

Vibrational and Homo-Lumo Analysis of L - Aspararginium Tartrate by Density Functional Theory

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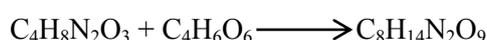
Abstract. L - Aspararginium Tartrate (LAsT), a semi organic nonlinear optical material was synthesized by slow solvent evaporation technique. Fourier transform infrared (FT-IR) spectroscopic studies were performed for identifying different functional groups present in the compound and was compared with the theoretical data obtained from DFT studies. Non-linear optical (NLO) behavior of the LAsT was investigated by the determination of the dipole moment μ and the hyper polarizability β obtained by B3LYP/6-31G (d, p) method. The calculated highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) with frontier orbital gap were presented.

1. INTRODUCTION

Nonlinear optical (NLO) crystals with high conversion efficiencies for second harmonic generation (SHG) and transparent in visible and ultraviolet ranges are required for numerous device applications. In the last few years, much progress has been made in the development of nonlinear optical (NLO) organic materials for second harmonic generation (SHG). However, most of the or Nonlinear optical (NLO) crystals with high conversion efficiencies for second harmonic generation (SHG) and transparent in visible and ultraviolet ranges are required for numerous device applications. In the last few years, much progress has been made in the development of nonlinear optical (NLO) organic materials for second harmonic generation (SHG). However, most of the organic NLO crystals are constituted by weak van der Waals and hydrogen bonds with conjugated π electrons [1]. In this respect, amino acids are interesting materials for NLO applications [2-3]. To the best of our knowledge, no density functional theory DFT wavenumber and structural parameters calculations of LAsT has been reported so far. The present work deals with the growth and characterization along with the detailed vibrational spectral investigation of LAsT.

2. EXPERIMENTAL PROCEDURE

L-Asparagine–L-tartaric acid (LAsT) was synthesized by dissolving one mole of L- Asparagine (Merck 99%) in double distilled water containing one mole of L-tartaric acid. The reaction is as follows



The synthesized salt was further purified by repeating the crystallization process at least thrice. The solubility of LAsT in deionized water (solvent) was determined by adding a solute in solvent till it is completely dissolved. The temperature dependence of solubility of LAsT is shown in Figure 1. Figure 2 shows the photograph of as grown crystal of LAsT.

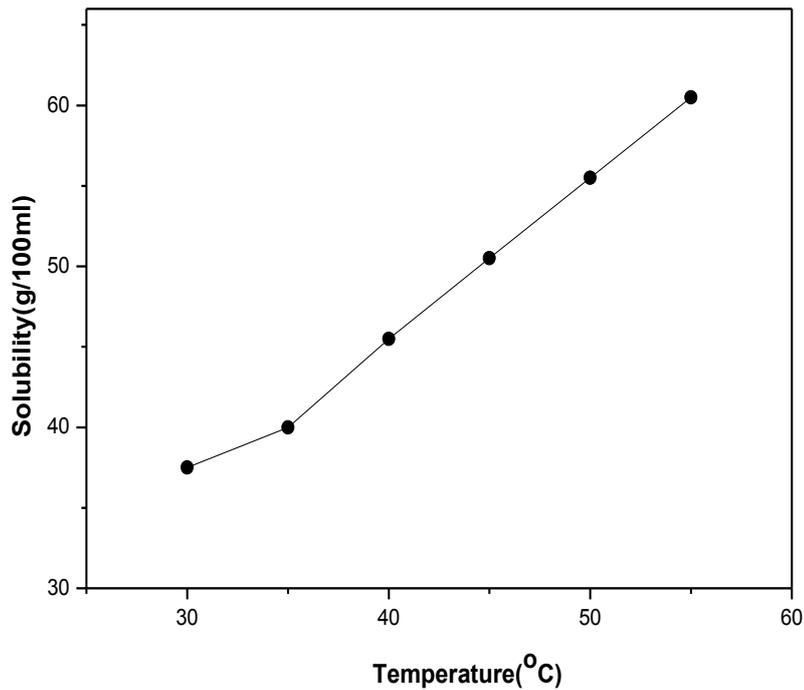


Figure 1.The solubility curve of LAsT crystal

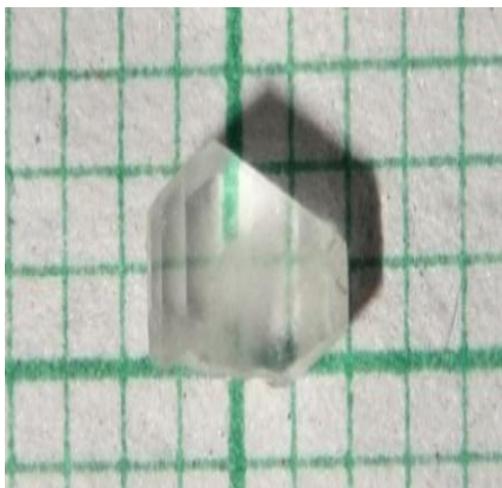


Figure 2.The grown LAsT crystal

3. RESULTS AND DISCUSSION

3.1 X-ray diffraction analysis

The selected well shaped, transparent, single crystal of LAsT was mounted on a BRUKER NONIUS CAD4/MAC4 X-ray diffractometer. Reflection data were measured at 20°C using graphite monochromated Mo-K α radiation and a ω -2 θ scan mode. The structure was solved by direct methods and refined by full-matrix least-squares method using the SHELXS-97 software package [4]. From the single crystal analysis, it was observed that the crystal belongs to monoclinic crystal system having non-centrosymmetry with P2₁ space group. A summary of the key crystallographic information is given in Table 1.

Table 1. Crystal parameters of LAsT single crystal

Crystal data	
Empirical formula	C ₈ H ₁₄ N ₂ O ₉
Crystal System	Monoclinic
Space Group	P2 ₁
a(Å)	5.086 Å
b(Å)	9.672 Å
c(Å)	11.834 Å
β(°)	95.31°

3.2 COMPUTATIONAL DETAILS

Quantum chemical density functional theory calculations were carried out with the 2003 version of the Gaussian program package using B3LYP functions [5] combined with the 6-31+G(d, p) basis set. The optimized geometrical parameters, fundamental vibrational frequencies, IR intensity, the atomic small charges, dipole moment, reduced mass and force constant were calculated.

VIBRATIONAL ASSIGNMENTS

The title molecule LAsT has 33 atoms. It has 93 (3N – 6) normal vibrational modes. The 93 normal modes of LAsT are distributed amongst the symmetry species as

$$\Gamma_{\text{vib}} = 63 A' \text{ (in-plane)} + 30 A'' \text{ (out-of-plane)}.$$

3.3 FT-IR ANALYSIS

FT-IR spectrum of the grown crystal was recorded in the range 500 cm⁻¹ to 4000 cm⁻¹, using KBr pellet technique on BRUKKER IFS FT-IR Spectrometer. The experimental IR spectrum is compared with the results of B3LYP/6-31+ G (d, p) calculation carried out for the title compound. The experimental FT-IR is shown in the Figure. 3.

C-H Vibrations

Presence of band in the region 2700–3000cm⁻¹ is the characteristic region for the identification of C–H stretching vibrations [6]. In this region the bands are slightly affected by the nature of the substituent. The IR vibrations are around 2900cm⁻¹. The experimental C–H vibrations are in good agreement with theoretical vibrations. For LAsT molecule prominent numbers of CH symmetric vibrations are obtained at frequencies 3092, 2977 and 2960cm⁻¹.

NH₂ Vibrations

The NH₂ asymmetric stretching vibrations [7] give rise to a strong band in the region 3390±60cm⁻¹ and the symmetric NH₂ stretching is observed as weak band in the region 3210±60cm⁻¹. In our title molecule the theoretically computed NH₂ asymmetric and symmetric stretching vibration by B3LYP/6-311(d,p) method is at 3369 and 3344 cm⁻¹. But the recorded spectrum does not show any kind of peak in this region. In the present work, NH₂ symmetric stretching is assigned at 3320 cm⁻¹ in IR region and also in 3280 cm⁻¹. The experimental values are well coincides with DFT values.

COO⁻ Vibration

Carboxyl group vibrations give rise to intense characteristic bands due to conjugation or formation of hydrogen bonds. These stretching and bending vibrations of acid group are generally expected in the region 1400–1200 cm⁻¹. In the present work COO symmetric stretching is at 1420 cm⁻¹ and 1553 cm⁻¹ have asymmetric stretching in IR region.

O–H Vibrations

The O–H group gives rise to three vibrations (stretching, in-plane bending and out-of-plane bending vibrations). The O–H group vibrations are likely to be the most sensitive to the environment, so they show pronounced shifts in the spectra of the hydrogen bonded species. The hydroxyl stretching vibrations are generally observed in the region around 3500cm⁻¹[8]. In the title compound the O-H vibrations is present at 3450 cm⁻¹ in IR region. The detailed vibrational assignments of LAsT for the experimental FT-IR along with the calculated frequencies for different basis sets are tabulated in Table 2.

Table 2. Vibrational Assignments of LAsT molecule

S.NO	FT-IR frequency		Vibrational Assignments
	Experimental	B3LYP	
1	3320	3327	νOH
2	3280	3308	νasym NH ₃ ⁺
3	1673	1678	βNH ₂
4	1310	1307	βCH, νCC
5	1065	1048	γCO
6	690	689	Sym ring breath
7	510	510	φNCN

ν-stretching; β-bending; δ-in-planebending; γ-out-of-plane bending;

ω- wagging; φ-rocking; τ-torsion

3.4 Hyperpolarizability

The non-linear optical properties play an important role for the design of materials in modern communication technology, signal processing, optical switches and optical memory devices [9]. The non-linear optical properties of the organic molecules arise from delocalized π electrons that move along molecule. The increase of the conjugation on molecule leads to an increase in its nonlinear optical properties. One another way to increase non-linear optical properties is to add donor and acceptor groups. Acceptor group is opposite of donor group in the organic molecules containing donor and acceptor groups and π electron cloud moves from donor group to acceptor group. If the donor and acceptor groups are powerful, delocalization of π electron cloud on organic molecules increases and as a result of this the polarizability and first hyperpolarizability of organic molecules

increase [10]. First-order molecular hyperpolarizability is a third rank tensor that can be described by $3 \times 3 \times 3$ matrix. The 27 components of the 3D matrix can be reduced to 10 components due to the Kleinman symmetry. The calculated polarizability α and first hyperpolarizability β of LAsT is 1.765808×10^{-30} esu that is greater than that of urea (0.37289×10^{-30} esu), respectively.

3.5 HOMO-LUMO energy gap

Both the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) are the main orbital take part in chemical stability. The HOMO represents the ability to donate an electron, LUMO as an electron acceptor represents the ability to obtain an electron. The HOMO and LUMO energy calculated by B3LYP/6-31G (d,p) method as shown in figure 4.

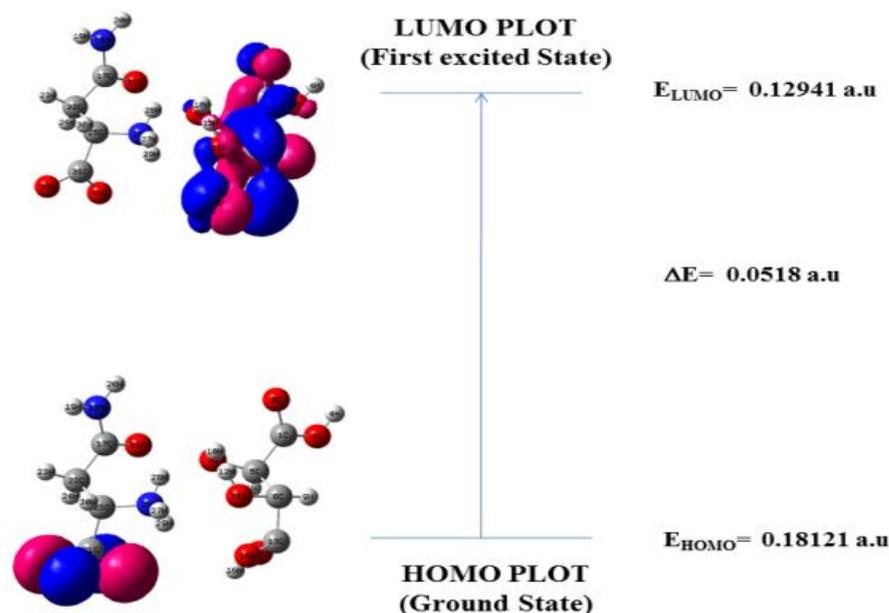


Figure 3. HOMO – LUMO plot of LAsT at B3LYP/6-31 G (d, p)

3.6 SHG efficiency studies

The second harmonic generation efficiency of the powdered material is measured using Kurtz and Perry method. A second harmonic signal of 161 mV is obtained for LAsT with reference to KDP (53 mV). Thus the SHG efficiency of LAsT is 3 times that of KDP.

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4. CONCLUSION

Single Crystals of L-Asparagine–L-tartaric acid (LAsT) of dimension $5 \times 3 \times 8 \text{ mm}^3$ are conveniently grown by slow evaporation technique at room temperature. The XRD analysis proves that LAsT crystal belongs to monoclinic in structure with a non centrosymmetric space group $P2_1$. Fourier transform infrared (FT-IR) spectroscopic studies were performed for identifying different functional groups present in the compound. Non-linear optical (NLO) behavior of the LAsT was investigated by the determination of the dipole moment μ and the hyperpolarizability β obtained by B3LYP/6-31G (d, p) method. The calculated highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) with frontier orbital gap were presented.

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