Theoretical and Experimental studies on nonlinear optical L-phenylalaninium maleate

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Abstract. Good quality single crystals of L-phenylalaninium maleate (LPM) were grown successfully by slow evaporation technique. The grown crystal was subjected to powder X-ray diffraction study at room temperature. From the powder XRD studies it was observed that the crystal belongs to monoclinic crystal system having non-centrosymmetry with P2₁ space group. Quantum chemical Density functional theoretical (DFT) computations were performed and the optimized structure parameters of LPM molecule calculated by DFT (B3LYP) level with 6-31G (d,p) basis set were obtained. The optical absorption spectrum is used to study various linear optical parameters as a function of incident photon energy. It is found that LPM is a suitable material for NLO applications. HOMO-LUMO calculations were performed and the energy band gap was obtained.

1. Introduction
Nonlinear optical chromopores have attracted great interest in recent years and their compounds are important for the development of high-speed optical modulators and switches. In this context, researchers have been focusing on the search for materials with large optical nonlinearities and for their application in the fields of high speed data transmission, processing and storage [1-3]. Considering the significance and influence of Aminoacids in NLO materials, in this paper, we study the molecular and nonlinear optical properties of L-Phenylalaninium maleate(LPM) using ab initio and density functional theory (DFT) calculations.

2. Experimental Procedure
High purity L-phenylalanine (Merck 99%) and maleic acid (AR grade) were taken in 1:1 molar ratio and dissolved in deionized water. The reaction is as follows,

\[ \text{C}_6\text{H}_5\text{CH}_2\text{CH(NH}_2\text{) + C}_4\text{H}_4\text{O}_4 \rightarrow \text{C}_6\text{H}_5\text{CH}_2\text{CH(NH}_3\text{)}^+ \text{C}_4\text{H}_3\text{O}_4^- \]

The photograph of as grown single crystals of LPM crystal is shown in Figure 1.

Figure 1 Photograph of as grown LPM single crystal
3. Computational details
Quantum chemical Density functional theoretical (DFT) computations were performed using closed-shell Becke–Lee–Yang–Parr hybrid exchange-correlation three-parameter functional (B3LYP) in combination with 6-31G (d,p) basis set to derive the complete geometry optimizations and normal-mode analysis on isolated entities. Above said task was achieved using Gaussian03W [4].

4. Results and Discussion

4.1 Powder X-ray Diffraction Analysis
The grown single crystal of LPM was subjected to powder X-ray diffraction. The powder form of the above-mentioned crystal was taken for analysis using a Rich powder diffractometer - RICH SIEFERT & CO with a scan speed of 1°/min.

The resulting powder X-ray diffraction pattern is shown in Figure 2. The obtained two-theta values were used for indexing by using the XRDA software package. It was confirmed that the crystal belongs to the monoclinic crystal system having non-centrosymmetry with P2₁ space group. Lattice parameters have been determined as a=11.056 Å, b=5.332 Å, c=11.471 Å, α=90.00°, β=101.070°, γ=90.00°.

4.2 Molecular geometry
The optimized molecular structure of the isolated LPM molecule calculated using DFT theory at B3LYP/6-31 level is shown in Figure 3. The optimized geometrical parameters such as bond length and bond angles are given in Table 1.

| S.No | Bondlength(Å) | Bond angles(°) |
|------|---------------|----------------|
| 1    | C₁-C₆         | C₁-C₆-C₅       | 119.999 |
| 2    | C₁-C₂         | C₆-C₁-C₂       | 119.998 |
| 3    | C₂-C₃         | C₁-C₂-C₃       | 120.008 |
| 4    | C₃-C₄         | C₂-C₃-C₄       | 119.994 |
| 5    | C₄-C₅         | C₄-C₅-C₆       | 119.994 |
| 6    | C₅-C₆         | C₄-C₃-C₁₂      | 119.993 |
| 7    | C₁₂-C₁₅       | C₁₂-C₁₅-O₂₂    | 109.471 |
| 8    | C₁₅-N₁₇       | O₂₋₂⁻C₁₂⁻O₂₂   | 119.99996 |
| 10   | C₁₅-C₂₁       | C₂-C₃⁻C₁₂      | 120.01277 |
| 11   | C₂₁-O₂₃       | H₁₉⁻N₁₇⁻H₁₈    | 109.47119 |
| 12   | C₂₁-O₂₂       | C₂₁-C₁₅-H₁₆    | 109.47122 |
| 13   | N₁₇-H₁₉       | C₁₂-C₁₅-C₂₁    | 109.47119 |
| 14   | O₂₂-H₂₄       | C₁₂-C₁₅-N₁₇    | 109.47123 |
4.3 HOMO-LUMO Analysis
The energies of the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) are computed at B3LYP/6-31G(d, p) level. HOMO and LUMO orbitals are shown in Figure 4. Generally, the energy values of LUMO, HOMO and their energy gap reflect the chemical activity of the molecule. The energies of the HOMO and LUMO, based on the optimized structure are computed as -0.10814 and -0.05570 a.u, respectively. The HOMO-LUMO energy gap is -0.05244 a.u. The calculated HOMO and LUMO energies clearly show that charge transfer occurs within the molecule.

Figure 4. HOMO – LUMO plot of LPM molecule.

4.4 Optical Properties of LPM
The optical properties of a material are important, as they provide information on the electronic band structures, localized states and types of optical transitions. To determine the transmission range and hence to know the suitability of LPM single crystals for optical applications, the UV-Vis-NIR spectra (Figure 5) were recorded in the range of 200–1200 nm. The spectrum reveals that the LPM compound has a wide transparency window in the region 240–1000 nm (~80%) and shows no remarkable absorption in the visible region. Figure 6 and Figure 7 shows the plot of extinction coefficient and refractive index against incident photon energy. It’s found that extinction coefficient remains constant for incident photon energy of 1.2 eV to 5.5 eV. The variation of refractive index with incident photon energy shows that initially the refractive index decreases with increasing photon energy then becomes constant.

Figure 5. Optical absorption spectrum of LPM
5. Conclusions
Optically good quality single crystals of LPM were grown by slow solvent evaporation technique. The grown crystal is subjected to Powder X-ray diffraction analysis and it is found that the crystal belongs to the monoclinic system with P2$_1$ space group. Density functional theory (DFT) computations using (B3LYP) level with 6-31 G (d,p) basis set gives optimized structure parameters of LPM molecule. It is understood that hydrogen bonds are prevalent in this material and the optimized C–C bond lengths of LPM fall in the range 1.39471–1.54000 Å. Molecular energy gap of LPM was found as -0.05244 au by HOMO-LUMO analysis. Optical absorption spectrum was recorded for the given crystal and it is found that it has minimum absorption between 240 -1000 nm. Linear optical constants like extinction coefficient and refractive index are calculated and related with incident photon energy. This optical analysis reveals the NLO behavior of the material.

6. References
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