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Structural and Density Functional Theory Investigation on L-Alaninium Maleate (LAM) single crystal an organic NLO Material

M. Victor Antony Raj[1] J.Madhavan[1] M. Gulam Mohamed [2*]

[1]*Department of Physics, Loyola College, Chennai*
[2]*Department of Physics, The New College, Chennai*

ABSTRACT

L-Alaninium Maleate (LAM) an efficient nonlinear optical material was synthesized and grown from aqueous solution. The crystal structure of LAM was solved by direct method using SHELXS-97 and it's found that it crystallizes in orthorhombic crystal system having non-centrosymmetry with $P2_12_12$ space group. The alaninium residue forms N-H...O and O-H..O hydrogen bonds with malaete anion and the later form O-H..O hydrogen bonds with each other. Density functional theory computations of equilibrium geometry and the first order hyperpolarizability of the crystal were calculated. The optimized geometric bond lengths and bond angles obtained by using DFT (B3LYP/6-31G (d,p)) show good agreement with the experimental data.

INTRODUCTION

Nonlinear optical (NLO) materials showing second harmonic generation (SHG) have been in demand over the last few decades due to technological importance in the fields of optical communication, signal processing, and instrumentation. In search of new non-linear optical (NLO) materials compared to inorganic materials, organic counterparts have high Second Harmonic Generation (SHG) efficiency [1-4]. The basic substituent's to polarize the π-electron system of organic materials have been illustrious for developing the NLO chromophores possessing large molecular non-linearity, good thermal stability, improved solubility and processability. In recent years much effort is being rendered to understand the origin of non-linearity and to relate the NLO responses to electronic structure and molecular geometry for designing and fabricating the NLO materials of large molecular hyperpolarizability. Amino acid family of materials are extensively researched for NLO activity due to the fact that all the amino acids except glycine contain chiral carbon atom and crystallize in noncentrosymmetric space groups an essential character for NLO activity [5,6]. A vast majority of organic crystals have

their absorption in the blue light region. Amino acids single crystals formed by L-alanine, L-arginine, L-histidine, etc., are found to be promising nonlinear optical (NLO) materials. Our research group has already found that the optical, thermal, spectroscopic and hardness parameter of LAM single crystals could be altered when doped with Mg and Cu ions [7]. This paper deals with structural and DFT investigation of L-alaninium maleate (LAM), an analog of L-alanine having high NLO active chromophores. Good quality single crystal of LAM was grown successfully by slow evaporation technique. The structure of LAM was solved by direct method and unit cell parameters are determined. In the LAM compound, a head-to-tail hydrogen bond is observed between the amino acid molecules. There are no direct hydrogen-bonded interactions between the semi maleate anions. Knowledge of molecular geometry may help researchers to predict the physiochemical properties of the compound material in different environment. Geometry optimizations were achieved using the Gaussian03W program package and inter atomic distances and angles were computed and compared with XRD parameters. The SHG efficiency of the LAM crystal were also studied using Nd:YAG Q-switched laser.

2. Synthesis and growth of l-alaninium maleate (LAM) single crystals

Analytical grade L-alanine (AR grade) and maleic acid was dissolved in double deionized water. In order to grow good quality crystals, it is essential to increase purity up to a respectable level. In the present study, the commercially available salt was dissolved in water and purified by repeated crystallization process and the recrystallized material was used to prepare the saturated solution. The solubility of LAM was measured at different temperatures and the drawn solubility curves are shown in Figure 1. It is seen that the solubility of LAM increases with temperature. The resulting aqueous solution was filtered and allowed to evaporate under optimized conditions to grow crystals by slow evaporation method at room temperature (30°C). The reaction that takes place between L-alanine and maleic acid in water medium is as follows:

$$C_3H_7NO_2 + C_4H_3O_4 + H_2O \longrightarrow C_3H_8NO_2^{+}.C_4H_3O_4^{-}$$

In a period of thirty days good transparent single crystal was harvested.

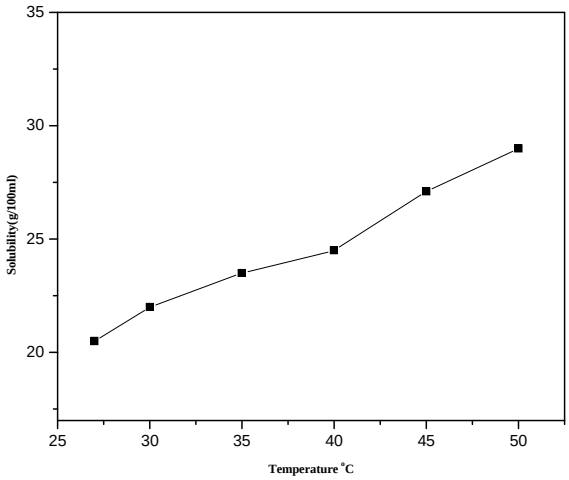


Figure 1. Solubility of LAM

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 [8] program package, invoking gradient geometry optimization. The absence of imaginary values of wave numbers on the calculated vibrational spectrum confirms that the structure deduced corresponds to minimum energy.

RESULTS AND DISCUSSION

4.1Single crystal XRD

Among the grown crystals of LAM well shaped, transparent, single crystals were selected and it was subjected to single crystal XRD analysis using ENRAF NONIUS CAD4/MAC4 X-ray diffractometer with MoK_{α} (λ=1.5418) radiation at room temperature. Intensity data were collected up and accurate unit cell parameters were obtained based on all reflections. Crystal structure was solved by direct method using the SHELXS-97 [9] and the positional parameters of the non hydrogen atoms were refined by full matrix least square with anisotropic thermal parameters to an R value of 0.0371.

Table-1 Crystal parameters of LAM

Empirical Formula	$C_7 H_{11} N O_6$
Formula weight	205.17
Temperature	293(2)
Wave length	1.5418
Crystal system, Space group	Orthorhombic, $P 2_1 2_1 2_1$
Unit cell dimensions	a=5.5873(11) Å alpha=90˚ b=7.3864(17) Å beta =90˚ c=23.688(3) Å gamma = 90˚
Cell volume	977.6(3) $Å^3$
Calculated Density	1.39391 g/cm^3
Absorption coefficient	1.078 mm^{-1}
F(000)	432
Crystal size	.33 x.23 x.12cm
Theta range for data collection	3.73 to 67.88 deg.
Limiting indices	0<=h<=6, 0<=k<=8, 0<=l<=25
Reflections collected/unique	1024/1024[R(int)=0.0000]
Completeness to theta = 67.88	100%
Refinement method	Full-matrix least squares on F^2
Data/restraints/parameters	1024/0/130
Goodness- of – fit on F^2	1.100
Final R indices [I>2sigma(I)] 80	R1=0.0354, wR2 =0.1060
R indicies (all data)	R1= 0.0371, wR2 =0.1123
Extinction coefficient	0.018(2)
Largest diff. peak and hole	.163 and -.159 $e.A^{\circ 3}$

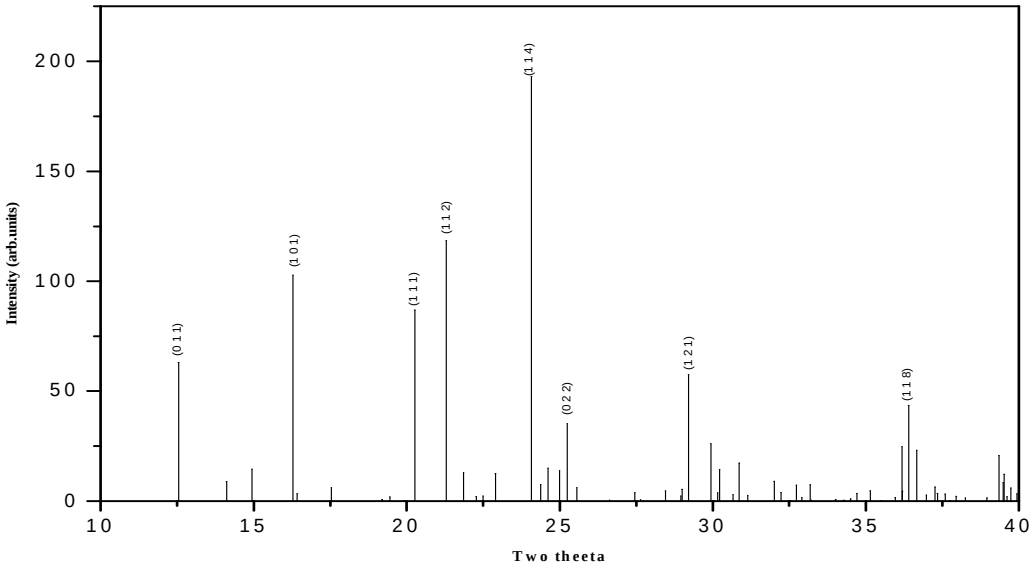
From the single crystal analysis it was observed that the crystal belongs to orthorhombic crystal system having non-centrosymmetry with $P2_12_12$ space group. Lattice parameters were determined as a=5.5873Å, b=7.3864Å, c=23.688Å, α=β=γ=90˚ and the volume of the unit cells is found to be 977.6045 $Å^3$. The details of crystal data, parameters used for data collection and reliability factor are summarized in Table 1.The alaninium residue forms N-H...O and O-H..O hydrogen bonds with malaete anion the later form O-H..O hydrogen bonds with each other. The C-O distances and O-C-C bond angles clearly show the presence of COOH group in the structure of LAM single crystal. Hydrogen centered donor acceptor distances and dihedral angles are listed in table.3.Theoretically Simulated XRD pattern of LAM single crystal with indexed peak is given in Fig 2. Experimental Powder XRD pattern is also shown in Fig 3. Both XRD patterns are almost similar in comparison.

Table-2. Hydrogen bonding (A˚)and angles(˚)

D-H…A	D(D-H)	d(H…A)	d(D…A)	<(DHA)
O1- H1- O4 (1)	.82	1.78	2.593(2)	174.0
O3- H3- O5 .	.82	1.63	2.425(3)	163.8
N1- H1A- O5(2)	.89	2.00	2.887(3)	174.8
N1- H1B -O2 (4)	.89	2.17	2.881(2)	136.8
N1- H1B- O4 (4)	.89	2.43	2.996(3)	121.6
N1- H1C -O6 (5)	.89	1.96	2.828(3)	164.5
C5- H5- O3 (6)	.93	2.45	3.264(3)	145.8
C6 -H6 -O5 (6)	.93	2.51	3.419(3)	164.8

Where, *#1) 1+x, y,-1+ z* *#4) 0.5+x, 1.5-y, 1-z*
#2) 0.5-x, 1-y,-0.5+ z *#5) 1.5-x, 1-y, -0.5+z*
#3) -0.5+x, 1.5-y, -z *#6) 1+x, y, z*

Figure2.Theoretically simulated powder XRD pattern of LAM



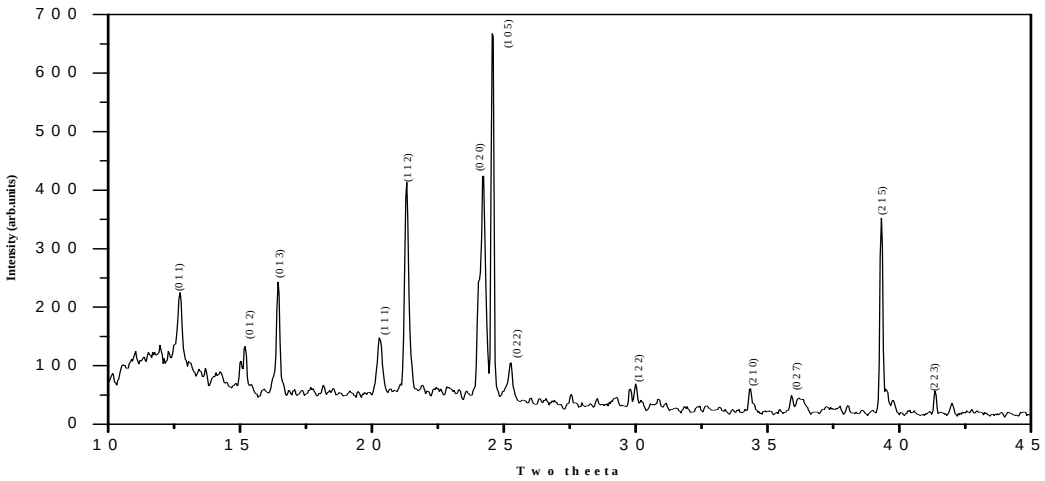


Figure 3.Experimentally obtained Powder XRD pattern of LAM

4.2Geometrical structure

The optimized structure parameters of LAM calculated by DFT (B3LYP) level with 6-31G(d,p) basis set show strong hydrogen bonding. The bond lengths of some selected atoms of a synthesized LAM molecule are given in Table-3. The C–C bonds are normal with lengths ranging between 1.3259 to 1.5072A˚. The hydrogen bond interaction of the type N1- H1- O2 could be the reason for bending of hydrogen towards L-alaninium cation. The crystal data confirms the zwitterions form adopted by L-alaninium cation with additional protonation of the Nitrogen atom. It is found from the table that experimentally obtained bond lengths are smaller in comparison with the optimized values from Gaussian 98 output. The differences between calculated and observed geometrical parameters can be attributed to the fact that the theoretical calculations were carried out with isolated molecules in the gaseous phase where the intermolecular columbic interactions with the neighboring molecules are absent but the experimental values were based on molecules in the crystalline state[10]. Some selected bond angles are listed in table.4. Atomic numbering system adopted in this study is shown figure 4.

4.3 Hyperpolarizability studies

The hyperpolarizability and non linear optical properties of an isolated molecule of potential NLO materials are considered as an extensive tool of research in molecular spectroscopy. The length of the conjugated π-electrons are vital factor in contributing to hyperpolarizability. It has been demonstrated that the first order hyperpolarizability increases with the third power of the number of π-electron bonds and the correlation of polarizability and hyperpolarizabilities with bond length alternation in the conjugated π-electron system from the neutral ground state structure to the resonance structure of a charge-transfer state of the system.. This electron cloud makes the molecule highly polarized and the intermolecular charge transfer interaction is highly responsible for the NLO properties of the title compound. Relation connecting non linear response, linear polarisability(α_{ij}) and first order hyperpolaraisability(β_{ijk}) can be represented as a Taylor expansion of the total dipole moment as

$$\mu_t = \mu_0 + \alpha_{ij}E_i + \beta_{ijk}E_iE_j + \ldots \quad (1)$$

The components of first order hyperpolarisability can be determined using the relation

Table-3. Selected bond length of LAM molecule

Bond length(A˚)	XRD	Gaussian	Bond length(A˚)	XRD	Gaussian
C_1-O_3	1.2294	1.43000	C_{16}-C_{18}	1.5072	1.5400
C_1-O_3	1.268	1.43000	C_{22}-H_{23}	0.9606	1.0700
C_1-C_5	1.4743	2.66735	C_{22}-H_{24}	0.9603	1.0700
C_4-H_9	0.93500	1.0700	C_{22}-H_{25}	0.9598	1.0700
C_4-C_7	1.4755	2.667358	O_2-H_8	0.8184	0.9600
C_5-C_4	1.3259	1.5400	N_{12}-H_{13}	0.8901	1.0000
C_5-H_6	0.9293	1.0700	N_{12}-H_{14}	0.8896	1.0000
C_7-O_{11}	1.2278	1.4300	N_{12}-H_{15}	0.8901	1.0000
C_7-O_{10}	1.2803	1.4300	N_{12}-C_{16}	1.4854	1.4700

Figure-4.Atomic numbering system adapted for ab initio computations of LAM molecule.

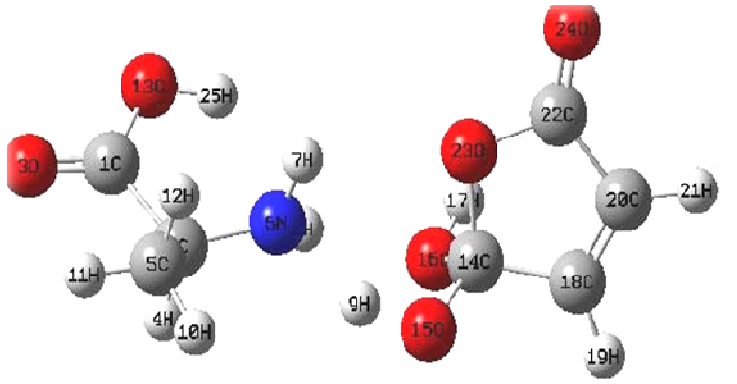


Table-4. Selected bond angles of LAM molecule

BondAngle(degree)	XRD	GAUSSIAN	BondAngle(degree)	XRD	GAUSSIAN
H2-N1-C3	121.6	120.	H7-C5-H8	109.5	109.4424
N1-C3-H4	109.5	109.5	C3-C5-H9	109.5	109.5
N1-C3-C5	109.2	111.1	H7-C5-H9	109.5	109.4424
H4-C3-C5	109.5	108.6358	H8-C5-H9	109.5	109.4424
N1-C3-C6	109.2	111.1	C3-C6-O10	120.8	120.
H4-C3-C6	109.5	108.6358	H2-N1-H11	109.5	120.
C5-C3-C6	110.3	107.7945	C3-N1-H11	109.5	120.
C3-C5-H7	109.5	109.5	C3-C6-O12	120.8	120.
C3-C5-H8	109.5	109.5	O10-C6-O12	121.6	120.

$$\beta_{ij} = \beta_{iii} + \frac{1}{3}\sum_{i \neq j}(\beta_{ijj} + \beta_{jij} + \beta_{jji}) \quad (2)$$

Using the x,y and z components the magnitude of first order hyperpolarisability (β_{tot}) tensor can be calculated by the following equation

$$\beta_{tot} = (\beta_x^2 + (\beta_y^2 + (\beta_z^2)^{1/2} \quad (3)$$

The complete equation for calculating the first order hyperpolarisability from GAUSSIAN 03W output is given as

$$\beta_{tot} = (\beta_{xxx} + \beta_{xyy} + \beta_{xzz})^2 + (\beta_{yyy} + \beta_{yzz} + \beta_{yxx})^2 + (\beta_{zzz} + \beta_{zxx} + \beta_{zyy})^2 \quad (4)$$

The β components of GAUSSIAN 03W output are reported in atomic units and the calculated values have to be converted into electrostatic units(1 a.u = 8.3693x 10^{-33} esu).The first order hyperpolarisability (β_{ijk}) of LAM is calculated using6-31G(d,p) basis set based on finite field approach. Hyperpolarisability is a third rank tensor that can be described by a 3x3x3 matrix. The 27 components of 3D matrix can be reduced to 10 components due to Kleinman symmetry. [11] The calculated first order hyperpolarisability values for LAM molecule are given in table 5. It is found from the table β_{zzz} value is maximum among the tensor values which indicates that more delocalization of electron could takes place in that particular direction. This may be due to π-electron cloud movement form donor to acceptor which make the molecule highly polarisable an essential behavior for NLO activity.

Table-5.Hyperpolarizability of LAM in esu

β_{xxx}	-244.8529961
β_{xxy}	4.0178705
β_{xyy}	-42.9225673
β_{yyy}	-35.0618471
β_{xxz}	-69.6276676
β_{xyz}	-16.5918869
β_{yyz}	-25.6566023
β_{xzz}	-66.4961103
β_{yzz}	-31.7199792
β_{zzz}	59.6206191
β_{tot}	3.02593461x10^{-30}

4.4NLO studies

Second harmonic generation (SHG) efficiency was measured to get an idea how much efficient the material is in transferring energy from fundamental laser beam to second harmonic beam. The grown crystal LAM were subjected to Kurtz [12] Second Harmonic Generation (SHG) test using the Nd:YAG Q-switched laser beam for the nonlinear optical (NLO) property. The second harmonic signal of 301 mW was obtained for LAM single crystal with reference to KDP (275 mW). Thus, the SHG efficiency of LAM single crystal is nearly 1.1 times greater than KDP. So the candidate material can be used for frequency conversion in NLO devices.

CONCLUSION

Good quality single crystals of L- Alaninium Maleate (LAM) were grown successfully by slow evaporation technique. Single crystal XRD studies were carried out for the grown crystal and the crystal structure was solved by direct method using the SHELXS-97 Programme package. From the single crystal analysis it was observed that the crystal belongs to orthorhombic crystal system

with $P2_12_12$ space group. Quantum chemical Density functional theoretical (DFT) computations reveals that the optimized structure parameters like bond lengths and bond angles of LAM molecule calculated by DFT(B3LYP) level with 6-31G(d,p) basis set were in good agreement with experimentally obtained values. First order hyperpolarizability for the optimized LAM molecule is calculated and its value is found to be $3.02593461x10^{-30}$ esu. SHG efficiency of the LAM single crystal is 1.1 times greater than KDP.

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