Journal of Computational Methods in Molecular Design, 2012, 2 (1):16-23

Scholars Research Library
(http://scholarsresearchlibrary.com/archive.html)

ISSN : 2231- 3176
CODEN (USA): JCMMDA

Synthesis, Structural and Density functional Theory Investigations on an efficient NLO material L-Arginine Maleate

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

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

ABSTRACT

L-Arginine Maleate (LArM) an efficient Non Linear optical (NLO) material was synthesized and grown by slow evaporation technique. Its crystal structure is solved by single crystal XRD using SHELXS-97. Density Functional Theory investigation of LArM molecular structure using Gaussian 03W is analysed and its interatomic distances and angles coincidence with experimental single crystal XRD parameters. The first order hyperpolarizability tensor of LArM is found to be as 6.30615227×10^{-30} *esu. Second Harmonic generating (SHG) efficiency of the candidate material is 3.8 times greater than that of KDP.*

INTRODUCTION

The DFT (density functional theory) is of particular interest owing to give satisfactory results with experiment by costing low computational demands compared to the computational methods developed for the calculation of the electronic structure and excitation energies of molecular systems [1.2]. Organic materials have been demonstrated in recent years to possess superior second- and third-order NLO properties compared to the more traditional inorganic materials. The structural flexibility of organic compounds is an asset for materials with optimized second-order nonlinear susceptibility, fast response, and tailor made flexibility. Due to their high molecular hyperpolarizabilities, organic materials display a number of significant nonlinear optical properties. Last decade NLO materials are extensively researched quantum mechanically to obtain an optimized molecular structure. Nonlinearity in organic chromophores can be synthetically modulated by varying the composition or length of conjugated p-systems, and by evaluating the effects of various electron-donor and electron-acceptor groups. In solid state, amino acid contains a deprotonated carboxylic acid group (COO−) and protonated amino group (NH3+). This dipolar nature exhibits peculiar physical and chemical properties in amino acids, thus making them ideal candidates for NLO applications [3 - 5].In order to widen the properties of amino acid family of materials and discover novel crystals with better NLO properties research on new crystals and growth mechanism are in progress in our lab.[6,7].Malic acid with relatively large π conjugation has attracted our attention. In this present communication, the synthesis, single crystal growth of L-arginine maleate (LAM) from its aqueous solution by slow cooling method has been reported. The grown crystals were then characterized by single crystal X-ray diffraction analysis, DFT analyses, first order hyperpolarizability studies and second harmonic generation efficiency measurements.

MATERIALS AND METHODS

2. Material synthesis, Solubility studies and crystal growth

Equimolar amount of strongly basic amino acid, L-arginine (Merck, 99%) and weak organic acid, maleic acid (Loba Chemie, 99.5%) were dissolved in double distilled water to synthesize LArM . During this crystallization, L-arginine maleate transformed to its hydrated form with the addition of two molecules of water of crystallization to its crystal lattice. The synthesized material was then purified by repeated recrystallization process. L-arginine maleate was dissolved in double distilled water and kept in a constant temperature bath with a cryostat facility and stirring was achieved continuously for 8 h. Solubility studies for different temperatures (30, 35, 40 and 45 °C) have been carried out.

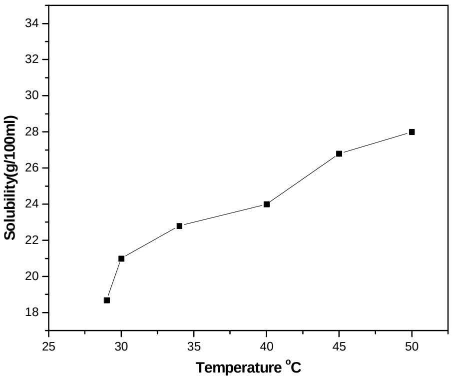

Figure.1 solubility diagram of LArM

Figure.2 Photograph of as grown LArM single crystal

The starting material L-arginine maleate was dissolved in double distilled water in accordance with the solubility diagram shown in Figure.1. 200 ml of saturated solution of LArM at 40 °C was prepared and the solution was filtered. Seeds obtained from slow evaporation technique were used for bulk growth. Optical quality crystal with dimension of $13 \times 15 \times 9$ mm^3 has been grown over a typical growth period of 3 weeks. Photograph of as grown single crystal is shown in figure.2.

Computational details

The molecular geometry is directly taken from the X-ray diffraction experimental results without any constraints. Initial molecular geometry was optimized using the DFT calculations with a hybrid Functional B3LYP (Becke's Three parameter Hybrid Functional Using the LYP Correlation Functional) at 6-31G basis set were performed with the Gaussian 03W software package and Gauss view visualization program [8] implemented on Pentium core 2 duo/3 GHz processor with 2GB RAM personal computer. The optimized geometries corresponding to the minimum potential energy surface have been obtained by solving self consistent field (SCF) equation iteratively. 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

The selected well shaped, transparent, single crystal of LArM was mounted on a ENRAF NONIUS CAD4/MAC4 X-ray diffractometer. Reflection data were measured at 20◦C using graphite monochromated Mo-K*α* (λ = 0.71073 A°) radiation and a ω-2θ scan mode. A total of 1762 independent reflections were collected in the range of 4.02° < θ < 27.34°, of which 1697 reflections with $I > 2\sigma(I)$ were considered to be observed and used in the succeeding refinement. The structure was solved by direct methods and refined by full-matrix least-squares method using the SHELXS-97 software package. All non-H atoms were anisotropically refined. The hydrogen atom positions were fixed geometrically at calculated distances and allowed to ride on the parent C atoms. The final least-square cycle gave R1=0.0303, wR2 =0.0693;the weighting scheme, $w = 1/[\sigma^2(F20\ ) + (0.0307P)^2 + 0.0785P]$,where $P = (F^20 + 2F^2c\ )/3$. From the single crystal analysis it was observed that the crystal belongs to triclinic crystal system having non-centrosymmetry with P_1 space group. Lattice parameters have been determined as a=5.27100Å, b=8.0481Å, c=9.7942Å, α=106.15°,β=97.26°,ν=101.649° and the volume of the unit cells is found to be 383.42 (3) Å^{3}A summary of the key crystallographic information is given in Table 1.From table-2 one can see that the hydrogen bonds between maleic acid and L-arginine are dominant in the crystal.The hydrogen bonds between guanidyl and carboxylate groups are little weaker. Water molecule binds to the cations as an acceptor by weaker hydrogen bonds. In the cell unit, both water molecules are interacted with L-arginine and maleic acid layers, while hydrogen bonds connect them together. Theoretically Simulated XRD pattern of LAM single crystal with indexed peak is given in Fig 3. Experimental Powder XRD pattern is also shown in Fig 4. Both XRD patterns are almost similar in comparison.

Table 1.Crystallographic information of LArM Single crystal

Empirical Formula	$C_{10}H_{22}N_4O_8$
Formula weight	326.32
Temperature	293(2)
Wave length	0.71073
Crystal system, Space group	Triclinic, P_1
Unit cell dimensions	a=5.27100(4) Å alpha=106.15° b=8.0481(2) Å beta =97.26° c=9.7942(2) Å gamma = 101.649°
Cell volume	383.42(2) Å^3
Calculated Density	1.413 g/cm^3
Absorption coefficient	0.122 mm^{-1}
F(000)	174
Crystal size	.25 x.23 x.19cm
Theta range for data collection	4.02 to 27.34 deg.
Limiting indices	-6<=h<=6, -10<=k<=10, -11<=l<=12
Reflections collected/unique	1762/1697[R(int)=0.0000]
Completeness to theta = 67.88	100%
Refinement method	Full-matrix least squares on F^2
Data/restraints/parameters	1762/7/220
Goodness- of – fit on F^2	1.012
Final R indices [I>2sigma(I)] 80	R1=0.0303, wR2 =0.0693
R indicies (all data)	R1= 0.0314, wR2 =0.0700
Extinction coefficient	0.019(2)
Largest diff. peak and hole	.164 and -.149 e.A$^{\circ 3}$

Table-2 Hydrogen bond lengths and angles of LArM Single crystal

D-H…A	D(D-H)	d(H…A)	d(D…A)	<(DHA)
N4 -H4AA- O2	0.89	1.98	2.843(2)	162
N1- H1A -O1.	0.86	2.18	2.935(2)	147
N1- H1B- O3	0.86	1.98	2.843(2)	176
N4- H4BB- O5	0.89	2.23	3.079(3)	160
N2- H2A -O2	0.86	2.10	2.948(2)	171
N2- H2B- O5	0.86	2.08	2.862(3)	152
N3- H3- O4	0.86	2.10	2.955(2)	172
N4- H4CC- O7	0.89	1.92	2.801(2)	173
O3 -H6A- O6	1.28(4)	1.13(4)	2.407(2)	173(3)
O7- H7A -O8	0.90(2)	1.91(2)	2.791(3)	165(5)
O7- H7B- O1	0.87(2)	2.35(4)	3.081(3)	142(5)
O7- H7B- O8	0.87(2)	2.57(5)	3.186(4)	129(5)
O8- H8A- O4	0.87(3)	2.01(2)	2.873(3)	170(4)
O8- H8B- O2	0.88(2)	1.97(3)	2.770(2)	152(5)

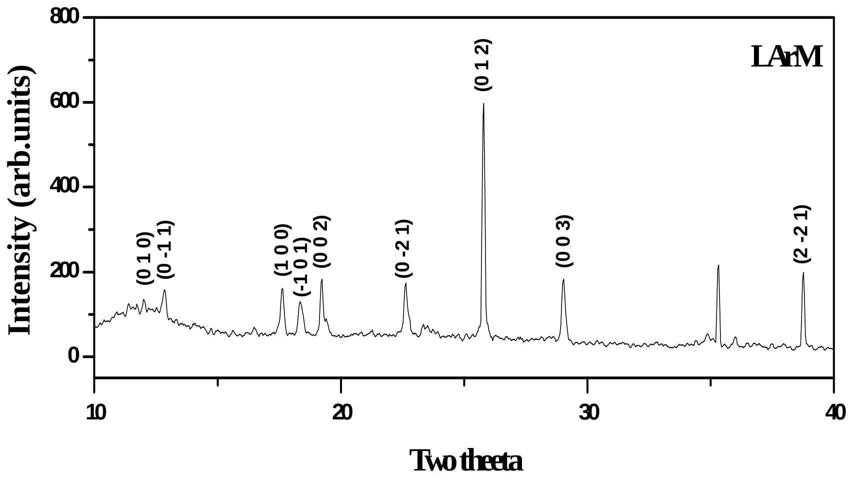

Fig 3. Experimental Powder XRD pattern of LArM crystal.

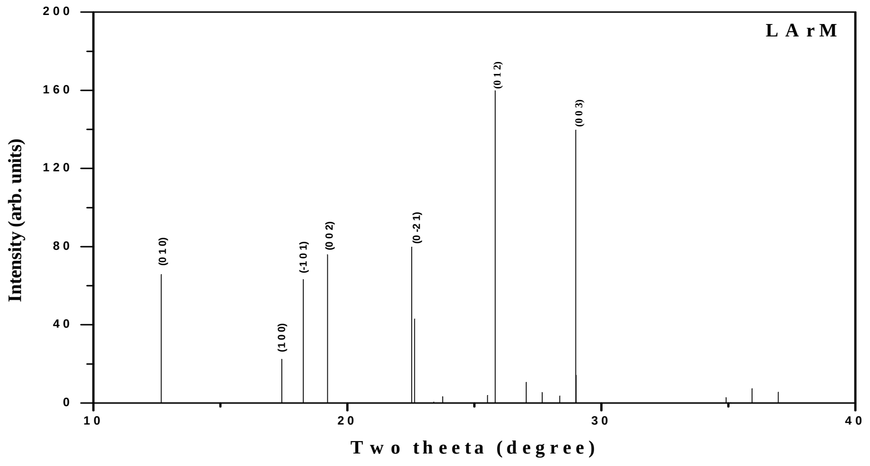

Fig-4.Simulated XRD pattern of LAM single crystal

4.2 Molecular geometry

Computational chemistry is an important tool to design and modeling the NLO materials [9]. The geometry of the investigated compound was treated as an isolated gas molecule Becke-Lee-Yang-Parr hybrid exchange correlation three parameter (B3LYP) level at 6-31G basis set is used to derive the optimized structure in Gaussian 03W. Optimized structure was confirmed to be minimum energy conformations. the optimized molecular structures of the isolated LArM is shown in figure .5. The selected bond lengths and angles of the candidate material obtained by calculations and single crystal XRD analysis are listed in Table .3.It is found from the table that C-C bond length varies from 1.39483 to 1.50328 A^o theoretically and from 1.333(3) to 1.495(3) A^o experimentally which interprets the strong correlation between calculated and experimental results. Existence of strongest hydrogen bond shall be understood by shortest length of O12-H13. The bond length of O(12)–H(14) (1.25(5)A ˚) is much longer than that of O(13)–H(13) (1.15(5)A ˚). The former exists as a donor while the later is an acceptor, which is consistent with the hydrogen bond length between O (12) and O(13). This indicates that the hydrogen bond between O(12) and O(13) is asymmetric. The coexistence of both forms of carboxylic groups resulting breaking of central-symmetry appears to be a fruitful idea for NLO property. The maleate anion with relatively large π-conjugation optimizes the orientation of L-arginine,namely the optically active L-arginine is arranged with the asymmetrical guanidyl and carboxyl groups with maleate anion. Therefore the introduction of maleate anion greatly enhances its NLO properties and susceptibility.

Table.3.Selected bond lengths and angles of LArM molecule

Bond Length(A^0)		**XRD**
C1-C4	1.39483	1.333(3)
C1-C2	1.50328	1.495(3)
C4-C3	1.39514	1.485(3)
C3-O7	1.43000	1.288(3)
C3-O8	1.39483	1.235(2)
C2-O11	1.43000	1.262(2)
C2-O10	1.01000	1.222(3)
O10-O15	1.24051	1.2305(2)
O12-H14	0.96000	1.25(5)
O13-H13	0.96000	1.15(5)
C18-O22	1.43000	1.235(3)
C18-O21	1.43000	1.269(3)
C18-C19	1.54000	1.521(3)
C19-N23	1.47000	1.496(3)
C19-C27	1.54000	1.531(3)
C35-N33	1.47000	1.454(3)
C35-N36	1.47000	1.330(2)
C35-N37	1.47000	1.324(3)
C42-C30	1.63080	1.531(3)
C27-C42	1.41764	1.520(3)

Bond Angle		**XRDA**
C1-C4-C3	120.00004	116.33(16)
C4-C3-O7	119.98399	119.6(2)
O7-C3-O8	120.01131	120.3(2)
O11-C2-O10	77.74370	78.60(3)
O11-C2-C1	118.66846	118.50(17)
C2-O10-O15	162.97858	165.50(5)
O10-O15-H16	151.30487	150.40(2)
H14-O12-H13	109.47121	109.19(5)
O21-C18-O22	120.00000	122.8(2)
O21-C18-C19	120.00001	120.2(2)
N23-C19-C27	109.47119	109.19(15)
N36-C35-N33	120.00000	119.20(18)
N33-C35-N37	120.00001	120.33(18)
C18-C19-C27	109.47123	108.94(15)
C18-C19-N23	109.47124	112.22(16)
N33-C30-C27	109.47127	111.67(15)

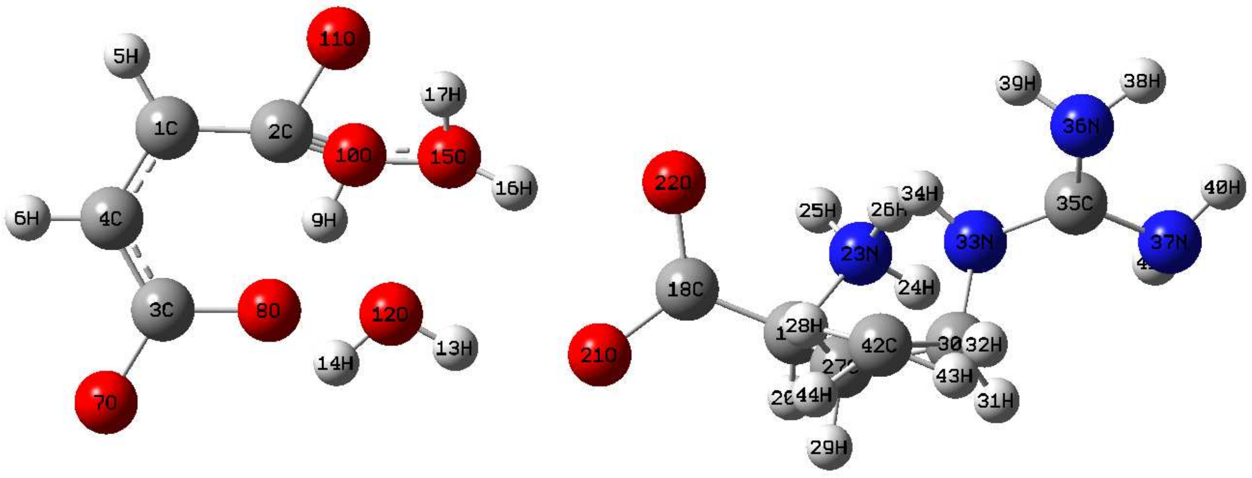

Figure.3. The optimized molecular structure of the isolated LArM

4.3 First order Hyperpolarizability studies

Experimental measurements and theoretical calculations on molecular hyperpolarizability β become one of the key factors in the second-order NLO materials design [9, 10, 11].Theoretical determination of hyperpolarizability is quite useful both in understanding the relationship between the molecular structure and nonlinear optical properties. It also provides a guideline to experimentalists for the design and synthesis of organic NLO materials. Nonlinearity in organic chromophores can be synthetically modulated by varying the composition or length of conjugated p-systems,and by evaluating the effects of various electron-donor and electron-acceptor groups. The non linear response, linear polarisability(α_{ij}) and first order hyperpolaraisability(β_{ijk}) can be related as a Taylor expansion of the total dipole moment as

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

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

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

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

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

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

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

The β components of GAUSSIAN 03W output are reported in atomic units and the calculated values are converted into electrostatic units (1 a.u = 8.3693x 10^{-33} esu). Hyperpolarizability 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 [12]. The calculated first order hyperpolarisability values for LArM molecule are given in table 5. The calculated first order hyperpolarizability of LArM is 6.30615227×10^{-30} esu, the compound having the higher β_{tot} value, correspond to the low HOMO-LUMO energy gap.

Table .5 Hyperpolarizability of LArM molecule

β_{xxx}	-154.0584244
β_{xxy}	-154.0584244
β_{xyy}	265.3935258
β_{yyy}	-80.3168278
β_{xxz}	1460.1973362
β_{xyz}	-673.076011
β_{yyz}	511.9064268
β_{xzz}	352.2447648
β_{yzz}	334.4451487
β_{zzz}	-2557.9267795
β_{tot}	6.30615227×10^{-30}

4.4 Second harmonic generation (SHG) efficiency studies

The NLO properties of the grown crystal is studued,Kurtz and Perry technique [13]. A high-intensity Nd:YAG laser with fundamental radiation of 1064 nm was used as the optical source and directed onto the powered sample of crystal. The SHG behaviour has been confirmed from the output of intense green light emission (k = 532 nm) from the crystal. KDP sample was used as the reference material and Intensity of the bright green emission is 3.8 times higher that of KDP.

CONCLUSION

Single crystals of LArM are conveniently grown by employing slow evaporation technique. Single crystal XRD studies confirm the crystalline nature of grown crystals and its structure was solved by direct method using the SHELXS-97 Programme package. From the single crystal analysis it was found that the crystal belongs to triclinic crystal system having non-centrosymmetry with P_1 space group. Optimized structure of the isolated LArM molecule was confirmed to be minimum energy. Existance of strongest hydrogen bond was understood from bond lengths. First order hyper polarisability of LArM in calculated and presented.

REFERENCES

[1] V.N. Nemykin, J.G. Olsen, E. Perera, P. Basu, *Inorg. Chem.* 45 (**2006**) 3557–3568

[2] G. Menconi, N. Kaltsoyannis, *Chem. Phys. Lett.* 415 (**2005**) 64–68.

[3] J. Madhavan, S. Aruna, K. Prabha, J. Packiam Julius, Ginson P. Joseph, S. Selvakumar, P. Sagayaraj., *Journal of crystal growth* 293(**2006**) 409.

[4] S. Senthil, S. Pari, P. Sagayaraj, J. Madhavan, *Physics B* 404(**2009**)1655.

[5] M. Gulam Mohammed, K. Rajarajan, G. Mani, M. Vimalan, K. Prabha, J. Madhavan, P. Sagayaraj., *Journal of crystal growth* 300(**2007**) 409.

[6] M.Victor Antony Raj and J.Madhavan, *Archives of physics Research*,**2011**, 2 (1), 160-168.

[7] P. Praveen Kumar , V. Manivannan , S. Tamilselvan , S. Senthil ,M. Victor Antony Raj , P. Sagayaraj , J. Madhavan, *Optics Communications* , May **2008**.

[8] M.J. Frisch, G.W. Trucks, H.B. Schlegel, G.E. Scuseria, M.A. Robb, J.R. Cheeseman, J...A. Montgomery Jr., T. Vreven, K.N. Kudin, J.C. Burant, J.M. Millam, S.S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G.A. Petersson, H. Nakatsuji, M. Hada,

M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J.E. Knox, H.P. Hratchian, J.B. Cross, C. Adamo, J. Jaramillo, R. Gomperts, R.E. Stratmann, O. Yazyev, A.J. Austin, R. Cammi, C. Pomelli, J.W. Ochterski, P.Y. Ayala, K. Morokuma, G.A. Voth, P. Salvador, J.J. Dannenberg, V.G. Zakrzewski, S. Dapprich, A.D. Daniels, M.C. Strain, O. Farkas, D.K. Malick, A.D. Rabuck, K. Raghavachari, J.B. Foresman, J.V. Ortiz, Q. Cui, A.G. Baboul, S. Clifford, J. Cioslowski, B.B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R.L. Martin, D.J. Fox, T. Keith, M.A. Al-Laham, C.Y. Peng, A. Nanayakkara, M. Challacombe, P.M.W. Gill, B. Johnson, W. Chen, M.W. Wong, C. Gonzalez, J.A. Pople, Gaussian 03, Gaussian, Inc., Pittsburgh, PA, **2003**.

[9] Kechen Wu, Jaap G. Snijders, and Chensheng Lin, *J. Phys. Chem* B 106, 8954 (**2002**).

[10] Rice JE, Handy NC (**1991**) *J Chem Phys* 94:4959–4971

[11] Li H, Han K, Shen X, Lu Z, Huang Z, Zhang W, Zhang Z, Bai L (**2006**) *J Mol Strut (Theochem)* 767:113–118

[12] D.A. Kleinman, *Phys. Rev*. 126 (**1962**) 1977.

[13] KurtzS.K. and PerryT.T.(**1968**), *J.Appl.Phys.*,Vol.39, pp. 3798–38l3