Study of Structural Simulation, Dielectric and Electronic Properties of Pyrazine-2, 3-dicarboxamide

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***Abstract*—The Pyrazine-2,3-dicarboxamide structure has been simulated and optimized using energy minimization technique of First-principles calculations based on DFT. The optimized structure of Pyrazine-2,3-dicarboxamide is matching very well with the structural parameters reported in the literature. Electron density of states calculation has been done which gives a Band gap of 1.6eV. The Phonon modes and Dielectric constant have been computed. Phonon modes at gamma point have also been computed in Pyrazine-2,3-dicarboxamide and they come out to be 151cm^{-1} to 3522cm^{-1}. The value of dielectric constant in Pyrazine-2,3-dicarboxamide comes out to be 2.94, 3.08 and 2.78 along X, Y and Z axes respectively and the average value comes out to be 2.93.**

***Index Terms*—Electron density of states, Band gap, Dielectric constant. Phonon modes, Pyrazine-2,3-dicarboxamide, First-principles calculation.**

I. 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. Aku Suhonen et. Al., [1] have studied crystal structures and molecular conformations of two foldamer-type oligoamides and have reported that the different modes of intra-molecular hydrogen bonding strongly affect the conformation and folding of the molecules. G. Caliendo et al. [2] 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. Brad A. Bovenzi et. Al., [3] have synthesized monoclinic single crystals of pyridine-2,6-dicarboxamideoxime, C7H9N5O2 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 co-ordination compounds of pyridine-2,6-dicarboxamideoxime. Alejandro Dorazco-González et. Al., [4] 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 [5]. Sneh L. Jain et. Al., [6] have synthesized and characterized seven new complexes of pyridine dicarboxamide. Yu. A. Ustynyuk et. Al., [7] 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.

Kazuhiko Mitsui et. Al., [8] 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 [9, 10]. Vishweshwar et. al., [11] have studied the structure of Pyrazine-2,3-dicarboxamide C6H6N4O2 using XRD and have reported that the linear tapes of carboxamide N-H O and pyrazine C-H N hydrogen-bond dimers are connected by N-H O bonds to form a staircase-like pattern. The reported triclinic lattice structure has the lattice parameters; a=5.025Å, b=7.098Å, c=10.1196 Å, alpha=70.826deg, beta=81.868deg and gamma=81.163deg with unit cell volume 335.25Å^3 having two molecules per unit cell.

A CCDC deposited Unit cell structure of Pyrazine2,3-Dicarboxamide at low temperature has reported a triclinic unit cell with a=5.0263Å, b=7.0968Å, c=10.1074Å, alpha=70.9deg, beta=81.73deg, gamma=81.03deg, cell volume=334.85Å^3 with two molecules per unit cell [12]. 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 [13, 14]. First-principles calculation based on Density Functional Theory [15] has been proved to be an effective tool in the study of structural, electronic and dielectric properties of organic materials [16]. Pyrazine-2,3-dicarboxamide and its coordination compounds have attracted the scientific community in various aspects. With this in view, structure of Pyrazine-2,3-dicarboxamide 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. 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. Author has used plane wave self consistent field (PWSCF) [17] implementation of density functional theory (DFT), with a Local density approximation (LDA) [18] to exchange correlation energy of electrons and ultrasoft pseudopotentials [19], 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 with appropriate k point mesh and occupation numbers were smeared using Methfessel-Paxton scheme [20] with broadening of 0.03 Ry. The structure was relaxed to minimize energy.

III. RESULTS AND DISCUSSION

A. Structural Simulation

In the present study, the Triclinic unit cell of Pyrazine-2,3-dicarboxamide was first simulated using "Avogadro" [20]. 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=4.95Å, b= 7.097Å, c=10.32Å, α =70.83 deg, β=81.87deg and γ=81.16deg with cell volume of 336.75 Å^3 having two molecules 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.

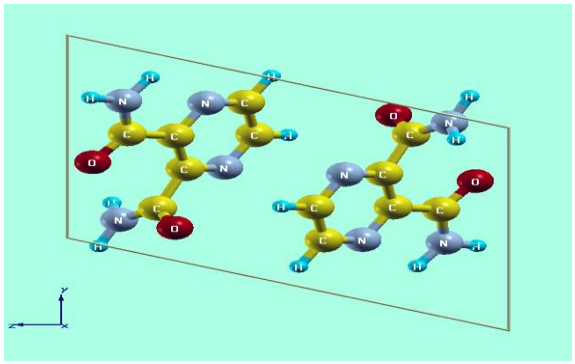

Fig. 1 Structure of unit cell of Pyrazine-2,3-dicarboxamide as viewed along X-axis.

Completely relaxed structure of the unit cell was visualized using the program "XcrysDen" [28] and the structure of unit cell of Pyrazine-2,3-dicarboxamide as seen along X-axis has been shown in Figure 1. The bond lengths and bond angles in the relaxed structure of Pyrazine-2,3-dicarboxamide have been tabulated in tables 1 and 2 respectively. Structural parameters in Pyrazine-2,3-dicarboxamide have been tabulated in table 3.

Table 1Bond lengths in Pyrazine-2,3-dicarboxamide

Bond	Bond length (Å)
C – H	1.09
C – C	1.40
C – O	1.25
C – N	1.34
N – H	1.02

Table 2 Bond angles in Pyrazine-2,3-dicarboxamide

Bond	Bond angle (deg)
C – N – C	119
O – C – C	120
N – C – C	114 – 120
N – C – O	123, 126
C – C – C	123 – 126
C – C – H	122
H – N – H	119
C – N – H	121
N – C – H	117

Table 3 Structural parameters in Pyrazine-2,3-dicarboxamide

Parameter	Present work	From literature [11]
a	4.95Å	5.025Å
b	7.097Å	7.098Å
c	10.32Å	10.1196Å
α	70.83 deg	70.826deg
β	81.87deg	81.868deg
γ	81.16deg	81.163deg
Volume of unit cell	336.75 $Å^3$	335.25$Å^3$
Molecules per unit cell	2	2

From the table 3, it is clear that the structural parameters of the simulated and optimized structure of Pyrazine-2,3-dicarboxamide in the present study is very close to the structure reported in the literature by Vishweshwar et. al., [11].

B. Dielectric constant and Phonon modes

Dielectric constant of the material has been computed in case of Pyrazine-2,3-dicarboxamide. The value of dielectric constant in Pyrazine-2,3-dicarboxamide comes out to be 2.94, 3.08 and 2.78 along X, Y and Z axes respectively and the average value comes out to be 2.93. Phonon modes at gamma point have also been computed in Pyrazine-2,3-dicarboxamide and they come out to be 151cm^{-1} to 3522cm^{-1}.

C. EDOS Calculation

Electron Density of States (EDOS) has been computed in Pyrazine-2,3-dicarboxamide using Electronic structure calculation code of Quantum espresso. EDOS in Pyrazine-2,3-dicarboxamide has been shown in Figure 2. Band gap in Pyrazine-2,3-dicarboxamide is found to be 1.6eV.

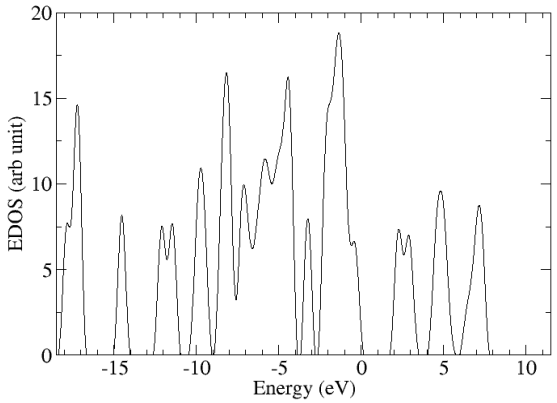

Fig. 3 Electron Density of States in Pyrazine-2,3-dicarboxamide

IV. CONCLUSIONS

The simulated and optimized structure of Pyrazine-2,3-dicarboxamide is matching very well with the structural parameters reported in the literature. Band gap in case of Pyrazine-2,3-dicarboxamide comes out to be 1.6eV. The value of dielectric constant in Pyrazine-2,3-dicarboxamide comes out to be 2.94, 3.08 and 2.78 along X, Y and Z axes respectively and the average value comes out to be 2.93. Phonon modes at gamma point have also been computed in Pyrazine-2,3-dicarboxamide and they come out to be 151cm^{-1} to 3522cm^{-1}.

ACKNOWLEDGMENTS

Authors thank the PG and RC Bharathicollege for permitting to carry out the research work. Also, author acknowledges the necessary facilities provided by the Bharathi Education Trust, Mandya.

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