Chemical Technology: An Indian Journal

Chemical Technology
ISSN: 0974-7443

Research | Vol11 Iss 5

Study of Electronic and Dielectric Properties of Fluorinated Pyridine-2-dicarboxamide

Sreepad HR*

Department of Physics, Government College (Autonomous), Research centre of University of Mysore, Mandya-571401, Karnataka State, India

***Corresponding author:** Sreepad HR, Associate Professor and Head P.G. Department of Physics Government College (Autonomous), Affiliated to University of Mysore, Mandya-571401, Karnataka State, India, Tel: 919449184109; E-mail: hrsreepad@gmail.com

Abstract

The structure of Pyridine-2-dicarboxamide has been simulated and optimized using energy minimization technique of First-principles calculations based on DFT. Then it is fluorinated by replacing two hydrogen atoms by two fluorine atoms and the structure was again optimized. Electron density of states calculation has been done which gives a Band gap of 0.6 eV. Dielectric constant and polarizability have been computed. The value of dielectric constant in fluorinated Pyridine-2-dicarboxamide comes out to be 3.84, 6.66 and 5.44 along X, Y and Z axes respectively and the average value comes out to be 5.31. Polarizability in fluorinated Pyridine-2-dicarboxamide is estimated to be 26.94 Å3, 36.20 Å3 and 33.03 Å3 along X, Y and Z axes respectively and the average value comes out to be 32.06 Å3.

Keywords: *Pyridine-2-dicarboxamide; First-principles calculation; Electron density of states; Band gap; Dielectric constant; Polarizability.*

Introduction

An amide is a compound with the functional group $R_nE(O)xNR'_2$ where R and R' refer to H or organic groups. Most common are organic amides with n = 1, E = C, x = 1. There are many other important types of amides. For example; phosphor amides with n = 2, E = P, x = 1 and many related formulae and sulfonamides with E = S, x= 2 [1]. Suhonen et al., [2] have studied crystal structures and molecular conformations of two foldamer-type oligoamides and have reported that the different modes of intramolecular hydrogen bonding strongly affect the conformation and folding of the molecules.

Caliendo et al. [3] have synthesized and studied several derivatives of Benzamide. It has been found that the N-substituted benzamides can be used as agents for combating pests, in particular as insecticides and nematicides [4]. Bovenzi et al., [5] have synthesized monoclinic single crystals of pyridine-2,6-dicarboxamideoxime, $C_7H_9N_5O_2$ with a = 7.569(1) Å, b = 4.695(1) Å, c = 12.534(2) Å having two molecules per unit cell and have synthesized and characterized the nickel and copper

Citation: Sreepad HR (2016) Study of Electronic and Dielectric Properties of Fluorinated Pyridine-2-dicarboxamide, Chemical Technology: An Indian Journal, 11

co-ordination compounds of pyridine-2,6-dicarboxamideoxime. Bates et al., [6] have studied the structural diversity in the first metal complexes of 2,5-dicarboxamidopyrroles and 2,5-dicarbothioamidopyrroles.

Dorazco-González et. al., [7] have studied the Fluorescent anion sensing by bisquinolinium pyridine-2,6-dicarboxamide receptors in water. 2,6-pyridinedicarboxamide coordination compounds have been found to be reliable circularly polarized luminescence calibration standards [8]. Jain et. al., [9] have synthesized and characterized seven new complexes of pyridine dicarboxamide. Ustynyuk et. al., [10] have first predicted using DFT simulation and then experimentally proved that the phenanthroline-2,9-dicarboxamides are efficient donor ligands with high and unusual selectivity for the extraction separation of lanthanides.Mitsui et al., [11] have studied the Dendritic effects on both the enantioselectivity and diastereoselectivity of the direct aldol reaction for dendrons terminated with L-prolinamides. Dicarboxamide fungicides are a family of agricultural fungicides that include vinclozolin, iprodione, and procymidone. Dicarboximides are believed to inhibit triglyceride biosynthesis in sclerotia-forming fungi, including Botrytis cinerea. These fungicides turn into 3,5-dichloroaniline in soil rapidly. But, repeated use of dicarboximides over several years reduce their effectiveness [12,13]. Munro et al. [14] have studied the structure of Pyridine-2-dicarboxamide $C_{16}H_{18}N_4O_2$ using XRD and have reported the triclinic unit cell with lattice parameters; a = 5.3215 Å, b = 7.2734 Å, c = 9.7993 Å, alpha = 83.509 deg, beta = 77.256 deg and gamma = 81.005 deg with unit cell volume 364.18 $Å^3$ having only one molecule per unit cell.

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 [15-17]. 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 [18] has been proved to be an effective tool in the study of structural, electronic and dielectric properties of organic materials [19,20]. Amide derivatives have attracted the scientific community in various aspects. With this in view, structure of fluorinated Pyridine-2-dicarboxamide has been simulated using First-principles calculations based on Density Functional Theory and computation of Electronic density of states, Dielectric constant and Polarizability have been done and the results have been reported in the present paper.

Computational Details

Several codes are available for the theoretical structure simulation [21]. 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 modeling. It is based on density-functional theory, plane waves, and pseudopotentials. Author has used plane wave self consistent field (PWSCF) [22] implementation of density functional theory (DFT), with a Local density approximation (LDA) [23] to exchange correlation energy of electrons and ultrasoft pseudopotentials [24], 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 [25] with appropriate k point mesh and occupation numbers were smeared using Methfessel-Paxton scheme [26] with broadening of 0.03 Ry. The structure was relaxed to minimize energy.

Results and Discussion

In the present study, the triclinic unit cell of fluorinated Pyridine-2-dicarboxamide was first simulated using “Avogadro” [27]. 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 = 4.776 Å, b = 5.701 Å, c = 8.837 Å, α = 84.24 deg, β = 75.82 deg and γ = 86.26 deg with cell volume of 231.93 $Å^3$ having only one molecule per unit cell. “scf” calculation was done using the final atomic positions obtained after relaxing the structure using the program 'pw.x' of Quantum espresso.

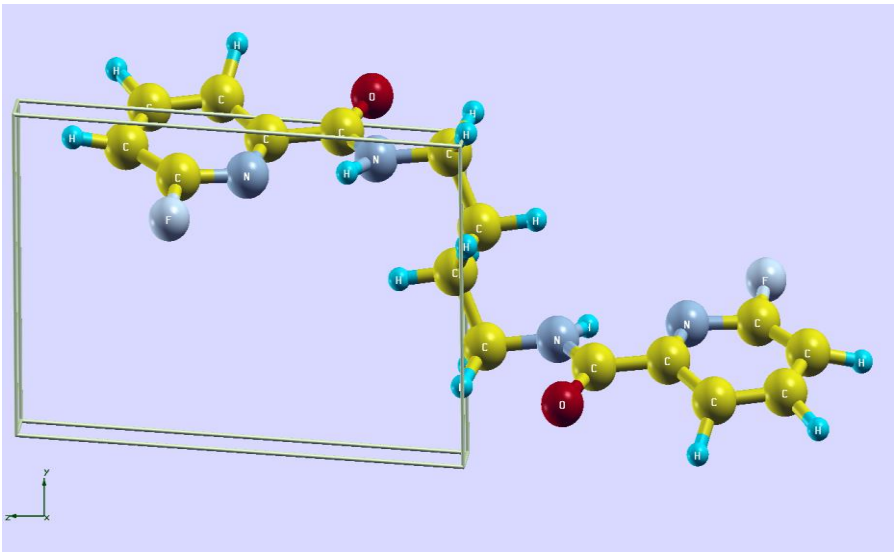

Figure 1**:** Structure of unit cell of fluorinated pyridine-2-carboxamide as viewed along X axis.

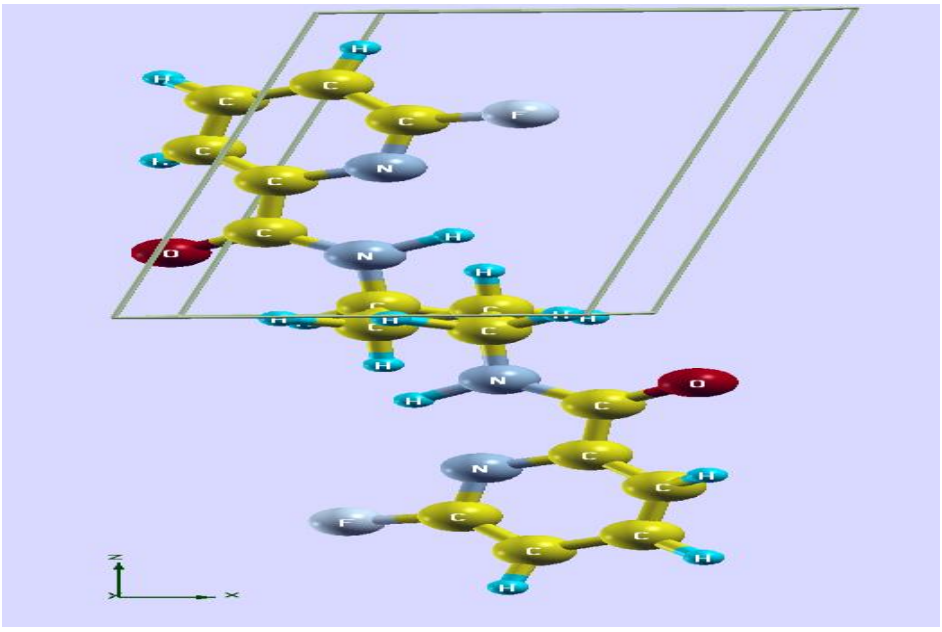

Figure 2: Structure of unit cell of fluorinated pyridine-2-carboxamide as viewed along Y axis.

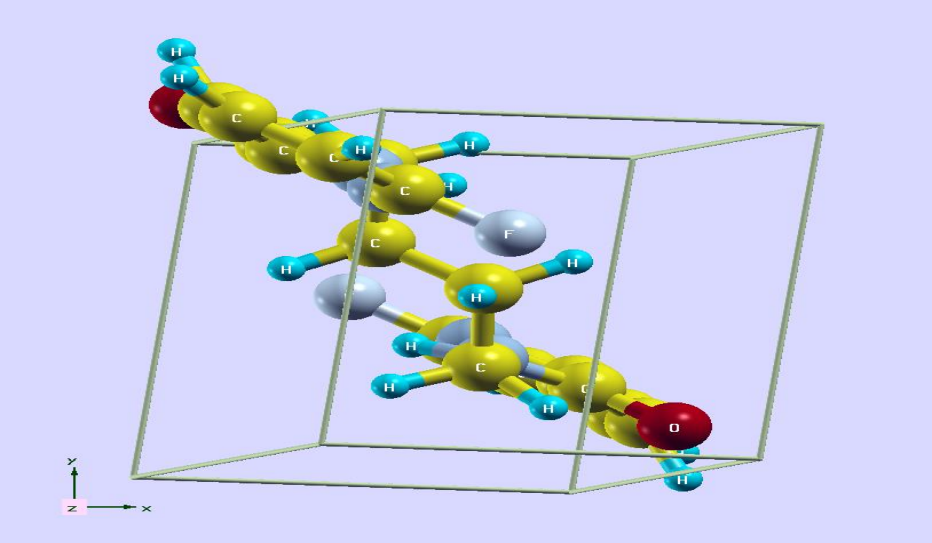

Figure 3: Structure of unit cell of fluorinated pyridine-2-carboxamide as viewed along Y axis.

Completely relaxed structure of the unit cell was visualized using the program "XcrysDen" [28] and the structure of unit cell of fluorinated Pyridine-2-dicarboxamide as seen along X, Y and Z axes are shown in Figures 1-3 respectively. From the figures, it is clear that the structural parameters of the simulated and optimized structure of fluorinated Pyridine-2-dicarboxamide in the present study is very close to the structure reported in the literature by Munro et al. [14].

EDOS calculation

Electron Density of States (EDOS) has been computed in fluorinated Pyridine-2-dicarboxamide using Electronic structure calculation code of Quantum espresso. EDOS in fluorinated Pyridine-2-dicarboxamide has been shown in Figure 4. Band gap in fluorinated Pyridine-2-dicarboxamide is found to be 0.6 eV. The value of Band gap indicates that the material is exhibiting the nature of semiconducting materials.

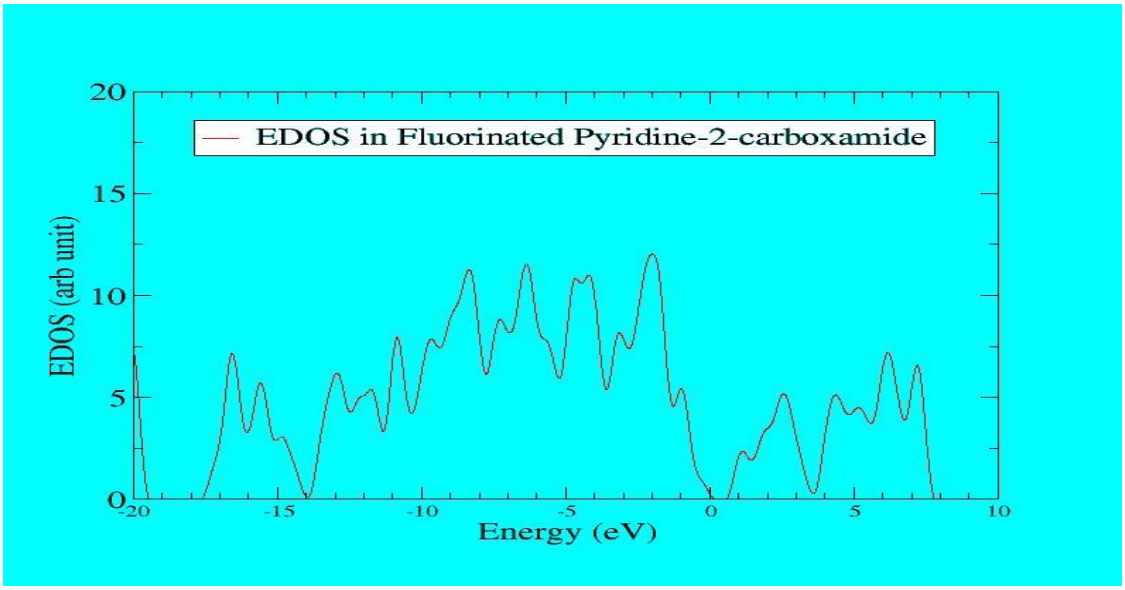

Figure 4: Electronic density of states in fluorinated pyridine-2-carboxamide.

Dielectric constant and polarizability

Dielectric constant of the material has been computed in case of fluorinated Pyridine-2-dicarboxamide. The value of dielectric constant in fluorinated Pyridine-2-dicarboxamide comes out to be 3.84, 6.66 and 5.44 along X, Y and Z axes respectively and the average value comes out to be 5.31. Polarizability in fluorinated Pyridine-2-dicarboxamide is estimated to be 26.94 Å^3, 36.20 Å^3 and 33.03 Å^3 along X, Y and Z axes respectively and the average value comes out to be 32.06 Å^3.

Conclusions

The simulated and optimized structure of fluorinated Pyridine-2-dicarboxamide is matching very well with the structure reported in the literature. Band gap in case of fluorinated Pyridine-2-dicarboxamide comes out to be 0.6 eV. The value of Band gap indicates that the material is exhibiting the nature of semiconducting materials. Hence the usage of the material under study as a semiconductor has to be explored. The value of dielectric constant in fluorinated Pyridine-2-dicarboxamide comes out to be 3.84, 6.66 and 5.44 along X, Y and Z axes respectively and the average value comes out to be 5.31. Polarizability in fluorinated Pyridine-2-dicarboxamide is estimated to be 26.94 Å^3, 36.20 Å^3 and 33.03 Å^3 along X, Y and Z axes respectively and the average value comes out to be 32.06 Å^3.

Acknowledgments

Author thanks the Department of Collegiate Education, Government of Karnataka for permitting to carry out the research work. Also, author acknowledges the necessary facilities provided by the Government College (Autonomous), Mandya (Affiliated to University of Mysore), India.

References

1. IUPAC, Compendium of Chemical Terminology, 2nd edn. (the "Gold Book") (1997). Online corrected version: (2006) "amides".
2. Suhonen A, Nauha E, Salorinne K, Helttunen K, Nissinen M (2012) Structural analysis of two foldamer-type oligoamides – the effect of hydrogen bonding on solvate formation, crystal structures and molecular conformation. Cryst Eng Comm 14: 7398-7407.
3. Caliendo G, Santagada V, Perissutti E, Severino B, Fiorino F, et al. (2001) Synthesis of substituted benzamides as anti-inflammatory agents that inhibit preferentially cyclooxygenase 1 but do not cause gastric damage. Eur J Med Chem 36: 517-530.
4. Patent US5082862 - N-substituted benzamides.
5. Bovenzi BA, Pearse GA, Pearse GA Jr. (1997) The synthesis and crystal structures of pyridine-2,6-dicarboxamideoxime, $C_7H_9N_5O_2$, and itsnickel(II) and copper(II) co-ordination compounds. J Chem Soc Dalton Trans 1997: 2793-2798.
6. Bates GW, Gale PA, Light ME, Ogden MI, Warriner CN (2008) Structural diversity in the first metal complexes of 2,5-dicarboxamidopyrroles and 2,5-dicarbothioamidopyrroles. Dalton Trans 2008: 4106-4112.
7. Dorazco-González A, Alamo MF, Godoy-*Alcántar C, Höpfl H,* Yatsimirsky AK *(*2014) Fluorescent anion sensing by bisquinolinium pyridine-2,6-dicarboxamide receptors in water. RSC Adv 4: 455-466.

8. Bonsall SD, Houcheime M, Straus DA, Muller G (2007) Optical isomers of N,N′-bis(1-phenylethyl)-2,6-pyridinedicarboxamide coordinated to europium(III) ions as reliable circularly polarized luminescence calibration standards. Chem Commun 2007: 3676-3678.
9. Jain SL, Bhattacharyya P, Milton HL, Slawin AM, Crayston JA, et al. (2004) New pyridine carboxamide ligands and their complexation to copper(II). X-Ray crystal structures of mono-, di, tri- and tetranuclear copper complexes. Dalton Trans 2004: 862-871.
10. Ustynyuk YA, Borisova NE, Babain VA, Gloriozov IP, Manuilov AY, et al. (2015) N,N′-Dialkyl-N,N′-diaryl-1,10-phenanthroline-2,9-dicarboxamides as donor ligands for separation of rare earth elements with a high and unusual selectivity. DFT computational and experimental studies. Chem Commun 51: 7466-7469.
11. Mitsui K, Hyatt SA, Turner DA, Hadad CM, Parquette J (2009) Direct aldol reactions catalyzed by intramolecularly folded prolinamide dendrons: dendrimer effects on stereoselectivity. Chem Commun 2009: 3261-3263.
12. Noon, Robert (2004) New developments in Fungicides. PJB Publications, p: 38.
13. Copping LG (1998) Review of major agrochemical classes and uses. In: Chemistry and Technology of Agro-chemical Foundations (D. Alan Knowles ed.). Dordrecht; Boston: Kluwer Academic Publishersm, p: 29.
14. Munro OQ, Wilson C (2010) Acta Crystallographica. Section C: Crystal Structure Communications 66: o535-o539.
15. Sreepad HR, Ravi HR, Khaleel Ahmed, Dayananda HM, Umakanth K (2013) First-principles study of fluorination of L-Alanine. AIP Conf Proc 1512: 836-837.
16. Sreepad HR, Hembram KPSS, Waghmare UV (2011) First-principles Study of Electronic and Dielectric Properties of Polyoxymethylene. AIP Conf Proc 1349: 871-872.
17. Sreepad, HR (2016) Structure Simulation and Study of Electronic and Dielectric Properties of Two Derivatives of Benzamide. Mol Crys Liq Cryst 625: 195-201.
18. Payne MC, Teter MP, Allan DC, Arias TA, Joannopoulos JD (1992) Iterative minimization techniques for ab initio total-energy calculations: molecular dynamics and conjugate gradients. Rev Mod Phys 64**:** 1045-1097**.**
19. Sreepad HR, Ravi HR, Khaleel Ahmed, Waghmare UV (2012) Radiation induced changes in electronic and dielectric properties of polyoxymethylene. AIP Conf Proc 1447: 793-794.
20. Sreepad HR, Ramegowda M, Ahmed K, Dayananda HM, Manohara (2013) First-principles study of structure and electronic properties of phenyl imidazole. AIP Conf Proc 1512: 802-803.
21. http://en.wikipedia.org/wiki/Molecular_modelling
22. http://www.pwscf.org
23. Perdew JP, Zunger A (1981) Self-interaction correction to density-functional approximations for many-electron systems. Phys Rev B 23: 5048-5079.
24. Vanderbilt D (1990) Soft self-consistent pseudopotentials in a generalized eigenvalue formalism. Phys Rev B 41: 7892-7895.
25. Monkhorst HJ, Pack JD (1976) Special points for Brillouin-zone integrations. Phys Rev B 13: 5188-5192**.**
26. Methfessel M, Paxton AT (1989) High-precision sampling for Brillouin-zone integration in metals. Phys Rev B 40: 3616-3621.
27. http://avogadro.openmolecules.net/wiki/
28. Kokalj A (2003) Computer graphics and graphical user interfaces as tools in simulations of matter at the atomic scale. Comp Mater Sci 28: 155-168