Research article

Crystal property and spectroscopic investigation on electro-optic and physico-chemical properties of NLO crystal; 3-(3,4-Dihydroxyphenyl)-L-Alanine

D. Vidhya, S. Ramalingam, S. Periandy, R. Aarthi

A R T I C L E   I N F O

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A B S T R A C T

In this attempt, in order to obtain high-quality NLO crystal, organic compound; 3-(3,4-Dihydroxyphenyl)-L-Alanine crystal was fabricated. The organic-composite crystal was characterized by crystallographic and spectroscopic tools. The NLO supported parameters like crystal lattice (orthorhombic) and space group (P212121) examined and validated by XRD examination. The SHG test was carried out and SHG efficiency was calculated that 1.29 and 1.35 times greater than solid KDP crystal. The laser damage threshold energy density was determined to be 14.51 GW/cm². By the application of mulliken charge assignment, multiple dielectric cavities were found in crystal material which is able to process the high degree of birefringence gradient. The oscillating chemical potential movement was observed by examining chemical shift, among the core carbons of hexagonal ring and bridge carbons of chain. The chemical softness insists the binding viability of further ligand groups. The π and δ-conjugated interactive complex orbitals recognized on molecular site and participation in optical active mechanism was identified. UV-Visible transmission characteristics of crystal were studied and UV-Visible absorption on degenerate energy states was noted and its band gap energy was estimated. The CT complex of the present case was acknowledged to be COOH group and it causing crystal properties of current organic composite. The hyperactive polarizability was determined as 1775.05/10^3 esu and it was found to be five times greater than thiourea. The depletion energy between highly electrophilic zones and protonic zones was estimated to be ±5.241 e 2 causing permanent dielectric characteristics for the title organic composite. The non-superposable on the molecular mirror image was displayed and thereby optical ability was validated.

1. Introduction

The nonlinear optical characteristics crystal made by the different combination of organic and semi organic materials and their characterization towards its optical quality and optically induced mechanism is technologically fast growing and emerging field of current research. It plays vital role in fabrication of optical modulator, high frequency optical switch, frequency shifter and optical data storage devices. The customization of tuned hyper active non linear optical mechanism in high degree of dielectric organic crystals is the fundamental need of enhancing the second and third harmonic generation in the crystals is extremely important for both laser spectroscopy and laser processing technology. The improvement of developing optical efficiency even in IR and UV regions by doping of chiral and symmetrical molecules with optically active amino acids is very significant for producing parametric oscillation process [1].

The dielectric crystal made by organic materials have great consideration over two past decades as a result of superior optical, opto-electronic and photoactive characteristics due to their NLO hyperactivity and pure optical transparency [2, 3]. Amino acid doped organic material are always having wide and tuned sharp UV-optical band width by the symmetrical arrangement of conjugated π and δ-electron systems exhibit various photo-optic responses [4]. Non-toxic organic-dielectric crystal complex is usually customized by the well symmetric hexagonal structured organic [5] or semi organic compound adopted with Alanine which is enabled with high helical controlled non linear mechanism, chemical potential flexibility, high degree of non centro-symmetry, first

* Corresponding author.
E-mail address: ramalingam.physics@gmail.com (S. Ramalingam).

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order donor and acceptor stability and good optical transmittance render organic enhanced photoactive process [6].

1. 2-dihydroxybenzene known as catechol, is the ortho isomer in which two hydroxyl groups are consecutively substituted in the benzene ring is basically used as a precursor to organic crystals and pharmaceuticals [7]. The present compound was fabricated using the base; catechol and the crystal perfection were improved by the addition of Alanine (professional organic NLO composite beneath of amino acid category). The L-alanine is an important non-polar characteristic hydrophobic nature amino acid belongs to non-centrosymmetric space groups. Due to an asymmetric carbon core sequence, it is enabled as optically active [8]. Usually, optically resonance active amino acids acquire wide optical transparency range in UV-Vis spectral region. The combination of hexagonal frame substitution in alanine is a supreme electronic operated composite material for nonlinear optical devices [9].

Even though, the suitable combination of catechol and Alanine crystals is making huge impact on the fabrication of efficient organic NLO crystals, so far, no work is available to carry out the crystal growth and the characterization on such organic composite. Here, the present crystal was grown by simple slow evaporation technique and it was characterized morphologically, structurally, optically and spectroscopically using quantum computational methods.

2. Experimental methods

A mixture of 27.2 g (0.1 mole) of LI, 67.8 ml (0.6 mole) of 47% HBr, and the temperature of 28 ml (0.32 mole) of phenyl hydroxide was increased with magnetic stirrer and refluxed about 3 h and the deposited brown solution was allowed to be evaporated to a reddish syrup. It was dissolved in 30 ml of n-BuOAc and extracted twofold with 30 ml and 10 ml of H$_2$O. The solution is kept in a refrigerator for 12 h and the corresponding powder was filtered.

For fabricating the present crystal compound, the L-Alanine and dihydroxy benzene were taken at 1:1 ratio and both are blended with one another by magnetic stirrer and boiled at 120 °C and also the combination was allowed to slow evaporation. The grown crystal was cleaved in its optical axis and it was allowed to characterize. The XRD pattern was recorded for raw sample of present case and the clear XRD pattern was determined for the analysis.

- The FT-IR spectral pattern was sequentially recorded using a Bruker IFS 66V with high resolution vib-rot spectrometer after making several scanning process in order to optimize the results.
- The FT-Raman spectral sequence was documented using Bruker spectrometer adopted with FT-IR instrument with Raman module equipped with a Nd:YAG laser source being operated at 1.068 μm line width with 500 mW power.
- The high resolution $^{1}$HNMR and $^{13}$CNMR spectra were recorded using 300 MHz and 75 MHz NMR spectrometer with high magnetic gradient.
- The UV-Visible spectral prototype was recorded in solid phase in the region of 50 nm–700 nm, with the scanning interval of 0.50 nm, using the UV-1800 series instrument.

3. Computational methods

The present compound is the combination of amino acid and dihydroxy benzene and appeared to be helical structure which is to be optimized by hybrid methods of calculations. Here, all the structural parametric values are determined by B3LYP/6-311++G(d,p) method of computations and scanning process was performed to find out the optimized form of structure and it was validated to insert in crystal structure. The vibrational assignments were made on the characteristics wave-number region which were calculated by B3LYP/B3PW91/6-311++G(d,p) methods and it was scaled in order to coincide the wave-numbers with observed spectral values. The molecular structure with minimized potential energy was depicted in which the molecular combination of alanine and dihydroxybenzene was clearly showed. The benzene structure was appeared at one plane and alanine was found to be helical form and other than benzene, the rest part of the molecule was become semicircle formation.

The structural parameters and Mulliken charge assignment was calculated on the optimized structure using B3LYP/6-311++G(d,p) which are tabulated in ascending order. The chemical shift from $^{13}$C and $^{1}$H was computed in terms of TMs values and the restoring of chemical potential was determined. The FMO orbital interactions were monitored from which the non bonding orbital transitions were illustrated to find the chemical potential in non radiative transitions. The non linear process was studied by observing the hyper active polarizability taking place among molecular site. For analyzing molecular dipole moment, the electrostatic potential gradient was drawn from the grid points of distributed field using B3LYP/6-311++G(2d,2p) method of calculation.

4. Results and discussion

4.1. XRD analysis

The XRD spectral pattern was recorded for the present solid crystal sample and it is displayed in Figure 1. The clear XRD peak sequence was obtained with maximum intensity. The peaks were observed at 16°, 18°, 26°, 28°, 29°, 32, 36, 40°, 42° and 45° for (200), (001), (020), (210), (121), (220), (212) and (301) planes. Except some, all the XRD crust was observed with greatest diffraction intensity. This pattern of well distinct peaks is assigned to be orthorhombic crystal formation for present compound. Usually, below 20° of 20, the diffraction peaks not possible for organic crystals. But in this case, number of peaks was found to represent the orthorhombic crystal formation using present molecular structure; 3-(3,4-Dihydroxyphenyl)-L-Alanine. Although, the present organic compound would be in helical form, the perfect array of optimized structure formed well aligned orthorhombic crystal nature. Normally, the organic or semi-organic complex molecules are having flexibility of molecular design to construct well amalgamated crystal structure, here, the helical structure as well as hexagonal base of present case was found to be arranged in the form of three different sequence such as unequal axes at right angles and thereby orthorhombic crystal configuration was strongly shaped. In this case, the characteristic condition $\alpha = \beta = \gamma = 90°$ was satisfied from the obtained distinct peaks in different planes of the crystal system and $P_2$ point group of symmetry was found to be adopted with the molecular system and thus, the $P_2_1$ space group was assigned according to the symmetry. From the above observation, it was clear that, the present crystal structure was customized on orthorhombic lattice and also confirmed that, the asymmetric
core carbon sequence and non-centrosymmetric space groups induced NLO mechanism in the present crystal.

4.2. Crystal profile

The crystal parameters were observed from different parametric experimentation and are presented in Table 1. The base molecular structure for the crystal process and the grown crystal are displayed in Table 1. Here, two solvents were used to fabricate crystal by slow evaporation method and the melting point of crystal was determined to be 108 °C by raising its temperature in heating furnace. As per the bravais lattice rules, the space group of present crystal was measured to be P212121 whereas the point group of molecular structure was to be C4v which is recognized as noncentro-symmetric. The unit cell dimension was determined to be a = 6.321 Å, b = 13.629 Å and c = 5.864 Å which confirmed the orthorhombic lattice for the present organic crystal structure. This variable plane length of the crystal was ensured elevation of crystal unit cell repetition in different lattice plane sequence that strongly represents optical birefringence effect in the crystal. Correspondingly, the refractive indices of the crystal was determined to be n1 = 1.661, n2 = 1.874 and n3 = 1.519 respectively in three unequal optical axes which established the translation operation was invariably taking place in different planes inside the crystal system. The observed parametric indices including optical birefringence were well agreed with the literature [10, 11, 12]. For present crystallographic material, the birefringence gradient Δn was measured to be 0.189, was moderate and it is enough to produce double refraction modulation of a ray of light resultant in polarization. This present case was already found to be molecularly ordered organic complex which are having different refractive indices regarding to different crystallographic directions and was able to facilitate the Intrinsic Birefringence.

The Nonlinear optical property of present organic crystal was performed by Kurtz powder second harmonic generation (SHG) test by using popular Q-switched laser beam (Source-Nd: YAG laser). The crystal sample with same dimension was irradiated by laser (TEM00 mode locked) with input pulse of 6.8 mJ at λ = 1064 nm. The second harmonic signals were found at 348 mV and 389 mV from the present crystal sample with the optimum reference material of KDP at 265 mV from which the SHG efficiency was calculated to be 1.29 and 1.35 times greater than solid KDP crystal and the result is agreed well with the reported literature [13, 14]. The laser damage threshold energy density was determined by the mode of multiple shots damage and was identified to be 14.51 GW/cm². When compared with standard KDP crystal, the experimental damage threshold energy value was found to be greater than KDP and other known organic crystals. The dielectric constant is the important factor which influences the NLO property of the organic material and composites directly. In this case, it was measured at 1 MHz frequency and it was to be 4.821 at 50 °C and 5.112 at 60 °C. The DC was increased much with respect to the temperature and decreased with frequency. The present crystal was Enantiomorphic and it was able to facilitate the interplanes with different refractive ability.

4.3. Structural property analysis

As per organic compositions of present case, the molecular geometry was arranged and thereby the crystal symmetry was spontaneously approved. All the structural parameters are depicted in the Table 2. In this case, according to the molecular arrangement, Hydrogen bond donor count, Hydrogen bond acceptor count and Rotatable bond count were

Table 1. Crystal parameters of 3-(3,4-Dihydroxyphenyl)-L-Alanine.

| S. No. | Parameters | Values | Molecular/crystal structure |
|-------|------------|--------|----------------------------|
| 1     | Space group | P212121|                           |
| 2     | Melting point | 108 °C |                           |
| 3     | Unit cell   |        |                           |
|       | a           | 6.321 Å|                           |
|       | b           | 13.629 Å|                          |
|       | c           | 5.864 Å|                           |
| 4     | Refractive index |      |                           |
|       | n1          | 1.661  |                           |
|       | n2          | 1.874  |                           |
|       | n3          | 1.519  |                           |
| 5     | Birefringence (Δn) KJ/t | 0.189  |                           |
| 6     | NLO efficiency |        |                           |
|       | λ²n = 15 X 1²n |        |                           |
| 7     | Transmittance |        |                           |
|       | 0.298-2.012 μm |        |                           |
| 8     | Complexity  | 210    |                           |
| 9     | Volume      | 480.11 Å³ |                         |
| 10    | Crystal lattice | Orthorhombic |               |
| 11    | Crystal type | Enantiomorphic |                |
| 12    | Dielectric constant (εr) [1MHz] | 50 °C = 4.821 & 60 °C = 5.112 |
Table 3. Optimized geometrical parameters for 3-(3,4-Dihydroxyphenyl)alanine.

| Geometrical Parameters | Methods    | HF       | HF       | B3LYP    | B3PW91   |
|------------------------|------------|----------|----------|----------|----------|
|                        | 6-31+G (d, p) | 6-311+G (d, p) | 6-311++G (d, p) | 6-311++G (d, p) |
| Bond length(Å)         |            |          |          |          |          |
| C1–C2                  | 1.377      | 1.378    | 1.391    | 1.389    |
| C1–C6                  | 1.398      | 1.394    | 1.404    | 1.402    |
| C1–O10                 | 1.351      | 1.349    | 1.366    | 1.360    |
| C2–C3                  | 1.394      | 1.389    | 1.394    | 1.392    |
| C2–H7                  | 1.077      | 1.077    | 1.086    | 1.087    |
| C3–C4                  | 1.381      | 1.382    | 1.395    | 1.393    |
| C3–H8                  | 1.075      | 1.076    | 1.084    | 1.085    |
| C4–C5                  | 1.398      | 1.393    | 1.400    | 1.398    |
| C4–C14                 | 1.514      | 1.514    | 1.512    | 1.507    |
| C5–C6                  | 1.379      | 1.380    | 1.392    | 1.390    |
| C5–H9                  | 1.078      | 1.077    | 1.087    | 1.088    |
| C6–O12                 | 1.349      | 1.348    | 1.365    | 1.359    |
| O10–H11                | 0.942      | 0.940    | 0.962    | 0.961    |
| O12–H13                | 0.942      | 0.940    | 0.962    | 0.961    |
| C14–H15                | 1.081      | 1.082    | 1.091    | 1.092    |
| C14–H16                | 1.081      | 1.083    | 1.092    | 1.093    |
| C14–C17                | 1.532      | 1.532    | 1.539    | 1.533    |
| C17–H18                | 1.093      | 1.093    | 1.105    | 1.107    |
| C17–N19                | 1.452      | 1.454    | 1.465    | 1.457    |
| C17–C22                | 1.518      | 1.518    | 1.524    | 1.519    |
| N19–H20                | 0.999      | 0.999    | 1.015    | 1.014    |
| N19–H21                | 0.999      | 0.999    | 1.014    | 1.013    |
| C22–O23                | 1.188      | 1.181    | 1.203    | 1.203    |
| C22–O24                | 1.330      | 1.330    | 1.357    | 1.350    |
| O24–H25                | 0.948      | 0.946    | 0.969    | 0.967    |

(continued on next page)
Table 3 (continued)

| Geometrical Parameters | Methods          |
|------------------------|------------------|
|                        | HF 6-31 + G (d, p) | HF 6-311 + G (d, p) | B3LYP 6-311 + G (d, p) | B3PW91 6-311 + G (d, p) |
|                        | H18-C17-N19      | H18-C17-C22         | C17-N19-H20             | C17-N19-H21               |
|                        | 112.3937         | 104.9525            | 108.8378                | 110.5972                  |
|                        | 125.9452         | 104.9516            | 108.8556                | 111.6626                  |
|                        | 108.4834         | 108.0321            | 125.9452                | 111.8693                  |
|                        | 112.2979         | 104.4348            | 110.2803                | 126.0233                  |
|                        | 112.5633         | 104.0313            | 110.8773                | 111.6915                  |
|                        | 112.736          | 110.495            | 110.8424                | 111.662                   |
|                        | 122.2492         | 122.3528            | 122.3859                | 107.3244                  |
|                        | 108.9006         | 106.9818            |                        |                         |
| Dihedral angle (°)     |                  |                   |                         |                         |
|                        |                  | C6-C1-C2-C3        | -179.5828               | -179.8735                |
|                        |                  |                    | 179.4582                | 179.4582                 |
|                        |                  |                    | 179.7928                | 179.7928                 |
|                        |                  |                    | 0.152                  | -0.2688                  |
|                        |                  |                    | -0.1631                | 0.2533                   |
|                        |                  |                    | 0.17                   | -179.9566                |
|                        |                  |                    | -179.9136              | -179.9136                |
|                        |                  |                    | -0.1785                | 0.0726                   |
|                        |                  |                    | -1.3775                | 2.1103                   |
|                        |                  |                    | -178.3608              | -177.6196                |
|                        |                  |                    | -178.5211              | -178.7735                |
|                        |                  |                    | -179.1466              | -179.5944                |
|                        |                  |                    | -179.553               | -179.561                 |
|                        |                  |                    | -0.0016                | 0.4406                   |
|                        |                  |                    | -179.4331              | -179.4331                |
|                        |                  |                    | -179.9435              | -179.9435                |
|                        |                  |                    | -179.7828              | -179.7828                |
|                        |                  |                    | -179.2147              | -179.2147                |
|                        |                  |                    | -0.5048                | 0.1296                   |
|                        |                  |                    | -178.2399              | -178.1691                |
|                        |                  |                    | -178.4797              | -178.5415                |
|                        |                  |                    | -179.3201              | -179.7735                |
|                        |                  |                    | -179.0941              | -179.0978                |
|                        |                  |                    | -179.4524              | -179.5238                |
|                        |                  |                    | -179.4625              | -179.5150                |
|                        |                  |                    | -179.4516              | -178.9435                |
|                        |                  |                    | -178.7019              | -178.7604                |
|                        |                  |                    | -178.5238              | -178.6184                |
|                        |                  |                    | -178.4797              | -178.4797                |
|                        |                  |                    | -179.8284              | -179.8284                |
|                        |                  |                    | -179.7891              | -179.7891                |
|                        |                  |                    | -0.5048                | 0.1296                   |
|                        |                  |                    | -178.2399              | -178.1691                |
|                        |                  |                    | -178.4797              | -178.5415                |
|                        |                  |                    | -179.3201              | -179.7735                |
|                        |                  |                    | -179.0941              | -179.0978                |
|                        |                  |                    | -179.4524              | -179.5238                |
|                        |                  |                    | -179.4625              | -179.5150                |
|                        |                  |                    | -179.4516              | -178.9435                |
|                        |                  |                    | -178.7019              | -178.7604                |
|                        |                  |                    | -178.5238              | -178.6184                |
|                        |                  |                    | -178.4797              | -178.4797                |
|                        |                  |                    | -179.8284              | -179.8284                |
|                        |                  |                    | -179.7891              | -179.7891                |
|                        |                  |                    | -0.5048                | 0.1296                   |
|                        |                  |                    | -178.2399              | -178.1691                |
|                        |                  |                    | -178.4797              | -178.5415                |
|                        |                  |                    | -179.3201              | -179.7735                |
|                        |                  |                    | -179.0941              | -179.0978                |
|                        |                  |                    | -179.4524              | -179.5238                |
|                        |                  |                    | -179.4625              | -179.5150                |
|                        |                  |                    | -179.4516              | -178.9435                |
|                        |                  |                    | -178.7019              | -178.7604                |
|                        |                  |                    | -178.5238              | -178.6184                |
|                        |                  |                    | -178.4797              | -178.4797                |
|                        |                  |                    | -179.8284              | -179.8284                |
|                        |                  |                    | -179.7891              | -179.7891                |
|                        |                  |                    | -0.5048                | 0.1296                   |

(continued on next page)
calculated to be 4, 5 and 3 respectively. All the above parameters ensured the molecular planes and helical nature of the molecular setup and anisotropic characteristics and here, all the parameters were support for enforcement of crystalline quality. The Topological Polar Surface Area is the significant factor to make impact on crystal density and morphological integrity and it was 104 Å², for the crystal quality it should be greater than 100 Å² and here the observed value showed superiority of the crystal.

The heavy atom count, Heteronuclear bonds counts and Homonuclear bond counts are consistently used to determine heterogeneity and anisotropic characteristics of the organic crystal material to provide Intrinsic Birefringence effect and they were found to be 14, 16 and 8.

Table 3 (continued)

| Geometrical Parameters | Methods | HF 6-31 + G (d, p) | HF 6-311 ++ G (d, p) | B3LYP 6-311 ++ G (d, p) | B3PW91 6-311 ++ G (d, p) |
|------------------------|---------|---------------------|-----------------------|--------------------------|--------------------------|
| H18–C17–N19–H21       | -56.6562| -58.4929            | -60.9613              | -61.1482                 |
| C22–C17–N19–H20       | -179.9672| 177.0908            | 174.2604              | 173.7564                 |
| C22–C17–N19–H21       | 59.123  | 57.2514             | 55.0087               | 54.782                   |
| C14–C17–C22–O23       | 10.7744 | 9.507               | 15.5278               | 18.8558                  |
| C14–C17–C22–O24       | -171.5895| -172.6458           | -167.103              | -164.0679                |
| H18–C17–C22–O23       | -106.3775| -107.497            | -100.4609             | -96.6285                 |
| H18–C17–C22–O24       | 71.2586  | 70.3502             | 76.9083               | 80.4477                  |
| N19–C17–C22–O23       | 133.1236 | 132.1398            | 138.5506              | 142.1262                 |
| N19–C17–C22–O24       | -49.2402 | -50.013             | -44.0802              | -40.7975                 |
| C17–C22–O24–H25       | -179.56  | -179.6453           | -178.9823             | -178.5659                |
| O23–C22–O24–H25       | -1.8201  | -1.7052             | -1.4975               | -1.3709                  |

Figure 2. Molecular structure of 3-(3,4-Dihydroxyphenyl)-L-Alanine.
respectively. According to the observed values, the present organic composite is able to have efficient heterogeneity in molecular site of crystal compound and thereby the dielectric constant was improved for the betterment of crystalline excellence. The Covalently-Bonded Unit Count was 1 and ionic character was recognized to be >1 and these parameters provide large hyperpolarizability character for the molecule of crystal which enhanced the SHG efficiency of the composite.

4.4. Molecular geometry analysis

The title organic composite is composed by alanine and dihydroxy benzene by this application, the bond length and bond angle parameters are altered. The bond parameters alternation was made with respect to the electrochemical forces existed among the atomic site. Here, according to the standard value (1.391Å) for core CC of benzene ring [15], the tri-substituted benzene was found to be fractured multiply and it was evidenced by the change of bond lengths of C1–C2, C2–C3, C3–C4, C4–C5, C5–C6 and C1–C6 as 1.391, 1.394, 1.395, 1.400, 1.392 and 1.404 Å respectively as in the Table 3. The core CC of hexagonal ring system was differed from standard value from 0.001 to 0.013Å and it was well pronounced at C1, C6 and C4 by the substitutions. Other than core, the bond length of C4–C14, C14–C17 and C17–C22 were 1.512, 1.539 and 1.524Å respectively and these bond lengths were very much stretched up to 0.121Å due to the further addition of electronegative atoms in the chain. The bond length of O–H in phenol mode was less stretched up to 0.007Å than O–H in acid group as shown in Figure 2. Here, the alternative polarized and non polarized bonds in the chain produced heterogeneity molecular atmosphere to induce anisotropic ambiance in the crystal morphology.

In the case of heteronuclear bond angle, such as C1–O10–H11, C6–O12–H13, H15–C14–H16, C17–N19–H20, C17–N19–H21, H20–N19–H21, O23–C22–O24 and C22–O24–H25 were found to be enlarged and was ranged from 2.182° to 3.169°. These bond angle changes were mainly due to electronic, Space Charge and oriental polarization taking place in different entities of the molecular sites. In the case of chain, the orientation of molecular dipoles were taking place, in the case of hexagonal ring, the separation or distortion of electron cloud around molecules with respect to the interactive and repulsive force constant. The movements of charges around molecular site were resulting in alignment of charge dipoles causing heterogeneous polarization which induced strong dielectric behavior of the material.

4.5. Mulliken charge assignment

Linear combination of atomic orbitals (LCAO) system overlapped with one another with respect to the spatial quantization for formation of molecular orbitals and produced degenerate orbital interactions in which the dipole and electronic polarization were observed to explore the inducement of local electrical field by the applied electric field. The magnitude of local field can be modified by chemical potential generated

Figure 3. Mulliken charge distribution of 3-(3,4-Dihydroxyphenyl)-L-Alanine.
around the molecular structure in the crystal which is quite significantly the space and electronic polarization of structure arrangement. The
invariable mulliken charge assignment is exhibited in Figure 3.

Here, the charges on molecular site were found to be reoriented with respect to the local field and such that the negative charges from hydroxyl groups were delocalized and moved towards the core CC of benzene ring and shifted to the chain via C4. The electron cloud was populated on C1, C3 and C6 and they drained along the chain. Similarly, the charge domain was getting moved from the acid group and displaced towards C14 at which the charged domain was repelled and thus the charged domains depleted and formed boundary between them. The depletion force existed between domains leading Lorentz force which usually acted on dielectric cavity in the organic composite crystal. When the field is applied, the local electric field was induced and was distinguished from entities to entities in crystal. The well distinct domains were distributed over the material such that formed dielectric cavities which is able to process the high degree of birefringence gradient.
| S.No | Symmetry Species \(C_s\) | Observed Frequency (cm\(^{-1}\)) | Methods | Vibrational assignments |
|------|-------------------------|----------------------------------|---------|------------------------|
|      |                         | FT-IR                            | FT-Raman|                        |
| 1    | A'                      | 3400 m                           | -       |                        |
| 2    | A'                      | -                                | 3395 w  |                        |
| 3    | A'                      | 3290 m                           | -       |                        |
| 4    | A'                      | 3280 m                           | -       |                        |
| 5    | A'                      | 3240 m                           | 3240 w  |                        |
| 6    | A'                      | 3030 m                           | -       |                        |
| 7    | A'                      | 3010 w                           | 3010 w  |                        |
| 8    | A'                      | -                                | 3005 m  |                        |
| 9    | A'                      | 2990 m                           | 2990 w  |                        |
| 10   | A'                      | 2985 m                           | 2985 w  |                        |
| 11   | A'                      | -                                | 2930 w  |                        |
| 12   | A'                      | 1650 vs                          | -       |                        |
| 13   | A'                      | 1610 m                           | -       |                        |
| 14   | A'                      | 1590 m                           | -       |                        |
| 15   | A'                      | 1575 wv                          | -       |                        |
| 16   | A'                      | 1570 wv                          | -       |                        |
| 17   | A'                      | 1520 wv                          | -       |                        |
| 18   | A'                      | 1500 m                           | -       |                        |
| 19   | A'                      | 1495 m                           | -       |                        |
| 20   | A'                      | 1460 m                           | -       |                        |
| 21   | A'                      | 1440 vs                          | 1440 wv |                        |
| 22   | A'                      | 1410 wv                          | 1410 wv |                        |
| 23   | A'                      | 1405 wv                          | -       |                        |
| 24   | A'                      | 1365 w                           | -       |                        |
| 25   | A'                      | 1360 w                           | -       |                        |
| 26   | A'                      | -                                | 1350 wv |                        |
| 27   | A'                      | -                                | 1330 wv |                        |
| 28   | A'                      | 1300 m                           | -       |                        |
| 29   | A'                      | 1295 m                           | 1295 wv |                        |
| 30   | A'                      | 1280 w                           | -       |                        |
| 31   | A'                      | -                                | 1270 wv |                        |
| 32   | A'                      | 1265 w                           | -       |                        |
| 33   | A'                      | 1260 w                           | -       |                        |
| 34   | A'                      | 1220 vs                          | -       |                        |
| 35   | A'                      | 1205 vs                          | -       |                        |
| 36   | A'                      | 1170 vs                          | 1170 wv |                        |
| 37   | A'                      | -                                | 1130 wv |                        |
| 38   | A'                      | 1120 w                           | -       |                        |
| 39   | A'                      | 1070 vs                          | 1070 wv |                        |
| 40   | A'                      | -                                | 990 w   |                        |
| 41   | A'                      | -                                | 985 w   |                        |
| 42   | A'                      | 980 s                            | -       |                        |
| 43   | A'                      | 950 vs                           | 950 wv  |                        |
| 44   | A'                      | -                                | 945 wv  |                        |
| 45   | A'                      | 920 vs                           | 920 wv  |                        |
| 46   | A'                      | -                                | 915 wv  |                        |
| 47   | A'                      | 880 vs                           | 880 wv  |                        |
| 48   | A'                      | -                                | 875 wv  |                        |
| 49   | A'                      | 840 vs                           | 840 wv  |                        |
| 50   | A'                      | 820 vs                           | 820 wv  |                        |
| 51   | A'                      | -                                | 815 wv  |                        |
| 52   | A'                      | 780 vs                           | 780 m   |                        |
| 53   | A'                      | -                                | 775 m   |                        |
| 54   | A'                      | 750 vs                           | -       |                        |
| 55   | A'                      | 740 vs                           | -       |                        |
| 56   | A'                      | 720 vs                           | 720 wv  |                        |

(continued on next page)
Table 4 (continued)

| S. No | Symmetry Species C_s | Observed Frequency(cm⁻¹) | Methods | Vibrational assignments |
|-------|----------------------|-------------------------|---------|------------------------|
|       |                      | FT-IR | FT-Raman | B3LYP | 6-311+G (d, p) | B3LYP | 6-31G (d, p) | B3LYP | 6-311+G (d, p) | B3LYP | 6-311+G (d, p) |
| 57    | A'                   | 715vw |          | 696   | 328            | 302   | 302           | (C–C) δ |
| 58    | A'                   | 680vw |          | 686   | 322            | 297   | 295           | (C–O) γ |
| 59    | A'                   | 620vw |          | 434   | 313            | 284   | 282           | (C–O) γ |
| 60    | A'                   | 590vw |          | 410   | 289            | 277   | 274           | (C–O) γ |
| 61    | A'                   | 560vw |          | 570   | 260            | 266   | 264           | (C–O) γ |
| 62    | A'                   | 470vw |          | 347   | 225            | 249   | 257           | (C–C) γ |
| 63    | A'                   | 410w  |          | 332   | 198            | 221   | 220           | (C–C) γ |
| 64    | A'                   | 390w  |          | 278   | 186            | 181   | 179           | (C–C) γ |
| 65    | A'                   | 340w  |          | 235   | 167            | 150   | 149           | (CNH₂) δ |
| 66    | A'                   | 300w  |          | 300   | 68             | 61    | 61            | (C(OH)₂) δ |
| 67    | A'                   | 220w  |          | 218   | 58             | 50    | 49            | (C(=O)H) δ |
| 68    | A'                   | 190w  |          | 192   | 49             | 26    | 43            | (CNH₂) γ |
| 69    | A'                   | 120w  |          | 120   | 32             | 26    | 23            | (C(COOH) γ) |

VS – Very strong; S – Strong; m – Medium; w – weak; as- Asymmetric; s – symmetric; v – stretching; δ – deformation, α – in-plane-bending; γ – out-of-plane bending; τ – Twisting.

Table 5. Experimental and calculated 1H and 13C NMR chemical shift in 3-(3,4-Dihydroxyphenyl)-L-Alanine.

| Atom position | Chemical Shift - TMS (ppm) | Experimental shift (ppm) |
|---------------|---------------------------|--------------------------|
|               | Gas | DMSO | Water | Gas | DMSO | Water |
| C1            | 162.348 | 162.374 | 162.348 | 155 |
| C2            | 126.863 | 126.837 | 126.863 | 121 |
| C3            | 132.365 | 132.347 | 132.365 | 128 |
| C4            | 150.655 | 150.653 | 150.655 | 151 |
| C5            | 132.02 | 131.997 | 132.02 | 138 |
| C6            | 164.074 | 164.099 | 164.074 | 158 |
| C14           | 37.2588 | 37.258 | 37.2588 | 32 |
| C17           | 61.9095 | 61.9053 | 61.9095 | 58 |
| C22           | 204.081 | 204.033 | 204.081 | - |
| H7            | 7.00041 | 6.9944 | 7.0004 | 6.8 |
| H8            | 7.00041 | 6.9944 | 7.0004 | 6.8 |
| H9            | 12.8702 | 12.8702 | 12.8702 | - |
| H11           | 4.04909 | 4.0372 | 4.0491 | 4.3 |
| H13           | 4.20945 | 4.1946 | 4.2094 | 4.3 |
| H15           | 2.68925 | 2.6875 | 2.6893 | 2.9 |
| H16           | 2.18612 | 2.1899 | 2.1861 | - |
| H18           | 4.04909 | 4.0372 | 4.0491 | 4.3 |
| H20           | 9.74455 | 9.7438 | 9.74455 | - |
| H21           | 1.3525 | 1.3443 | 1.352 | - |
| H25           | 6.20583 | 6.1963 | 6.2058 | 6.0 |

In this case, there were 16 heteronuclear and 8 homonuclear bonds appeared in which the dipoles formed electronic polarizability and homonuclear bonds created space charge polarization. At this juncture, the heteronuclear bonds C1–O10, C6–O12, C17–N19, C22–O23 and the heterogeneity was produced even on homonuclear bonds such as C4–C14, C2–C3 and C3–C4 by the charge delocalization due to space charge polarization and these were produced the strong σ and π-conjugative interactions which persuade spontaneous optical axes in different coordinates that making different refractive indices in different coordinates which making different refractive indices in the organic composite material. The composition of chemi-potential on the molecular structure was illustrated in Figure 4. According to the hyper-chemical calculation, the hyper and hypo-chemical potential was demonstrated by the red and blue colour gradient respectively. The molecular structure was appeared to be chair form and folded view showed helical manifestation and the topological surface area was drawn by electrostatic field grid points around the compound. The parametric potential oscillation was seen between ring and chain to explore resultant chemical hardness gradient.

4.6. Vibrational analysis

4.6.1. Vibrational assignment

The title composite was fabricated by amino acid species and organic compound by which the vibrational pattern was recorded and was synchronized with calculated wavenumbers. The finger print and group frequencies were assigned with respect to the characteristic vibrational regions and mutual exclusion principle. The obtained frequency pattern along with simulated spectra in terms of IR and Raman bands are illustrated in Figures 5 and 6 respectively and the related IR and Raman assignment are depicted in Table 4. As per the selection rule and point group of symmetry (C₅), the in plane and out of plane vibrations were calculated to be 69 in which the in plane and out of plane vibrations are classified as 48 and 23 respectively. In the observed wavenumbers, the peaks were obtained with from very strong to weak intensity according to the force constant of bonds.

4.6.2. O–H vibrations

In the present case, the O–H is present in phenol as well as acid groups at which the O–H vibrations may be differed between two groups. In the absence of intra-molecular hydrogen bonding, phenols have an absorption band at 3400-3240 cm⁻¹ for O–H stretching, at 1350-1200 cm⁻¹ for O–H in plane bending and at 720-600 cm⁻¹ [16-17]. According to the Table 4, the O–H stretching, in plane and out of plane bending modes were observed at 340, 3395, 3210 cm⁻¹ for O–H stretching, at 1350-1200 cm⁻¹ for O–H in plane bending and at 720-600 cm⁻¹ [16-17]. According to the Table 4, the O–H stretching, in plane and out of plane bending modes were observed at 340, 3395 & 3210 cm⁻¹, 1570, 1520 & 1500 cm⁻¹ and 1120, 1070 & 990 cm⁻¹ respectively for the current case. Except stretching, all the observed wavenumbers were found to be elevated well above the expected region which was due to the chemical energy reservoir at phenol group. Here, the O–H bond in two different places was greatly pronounced at prominent place of vibrational band.

4.6.3. COOH vibrations

The acid group is placed on the amino acid chain which very dominant usually and play important role in activation of vibrational activity of the molecule and in that way, the structural significance is exposed in the molecular structure. In amino acid, the C=O stretching band usually
Figure 7. Experimental and calculated NMR spectra of 3-(3,4-Dihydroxyphenyl)-L-Alanine.

Figure 8. Frontier molecular orbital interaction of 3-(3,4-Dihydroxyphenyl)-L-Alanine.
Table 6. Frontier molecular orbitals with energy levels 3-(3,4-Dihydroxyphenyl)-L-Alanine.

| Energy levels | IR region | UV-Visible region |
|---------------|-----------|------------------|
|               | B3LYP/6-311++G(d,p) | B3PW91/6-311++G(d,p) |
| H10           | 10.7613   | 10.7309          |
| H9            | 10.3406   | 10.2766          |
| H8            | 10.1686   | 10.0881          |
| H7            | 9.8170    | 9.6252           |
| H6            | 9.6731    | 9.3544           |
| H5            | 9.3359    | 9.2955           |
| H4            | 9.1011    | 8.9112           |
| H3            | 8.1667    | 8.1242           |
| H2            | 7.0687    | 7.2611           |
| H1            | 6.8965    | 6.9409           |
| L             | 6.0458    | 6.5701           |
| L1            | 0.6833    | 1.0391           |
| L2            | 0.5826    | 1.0432           |
| L3            | 0.4131    | 0.6305           |
| L4            | 0.3720    | 0.6259           |
| L5            | 0.2490    | 0.3780           |
| L6            | 0.0816    | 0.3532           |
| L7            | 0.1518    | 0.1059           |
| L8            | 0.3087    | 0.3687           |
| L9            | 0.5883    | 0.4993           |
| L10           | 0.7280    | 0.7333           |

allotted in the region 1680-1650 cm⁻¹ [18]. In this acid adopted molecule, the C=O stretching mode was recognized with very strong intensity at 1650 in IR spectrum which represent acid group in the spectra very consistently.

The C-O stretching vibration for mono and di-substituted phenols is observed in the region of 1300-1200 cm⁻¹. The connected in plane and out of plane bending modes are usually found in the region 450-375 cm⁻¹ and below 350 cm⁻¹ respectively [19]. Here, C-O stretching, in plane and out of plane deformation was identified with medium intensity at 1365, 1360 & 1350 cm⁻¹, 775, 750 & 740 cm⁻¹ and 620, 590 & 560 cm⁻¹ respectively. The phenol vibrations were supported here by adjoining nodal group of phenol.

4.6.4. Amino group vibrations

In primary amino acid molecule, typically N-H stretching vibrations suitably take place in the region 3500-3300 cm⁻¹ [20]. The NH₂ group has normally classified in to two vibrations; asymmetric and symmetric mode of vibrations. The asymmetric frequency is always elevated than symmetric and such asymmetric and symmetric N-H stretching vibrations of were acknowledged at 3280 cm⁻¹ and 3240 cm⁻¹ respectively for this case. In addition to that, the asymmetric mode is always more intense than symmetric whereas here, both were observed with medium intensity. The N–H in plane bending (scissoring mode) are regularly found in the region 1610-1630 cm⁻¹, rocking signal is assigned in the range 1100–1200 cm⁻¹ and the wagging and twisting (out of plane bending) vibrations are recognized under 900 cm⁻¹ [21]. In this molecule, the N–H in plane bending vibrations as scissoring mode was looked at 1495 and 1460 cm⁻¹. Relatively, N-H out of plane bending as wagging mode have been assigned at 1170 and 1130 cm⁻¹. As per the expected region of N-H modes, all the bending vibrational bands were recognized to be moved up to the higher region of spectrum due to the consistency of dipole bonds and it involved in the molecular typical character and participated in the hyper active polarization taking place in the molecule.

4.6.5. C-H vibrations

The phenol derivatives usually having stretching bands of C-H bonds arranged in the region 3100-3000 cm⁻¹ and such vibrational region may be infected by the addition of substitutions in the hexagonal ring. Associated in plane and out of plane bending vibrational bands are assigned as usual manner in the region 1300-1000 cm⁻¹ and 950-809 cm⁻¹ respectively [22, 23]. The present case was having stretching and in plane and out of plane deformation bands have been assigned at 3030, 3010 & 3005 cm⁻¹, 1280, 1270 & 1265 cm⁻¹ and 985, 980 & 950 cm⁻¹ in that order. All the C-H vibrations have been found well within the expected region. Except substitutions at core, three C-H bonds have been identified by the observation of vibrational characteristics. This vibrational process of allied dipole bonds are concerned in the molecular property in physical sense.

In the case of aliphatic chain, the C–H stretching vibrations of the same is usually arranged in the region 3000-2800 cm⁻¹ [24]. The related in plane and out of plane bending vibrations are normally observed in the range 1260-960 cm⁻¹ and 900-670 cm⁻¹ correspondingly [25]. At this time, the stretching, bending vibrations were particularly assigned at 2990, 2985 & 2930 cm⁻¹, 1260, 1220 & 1205 cm⁻¹ and 945, 920 & 915 cm⁻¹ respectively for the present crystal compound. The stretching and in plane bending signals were obtained within the expected limit whereas the out of plane bending modes were observed well above the allowed region which indicates that, the vibrational energy have not affected by allied bonds and the consistent participation in crystal property.

4.7. NMR examination

In the molecular orbital formation, electron cloud related to the atom is usually redistributed with respect to the chemical equilibrium forces among the molecular sites. The polarization of charges in both form among the molecular site are concentrated normally in electronegative and propositose regions. In this fashion, the electron clouds are forced to be delocalized and associated chemical shift is totally modified. For the current case, the chemical shift is monitored in Table 5 and the corresponding experimental and simulated spectra are demonstrated in Figure 7. Due to the solvent and state of the crystal sample, the recorded and calculated chemical shifts were differed and they were corrected as per the correction factors.

Generally, in aromatic case with substitutions, the chemical shift of core carbons of ring is always observed greater than 100 ppm [26]. In this case, the benzene was triply substituted hexagonal ring in which, except C1, C4 and C6, all the core carbons like C2, C3 and C5 were shifted chemically by 126, 132 and 131 ppm (Expt- 121, 128 and 138 ppm) respectively. The chemical shift was comparatively high since core carbons positioned around the substitutional place. The chemical shift of C1, C4 and C6 were observed to be 163, 150 and 164 ppm (Expt- 155, 151 and 158 ppm) respectively. The chemical shift of C1 and C6 was found to be high which was mainly due to the hydroxyl group where the paramagnetic shield was broken randomly since they acted as chemical nodal region of hexagonal ring. At C4, the electron delocalization taking place due to the bridge point of electron cloud harmonic oscillation. The C14 and C17 were determined to be having small chemical shift of 37 and 61 ppm and this was purely due to the intermediate allied carbons where during the chemical energy oscillation, electron cloud was virtually filled and simultaneously, paramagnetic shield was concealed and protected. The C22 was calculated to have large chemical shift of 204 ppm where the acid group pulled the electron cloud and send them in to the ring via chain. The charge oscillation restricted point was found to be acid group, from which the electron cloud was partially discharged towards the bridge point C of ring. In this case, the chemical shift clearly elucidated that, the oscillating chemical potential movement was observed among core carbons of hexagonal ring and bridge carbons of chain. The resultant oscillating charge cloud was strongly showed the chemical potential...
Figure 9. UV-Visible and transmission spectra of 3-(3,4-Dihydroxyphenyl)-L-Alanine.

Table 7. Theoretical electronic absorption spectral values of 3-(3,4-Dihydroxyphenyl)-L-Alanine.

| λ (nm) | E (eV) | (f) | Transition levels | Major contribution | Assignment | Region | Bands |
|--------|--------|-----|-------------------|--------------------|------------|--------|-------|
|        |        |     |                   |                    |            |        |       |
| **Gas** |        |     |                   |                    |            |        |       |
| 268.46 | 4.6183 | 0.0057 | H+1→L(42%) | H+1→L(42%) | n→π* | Quartz UV | R-band (German, radikalartig) |
| 265.68 | 4.6667 | 0.0102 | H→L(48%) | H→L(48%) | n→π* |
| 257.58 | 4.8134 | 0.0133 | H→L(32%) | H→L(57%) | n→π* |
| **DMSO** |        |     |                   |                    |            |        |       |
| 269.02 | 4.6087 | 0.0028 | H+2→L(36%) | H+1→L(49%) | n→π* | Quartz UV | R-band (German, radikalartig) |
| 264.49 | 4.6878 | 0.0077 | H+1→L(21%) | H→L(60%) | n→π* |
| 257.37 | 4.8173 | 0.0256 | H+1→L-2(23%) | H→L-1(59%) | n→π* |
| **Water** |        |     |                   |                    |            |        |       |
| 268.96 | 4.6098 | 0.0026 | H+1→L(36%) | H+1→L(49%) | n→π* | Quartz UV | R-band (German, radikalartig) |
| 264.40 | 4.6892 | 0.0070 | H+1→L(21%) | H→L(61%) | n→π* |
| 257.26 | 4.8194 | 0.0241 | H+1→L-2(24%) | H→L-1(59%) | n→π* |
empty orbitals were available to accept electronic energy and here, the $\sigma$ and $\pi$-orbitals were interacted by space charge polarization and chain and ring reserved its own. These are direct acceptor interactive orbitals and quantized to allowed chemical potential as splitted electronic transitions.

The HOMO was appeared as $\pi$ and $\delta$–interactive system of orbitals concentrated on semicircle core carbons of hexagonal frame. Here, all the interactive orbitals are appeared to be merged by overlapping and all electrons in such orbitals are clubbed together and able to make resultant transitions to all available unoccupied orbitals. In this HOMO, all were seem to be $\pi$ and $\delta$-conjugated complex orbitals where the energy of all possible excited molecular energy states were blended and thereby the new properties are exposed from the product organic crystal. In HOMO-1, the space charge polarization made all excited orbitals of all core carbons and part of chain together which was observed to be more intense than HOMO. So it was inferred that, when going from lower order orbital to higher level, the degenerate orbital interaction increased more and more and finally all orbitals of particular energy are linked and thus, the peculiar properties were persuaded. Accordingly, all types of higher order and lower order orbital interactions in this compound made electro-optical properties. The energy gap of present case in first order and second order were 5.26 and 5.36 eV correspondingly which confirmed high degree of dielectric constant of present organic crystal and simultaneously the present case possessed SHG and THG characteristics.

### 4.9. UV-visible absorption/transmission analysis

The UV-Visible absorption spectral simply described existing electronic energy levels and their important transitions associated with Charge transfer complex causing fundamental properties of the organic complex [27] whereas UV-visible transmission spectral pattern used for investigating linear optical characteristics of the chemical compound. Here, both absorption and transmission curves are obtained for the present organic complex and are shown in Figure 9. The electronic absorption parametric values are portrayed in Table 7.

According to the table, three excited transitions observed at 268, 265 and 257 with the energy gap of 4.61, 4.66 and 4.81 eV at oscillator strength of 0.005, 0.01 and 0.013 respectively. All those transitions were assigned to $n\rightarrow\pi^*$ system in Quartz UV region with the band of R-Band (German, radikalatig). These transitions are observed in real molecular phase and all those values are repeated in solvent phase also that confirmed solvent has taken no effect on absorption spectra. According to the assigned wavelengths of transitions, the CT of the present case was identified to be COOH group. Even though, partial transitions represent as H→L-1, H→1→L, H→2→L and H+1→L-2 which are belong to $n\rightarrow\sigma^*$ and $\sigma\cdot\sigma^*$ interactive orbital systems. The resultant electronic absorption was represented by transitions among three vibrational energy states. The UV-Visible energy gap was found to be 4.6–4.8 eV invariably and it is controlled by applied electric potential.

The UV-Visible transmission curves were observed to be flat from 400 nm to 700 nm which showed the good optical response of the present organic composite. The optical transmission response is also recognized even below 400 nm which described that, the present case able to reproduce UV signals with more than 60% intensity. If, the distinct wavelengths are looked out, the absolute optical response for actual wavelength will be determined. From the above observation, it is clear that, the present case is able to produce even laser if it is properly electronically pumped.

### 4.10. Physico-chemical parameters

As in Table 8, the zero point vibrational energy state of this case was found to be 705 Hartree in both regions since there was no structural difference observed between two regions. The resultant dipole moment of molecule; 3-(3,4-Dihydroxyphenyl)-L-Alanine was 2.22 and 3.20 dyne.
in IR and UV region respectively. Here, dipole moment was higher in UV than IR since the optical polarizability was greater in present case than electronic polarizability. The electron affinity and ionization potential was found to be 6.0459 eV & 0.6833 eV and 5.261 eV & 1.309 eV in IR and UV-Visible region in that order. Here, the forbidden energy gap formed in IR was greater than UV-Visible region that ensured current crystal was UV-Visible active.

The Chemical hardness ($\eta$) of the organic composite reflect the chemical inertness of crystal and here it was 2.68 which was moderate and present organic composite was rather hard to receive other chemical species to fuse. The Chemical softness($S$) of this case determined to be 10.7252 which were large and it was enough to accept further organic or inorganic species to produce new compound and thereby properties of the product is different. The Electronegativity ($\chi$) is used to measure the electronegative characteristics of organic complex and here, the same was found to be 3.3646 and 3.9396 in IR and UV region respectively. In both regions, the specific parameter was traced to be high which showed heterogeneity atmosphere in charge levels and hence, it proved the existence strong polarizability. The Electrophilicity index ($\omega$) of present composite was to be 2.11 and 2.95 in both regions and these values illustrated that, distributed anomalous charge domains were found to be present in different coordinates of the crystal composite. The ECT gradient was observed to be $+0.0918$ and it showed the chemical equilibrium of the compound by which it is acted as saturated chemical species.

### 4.11. NLO activity analysis

The non linear optical activity is usually customized by the induce-ment of frequency dependent polarization occurred in the crystal materials. The first order and second order polarizability was calculated and are presented in the Table 9. For this compound, the average and net polarizability were calculated in different coordinates of the molecular complex. It was found to be 83.79 in XX coordinate and it was represented as $\alpha_{xx}$. Similarly, the polarizability was found to be 74.56 in YY component and it was symbolized to be $\alpha_{yy}$. In ZZ component it was determined to be 82.71 denoted as $\alpha_{zz}$. Form these values, it is observed that, in three coordinates (X,Y,Z), the polarizability was taking place and hence such values offering different refractive indices for optical waves. Thus, the birefringence effect is ensured in the crystal composite. In addition to that, the total polarizability $\alpha_{tot}$ and average polarizability $\Delta \alpha$ are observed to be $168 \times 10^{-33}$ esu and $225 \times 10^{-33}$ esu respectively. These parameters were validated the hypo-polarizability in the material and thereby it was optically active. The hyper active polarizability is found to be $91.2 \times 10^{-33}$ esu, $26.63 \times 10^{-33}$ esu and $44.67 \times 10^{-33}$ esu at xxx, xxy and xyy coordinates and these are represented as $\beta_{xxx}$, $\beta_{xxy}$ and $\beta_{xyy}$ respectively. From this view, it was clear that, the hyper action first coordinate is more than rest of two coordinates. The resultant hyper-polarizability is calculated to be $1775.05 \times 10^{-33}$ esu which is five times greater than hyperpolarizability of thio urea. So, in this case, the SHG and THG will be possible with maximum slew rate.

### 4.12. MESP analysis

The electrostatic potential energy Laplacian distribution on the molecular complex showed the charge displacement due to the existence of depletion potential. The molecular charge delocalized according to the electronegative (electrophilic) and protopositive (nucleophilic) enforce-ment in the molecular site. It gives clear cut evidence of hypo and hyper polarization due to the homo and heteronuclear interactions and repulsions [28]. Here, the molecular structures are arranged periodically.
Table 10. The calculated NBO of 3-(3,4-Dihydroxyphenyl)-L-Alanine by second order Perturbation theory.

| Donor (i) | Type of bond | Occupancy | Acceptor (j) | Type of bond | E2 kcal/mol | Ej – Ei au | F(I) au |
|-----------|--------------|-----------|--------------|--------------|-------------|------------|--------|
| Cl-C2     | π            | 1.98366   | Cl-C6       | σ            | 2.01        | 1.13       | 0.043  |
| Cl-C2     | π            | 1.98098   | C4-C5       | σ            | 9.93        | 0.29       | 0.049  |
| Cl-C2     | C6-O12       | C4-C5     | σ            | 2.99         | 0.71        | 0.043     |
| Cl-C2     | C5-C4        | C4-C5     | σ            | 1.97923      | 2.16        | 1.63       | 0.053  |
| Cl-H8     | C4-C5        | C4-C5     | σ            | 6.63         | 0.93        | 0.070     |
| Cl-C8     | C4-C5        | C4-C5     | σ            | 1.97923      | 2.62        | 1.16       | 0.049  |
| Cl-C6     | C1-C2        | C1-C2     | σ            | 9.52         | 0.31        | 0.050     |
| Cl-C6     | C3-C4        | C3-C4     | σ            | 1.175        | 0.33        | 0.056     |
| Cl-C9     | C1-C6        | C1-C6     | σ            | 4.92         | 0.92        | 0.061     |
| Cl-C9     | C1-C6        | C1-C6     | σ            | 51.34        | 1.16        | 0.219     |
| Cl-C10    | C1-C6        | C1-C6     | σ            | 4.47         | 0.52        | 0.045     |
| C11-H20   | C1-C6        | C1-C6     | σ            | 20.07        | 1.21        | 0.139     |
| N19-H20   | C1-C6        | C1-C6     | σ            | 17.78        | 0.36        | 0.074     |
| O10       | C1-C6        | C1-C6     | σ            | 18.53        | 0.36        | 0.076     |
| O10       | C1-C6        | C1-C6     | σ            | 19.9937      | 6.45        | 0.74       | 0.062  |
| O12       | C22-C22      | C22-C22   | σ            | 20.07        | 1.21        | 0.138     |
| N19       | C1-C6        | C1-C6     | σ            | 3.28         | 1.71        | 0.069     |
| O23       | C1-C6        | C1-C6     | σ            | 13.18        | 0.62        | 0.082     |
| O23       | C1-C6        | C1-C6     | σ            | 30.57        | 0.52        | 0.113     |
| O24       | C1-C6        | C1-C6     | σ            | 5.55         | 1.12        | 0.071     |
| C1-C2     | C3-C4        | C3-C4     | σ            | 24.04        | 0.35        | 0.082     |
| C5-C6     | C3-C4        | C3-C4     | σ            | 70.82        | 0.02        | 0.062     |
| C5-C6     | C3-C4        | C3-C4     | σ            | 53.50        | 0.02        | 0.064     |

Figure 11. VCD spectra of 3-(3,4-Dihydroxyphenyl)-L-Alanine.

by performing translation symmetry operation in the crystal structure and hence, the two dissimilar charge domains in the molecular site were displaced and retained at particular places around the atoms that were displayed in Figure 10. After the completion of fusion of alanine and dihydroxybenzene, the molecular charges were settled down; this was rated by color gradient from red (electrophilic) to blue (nucleophilic).

Highly electrophilic zones were appeared over the OH and COOH groups in which the potential is measured to be -5.241 e⁻². Extremely positive region known as protonic zones are found around H of hydroxyl, benzene ring and COOH groups in which the potential is calculated to be -5.241 e⁻². The entire Laplacian charge distribution is controlled by acidic static field and in this case, the phenol, amino group and acid groups are acted as main field source and from which the field is distributed. This entire electrostatic field of molecular structure formed the enantiometric scale that causing binding of molecular structures in the crystal.

4.13. NBMO studies

Except bonding orbitals in the molecule, all the orbitals called non bonding molecular orbitals and the quantized transitions among
important entities are used to validate the chemical potential exchange to produce chemical, optical, electrical and biological properties [29]. The chemical potential energy was measured usually from the transitional energy which is directly proportional to the energy difference between two any orbitals with occupation energy [30]. Many transitions were observed in the interactive orbitals of present molecular complex of which some important transitions were presented in Table 10.

In the ring, the transitions were obtained from donor of (C1–C2) (occup. Energy-1.98366) to C3–C4 and C5–C6 by taking energy of 10.01 and 11.07 kcal./mol. at \( \pi \rightarrow \pi^* \) interactive systems. Similarly, from C3–C4 (occup. energy-1.98098) to C1–C2 and C5–C6 by absorbing energy of 10.90 and 9.93 kcal./mol. at \( \pi \rightarrow \pi^* \) interactive system. The transitions from C5–C6 to C1–C2 and C3–C4 by consuming energy of 9.52 and 11.75 kcal./mol. in same \( \pi \rightarrow \pi^* \) interactive system. Other significant transitions were observed from C5–C9 to N19–H20 and reversely from N19–H20 to C5–H9 by taking energy of 51.34 and 20.07 kcal./mol. in \( \sigma \rightarrow \sigma^* \). From the lone pair of O10 to C1–C2 and C5–C6 with the energy gap of 17.78 and 18.53 kcal./mol. another lone pair of O12 to C5–C6, O23 to C22, O23 to C17–C22 and C22–O24 by consuming energy of 18.53, 14.81, 13.18 & 30.57 kcal./mol. in \( n \rightarrow \sigma^* \), \( n \rightarrow \sigma^* \) and \( n \rightarrow \pi^* \) interacting systems of chain and ring. Consequently, from O24 to C22–O23, C1–C2 to C3–C4 and C5–C6 to C3–C4 by taking energy of 24.04, 70.82 and 53.50 kcal./mol in \( \pi \rightarrow \pi^* \) linking system. Most of the energy transactions were obtained from ring to chain and only less amount of energy observed from chain to ring. Large amount of energy was utilized for those transitions and generates chemical potential called activation potential that is the background of electronic controlled optical property inducement in the crystal material.

4.14. VCD and biaxial crystal analysis

Chirality is a physical property of the inorganic or organic molecule that results from its structure formation. The optical activity is directly recognized by identifying molecular structure in 3-D form in crystal materials. Normally, if the molecule is chiral, that molecule will be optically active and thus the formation of crystal is also optically dynamic [31]. The chiral like molecular compound is non-superposable on its mirror image which is usually formulated by the presence of asymmetric carbon nodal centre with electronegative groups of different masses. The vibrational circular dichroism techniques are not only used in biology for studying toxicity characteristics and also used to evaluate the optical properties in NLO crystallography and organo-metallic material research [32].

In this case, the L-Alanine has already having asymmetrical carbon centers for providing optical activity process in the molecule, and it was fused with dihydroxy benzene, so the optical nodal carbon centers were absolutely improved that guides enriched optical propagation with different velocities. It was validated by the observation of 3D molecular as well as crystal structures. As per Figure 11, the vibrational circular dichroic properties of the present compound were validated. The sequential arrangement of molecular structures within crystal material was detail shown in Figure where in the vibrational circular characteristics have been monitored as per the far-IR, mid-IR and near-IR region along with Raman scattering transmission peaks.

According to the mutual exclusion principle, the active bands in IR were found to be weak in Raman which was validated by the observed VCD spectrum for this case. The alternative peaks in IR and Raman at far-IR were observed to be weak whereas in mid and near IR, the peaks were obtained with moderate intensity. This arrangement in the VCD spectrum ensured non-superimposable mirror-image forms of present molecular structures and here, optimized molecular geometry and associated symmetry point groups (Cs) employed chirality functions that customized by uniquely associated with specific chiral chromophores present in the molecules. From this observation, it was concluded that, the present case was ensured to be biaxial symmetry crystal.

5. Conclusion

The organic-composite crystal; 3-(3,4-Dihydroxyphenyl)-L-Alanine, for optical applications was grown by slow evaporation method. The molecular (C5) and crystal symmetry (Lattice-orthorhombic) (Space group-P212121) were validated by examining the optimized molecular symmetry operation and XRD spectral pattern. The crystal parameters were evaluated and justified for the crystal physical chemical and structural properties. The formation of birefringence effect in the geometry of the crystal was confirmed by observing different refractive indices. The distortion of bond length and bond angles supported to dipole and oriental and electronic polarization for inducing non linear optical activity was proved. The asymmetric charge levels inside the molecule and crystal structure was monitored by the observation of Mulliken charge assignment. The molecular heterogeneity was proved by the homo and heteronuclear bond orientation in the crystal compound. The anisotropic characteristics of present organic composite crystal was studied by the activeness of dipole and polarized bonds in different entities. The role compositional bonds in the crystal to customize the dielectric property were studied from the vibrational analysis. The chemical reaction path for finding the oscillation of chemical potential was monitored by the examination of chemical shift. The \( \sigma, \pi, \delta \)- orbital conjugation interaction system in HOMO and LUMO arrangement was displayed and the exchange of interaction energy was studied and the linked energy gap mechanism was deliberated. The chemical parametric oscillation in terms of kinetic potential was measured from the non bonding molecular orbital interaction complex and maximum contribution of chemical energy to produce all properties was illustrated.

Declarations

Author contribution statement

D. Vidhya: Analyzed and interpreted the data. S. Ramalingam: Conceived and designed the experiments; Wrote the paper. R. Aarthi: Performed the experiments.

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Additional information

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