by the NBO analysis, it could strengthen the analysis of intra- and intermolecular bond analysis.

| Table 5. Early reported BLSOD (Marta Kulik et al(2013)) - Selected NBOs. |
|--------------------------|--------------------------|--------------------------|
| S.no | Donor NBO (i) | Acceptor NBO (j) | E(2) kcal/mol | E(i)-E(j) (a.u.) | F(i,j) (a.u.) |
| 1 | $\Sigma$ | C22 - C23 | RY*( 1) | O32 | 2.42 | 2.27 | 0.066 |
| 2 | $\Sigma$ | C25 - H27 | $\sigma^*$ | C23 - N28 | 6.54 | 1.21 | 0.079 |
| 3 | $\Sigma$ | C2 - C4 | $\pi^*$ | C1 - O11 | 4.97 | 1 | 0.065 |
| 4 | $\sigma^*$ | C16 - C17 | RY*(3) | C17 | 4.19 | 0.43 | 0.15 |
Table 6. Present work- selected NBOs.

| S.n | Donor NBO (i) | Acceptor NBO (j) | $E(2)$ kcal/mol | $E(j)-E(i)$ (a.u.) | $F(i,j)$ (a.u.) |
|-----|---------------|------------------|-----------------|--------------------|----------------|
| 1   | $\Sigma$ O37 - H38 | RY*(1) H39 | 3.69 | 1.95 | 0.076 |
| 2   | $\Sigma$ C12 - H15 | $\sigma*$ N10 - C11 | 7.34 | 1.19 | 0.084 |
| 3   | $\Sigma$ C11 - C12 | $\pi*$ O9 - C13 | 3.58 | 1.06 | 0.058 |
| 4   | $\sigma*$ C5 - C6 | RY*(3) C6 | 3.34 | 0.96 | 0.196 |

Overall, we conclude that, stabilization energy increases by $\sigma$-bond in my present work compared to the early reported work and are tabulated in table 5 and 6.

4. Conclusion

Our investigation differs from earlier work [5] due to the following reason. The guessed inputs of hydrogen bond information result in intensity variation of reflection. This will have different kl values in hkl assignments. Additionally, small difference in lattice parameter can also lead to different intensity distribution and assignment of hkl. The difference in the molecular orientation, compared to the earlier reported structure results in enhancement of the optical behavior of the BLSOD (present work).

Acknowledgement

The authors acknowledge the Director, Sophisticated Test and Instrumentation Centre, Cochin University, Kerala, India, for the data collection, the managements of Srimad Andavan Arts and Science college, Trichy and St Joseph’s College, Trichy, Tamil Nadu, India, for their appreciation.

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