A Quantum Chemical and Nonlinear Optical Investigation on L-Tryptophan Hydrochloride Single Crystals for Optoelectronic Device Applications

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Abstract: In this study, a semi-organic crystal of L-tryptophan hydrochloride (LTHC) has been synthesized and quality crystals has been grown using a slow evaporation technique. Singe crystal XRD confirms the monoclinic system with space group $P2_1$. UV optical studies displays the transmittance in the entire visible region. The Mulliken charge distribution and MEP mapping show significant charge transfer due to nucleophilic and electrophilic moieties. The molecule's chemical reactivity was examined using HOMO-LUMO and MESP investigations. The crystal's nonlinear properties were studied using the Kurtz-Perry method. These findings suggest that LTHC crystals may have potential applications in the field of nonlinear optics.

Keywords: Semi-organic, Single crystal, Optical, SHG, Nonlinear.

1. Introduction

Over the past two decades, data transmission has experienced exponential growth, with estimates suggesting that approximately 1 billion Gigabytes of data are transmitted on a daily basis. It is clear that the industry stands to greatly benefit from the adoption of nonlinear optical materials as a replacement for standard cables. These materials possess high optical and structural properties, making them highly promising for the development of optical communication systems [1, 2]. However, in order to fabricate successful devices for these sectors, it is essential that the crystals possess specific qualities, such as strong nonlinear optical performance [3, 4].

Amino acids are important chemical compounds that possess amino groups (NH2) and carboxylic acid (COOH) functional groups that can form hydrogen bonds, enabling the creation of innovative organic materials with remarkable nonlinear optical (NLO) and electro-optic properties. L-tryptophan, the most common amino acid, is similar to L-alanine but with an indolyl group replacing a hydrogen atom in the methyl group. Amino acids can react with both organic and inorganic acids to produce various compounds, including simple salts with distinct cations and anions. L-tryptophan has

been synthesized and structurally characterized in various simple salts, including L-tryptophanium chloride and bromide, which were shown to be extremely anisotropic by Takigawa *et al* in which L-tryptophan hydrochloride was crystallized in the monoclinic non-centrosymmetric space group $P2_1$ [5]. The demand for hybrid materials has significantly increased due to their unique structural, chemical, and biological properties. Thus, this study evaluated both the experimental and theoretical properties of L-tryptophan hydrochloride using various methods, such as Mulliken analysis, HOMO-LUMO analysis, molecular electrostatic potential, theoretical first hyperpolarizability UV analysis and powder SHG.

2. Experimental
2.1 Synthesis and Crystal growth

L-tryptophan hydrochloride single crystal was produced by gradually evaporating L-tryptophan and saturated 1 N HCl solutions using a progressive evaporation method. The saturated 1 N HCl solution was prepared by dissolving a predetermined volume of hydrochloric acid into double-distilled water and then gradually adding it to tryptophan while briskly stirring to

create a homogeneous solution. After filtering, the saturated solution was maintained at a specific temperature to allow for evaporation. The crystal's quality was improved by several recrystallization procedures. Over the course of 28 days, LTHC single crystals of exceptional purity and clarity were gathered (Figure 1).

Figure 1. As grown crystals of LTHC.

2.2 Computational Details

The calculation of DFT (B3LYP) was done with a GAUSSIAN 09w programme package without any geometry restrictions [6, 7]. The LTHC model was optimized initially, and the resulting geometries were utilized as inputs for additional calculations at the B3LYP/6-311++ G (d, p) level in the potential energy surfaces. Selected molecules were also examined using the GAUSSVIEW software. The as grown single crystals of LTHC were subjected to single crystal XRD using an Oxford-Diffraction Xcalibur with a sapphire CCD detector and enhance diffractometer (MoKα radiation, graphite monochromator; λ=0.71073A). The optical transmittance spectrum was recorded with a Perkin-Elmer Lambda 35 Spectrophotometer. Theoretical quantum chemical studies were performed using the DFT method with the B3LYP/6-31++G (d,p) basis set and Gaussian 09 program. The molecular structure was optimized from the crystallographic information file (CIF), and the GaussView 5.0 program was used to visualize the HOMO and LUMO orbitals [8].

3. Results and Discussion
3.1 Single crystal XRD

The obtained results indicate that the title compound belongs to the monoclinic system with a space group of $P2_1$. The lattice parameter values are found to be a (Å) =7.442, b (Å) =5.311, c (Å) =14.642 and α=90°, β= 98.786, γ= 90°. The volume of the LTHC crystal was found to be 569. 32 (Å³) [5]. The results are in well agreement with the earlier literature.

3.2 UV-Vis-NIR spectroscopy

In various device applications such as frequency conversion and optoelectronics, the optical properties of crystals play a crucial role. To determine important parameters like band gap energy, cut-off wavelength,

and optical transmittance, UV-Vis-NIR spectroscopy is commonly employed. In this study, the transmittance spectrum of LTHC crystal was measured in the range of 190–1100 nm, as depicted in Figure 2. The obtained spectrum demonstrates that LTHC crystal is highly transparent in the entire visible region and also exhibits a lower cut-off wavelength at 240 nm. The low cut-off wavelength confirms the transparency of the crystal in the ultraviolet and visible regions, indicating its potential for nonlinear optical device applications [9, 10].
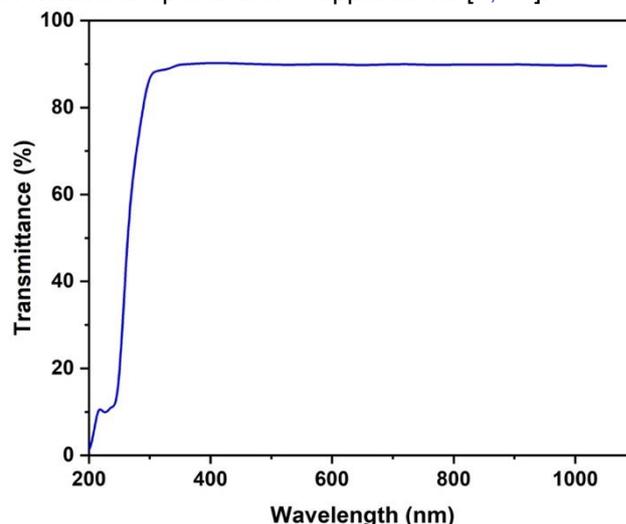
Figure 2. Optical transmittance spectrum of LTHC.

3.3 Optimized molecular geometry

The LTHC molecule's geometry was optimized through the DFT method using the B3LYP/6-311++G(d,p) basis set, and the resulting calculated energy value was -1147.361 atomic units. The optimized molecular structure of LTHC is shown in Figure 3. The carboxylic acid group C1-O1 bond displayed the value of 1.325 Å for XRD and 1.333 Å for DFT structure respectively. But C1=O2 bond exhibited the bond distance value of 1.147 Å (XRD) and 1.206 Å (DFT). The C-N (C4-N1= 1.505 Å and C7-N2 = 1.376 Å) distances of cation were found to be have same length for both DFT and XRD structure (Table 1).
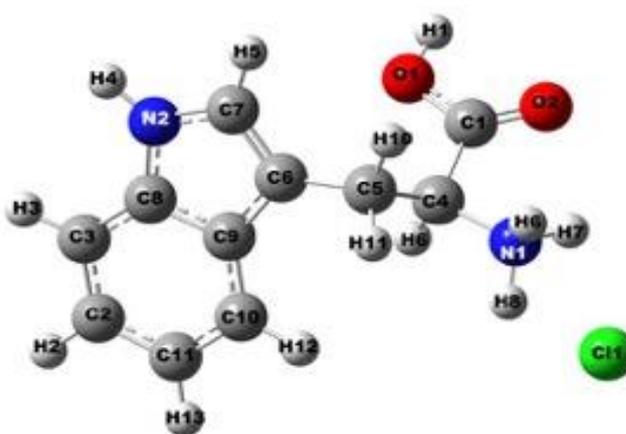
Figure 3. The optimized molecular structure of LTHC by DFT/B3LYP method 6-311++G (d,p) basis set.

Table 1 XRD geometrical parameters comparison with DFT optimized structural parameters of LTHC

Parameters	(XRD)	6311++ G(d,p)	
Bond length values (Å)			
C1-C4	1.54	1.526	
C1-O1	1.325	1.333	
C1-O2	1.147	1.206	
C2-C3	1.399	1.387	
C2-C11	1.386	1.407	
C3-C8	1.4	1.396	
C4-C5	1.54	1.554	
C4-N1	1.505	1.505	
C5-C6	1.53	1.495	
C6-C7	1.345	1.371	
C6-C9	1.451	1.442	
C7-N2	1.376	1.376	
C8-C9	1.382	1.419	
C8-N2	1.391	1.381	
C9-C10	1.412	1.405	
C10-C11	1.398	1.386	
Bond angle values (°)			
C4-C1-O1	106.84	112.51	
C4-C1-O2	125.7	122.68	
O1-C1-O2	127.45	124.78	
C3-C2-C11	119.71	121.23	
C2-C3-C8	116.4	117.51	
C1-C4-C5	115.05	116.27	
C1-C4-N1	106.95	106.04	
C5-C4-N1	109.66	109.202	
C4-C5-C6	114.18	113.83	
C5-C6-C7	128.04	126.81	
C5-C6-C9	126.46	126.43	
C7-C6-C9	105.49	106.75	
C6-C7-N2	111.54	109.77	
C3-C8-C9	123.2	122.31	
C3-C8-N2	128.99	130.48	
C9-C8-N2	107.79	107.19	
C6-C9-C8	107.73	106.89	
C6-C9-C10	131.14	134.29	
C8-C9-C10	121.12	118.8	
C9-C10-C11	114.64	119.05	
C2-C11-C10	124.77	121.06	
C7-N2-C8	107.46	109.38	

Torsion angle values (°)

O1-C1 C4-C5	51.81	55.99
O1-C1-C4-N1	173.86	177.57
O2-C1-C4-C5	-128.21	-125.16
O2-C1-C4-N1	-6.17	3.57
C11-C2-C3-C8	-3.97	0.42
C3-C2-C11-C10	4.48	-0.42
C2-C3-C8-C9	2.97	0.18
C2-C3-C8-N2	-178.73	-179.13
C1-C4-C5-C6	57.85	81.42
N1-C4-C5-C6	-62.72	-158.67
C4-C5-C6-C7	-77.96	-112.11
C4-C5-C6-C9	102.88	68.29
C5-C6-C7-N2	-178.92	-179.81
C9-C6-C7-N2	0.38	-0.52
C5-C6-C9-C8	178.72	179.81
C5-C6-C9-C10	0.22	1.42
C7-C6-C9-C8	-0.6	0.52
C7-C6-C9-C10	-179.09	-178.23
C6-C7-N2-C8	-0.03	0.32
C3-C8-C9-C6	179.21	179.79
C3-C8-C9-C10	-2.12	-0.8
N2-C8-C9-C6	0.59	-0.33
N2-C8-C9-C10	179.27	178.65
C3-C8-N2-C7	-178.87	-179.41
C9-C8-N2-C7	-0.36	0.01
C6-C9-C10-C11	-179.59	-179.4
C8-C9-C10-C11	2.08	0.79
C9-C10-C11-C2	-3.35	-0.21

Table 2. Mulliken atomic charge distribution of LTHC.

Atoms	Charges	Atoms	Charges
N1	0.171	C10	-0.543
H6	0.318	H4	0.319
C4	-0.72	C3	-0.465
H9	0.249	C11	-0.549
C5	-0.314	H12	0.12
C1	0.092	H3	0.149
H11	0.223	C2	-0.094
H10	0.206	H13	0.174
C6	0.613	H2	0.172
O2	-0.245	O1	-0.132
C7	-0.15	H1	0.337
C9	0.702	H7	0.311
H5	0.178	H8	0.35
N2	-0.103	Cl1	-0.815
C8	-0.211		

The phenyl ring of Tryptophan cation has the C-C bond distances values between 1.386 Å and 1.540 Å for XRD structure whereas in DFT structure it was obtained between 1.387 Å and 1.554 Å. There was no considerable deviation has been observed in bond distances between DFT and XRD molecular structure. The carboxylic acid involved bond angles such as (C4-C1-O1, C4-C1-O2 and O1-C1-O2) showed minimum deviations of 5.67 º, -3.02 º and -2.67 º respectively. The C-C-C bond angles (C6-C9-C10, C8-C9-C10, C9-C10-C11 and C2-C11-C10) of cation exhibited some deviations of 3.15 º, -2.32 º, 4.41 º and -3.71 º respectively. The remaining bond angles obtained in optimized molecular structure were found to be have similar values with respect to XRD bond angle values. Most of the dihedral angles of DFT structure were determined to be comparable with XRD structure. Some dihedral angles including C1-C4-C5-C6, N1-C4-C5-C6, C4-C5-C6-C7, C4-C5-C6-C9 and C9-C10-C11-C2 were displayed some considerable deviations of with 23.57 º, -95.95 º, -34.15 º, -34.59 º and 3.14 º XRD molecular structure respectively. The DFT-optimized molecular structure was compared to the XRD molecular structure, and the root mean square deviations were calculated for bond lengths, bond angles, and dihedral angles. The values obtained were 0.016 Å, 0.064 º, and 4.26º, respectively. The hydrogen bond distances were found to be mostly within the range of 2.42-2.48 Å (approximately 71%), with an average value of 2.45 ± 0.01 Å [11].

3.4 Mulliken atomic charge distribution analysis

The LTHC molecule displayed a complex distribution of charges among its atoms (Figure 4). Nitrogen atoms N1 and N2, oxygen atoms O1 and O2, and chlorine atom Cl1 exhibited negative charges. Carbon atoms C6 and C9 displayed positive charges due to electron delocalization within the molecule.
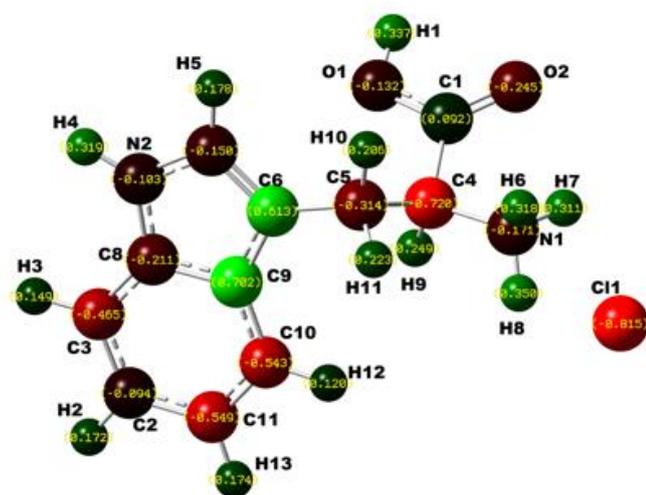

Figure 4. The Mulliken atomic charge distribution of LTHC.

Carbon atom C1 of the carboxylic acid group held a positive charge because of the strong influence of its neighboring electronegative oxygen atoms O1 and O2. All hydrogen atoms (H1-H13) possessed positive charges, with H1, H4, H6, H7, and H8 atoms exhibiting higher positive values and forming intermolecular interactions with electronegative atoms (Table 2).

3.5 Frontier molecular orbital analysis

The significance of the energy separation between the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) in determining the optical properties of a nonlinear optical (NLO) material [12, 13]. The study utilized the DFT/B3LYP-6311G (d,p) basis set to calculate the HOMO and LUMO orbitals, which were found to have energy values of -4.51 eV and -2.29 eV, respectively. The HOMO region was localized near the chlorine anion, while the LUMO region was situated near the tryptophan cation. The molecule exhibited charge transfer between the chlorine anion and the tryptophan cation, with a small energy gap of 2.21 eV (Figure 5). The results suggest that LTHC could have potential as an NLO material in future optical communication technology.
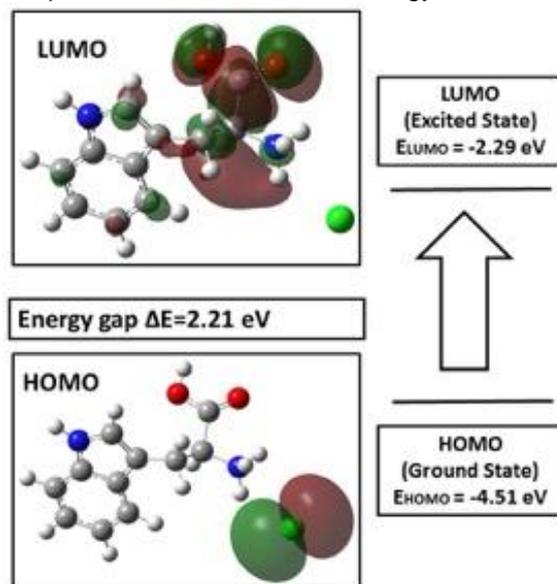

Figure 5. The frontier molecular orbitals (FMOs) of (LTHC) molecule.

3.6 Molecular electrostatic potential map analysis

The electrophilic and nucleophilic reactive sites of the LTHC molecule were investigated through the use of iso-electron density surface mapping in combination with electrostatic potential surface analysis. This widely-used technique provides information on molecular shape and size as well as electrostatic potential distribution. The electrostatic potential surface of LTHC was visualized in Figure 6, using a predicted MEP surface. The red color indicates highly electronegative regions, while blue represents highly electropositive areas. As seen in Figure 6, the chlorine (Cl1) anion is surrounded by a negative electrostatic potential and is thus a

possible site for electrophilic attack. On the other hand, positive electrostatic potential is located over the hydrogen (H1, H4, H7, and H8) atoms, which are promising sites for nucleophilic attack. These findings are consistent with crystallographic studies and are supported by the formation of N__H…Cl and O__H…Cl intermolecular interactions.
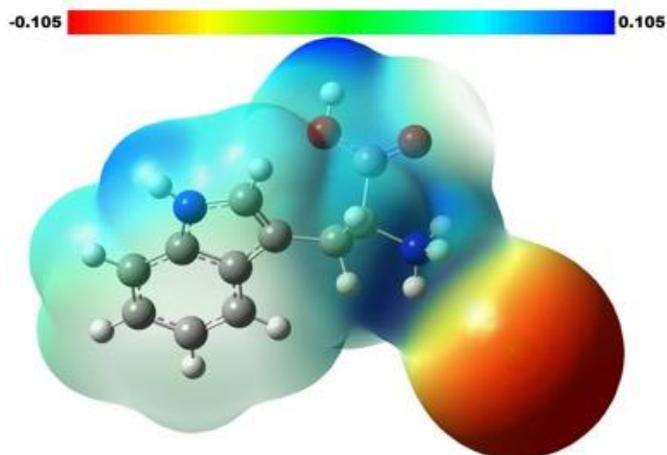
Figure 6 The molecular electrostatic potential surface of (LTHC) with the potential increases in the order of red < orange < yellow < green < blue.

3.7 NLO calculations

Density functional theory (DFT) is a frequently used method to enhance our understanding of the molecular structure and non-linear optical (NLO) properties of organic molecules. Using DFT/B3LYP-6-311G (d,p) basis set, the NLO properties of LTHC were computed and presented in Table 3, including electric dipole moment (μ_0), mean polarizability (α_0), and first-order hyperpolarizability (β_{total}). It was observed that the β_{yyy} component of the first hyperpolarizability had a large value of 10221.53 esu x 10^{-33}, indicating high electron charge mobility in that direction. Typically, the first hyperpolarizability value of urea is utilized as a benchmark to assess the NLO effectiveness of an organic molecule. The DFT/B3LYP-6-311G (d,p) basis set was utilized to calculate the first hyperpolarizability value of urea, which was found to be 0.51 x 10^{-30} esu. In contrast, the first hyperpolarizability value of LTHC was calculated to be 40.56 x 10^{-30} esu, which is 79.3 times greater than that of urea. This high value is attributed to the intermolecular charge transfer between the chlorine anion and tryptophan cation in LTHC.

3.8 Second Harmonic Generation (SHG) experimental studies

From Kurtz-Perry powder technique [14] using the ratio of output signal amplitudes corresponding to the sample to that of reference (KDP) for same input power, relative powder second harmonic generation conversion efficiency of the sample was computed. The PSHG output signal of the LTHC was found to be 18 mV, which was 2.27 times greater than standard KDP powder

output signal (41 mV). The relatively high SHG efficiency is attributed to the quality of the grown crystals.

Table 3 The electric dipole moment (μ_0), mean polarizability (α_0), and first-order hyperpolarizability (β_{total}) components of the **LTHC** molecule were calculated.

α components (esu x 10^{-24})		β components (esu x 10^{-24})	
α_{xx}	34.05	β_{xxx}	-15888.45
α_{xy}	-0.06	β_{xxy}	9782.66
α_{yy}	26.2	β_{xyy}	-6631.22
α_{xz}	1.15	β_{yyy}	10221.53
α_{yz}	3.61	β_{xxz}	-6589.65
α_{zz}	21.46	β_{xyz}	1660.63
α_0	184.05	β_{yyz}	-2999.55
μ_x	-16.12	β_{xzz}	-5325.65
μ_y	11.05	β_{yzz}	3301.11
μ_z	-2.93	β_{zzz}	-5432.9
μ_0	19.76	β_{total}	40562.14

4. Conclusions

The good quality crystals were grown by slow solvent evaporation technique and crystallographic properties were confirmed through single crystal XRD. The crystal was found to be monoclinic and exhibit significant charge dispersion and transfer due to nucleophilic and electrophilic moieties present in the molecule. The crystal's nonlinear effectiveness was evaluated using the Kurtz-Perry method, which showed promising results for its use in nonlinear optics. Additionally, HOMO-LUMO and MESP studies were utilized to demonstrate the chemical reactivity of the molecule. The crystal high transparency and low cut-off wavelength indicate its potential for use in optoelectronic and photonic applications. Overall, LTHC crystals hold promise for use in various device applications due to their unique properties.

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Has this article screened for similarity?
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Author Contribution Statement
Mohamed Ibrahim -Methodology, Data collection, Analysis, Writing—original draft; **S. Arunachalam** - Conceptualization, Supervision, Validation, Writing—review & editing; **J. Suryakanth** - Writing—review & editing; **M. Velayutham Pillai** —original draft, review & editing. All authors read and approved the final manuscript.

Conflict of Interest
The Authors have no conflicts of interest on this article to declare.