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# Studies on the growth, spectral, thermal, and optical properties of L-arginine adipate crystal

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ABSTRACT

Single crystals of L-arginine adipate were grown by liquid diffusion technique. The unit cell parameters were characterized by single crystal X-ray diffraction analysis. The structure of grown crystals was determined from Nuclear Magnetic Resonance spectral analysis. The UV–vis–NIR spectrum and Second Harmonic Generation were used to find its optical characteristics feature. The fundamental functional groups were identified from Fourier Transform Infra Red spectral analysis. The thermal behavior of the crystal has been found out by Thermal Gravimetric Analysis and Differential Thermal Analysis.



## 1. Introduction

Organic crystals exhibit unique properties due to its high chemical purity, which founds a lot of interest in the field of solid-state lasers. In the case of optical gain materials, the stimulated emission of cross-section is high and has a broad tunable emission of wavelength. Organic crystals shows excellent optical nonlinear activity than inorganic crystals [1,2]. Being highly pure it possess properties like high thermal stability and high polarized emission of radiation and low scattering densities [3]. The centrosymmetric nature of the crystal possesses the properties of third order non-linearity and the third order non-linear susceptibilities are useful for all optical switching, modulating and computing devices [4]. The third order non-linear optical materials have weak non-linear absorption and have considerable attention of their potential use in the optical signal processing devices [5]. Arginine is the most common amino acid with a proton acceptor carbonyl (—COO) group and the proton donor ($—NH_2$) group. α-Amino acid compounds have some special features such as molecular chirality, high transparency in UV and visible regions, and the zwitterionic nature of the molecule, which hardens the crystal [6]. L-Arginine found advantages with different salts, and a number of different acids on reaction with arginine were synthesized and grown. The crystal structure of L-arginine adipate was first reported by Roy et al. [7]. It crystallizes in the monoclinic crystal system, having $P2_1$ space group, with the values of $a = 12.494(4)$ Å, $b = 5.9510(7)$ Å, $c = 16.719(5)$ Å, $\beta = 105.977(5)^\circ$, $Z = 2$, and $V = 1195.1(6)$ Å$^3$. In the present work, the studies on the growth of L-arginine adipate crystal are carried out by liquid diffusion method. And the grown crystals were characterized by X-ray Diffraction analysis (XRD), Fourier Transform Infra Red Spectroscopy (FTIR), Nuclear Magnetic Resonance Spectroscopy (NMR), Thermal studies, optical characterization like UV–vis–NIR Spectroscopy, and Second Harmonic Generation (SHG) property.

## 2. Experimental

Crystals of L-arginine adipate were obtained from liquid diffusion method by making aqueous solution of L-arginine and adipic acid in equimolar ratio with the addition of ethanol or acetonitrile as the precipitant. Transparent crystals of L-arginine adipate were

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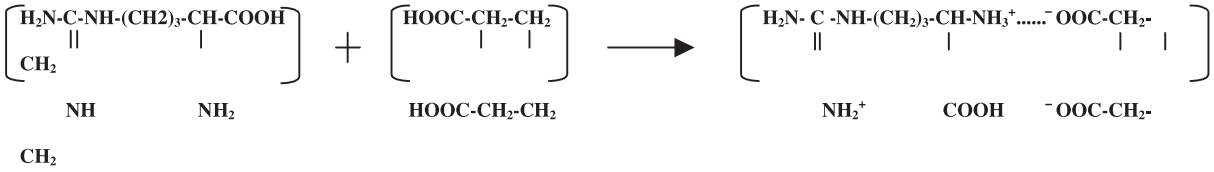
grown in a period of one week. The formation of the complex L-arginine adipate is given below.




L- arginine adipic acid L- arginine adipate

### 2.1. Characterisation

Single crystal XRD study was carried out using Nonius CAD4/MACH 3 single crystal X-ray diffractometer with Mo$K\alpha$ ($\lambda = 0.71069$ Å) radiation. The $^1$H NMR and $^{13}$C NMR spectra were recorded for the crystals by dissolving in heavy water ($D_2O$) using Bruker 300 MHz (ultrasheild)$^{TM}$ instrument at room temperature (300 MHz for $^1$H NMR (Nuclear Magnetic Resonance) and 75 MHz for $^{13}$C NMR) for the confirmation of molecular structure. The transparency range was investigated by λ35 model PerkinElmer double beam UV–vis–NIR spectrometer in the range from 190 nm to 1100 nm. FTIR (Fourier Transform Infra Red) spectrum was recorded by the KBr pellet technique using a SPECTROMRX1 FTIR spectrometer to confirm the functional groups. TGA (Thermal Gravimetric Analysis)/DTA (Differential Thermal Analysis) were carried out using the instrument SDT Q600 V20.9 Build 20 at a heating rate of 20 °C/min in nitrogen atmosphere in temperature range 30–1100 °C. The measurement of the SHG efficiency was determined using powder technique developed by Kurtz and Perry. The SHG measurement was carried out using *Q*-switched mode locked Nd:YAG laser with first harmonic output at 1064 nm, with an input energy of 1.9 m J/pulse and a pulse width of 10 ns at a repetition rate of 10 Hz.

## 3. Result and discussion

### 3.1. Single crystal XRD

Single crystal X-ray diffraction analysis was carried out to find the lattice parameters. This study reveals that the grown crystals of L-arginine adipate belong to the monoclinic system. The determined unit cell parameters are listed in Table 1. The observed values of L-arginine adipate crystal is found to be in good agreement with the reported values [7].

### 3.2. NMR studies

In order to analyse carbon-hydrogen bonded network of the crystal, $^1$H NMR and $^{13}$C NMR spectra were recorded using $D_2O$ solvent in Bruker 300 Hz(Ultrasheid) instrument at room temperature. The $^1$H NMR and $^{13}$C NMR spectrum of L-arginine adipate are shown in Figs. 1 and 2. The chemical shifts are tabulated in Tables 2 and 3.

In the $^1$H NMR spectrum the appearance of an intense peak at $\delta = 4.676$ ppm due to the presence of $D_2O$ solvent. The spectrum shows two triplet peaks at $\delta = 3.601$ ppm and $\delta = 3.075$ ppm corresponds to the proton of —CH— and —$CH_2$— groups of L-arginine. Two multiplets at $\delta = 1.764$ ppm and $\delta = 1.382$ ppm corresponds to the two —$CH_2$— groups of L-arginine. Similarly the two —$CH_2$— protons of adipate appeared at $\delta = 2.028$ ppm and $\delta = 1.565$ ppm. There is no peaks appeared for —$NH_2$— and —COOH— groups in $^1$H NMR, indicates that they are ionic in nature and are involved in secondary forces.

The $^{13}$C NMR spectrum of L-arginine adipate crystals showed nine different peaks corresponds to nine carbon atoms. The signal at $\delta = 183.57$ ppm and $\delta = 174.34$ ppm confirms the presence of carbonyl groups of L-arginine and adipic acid respectively. The carbon attached to NH═C—$NH_2$ group shows the signal at $\delta = 156.70$ ppm. The signal at $\delta = 54.19$ ppm is due to the carbon atom attached to amino group. The signals at $\delta = 40.41$ ppm, $\delta = 27.77$ ppm and $\delta = 25.03$ ppm owes to three —$CH_2$— groups of L-arginine moiety. Similarly the signals for two —$CH_2$— groups in adipic acid appeared at $\delta = 37.32$ ppm and $\delta = 23.84$ ppm.

**Table 1**
Unit cell parameters of L-arginine adipate.

| Cell parameters | Values |
|---|---|
| $a$ (Å) | 12.47 |
| $b$ (Å) | 5.99 |
| $c$ (Å) | 16.65 |
| $\alpha^\circ$ | 90 |
| $\beta^\circ$ | 105.88 |
| $\gamma^\circ$ | 90 |
| $V$ (Å$^3$) | 1197 |
| Crystal system | Monoclinic |

### 3.3. UV–vis–NIR spectral analysis

The UV Visible spectrum of the crystal in Fig. 3 shows an excellent transparency in the entire UV–vis–NIR region. All amino acids possess the property, that the absorption of radiation is absent in the entire visible region [8,9]. From the spectrum it is clear that

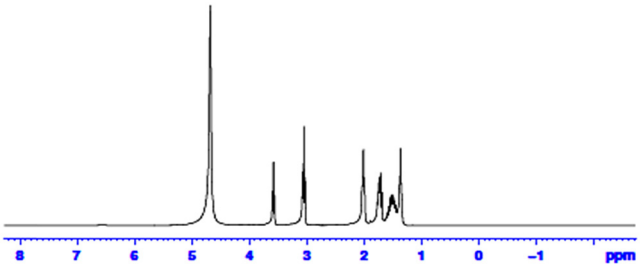



**Fig. 1.** $^1$H NMR spectrum of L-arginine adipate.

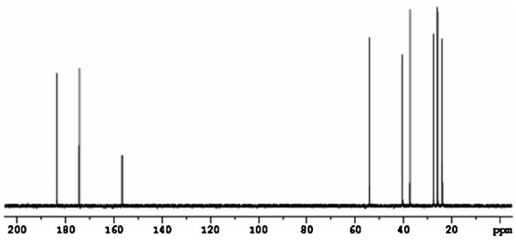



**Fig. 2.** $^{13}$C NMR spectrum of L-arginine adipate.