



FIRST ORDER HYPERPOLARIZABILITY, HOMO-LUMO AND VIBRATIONAL ANALYSIS OF L-ISOLEUCINE, L-ISOLEUCINE MALEATE (LIM) AND L-ISOLEUCINE OXALATE (LIO) BY DFT METHODS

A. Zeenath Bazeera^{1,2}, S. Selvaraj³, A. Syed Mohamed⁴

¹Research Scholar, Reg.No.12100 Department of Physics, M.D.T.Hindu College, Tirunelveli

²Department of Physics, Sadakathullah Appa College, Tirunelveli, Tamilnadu, India

³Department of Physics, M.D.T.Hindu College, Tirunelveli, Tamilnadu, India

⁴Department of Chemistry, Sadakathullah Appa College, Tirunelveli, Tamilnadu, India

Affiliated to Manonmaniam Sundaranar University, Tirunelveli, Tamilnadu, India

*Corresponding author: meeran.jull@gmail.com

ABSTRACT

In this work, the molecular structure, harmonic vibrational frequencies of L- isoleucine (LI), L-isoleucine Maleate (LIM) and L-isoleucine Oxalate (LIO) have been investigated. The optimized molecular geometries, first order hyperpolarizabilities and vibrational frequencies have been calculated using B3LYP/6-31G. The HOMO and LUMO energy calculation reveals that the charge transfer exist within the molecules. The Fourier Transform Infrared (FT-IR) of LIM and LIO are recorded in the regions 4000-400 cm^{-1} . The observed and calculated wave numbers are found to be in good agreement. The experimental spectra also coincide satisfactorily with those of theoretically constructed spectra.

Keywords: *ab initio*, L-isoleucine, non-linear optics, hyperpolarizability, Density Functional Theory (DFT)

1. INTRODUCTION

During the previous decades organic nonlinear optical materials have been fascinated much attention because of their optical nonlinearity, fast response, relatively low cost, ease of fabrication and integration into devices [1, 2]. NLO materials have gained interest in modern years with respect to their future potential applications in the field of optoelectronic such as optical communication, optical computing, optical switching and dynamic image processing [3].

Experimental measurements and theoretical calculations on molecular hyperpolarizability β become one of the significant factors in the second – order NLO materials design. Theoretical determination of hyperpolarizability is fairly helpful both in understanding the relationship between the molecular structure and nonlinear optical properties.

The vibrational spectral studies of the molecule can afford deeper knowledge about the relationships between molecular architecture, nonlinear response and hyperpolarizability. In this study molecular geometry, optimized parameters are computed and the performance of the computational method for B3LYP at 6-31G basis set [4]. This method predicts comparatively accurate molecular structure with moderate computational effort.

Recently, vibrational spectra combined with DFT calculations have been used as an effective tool in the study of NLO active compounds [5]. This study is extended to find out the electric dipole moment and hyperpolarizability of the title compounds.

Organic molecules with conjugated π electron identified to exhibit tremendously large optical nonlinear responses in terms of their molecular hyperpolarizabilities. Both theoretical and experimental studies have shown that large polarizabilities generally arise from a combination of strong electron donor and acceptor positioned at opposite ends of a suitable conjugation path and hyperpolarizability values depending not only on the strength of donor and acceptor groups but also on the path length between them [3].

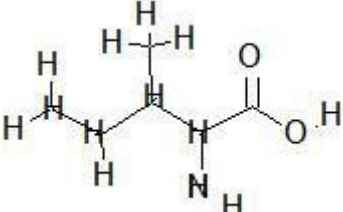
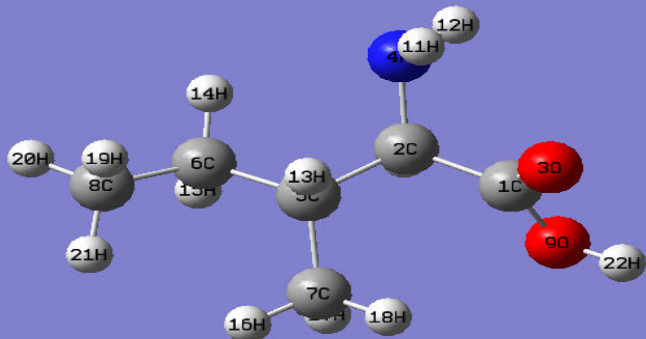
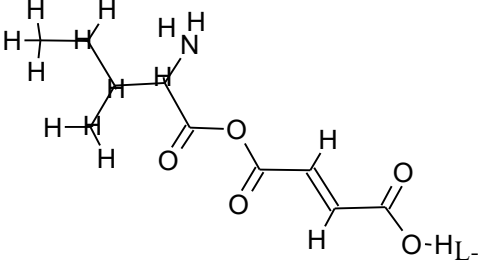
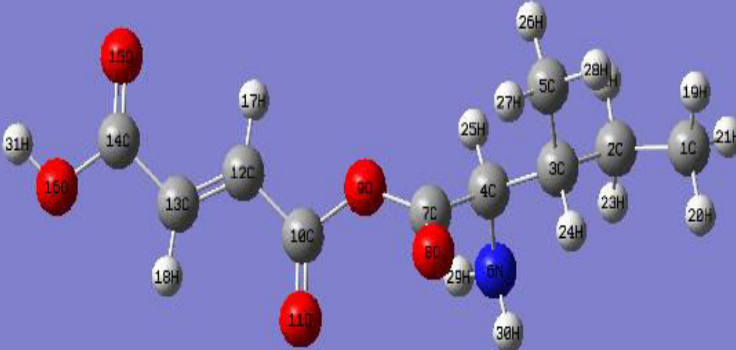
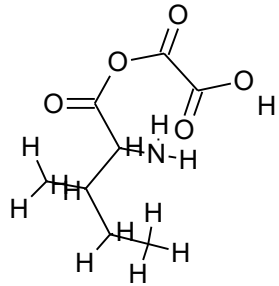
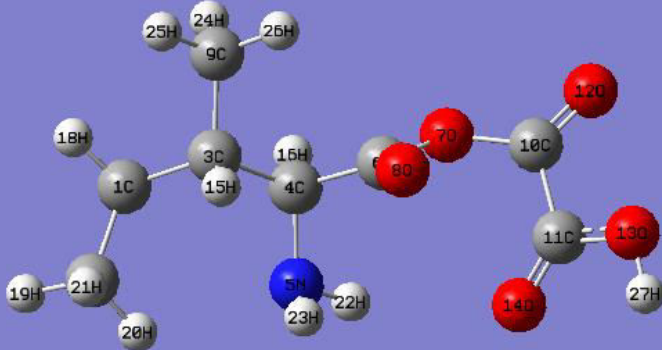
The progress of pi-electron cloud from donor to acceptor makes the molecule to be extremely polarized. L-Isoleucine is both glucogenic and ketogenic amino acid. This is one of the amino acids having branched hydro carbon side chains. It is non polar and aliphatic in nature. On the basis of infra red spectroscopic study, the crystal of L-Isoleucine was assumed to belong a rather unusual type in which molecules two type of conformation [6, 7].

2. COMPUTATIONAL ASPECTS

All hyperpolarizabilities calculations of LI, LIM and LIO were performed using GAUSSIAN 09 [8]. NLO calculations were performed at density functional theory using B3LYP/6-31G basis set, which has been found to

be more than enough for obtaining reliable trends in β values [9,10]. The optimized geometry of LI, LIM and LIO calculated by DFT levels were shown in Table 1.

Table 1: Molecules and their Geometries

STRUCTURE	GEOMETRY
 <p style="text-align: center;">L-Isoleucine (LI)</p>	
 <p style="text-align: center;">Isoleucine maleate (LIM)</p>	
 <p style="text-align: center;">L-Isoleucine Oxalate (LIO)</p>	

3. HYPERPOLARIZABILITY STUDIES

Molecules that show asymmetric polarization induced by electron donor and acceptor groups in pi- electron conjugated molecules are candidates for electro optic and NLO applications, such as frequency doubling or SHG

[6]. The study involves the calculation of first hyperpolarizability tensor for all 3 organic molecules. First hyperpolarizability is a third rank tensor that can be described by a 3x3x3 matrix. It can be specified in the lower tetrahedral format.

The output from GAUSSIAN 09 provides 10 components of this matrix as β_{xxx} , β_{xxy} , β_{xyy} , β_{yyy} , β_{xxz} , β_{xyz} , β_{yyz} , β_{zzz} , β_{yzz} , β_{zzz} , respectively. Many types of hyperpolarizabilities have been discussed in the literature denoted as β_{vec} (β vector), $\beta_{||}$ (β parallel), β_{tot} (β total). The components of β can be calculated using the following equation.

$$\beta_i = \beta_{iii} + 1/3 \sum_{i \neq j} (\beta_{ijj} + \beta_{jii} + \beta_{jji})$$

Using the x,y,z components of β , the magnitude of the first hyperpolarizability tensor can be calculated.

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

The comprehensive equation for calculating the magnitude of β from GAUSSIAN 09 output is given as follows.

$$B_{tot} = [(\beta_{xxx} + \beta_{xxy} + \beta_{xxz})^2 + (\beta_{yyy} + \beta_{yyz} + \beta_{yxx})^2 + (\beta_{zzz} + \beta_{zzx} + \beta_{zyy})^2]^{1/2}$$

Since the values of the first hyperpolarizability tensors of the output file of GAUSSIAN 09 are reported in atomic units (a.u.), the calculated values converted into electrostatic units (1 a.u. = 8.6393x 10⁻³³ esu).

The first order hyperpolarizability, total molecular dipole moment and HF values of LI, LIM and LIO are listed in the Tables 2 and 3. The connection between the electric dipole moments of an organic molecules having donor-acceptor substituent and first order hyperpolarizability is widely recognized in the literature.

Table 2: All β components and β_{tot} calculated at B3LYP/6-31G basis set for LI, LIM and LIO

Molecule	β_{xxx}	β_{xxy}	β_{xyy}	β_{yyy}	β_{xxz}	β_{xyz}	β_{yyz}	β_{zzz}	β_{xzz}	β_{xyy}	β_{yzz}	$\beta_{tot} \times 10^{-30}$ (esu)
LI	40.69	-10.64	2.66	1.72	-9.71	-4.61	-2.02	-1.13	20.76	3.521	0.5290	
LIM	-72.01	20.20	-2.47	-2.17	18.89	19.43	7.43	-11.01	-17.16	-0.96	0.9018	
LIO	53.42	-38.75	12.12	-8.42	25.43	-3.18	-2.54	17.65	16.05	-6.96	0.9363	

Table 3: Calculated dipole moment of LI, LIM and LIO

Molecule	Dipole Moment	Exact Polarizability	Approximate Polarizability
LI	X= 0.6900	86.247	103.349
	Y=-0.6528	-2.479	-3.306
	Z=-0.9383	73.489	101.515
	Tot=1.3352	1.037	4.115
		2.318	8.082
		67.422	109.940
HF=-441.6780785			
LIM	X= -1.4332	153.149	189.582
	Y=1.2256	6.602	20.643
	Z=-0.7925	122.019	188.328
	Tot=2.0456	6.166	14.819
		-2.119	7.564
		102.237	164.121
HF=-820.9602742			
LIO	X= -0.3420	127.834	158.353
	Y=-1.6330	7.569	20.476
	Z=0.5172	98.900	148.185
	Tot=1.7467	2.095	5.413
		-1.760	-2.343
		83.843	140.522
HF=-743.5559813			

4. HOMO-LUMO Analysis

The highest occupied molecular orbital and lowest unoccupied molecular orbital are very important

parameters for quantum chemistry. This is also used by the frontier electron density for predicting the most reactive site in π -electron systems and also explains

several types of reaction in conjugated system[11].The conjugated molecules are characterized by a small highest occupied molecular orbital lowest unoccupied molecular orbital (HOMO-LUMO) separation, which is the result of a sizeable degree of intermolecular charge transfer from the end capping electron donating groups to the efficient electron acceptor groups through π conjugated path [12]. Both the highest occupied molecular orbital and lowest unoccupied molecular orbital are the main orbitals that take part in chemical stability [13]. Energy difference between HOMO-LUMO orbital is called energy gap that is important for stability of structures. The HOMO-LUMO energy gap of LI, LIM and LIO were calculated at B3LYP/6-31G level, which reveals that the energy gap reflects the chemical activity of the molecule. The results of HOMO-LUMO analysis for LI, LIM and LIO are shown in Table-4. The LUMO as an electron acceptor represents the capacity to obtain an electron and HOMO represents the ability to donate an electron.

The intense charge transfer interaction through π -conjugated bridge results in substantial ground state donor-acceptor mixing and the appearance of a charge transfer band in the electron absorption spectrum.

Table 4: Calculated HOMO-LUMO values of LI, LIM and LIO

Molecule	HOMO(a.u.)	LUMO(a.u.)	Energy gap(a.u.)
LI	-0.244	+0.004	0.24
LIM	-0.251	-0.080	0.171
LIO	-0.252	-0.081	0.171

5. VIBRATIONAL ANALYSIS

The FT-IR analysis of LIM and LIO had been carried out in the wave number range of 4000 to 400 cm^{-1} , shown in Fig.1a and 1b .In LIM the highest energy region, peak at 2961 cm^{-1} is assigned to C-H stretching vibration [14]. The C-O and C=O stretching modes produce peaks at 2878 cm^{-1} and 1720 cm^{-1} . Multiple fine structures at the lower energy mode of the envelope indicates the strong hydrogen bonding interaction of NH_3^+ group with strong absorptions of COO^- group at 1568 cm^{-1} [15]. The C-O stretching mode is observed at 1307 cm^{-1} . The CH_2 wagging and rocking modes produce peaks at 1240 and 866 cm^{-1} , respectively. Further medium band observed at about 1069 cm^{-1} is due to C-N stretching. The COO^- scissoring (694 cm^{-1}) vibration is also observed [16].

Investigating the absorption bands of LIO below 1000 cm^{-1} four characteristic bands were identified ,one at 675 cm^{-1} (COO^- in plane deformation),the second one at 580 cm^{-1} (COO^- wagging mode), the third at 851 cm^{-1} (C-C stretching)and the fourth peak at 478 cm^{-1} (N-H deformation). The band corresponding to NH_3^+ asymmetric deformation vibration occurs at 1683 cm^{-1} , COO^- asymmetric stretching at 1512 cm^{-1} .High wave number region (3377-2350 cm^{-1}) contains NH and CH stretching vibration and combination of them.

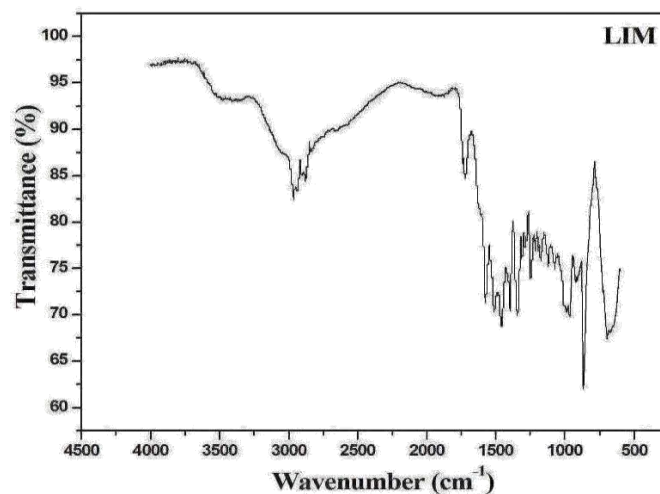


Fig. 1 (a)

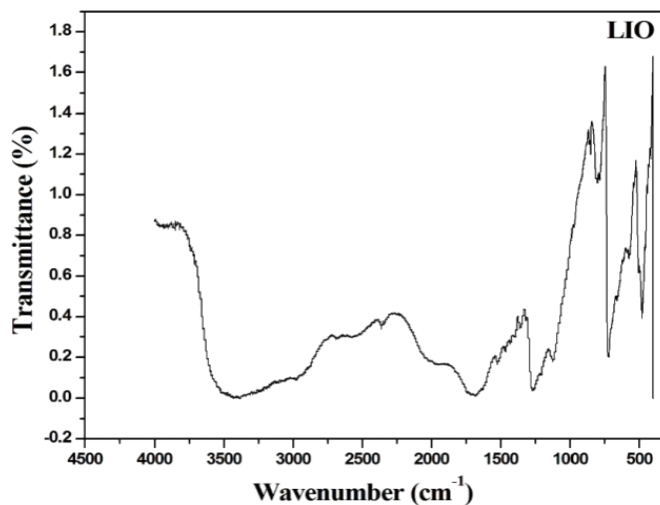


Fig. 1 (b)

Fig. 1: FT-IR analysis of LIM and LIO

The calculated spectra of LIM and LIO are shown in Fig.2a and 2b. The calculated spectra have been compared with the experimental FTIR Spectra and it can be observed that the vibrational frequencies obtained from DFT are in good agreement with the experiment.

The comparative band assignments of LIM and LIO are given in the Table 5 and 6.

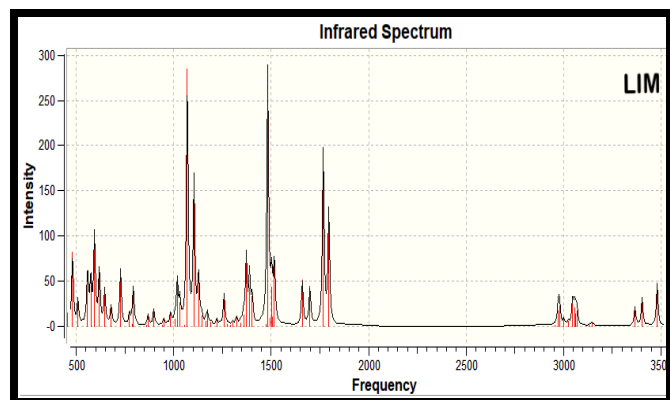


Fig. 2 (a)

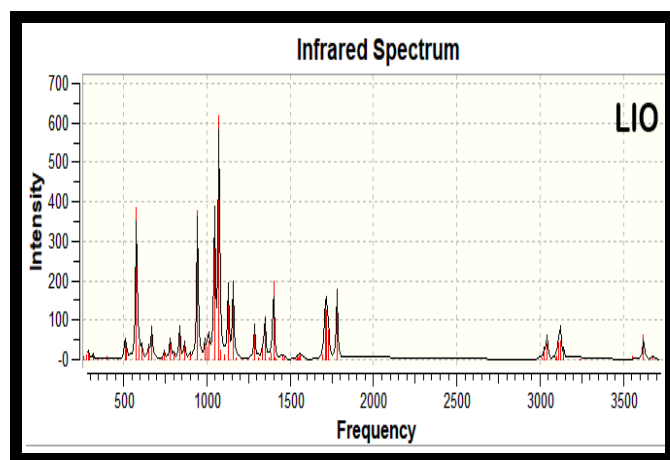


Fig. 2 (b)

Fig. 2: Calculated spectra of LIM and LIO

Table 5: The Experimental and Theoretical Band Assignments of LIM

Wave number cm ⁻¹ (Experimental)	Wave number cm ⁻¹ (Theoretical)	Assignments
2961	2955	C-H stretching
2878	2902	C-O stretching
1720	1767	C=O stretching
1568	1660	COO ⁻ asymmetric stretching
1307	1303	C-O stretching
1240	1258	CH ₂ wagging
1069	1070	C-N stretching
866	868	CH ₂ rocking
694	679	COO ⁻ scissoring

Table 6: The Experimental and Theoretical Band Assignments of LIO

Wave number cm ⁻¹ (Experimental)	Wave number cm ⁻¹ (Theoretical)	Assignments
3377-2350	3464	NH and C-H stretching vibration
1683	1697	NH ₃ ⁺ asymmetric deformation
1512	1515	COO ⁻ asymmetric stretching
1262	1249	CH ₂ wagging
1080	1087	C-N stretching
851	851	C-C stretching
675	680	COO ⁻ plane deformation
580	598	COO ⁻ wagging mode
478	456	N-H deformation

6. CONCLUSION

Attempts have been made in the present work for the molecular parameters and frequency assignments for the molecules LI, LIM and LIO from the FT-IR spectra. The equilibrium geometries, first hyperpolarizabilities and vibrational analysis for the title compounds were determined and analyzed at DFT level of theory utilizing 6-31 G basis set. The remarkable agreement of the calculated and observed vibrational spectra reveals the advantages of a smaller basic set for quantum chemical calculations. HOMO and LUMO energy gap explains an eventual charge transfer interactions taking place within the molecule.

7. ACKNOWLEDGEMENT

The authors thank the Manonmaniam Sundaranar University, Tirunelveli for providing the research support.

8. REFERENCES

1. Madhavan J, Aruna S, Prabha K, Packiam JJ, Ginson P, Joseph, Selvakumar S, Sagayaraj P. *Journal of crystal growth*, 2006; **293**:409.
2. Senthil S, Pari S, Sagayaraj P, Madhavan. *J Physics B*, 2009; **404**:655.

3. Sun GH, Sun XT, Sun ZH, Wang XQ, Liu XJ, Zhang GH, Xu D. *Journal of crystal growth*, 2009; **311**:3904.
4. Musa E Mohammed, Christina Y Ishak, Hajir I. Wahbi. *Der Chemica Sinica*, 2011; **2(4)**:133-139.
5. Wang LN, Wang XQ, Zhang GH, Liu XT, Sun ZH, Sun GH, Wang L, Yu WT, Xu D, *Journal of crystal growth*, 2011; **327**:13.
6. Tsuboi M, Takenishi T, Iitaka Y. *Bull. Chem. Soc. Japan*, 1959; **32**:305.
7. Kazuo Torji, Yoichi Iitaka, *Acta Cryst.*, 1971; **B27**:2237.
8. Frisch MJ, Trucks GW, Schlegel HB, Scuseria GE, Robb MA, Cheeseman JR, Scalmani G, Barone V., B. Mennucci, G. A. Peterson, *Int. J. Quantum Chem.*, 1974; **8**:61.
9. Nakatsuji H, Caricato M, Li X, Hratchian HP, Izmaylov AF. Gaussian 09 (Gaussian, Inc., Wallingford CT, 2009.
10. Chemla DS, Zyss J, *Nonlinear Optical Properties of Organic Molecules and Crystals*, Academic Press, Orlando, 1987.
11. Hann RA, Bloor D, *Organic Material of Non-linear Optics II*, The Royal Society of Chemistry, Cambridge, 1991.
12. Fukuli K, Yonezawa T, Shingu H. *Journal of Physical chemistry*, 1952; **20(4)**:722.
13. Choi CH, Kertesz M. *Journal of Physical chemistry A*, 1997; **101(20)**:3823-3831, 1997.
14. Gunasekaran S, Arun Balaji R, Kumaresan S, Anand G, Srinivasan S, *Canadian Journal of Analytical Sciences and Spectroscopy*, 2008; 53(4):149-162,
15. Geetha P, Arulmozhi S, Madhavan J, Victor Antony Raj M. *International Journal of Chem Tech Research*, 2014; **6(3)**:1647-1650.
16. Dinesh Raja M, Arulmozhi S, Madhavan J, Senthil S. *International Journal of Chem Tech Research*, 2014; **6(1)**:31-35.