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Study of Electronic and Dielectric Properties of L-Arginine Semimalonate

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***Abstract* - First-principles calculations have been done on the L-arginine semimalonate $C_9H_{18}N_4O_6$ crystal based on Density Functional Theory. The Triclinic structure of Nitrilotrisethylene carbamic acid has been simulated using this formalism and the structural parameters have been found out. The Electron Density of States (EDOS) has been computed in the material using the Electronic structure calculation code of the software Quantum-Espresso which gives a Band gap of 2.35 eV. This value is found to be close to the value exhibited by semiconducting materials and photonic band gap materials. The value of polarizability has also been calculated. Its value comes out to be 77.40 Å^3, 77.08 Å^3, 76.55 Å^3 along x,y and z axis with average value of 77.01 Å^3. The values of Phonon modes have been computed using the ph.x program code of quantum espresso software. The values of computed phonon modes range from 0 cm^{-1} to 8012 cm^{-1}.**

***Keywords*: L-Arginine Semimalonate, First-Principles Calculation, Electron Density of States, Band Gap, Semiconductor**

I. INTRODUCTION

Non-steroidal anti-inflammatory drugs play an important role in the treatment of the inflammation and they show their therapeutic and side effects in a greater part to the inhibition of cyclooxygenase (COX). The separation of these therapeutic effects from the side effects has become a major goal in the design and also synthesis of these drugs. Several derivatives of Benzamide have been synthesized and studied by G. Caliendo *et al.,* [1]. It is found that the N-substituted benzamides can be used as agents for combating pests, in particularly as insecticides and nematicides [2].

It is very much essential to have the knowledge of molecular interactions for the design and synthesis of macromolecules which adopt required conformations. Since these interactions are strongly temperature and pH dependent, not only their interplay dominant in the crystallization and stability of the macromolecules [3], but also govern the conformational properties enabling the pharmacological activity of several molecules [4]. Suryaprakash *et al.,* [5] have investigated few weak molecular interactions in isomeric fluorinated benzanilides using the spectroscopic techniques of 19 F and 1 H-NMR (with 14 N decoupling) along with the density functional theoretical (DFT) calculations.

Non-covalent forces found to play an important role in the processes like folding and also self-assembly [6]. In the recent years, chemists are engaged in the development of foldamers [7] and several artificial molecules which utilize non-covalent forces for modulating the folding or helical architectures. In this regard it has been found that the strong directional characteristics associated with the hydrogen bonds like O–H...O, N–H...O and N–H...N [8 - 12] are found to be highly effective in the assembly of supra-molecular structures.

If any little modification is done in the structure and composition of a material, it will bring in sufficient changes in the properties of the material [13, 14]. Thus it is very important to study the structure of the materials and also look at the parameters that can be altered to get a better material for several technological applications.

First-principles calculation based on Density Functional Theory [15] has been very well proved to be an effective tool in the study of structural also, electronic and dielectric properties of several organic materials [16, 17]. With this in view, the structure of L-arginine semimalonate has been simulated using First-principles calculations based on Density Functional Theory. Also, computation of Electronic density of states and the values of phonon modes have been done and the results have been reported in this present paper.

II. COMPUTATIONAL DETAILS

It is found that for the theoretical structure simulation several codes are available [18]. The approach based on density functional theory has emerged as a well established computational method. It has been largely employed to arrive at the conformations of a large number of molecular systems. It is found that the practical applicability of DFT is strongly sensitive to the better choice of exchange-correlation function along with the appropriate basis set.

Quantum espresso is a well known integrated suite of Open-Source computer codes for electronic-structure calculations and also the materials modelling. It is based on density-functional theory, plane waves, and pseudo potentials. In the present study the author has employed the plane wave self consistent field (PWSCF) [19] implementation of density

functional theory (DFT), with the Local density approximation (LDA) [20] to the exchange correlation energy of electrons and ultrasoft pseudopotentials [21], to represent the interaction between ionic cores and valence electrons. Kohn-Sham wave functions have been represented with a plane wave basis with an energy cutoff of 30 Ry and charge density cutoff of 180 Ry.

Integration over Brillouin zone was sampled with the Monkhorst-Pack scheme [22] with appropriate k point mesh and occupation numbers have been smeared using Methfessel-Paxton scheme [23] with a broadening of 0.03 Ry. The structure has been relaxed to minimize energy.

III. RESULTS AND DISCUSSION

A. Structure of L-Arginine Semimalonate

In the present investigation, the Triclinic unit cell of L-arginine semimalonate was first simulated using the "Avogadro" [24]. Later, atomic positions of the molecules have been used in the plane wave self consistent field calculations. The structure has been relaxed and the optimized values of the unit cell parameters so arrived through minimization of energy are; a = *5.353 Å*, *b = 6.931 Å*, *c = 9.922 Å*, *α = 69.53°*, *β = 89.03°*, *γ = 71.12°*. "scf'" calculation was done using the final atomic positions obtained after relaxing the structure using the program 'pw.x' code of Quantum espresso.

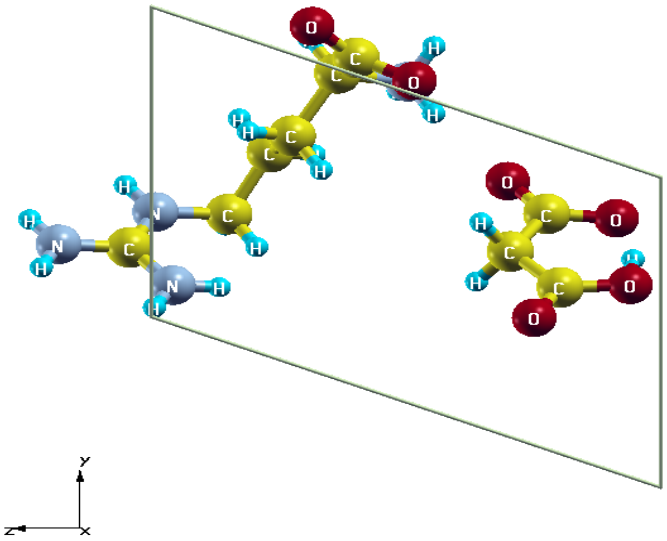

Fig. 1 Structure of the unit cell of L-arginine semimalonate as viewed along X axis

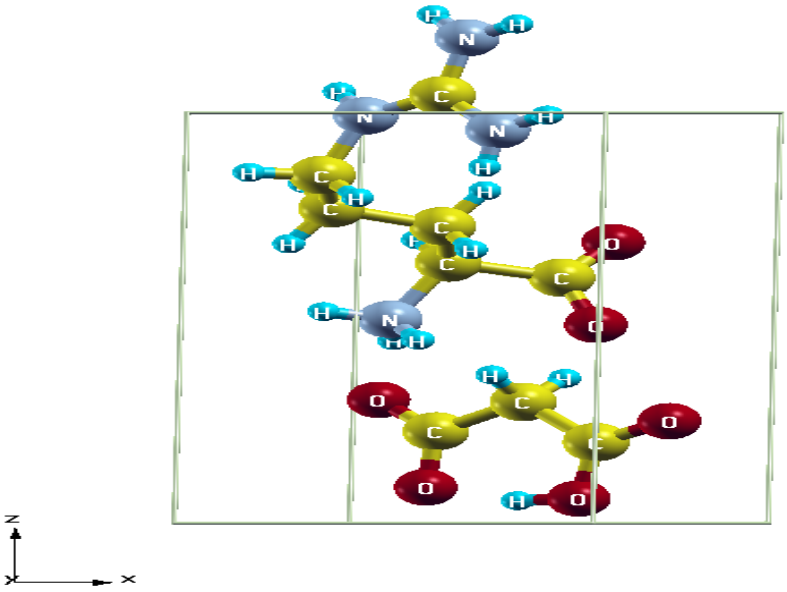

Fig. 2 Structure of the unit cell of L-arginine semimalonate as viewed along Y axis

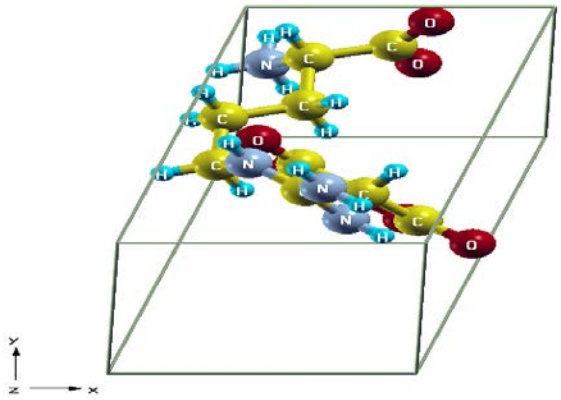

Fig. 3 Structure of the unit cell of L-arginine semimalonate as viewed along Z axis

The completely relaxed structure of the unit cell was visualized using the program "XcrysDen" [25] and the structure of L-arginine semimalonate as viewed along X, Y, and Z axes are shown in Figures 1, 2 and 3 respectively. The values of bond lengths and bond angles in the relaxed structure of L-arginine semimalonate are tabulated in tables I and II respectively.

TABLE I BOND LENGTHS IN L-ARGININE SEMIMALONATE

Bond	Bond length (Å)
C – H	1.00
C – C	1.51
C – O	1.25
N – H	1.00

TABLE II BOND ANGLES IN L-ARGININE SEMIMALONATE

Bond	Bond angle (deg)
H – N – H	120
O – C – O	124
N – C – N	119, 122
C – C – C	110 – 117

It is found that the structural parameters of L-arginine semimalonate are matching very well with the XRD studies found in the literature [26].

IV. EDOS CALCULATION

Electron Density of States (EDOS) are computed in L-arginine semimalonate using the Electronic structure calculation code of Quantum espresso. EDOS in L-arginine semimalonate has been shown in Figure 4. The band gap is found to be 2.35eV. The band gap is found to be similar to that exhibited by semiconductors and photonic band gap materials. Bang gap lies in the range of values exhibited by the Non-Linear Optical (NLO) materials [27] and the liquid crystalline materials [28]. It has been observed that several inorganic NLO materials show a band gap in the range 2eV to 4eV. For example, a band gap of 4eV has been observed in Lithium niobate. A band gap of 3.2eV has been observed in Barium titanate. BSO crystals show a value of 4.02eV and also KTN nanoparticles show a band gap of 3.26eV. An optical band gap of 3.65eV has been observed in the organic NLO material L-Tartaric acid. It is found that the tuning of the band gap plays an important role in the field of photonic crystals.

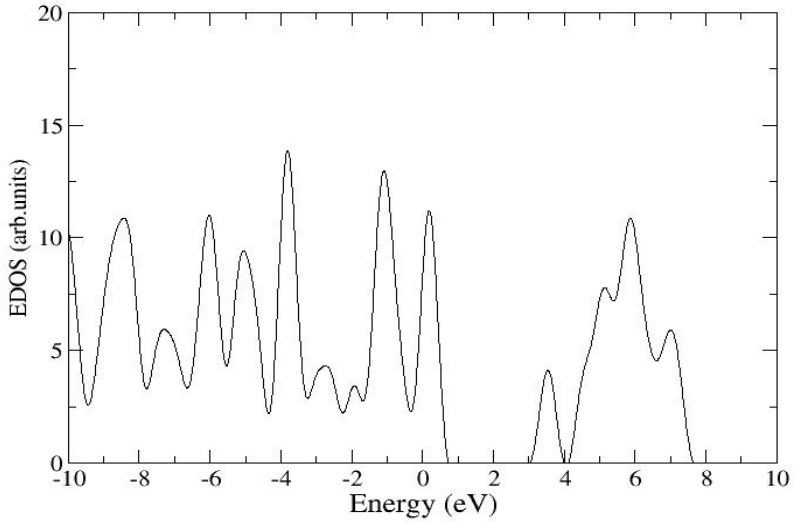

Fig. 4 Electron Density of States in L-arginine semimalonate

V. POLARIZABILITY AND PHONON MODES

The polarizability volume has also been calculated using the phcg.x code of Quantum espresso software. Its value comes out to be 77.40 $Å^3$, 77.08 $Å^3$, 76.55 $Å^3$ along X, Y and Z axes respectively with an average value of 77.01 $Å^3$. Values of phonon modes have also been computed using the ph.x program of quantum espresso software. The computed phonon modes so computed range from 0 cm^{-1} to 8012 cm^{-1}.

VI. CONCLUSION

The structure of the unit cell of L-arginine semimalonate crystal is found to be triclinic. Band gap in L-arginine semimalonate is found to be 2.35 eV. This value is close to the values exhibited by NLO materials and liquid crystalline materials. The polarizability value comes out to be 77.40 $Å^3$, 77.08 $Å^3$, 76.55 $Å^3$ along X, Y and Z axes respectively with an average value of 77.01 $Å^3$. Values of phonon modes range from 0 cm^{-1} to 8012 cm^{-1}.

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