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Structure Simulation and Study of Electronic and Dielectric Properties of Unfluorinated and Fluorinated 3,4-Dihydroxy-5-(Hydroxymethyl)Proline

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Abstract **- First-principles calculations based on Density Functional Theory have been done on the technologically important Proline derivative (3,4-Dihydroxy-5-(hydroxymethyl)(proline) [$C6H11NO5$]. The triclinic structure of the material has been simulated and the structural parameters are found to be a=4.309Å, b=6.004Å, c=6.967Å, α=103.47^o, β=103.17^o, γ=99.80^o. After fluorination the structural parameters are found to be a=4.301Å, b=6.214Å, c=7.113Å, α=105.10^o, β=104^o, γ=97.68^o. Electron Density of States (EDOS) has been computed in the material using the Electronic structure calculation code of Quantum-Espresso which gives a Band gap of 4.47 eV. After fluorination the Band gap is found to be 3.34 eV. The value of dielectric constant in the material comes out to be 2.32, 2.70 and 2.61 along x, y and z axes respectively and the average value comes out to be 2.54. After fluorination the dielectric constant of the compound comes out to be be 2.38, 2.56 and 2.56 along x,y and z axes respectively the average value comes to be 2.50. The computed phonon modes range from 101cm^{-1} to 3157cm^{-1}. After fluorination the phonon modes range from 306cm^{-1} to 3563cm^{-1}.**

Keywords **: Proline derivative, First-principles calculation, Electron density of states (EDOS), Band gap, Dielectric constant, Phonon modes.**

I. INTRODUCTION

Proline is an α-amino acid that is used in the biosynthesis of proteins. It contains an α-amino group, an α-carboxylic acid group, and a side chain pyrrolidine. It is classified as a nonpolar, aliphatic amino acid. It is considered as a non-essential in humans. It means that the body can synthesize it from the non-essential amino acid L-glutamate. Proline is the only proteinogenic amino acid with a secondary amine in which the alpha-amino group is attached directly to the side chain. This makes the alpha carbon a direct substituent of the side chain.

Proline and its derivatives are used as asymmetric catalysts in proline organocatalysis reactions. In brewing, proteins rich in proline combine with polyphenols to produce haze. L-Proline is known as an osmoprotectant. It is used in several pharmaceutical and bio-technological applications. It has been found that the growth medium used in plant tissue culture may be supplemented with proline. This can increase the growth, because it helps the plant in tolerating the stresses of tissue culture[1].

L-Proline has been found to act as a weak agonist of the glycine receptor and of both NMDA and non-NMDA ionotropic glutamate receptors. It has been proposed to be a potential endogenous excitotoxin [2-4].

Jianxin Gu and Mark E. Ruppen [5], Stephane Sabelle, Eric Terranova [6], Laurent Vidal and Aziz Fadli [7], Gianni Chessari, Miles Stuart Congreve [8], Astex Therapeutics Ltd, Michael J. Betts et.al., [9] have obtained patents on various aspects of proline derivatives. Best et. al., [10] have studied the structure of the Proline derivative 3,4-Dihydroxy-5-(hydroxymethyl)proline [$C6H11NO5$] using XRD [11].

It has been found that any little modification in the structure and composition of a material will bring in sufficient changes in the properties of the material [12, 13]. Thus it is important to study the structure of the materials and look at the parameters which can be altered to get a better material for technological applications. First-principles calculation based on Density Functional Theory [14] has been proved to be an effective tool in the study of structural, electronic and dielectric properties of organic materials [15, 16]. With this in view, structure of Proline derivative (3,4-Dihydroxy-5-(hydroxymethyl)proline [$C6H11NO5$] has been simulated using First-principles calculations based on Density Functional Theory and computation of Electronic density of states, Dielectric constant and phonon modes have been done and the results have been reported in the present paper.

II. COMPUTATIONAL DETAILS

Several codes are available for the theoretical structure simulation [17]. The density functional theory approach has emerged as a well established computational method. It has been widely employed to arrive at the conformations of a large number of molecular systems. The practical applicability and sophistication of DFT is strongly sensitive to the good choice of exchange–correlation function along with the appropriate basis set.

Quantum espresso is an integrated suite of Open-Source computer codes for electronic-structure calculations and materials modelling. It is based on density-functional theory, plane waves, and pseudopotentials. Authors have

used plane wave self consistent field (PWSCF) [18] implementation of density functional theory (DFT), with a Local density approximation (LDA) [19] to exchange correlation energy of electrons and ultrasoft pseudopotentials [20], to represent interaction between ionic cores and valence electrons. Kohn-Sham wave functions were 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 a Monkhorst-Pack scheme [21] with appropriate k point mesh and occupation numbers were smeared using Methfessel-Paxton scheme [22] with broadening of 0.03 Ry. The structure was relaxed to minimize energy.

III. RESULTS AND DISCUSSION

In the present study, the Triclinic unit cell of Proline derivative (3,4-Dihydroxy-5-(hydroxymethyl)proline [$C6H11NO5$] was first simulated using "Avogadro" [23]. Later, atomic positions of the molecules have been used in the plane wave self consistent field calculations. The structure was relaxed and the optimized values of the unit cell parameters thus arrived at through minimization of energy are; a=4.309Å, b=6.004Å, c=6.967Å, α=103.47^o, β=103.17^o, γ=99.80^o. "scf"' calculation was done using the final atomic positions obtained after relaxing the structure using the program 'pw.x' of Quantum espresso. Fluorination of Proline derivative was done by replacing one hydrogen atom by fluorine atom. Again the structure was relaxed to minimize the energy and the lattice parameters thus arrived are; a=4.301Å, b=6.214Å, c=7.113Å, α=105.10^o, β=104^o, γ=97.68^o.

The completely relaxed structure of the unit cell was visualized using the program "XCrysDen" [24] and the structure of unit cell of Proline derivative and fluorinated Proline derivative as seen along X-axis and Y-axis are shown in Figures 1-4. The bond lengths and bond angles in the relaxed structure of $C6H11NO5$ have been tabulated in tables 1 and 2 respectively.

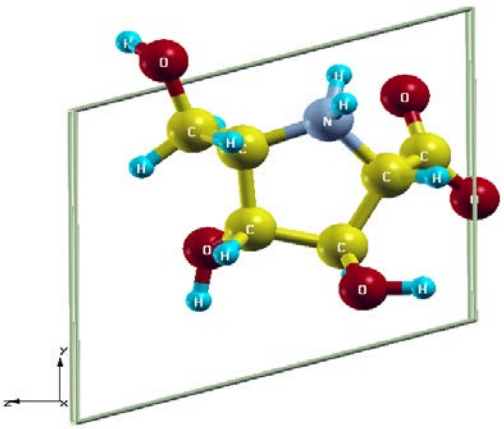

Fig.1 Structure of unit cell of $C6H11NO5$ as seen along x direction

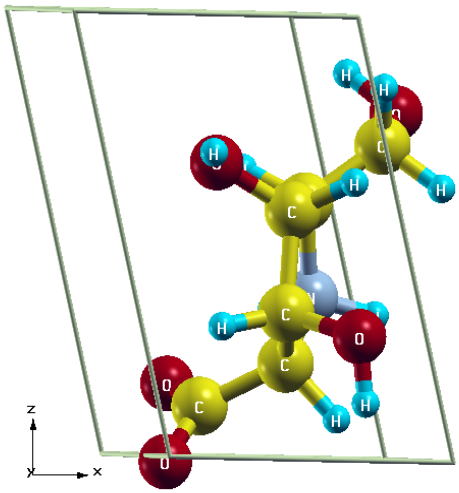

Fig.2 Structure of unit cell of $C6H11NO5$ as seen along y direction

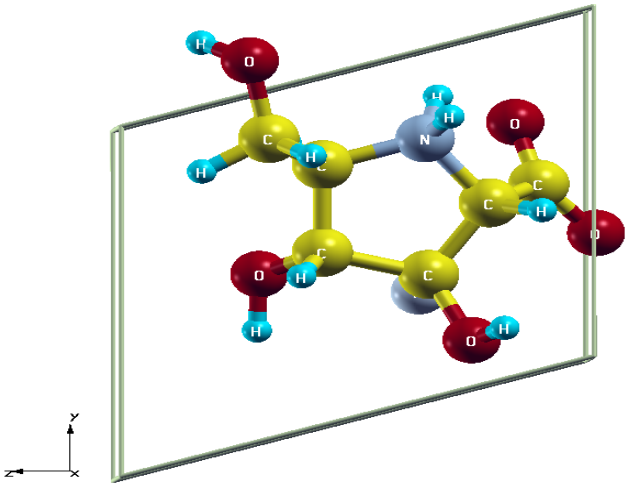

Fig.3 Structure of unit cell of fluorinated proline derivative as seen along x direction

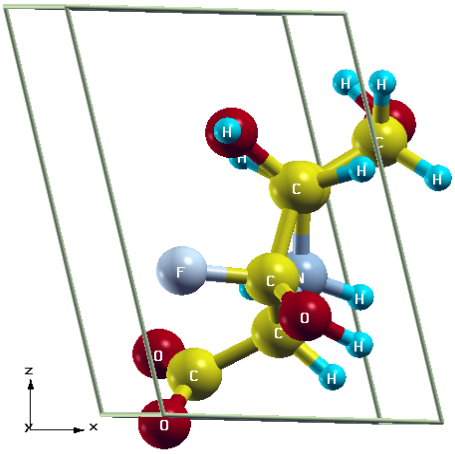

Fig.4 Structure of unit cell of fluorinated proline derivative as seen along y direction

TABLE 1 BOND LENGTH IN PROLINE DERIVATIVE

Bond	Bond length (Å)
C-H	1.12
O-H	1.00
C-O	1.34
C-C	1.51
N-H	1.05
N-C	1.49

TABLE 2 BOND ANGLE IN PROLINE DERIVATIVE

Bond	Bond angle (deg)
O-C-O	125
H-C-H	106
H-C-C	108
C-O-H	111
C-C-O	113
O-C-H	111
C-C-C	107
H-N-H	105
C-N-C	110
N-C-C	108
H-C-N	109

A. EDOS Calculation

Electron Density of States (EDOS) has been computed in proline derivative using Electronic structure calculation code of Quantum espresso. EDOS in proline derivative and fluorinated proline derivative have been shown in Figures 5 and 6. Band gap in proline derivative and fluorinated proline derivative is found to be 4.47 eV and 3.34 eV respectively. This value is close to that exhibited by Non-linear optical (NLO) materials [25] and organic semiconducting materials.

Presently, the organic semiconducting materials have very much attracted the scientific community owing to their technological advantages over traditional silicon-based semiconductor devices. Most organic materials are much less expensive to generate than highly crystalline inorganic semiconductors, and also may be used to make devices with inexpensive fabrication methods. Also, most organic materials are soluble in one or more common solvents which allows for the possibility of solution processing which can produce many devices at very low cost [26-28].

Several inorganic NLO materials show a band gap in the range 2eV to 4eV. For example, Lithium niobate shows a band gap of 4eV. Barium titanate shows a value of 3.2eV. BSO crystals show a value of 4.02eV and KTN nanoparticles show a band gap of 3.26eV. The organic NLO material L-Tartaric acid shows an optical band gap of 3.65eV. Tuning of the band gap plays an important role in the field of photonic crystals.

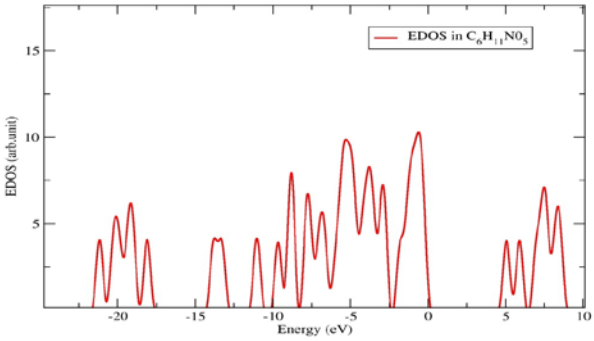

Fig.5 Electronic Density of States in proline derivative

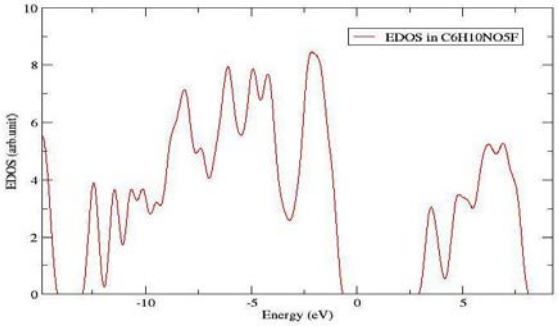

Fig.6 Electronic Density of States in fluorinated proline derivative

B.Dielectric constant and Phonon modes

The Dielectric constant and Phonon modes of the material have been computed in unfluorinated and fluorinated state using the ph.x code of Quantum espresso. Dielectric constant of the material has been computed. The value of dielectric constant in proline derivative comes out to be 2.32, 2.70 and 2.61 along x, y and z axes respectively and the average value comes out to be 2.54. After fluorination the dielectric constant of the compound comes out to be be 2.38, 2.56 and 2.56 along x,y and z axes respectively the average value comes to be 2.50.

This value is in the range exhibited by low k dielectric materials used in the semiconductor industry. For example; Dielectric constant of Fluropolyimide is 2.8, Benzo-cyclo-butane is 2.7, Black diamond is 2.7, Polyethylene is 2.4, Polypropylene is 2.3, Fluoropolymer is 2.24, Perylene is 2.2 and in Dupont PTFE-based copolymer AF 2400 it is 2.06. They have applications in the fabrication of semiconducting devices [29]. This also shows that the material under study can be used in semiconductor devices.

Phonon modes have been computed using the ph.x program of quantum espresso. The computed phonon modes range from $101cm^{-1}$ to $3157cm^{-1}$. After fluorination the phonon modes range from $306cm^{-1}$ to $3563cm^{-1}$. Values of various parameters in Unfluorinated and fluorinated proline derivative are tabulated in Table 3.

TABLE 3 DIFFERENT PARAMETERS IN UNFLUORINATED AND FLUORINATED PROLINE DERIVATIVE

Parameter	Unfluorinated proline derivative	Fluorinated proline derivative
a (Å)	4.309	4.301
b (Å)	6.004	6.214
c (Å)	6.967	7.113
α (deg)	103.47	105.10
β (deg)	103.17	104
γ (deg)	99.80	97.68
Crystal system	Triclinic	Triclinic
Band gap (eV)	4.47	3.34
Average Dielectric constant	2.54	2.50
Phonon modes (cm^{-1})	101 – 3157	306 – 3563

IV. CONCLUSIONS

The lattice parameters arrived at by the structural optimization using the first-principles calculations are a=4.309Å, b=6.004Å, c=6.967Å, α=103.47^o, β=103.17^o, γ=99.80^o. After flourination lattice parameters are found to be a=4.301Å, b=6.214Å, c=7.113Å, α=105.10^o, β=104^o, γ=97.68^o. The lattice parameters of the present study are matching well with the experimentally found values in the material. The material shows a band gap of 4.47 eV. After fluorination the band gap of the material reduces to 3.34 eV. These values of band gap tell that this material is behaving as an organic semiconductor. The material shows an average dielectric constant of 2.54 and after fluorination the average dielectric constant is reduced to 2.50. The computed phonon modes in the material range from 101cm^{-1} to 3157cm^{-1}. After fluorination the phonon modes range from 306cm^{-1} to 3563cm^{-1}. Thus it is demanding for further investigations in the material to explore the applications of this material in organic semiconductor electronics and other applications.

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