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Studies on Third Order Nonlinear Optical Property and Biological Activity of DL-Methioninium Maleate for the Applications in Optoelectronics and Biomedical Field

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Abstract. DL-methioninium maleate [DLMM] compound is one of the amino acid compounds exhibiting antibacterial activity besides nonlinear optical behavior. The compound was grown by using slow evaporation technique based on the knowledge of the classical theory of nucleation kinetics. The lattice parameters of the grown crystal were determined as $a = 11.06$ Å, $b = 5.67$ Å, $c = 19.70$ Å, $\alpha = 90^\circ$, $\beta = 102.59^\circ$ and $\gamma = 90^\circ$ with the volume of unit cell as 1229 Å^3 by single crystal X-ray diffractometer. The functional groups present in the grown material were confirmed by FTIR study. The molecular structure of the grown compound was analyzed by ^{1}H NMR and ^{13}C NMR spectral studies. The third order nonlinear optical parameters of the material were calculated as $n_2 = 3.32$ cm^2/W, $\beta = 3.20$ cm/W, and $\chi^{(3)} = 1.02$ esu by using Z-scan technique. Finally, Agar disc diffusion method was employed to discuss the biological activity of the grown compound. The grown DLMM compound is therefore an useful material to find applications in optoelectronics and biomedical field due to its third order nonlinear behavior and biological activity.

KEY WORDS: Biological activity, FTIR study, NMR study, Nucleation kinetics, Single crystal XRD, Z-scan technique.

1 Introduction

Several researchers have been searching for new nonlinear optical materials over the last two decades, combining organic and inorganic chemical compounds from the amino acid family because of their zwitterion nature to find

useful applications [1–4]. Amino acid compounds mix well with any inorganic compound and prefer to form single crystals, which are advantageous for nonlinear optical applications. Telephony, solid-state lasers, light-emitting transistors, photodynamic treatment, energy storage devices, photonics, high-resolution spectroscopy, optical fibers, optoelectronics, and optical switching are interesting applications of the nonlinear optical materials [5–7]. Recently, amino acid materials have been combined with organic or inorganic compounds to create interesting new nonlinear optical materials, such as L-alanine barium chloride [8], glycine sodium fluoride [9], L-alanine P-toluene sulfonic acid [10], L-methionine barium bromide [10], L-proline guanidine carbonate [12], DL-methionine doped ammonium dihydrogen phosphate [13] and others. The results of research on the amino acid family of crystals [14–16] are more encouraging to continue the research in this direction. As a result of a keen interest in the amino acid family of compounds, the compound DL-methioninium maleate is grown in the present study by combining DL-methionine and maleic acid with equimolar ratio. The sulphur component present in DL-methionine amino acid is active to synthesize proteins making the material more bioactive [17, 18]. After growing the crystal, the crystal nature and crystal structure were confirmed by XRD analysis. The material was then characterized first time by using NMR studies, Z-scan technique and Agar disc diffusion method to analyze the molecular structure, third order nonlinear optical property and antibacterial activity. A brief description of nucleation kinetics [19, 20] is also discussed to achieve proper supersaturation for obtaining good quality crystals. The FTIR study is included to confirm the functional groups present in the compound.

2 Synthesis of DLMM Compound

Before growing the compound, the critical supersaturation was estimated from the following expressions for nucleation rate (J), critical free energy change (ΔG^*) and volume energy change (ΔG_v),

$$J = A \exp\left(\frac{-\Delta G^*}{kT}\right), \tag{1}$$

$$\Delta G^* = \frac{16\pi\sigma^3}{3kT\Delta G_v^2}, \tag{2}$$

$$\Delta G_v = -\frac{kT}{v} \ln S, \tag{3}$$

where the symbols have usual meanings. The critical supersaturation was estimated as 1.22 by setting $J = 1$ at room temperature 300 K. At ambient temperature, a solution of maleic acid (Loba chemie – 99%) and DL-methionine (Loba chemie – 99%) was prepared with a molar ratio 1:1. It was ensured to keep the solution undersaturation, that is, below 1.22. The solution was stirred well for homogenization and kept undisturbed for slow evaporation in a constant temperature bath. After 10 days, DLMM single crystals with higher transparency were

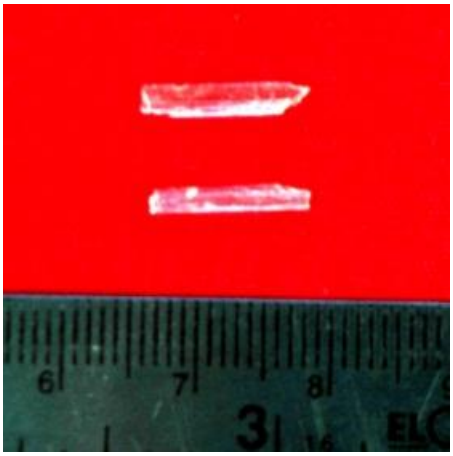


Figure 1. As-grown DLMM single crystals.

obtained when the solution reached supersaturation just above critical supersaturation. The crystals were purified by repeated crystallization. Figure 1 shows the as-grown DLMM single crystals. The reaction formula is as follows:

$$C_5H_{11}NO_2S + C_4H_4O_4 \rightarrow [C_5H_{12}NO_2S]^+[C_4H_3O_4]^- \ . \qquad (4)$$

3 Characterization Techniques

The lattice parameters of the grown DLMM crystal were calculated by using a BRUKER SMART APEX II single crystal X-ray diffractometer. The molecular structure of the grown crystal was examined using the SHELXT-2014/n programme. FTIR spectra of the compound were recorded by using Burger IFS 66V spectrometer with KBr pellet technique. NMR spectra were recorded at 22°C using D_2O as a solvent on a BRUKER AV II 500 MHz FT NMR spectrometer. Z-scan set up was arranged to evaluate the third order NLO parameters and finally the antibacterial activity was analyzed using the Agar disc diffusion method.

4 Results and Discussion

4.1 Single crystal XRD

To estimate and confirm the crystal data of the grown crystal, single crystal XRD analysis was carried out separately for the grown DL-methioninium maleate crystal using single crystal X-ray diffractometer with MOKα ($\lambda = 0.71073$ Å)

radiation. From the XRD measurement, the lattice parameters were estimated as $a = 11.06$ Å, $b = 5.67$ Å, $c = 19.70$ Å, $\alpha = 90°$, $\beta = 102.59°$ and $\gamma = 90°$ with the volume of unit cell as 1229 Å^3. The results reveal that the grown crystal belongs to monoclinic crystal system with $P_{21/c}$ centrosymmetric space group. It is observed that the lattice parameters of DLMM are found to be in good agreement with the published values [21]. Since it is known that the material belongs to centrosymmetric space group, it can exhibit third order nonlinear optical behavior.

4.2 Crystal structure

The molecular structure of the DLMM crystal is shown in Figure 2. The cationic form of DL-methioninium maleate contains a protonated amino group and an unmodified carboxylic group. The oxygen atoms in the semi-maleate ion form an intramolecular hydrogen bond. Methioninium cations on either side of these layers produce alternately hydrophobic and hydropolic layers. The six methioninium cations are found beside a pair of maleate ions. The presence of sulphur in methionine amino acid is primarily responsible for protein synthesis, making the substance bioactive.

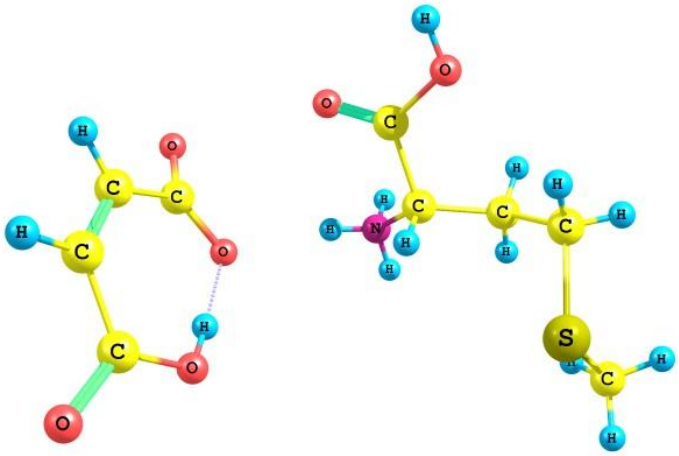


Figure 2. Molecular structure of DLMM crystal.

4.3 FTIR study

The FTIR spectra of the grown crystal are shown in Figure 3. It is observed that N-H asymmetric stretching vibrations, CH_2-S asymmetric stretching, NH out of plane bending, $(NH_3)^+$ asymmetric stretching vibrations and CH_3 asymmetric deformation correspond to 3432 cm^{-1}, 2918 cm^{-1}, 1618 cm^{-1}, 3186

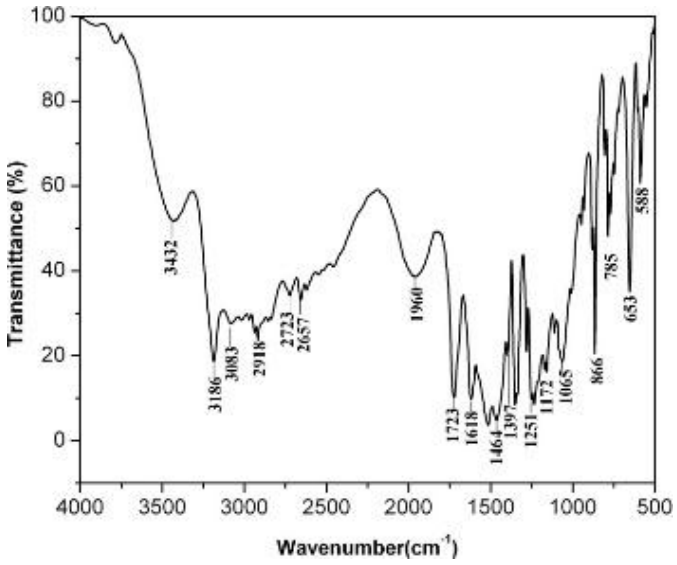


Figure 3. FTIR spectra of DLMM crystal.

and 3083 cm^{-1} and 1464 cm^{-1} respectively. Overtones and combination bands have been assigned to the wave number range 1700–2900 cm^{-1}. The absorption band at 1397 cm^{-1} is due to symmetric stretching COO, whereas the absorption bands at 1172 cm^{-1} and 588 cm^{-1} are related to the rocking and wagging mode of COO. The vibrational peaks of CH_2 asymmetric stretching (2938 cm^{-1}) and wagging (1350 cm^{-1}) are also discernible and both twisting (1281, 1251, 1235 cm^{-1}) and rocking modes (1009, 719, 653 cm^{-1}) are observed with the peak of NH_2 rocking at 866 cm^{-1} [22]. The functional groups present in the grown molecule are thus confirmed.

4.4 NMR studies

The study of proton nuclear magnetic resonance (^{1}H NMR) is effective to identify organic compounds. The DLMM signals and associated chemical shifts are shown in Figure 4. Maleic acid –CH=CH– is responsible for the peak at 6.232 ppm, which is a doublet. The triplets at 3.937 ppm, 3.949 ppm, and 3.962 ppm identify the esters from the COO–C–H group.

^{13}C NMR spectrum analysis is another important analytical tool used to analyse the structure of DLMM single crystal. The signal at 13.869 ppm is due to the presence of a CH_3 sulphur group containing DL-methionine (Figure 5). Protein accumulates and becomes physiologically active in the compound because of sulphur in DL-methionine. The signals at 28.623 and 29.137 ppm are

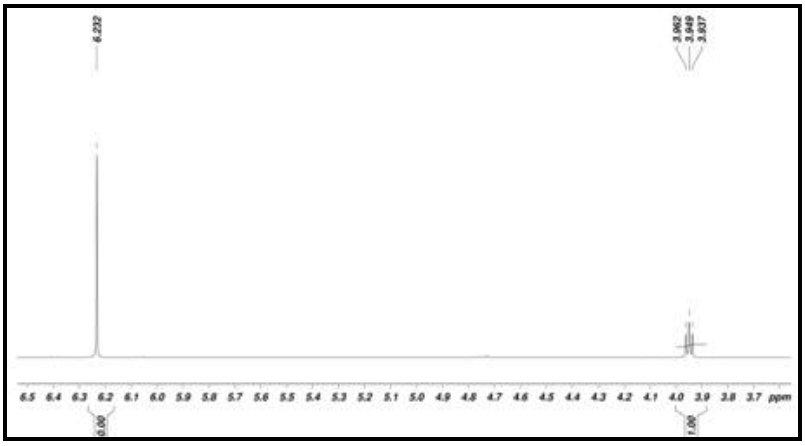


Figure 4. ^{1}H NMR spectra of DLMM single crystal.

combined into a doublet due to the influence of the nearby CH group. The signal at 133.03 ppm is caused by aromatic carbon groups. The CH_2 and CH carbons provide a signal at 52.534 ppm. The doublet peaks at 170.223 ppm and 172.615 ppm are caused by the carbonyl carbon of the COOH group in

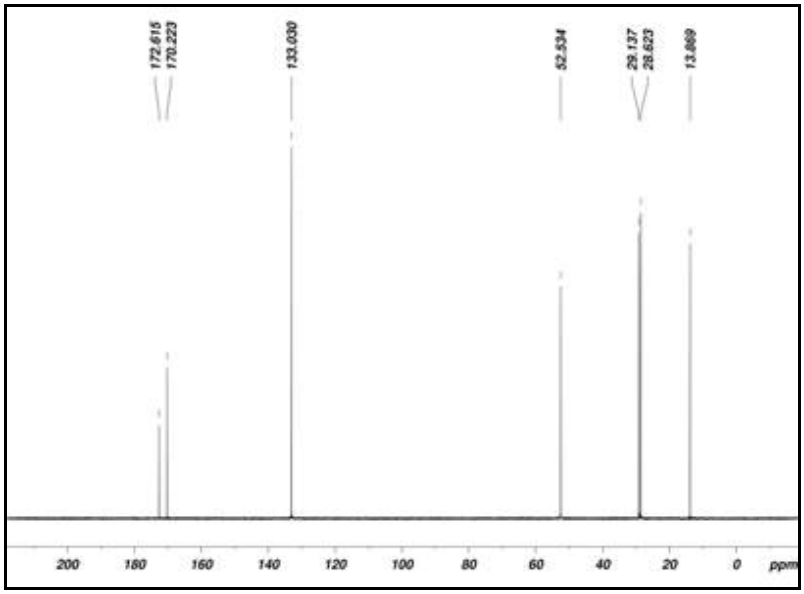


Figure 5. ^{13}C NMR spectrum of DLMM single crystal.

maleic acid. FTIR and NMR studies are thus useful to study the molecular structure of the title compound. It is understood that the maleate derivative of DL-methioninium exhibits bioactivity due to sulphur components.

4.5 Z-Scan technique

DLMM crystal possesses inversion symmetry because of centrosymmetric nature of the material. The absence of second order susceptibility was confirmed from Kurtz and Perry powder technique. The third order nonlinear parameters: nonlinear absorption coefficient (β), nonlinear refractive index (n_2) and the third order nonlinear susceptibility $\chi^{(3)}$) were evaluated using experimental data obtained from Z-scan technique. The expressions are given as follows [23]:

$$\beta = 2\sqrt{2}\frac{\Delta Tp}{I_0 L_{\text{eff}}} \tag{5}$$

and

$$L_{\text{eff}} = [1 - \exp(-ad/\alpha)]\,, \tag{6}$$

where I_0 is the intensity value at the focus, ΔTp is obtained from the experimental data. The phase shift

$$\Delta\varphi = \beta I_0 L_{\text{eff}}/Z_0\,, \tag{7}$$

where Z_0 is the propagation depth corresponding to $Z = 0$. The nonlinear refractive index n_2 is given by

$$n_2 = \Delta\varphi_0/kI_0 L_{\text{eff}}\,, \tag{8}$$

where k is the wave vector. The real and imaginary part of the nonlinear susceptibility are expressed as

$$\chi_R^{(3)} = 10^{-4}\varepsilon_0 c^2 n_0^2 n_2/\pi\,, \tag{9}$$

$$\chi_I^{(3)} = 10^{-2}\varepsilon_0 c^2 n_0^2 \lambda\beta/4\pi^2\,, \tag{10}$$

$$\chi^{(3)} = \left[(\chi_R^{(3)})^2 + (\chi_I^{(3)})^2\right]^{1/2}\,, \tag{11}$$

where ε_{0o} is the permittivity of vacuum, n_0 is the refractive index of the sample and c is the velocity of light in vacuum.

Table 1 presents the third order NLO coefficients of the grown crystal DLMM. The NLO property is due to non-linear absorption, two-photon absorption, etc. The presence of sufficient number of intrinsic defects and intermolecular attraction also contribute to the NLO property. It is observed that ($\chi_I^{(3)}$) is greater than ($\chi_R^{(3)}$) which means the contribution of nonlinear absorption is more dominant than that of nonlinear refraction. The absence of SHG efficiency confirms the centrosymmetric group of the material. Hence, DLMM is a third order NLO material to find applications in optoelectronics, photonics and holography.

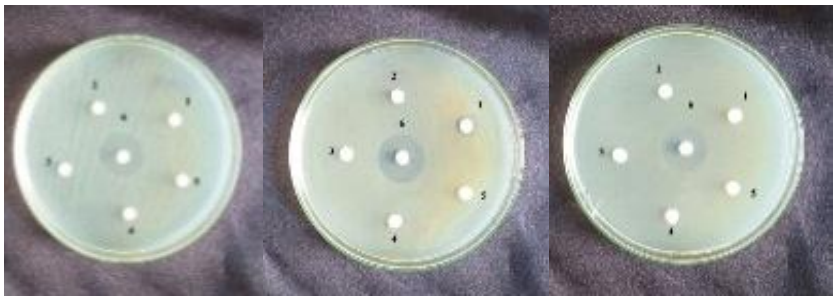
Table 1. Nonlinear optical coefficients of DLMM crystal

Parameters	**Values**
$n_2 \times 10^{-14}$ cm^2/w	3.32
$\beta \times 10^{-7}$ cm/w	3.20
$\chi^{(3)} \times 10^{-4}$ esu	1.02

4.6 Biological activity studies

The experiment was carried out using the Agar well diffusion method [24, 25]. After dissolving the 3.8 g Muller Hinton agar medium in 100 ml of distilled water, Agar (1 g) was added. The medium was then sterilised and stored. After sterilisation, the media was placed in sterile petri dishes for one hour to solidify. After the medium was firmly setup, sterile swabs moist with the bacterial suspension were used to apply the inoculums to the solid plates.

The discs were formed with 20 μl of the DLMM sample at the specified concentrations (1000 μg, 500 μg, 250 μg, and 125 μg). To 20 μl of MHA plates, DMSO was added, and Streptomycin (1 mg/ml) was also added as a positive control. These plates were incubated for 24 hours at 37°C. The sizes of the zones of inhibition for the pathogens *Klebsiella pneumonia, Staphylococcus aureus*, and *Enterococcus faecalis* are shown in Figures 6(a), 6(b), and 6(c). The diameter of the zone of inhibition was then measured in order to assess the rate of microbial growth. The experimental results reveal that the sample with positive control 20 μl of streptomycin can suppress the growth of microorganisms shown in Table 2. This antibacterial activity is due to presence of sulphur components in the sample and this biological activity can be used for the treatment of liver diseases and the prevention of hypercholesterolemia.



(a) (b) (c)

Figure 6. Zones of inhibition.

Table 2. The diameters of zone of inhibition

Microorganisms	Zone of inhibition in mm					
	Concentrations (μg)				DMSO	Streptomycin
	1000	500	250	125	(20 μl)	(20 μl)
Klebsiella pneumonia (mm)	12	10	—	—	—	22
Staphylococcus aureus (mm)	13	11	—	—	—	19
Enterococcus faecalis (mm)	14	12	—	—	—	21

5 Conclusion

The slow evaporation method was used to grow single crystals of DL-methioninium maleate (DLMM) at room temperature, with the knowledge of nucleation kinetics. The grown crystal possesses monoclinic system and centrosymmetric space group confirmed by XRD investigation. According to the molecular structural data, the cationic DL-methioninium molecule contains a protonated amino group and an uncharged carboxylic acid group. Maleic acid is a single-ionized molecule. FTIR spectroscopy was used to identify the vibrational functional groups of the DLMM. NMR spectroscopy confirmed the molecular structure of DLMM. The presence of sulphur components is primarily responsible for the antibacterial activity. The antibacterial activity of the compound DL-methioninium maleate can find medical applications such as the treatment of liver disease and the prevention of hypercholesterolemia. In addition, the synthesised compound exhibits third order NLO property to find applications in optoelectronics, photonics, holography and related fields.

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