Growth and Hirshfeld Surface Analysis of Imidazolium Fumarate (IMF) Single Crystal and DFT Computational Calculations for Third harmonic Generation

Abstract No:P29

C. Elavarasi, S. Mugundan*

Sri Vijay Vidyalaya College of Arts and Science, Nallampalli, Tamil Nadu, India -636807

elachinnakannu@gmail.com

Abstract

Imidazolium fumarate (IMF) is a third harmonic Generation crystal that has been synthesized by the process of slow evaporation at room temperature. The Crystal structure has been identified by Single crystal X-ray diffraction analysis which is in monoclinic structure with a space group of PT. Through FTIR analysis, functional groups for Imidazolium fumarate (IMF) single crystal have been found out. The UV-Vis-NIR spectrum shows that there is no considerable absorption peak after 380 nm. To understand the different intermolecular interactions of the synthesized crystal, Hirshfeld surface analysis was carried out and, in the 3D hirshfeld surface, shape index is hollow red and blue bump region which indicates closer contact of the molecule. The theoretical calculations were done by using the density functional theory (DFT/B3LYP) with 6-311G (d,p) basis set. In Natural Bond Orbital (NBO) analysis, due to σ*(C1 - N7) to π*(C2 - C3) interaction which has high stabilization energy of 60.26 kJ mol^{-1} that involve in the intermolecular charge transfer within the IMF molecule. From HOMO-LUMO the energy gap of this molecule is 4.83 eV has been calculated. In Molecular Electrostatic Potential (MEP) surface, hydrogen atoms attached to nitrogen and oxygen have positive potential that represents the nucleophilic attack were evaluated. The bonding and antibonding are identified using Density of States (DOS). Through the Mulliken charges, the highest positive value is noted for C9 atom..

Keywords: Imidazolium Fumarate, FTIR, DFT, NBO analysis, MEP, DOS.

Introduction

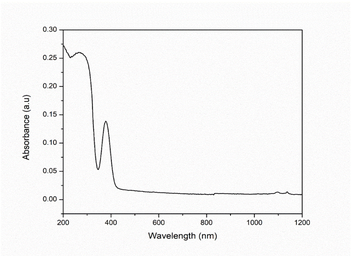
- Designing Organic crystals that exhibit useful solid-state properties - nonlinear optical behavior, electrical conductivity, solid-state reactivity and so on.
- Organic synthesis has advanced to the point where we can design organic molecules with almost any desired structure and chemical properties.
- To investigate a series of salts between imidazole and dicarboxylic acids, as molecular building blocks for several reasons.
- Imidazolium carboxylate salts of dicarboxylic acids form polar hydrogen-bonded layers composed of N-H-O and O-H-O hydrogen bonds. Imidazole belongs to an aromatic heterocyclic compound, and it has potentially active strategy for making NLO materials. It is to used design derivates of imidazole crystals with molecular hyperpolarizability [1].
- Fumaric acid and some organic acid having the capability of forming dimers in their structures. Because of dimers, the fumaric acid decompose and form a new and strong hydrogen bond with the imidazole molecule [2].
- Few researchers have synthesized and characterized the single crystal of imidazole derivates such as 1H-Imidazolium hydrogen L-tartrate (ImiLT) , Imidazolium adipate (IA), Imidazolium L-tartrate, Imidazo-Imidazolium picrate monohydrate [6] due to its optical properties. The Imidazolium Fumarate (IMF) single crystal has been already grown and structure has been already reported [3].

Single X-Ray Diffraction

Imidazolium fumarate single crystal structure is shown in the table.

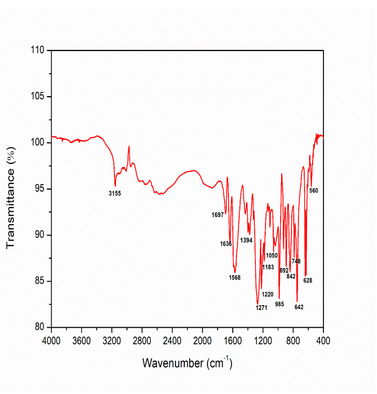
Parameters	Present work	Reported literature [3]
Unit cell parameters	a = 7.480 Å b = 7.765 Å c = 8.422 Å	a = 7.4794 Å b = 7.7522 Å c = 8.4231 Å
Space group	$P\bar{1}$	$P\bar{1}$
Crystal system	Triclinic	Triclinic

UV-Vis-NIR Absorption Spectrum



- Absorption peak at 380 nm due to the imidazole ring [4].
- No absorption peak after 380 nm to 1100 nm - used for optical applications.

FTIR spectrum



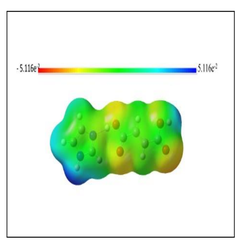
- The bands at 1500-1640 cm^{-1} and 650-750 cm^{-1} - presence bending and stretching vibrations of aromatic and imidazole ring [5].
- 3155 cm^{-1} - O-H or N-H stretching vibrations.
- 1568 cm^{-1} - carboxylate stretching vibrations or NH_2 symmetric vibrations
- 1697 cm^{-1} - C=O stretching vibration .
- C-H deformation of Imidazole ring is present at 1394 cm^{-1} in the spectrum [6].
- C-O stretching vibration is due to 1183 cm^{-1}. The intense peak at 1284 cm^{-1} - CO stretching band of the fumarate [5].
- Band at 985 cm^{-1} N-H deformation or O-H stretching of carboxylic acid .
- 892 cm^{-1} - C-H out of plane bending.
- Band at 642, 628 cm^{-1} - C-C-C bending vibration.
- 560 cm^{-1} - C-C-O in plane bending vibration.

Mulliken atomic charges

Atoms with numbering	Mulliken atomic charge (e)
1 C	0.210638
2 C	-0.017093
3 C	-0.007892
4 H	0.111057
5 H	0.119093
6 N	-0.325590
7 N	-0.411728
8 H	0.239441
9 C	0.394597
10 C	-0.131822
11 H	0.139605
12 C	-0.148292
13 H	0.143839
14 C	0.381326
15 O	-0.355717
16 H	0.296891
17 O	-0.379162
18 O	-0.332519
19 H	0.252198
20 O	-0.332207
21 H	0.153336

- All the oxygen and nitrogen atoms have negative charges.
- All the hydrogen atoms and C1, C9, C14 have positive charges and remaining carbon atoms has negative charges.
- The highest positive value - C9 is 0.394597, highest negative value - N7 is -0. 411728

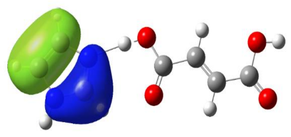
Molecular Electrostatic Potential (MEP)



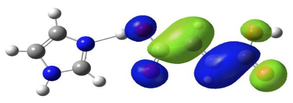
- The MEP are given in the order of Red < Orange < Yellow < Green < Blue .
- The oxygen atom indicate that it has negative potential (electrophilic attack) and hydrogen atom attached to the nitrogen atom has positive potential (nucleophilic attack). The remaining atoms in the molecules are to be neutral particles that is it has zero potential.

HOMO-LUMO

HOMO

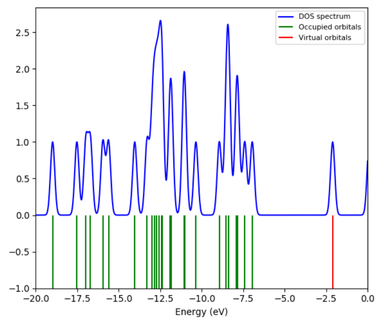


LUMO



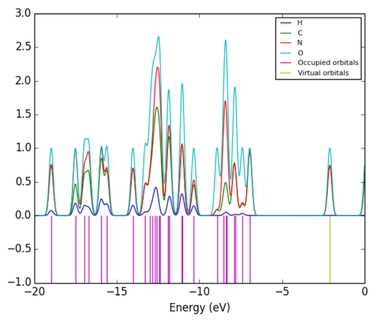
- HOMO is localized on the imidazole molecule of carbon, hydrogen and nitrogen.
- LUMO is mostly localized on the carbon, hydrogen and oxygen.
- The energy gap of this molecule is 4.83 eV.

Density of states (DOS)



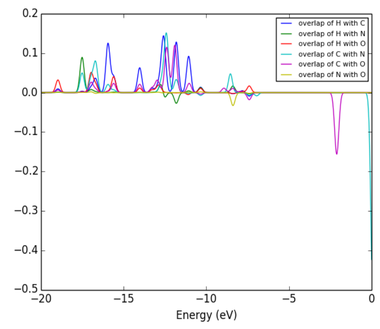
Total Density of States (TDOS)

- TDOS plots are necessary for the determination of molecular orbital compositions and chemical bonding.
- In this figure, the green line represents the filled orbitals, and the red line represents the virtual orbitals



Populated Density of States (PDOS)

- The basic structure of the shared orbitals that contribute to the electronic states is seen in the PDOS plots.
- Indigo line - hydrogen orbitals , green line - carbon orbitals,
- red line - nitrogen orbitals, the blue line - oxygen orbitals,
- pink line indicates the filled orbitals and the yellow line designates virtual orbitals.



Overlap Population Density of States (OPDOS)

- H with C (Indigo line) is strongly overlapping orbital when compared all other overlapping orbital.
- N with O (yellow line) is the slightly overlapping orbital when compared to all other overlapping orbital.
- The pink line is overlapping of C with O is in the negative population overlap which represent antiboding interaction.

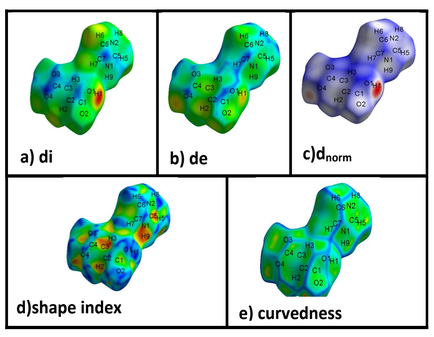
Natural Bond Orbital Analysis (NBO)

Donor (i)	Occupancy (e)	Acceptor (j)	Occupancy (e)	E(2)kcal/mol	E(j)-E(i) (a.u)	F(i,j) (a.u)
π (C1- N7)	1.87722	π*(C2 - C3)	0.28415	20.73	0.34	0.078
π (C2 - C3)	1.85976	π*(C1- N7)	0.38840	14.34	0.27	0.059
LP (1) N6	1.57528	π*(C1 - N7)	0.38840	52.20	0.28	0.108
LP (1) N6	1.57528	π*(C2 - C3)	0.28415	30.34	0.30	0.088
LP (1) N7	1.86835	σ*(C2 - C3)	0.01676	4.93	0.96	0.063
σ*(C1 - N7)	0.38840	π*(C2 - C3)	0.28415	60.26	0.02	0.058
LP (1) N7	1.86835	σ*(O15 - H16)	0.08373	33.48	0.78	0.146
σ (C10 - H11)	1.97933	σ*(C12 - H13)	0.01594	4.68	0.98	0.060
π (C10 - C12)	1.86419	π*(C9 - O17)	0.27886	15.87	0.30	0.064
π (C10 - C12)	1.86419	π*(C14 - O20)	0.23861	18.40	0.30	0.068
σ (C12 - H13)	1.97511	σ*(C10 - H11)	0.01540	5.08	0.97	0.063
π (C14 - O20)	1.97512	π*(C10 - C12)	0.04323	5.69	0.42	0.044
σ (O15 - H16)	1.98479	σ*(C9 - C10)	0.06673	4.09	1.14	0.062
LP (2) O15	1.76561	π*(C9 - O17)	0.27886	56.44	0.32	0.122
LP (2) O17	1.85993	σ*(C9 - C10)	0.06673	18.58	0.67	0.101
LP (2) O17	1.85993	σ*(C9 - O15)	0.08054	27.23	0.67	0.122
LP (2) O18	1.82893	π*(C14 - O20)	0.23861	43.61	0.34	0.111
LP (2) O20	1.85012	σ*(C12 -C14)	0.05867	17.42	0.69	0.100
LP (2) O20	1.85012	σ*(C14 - O18)	0.10058	32.60	0.61	0.128
π*(C9 - O17)	0.27886	π*(C10 - C12)	0.04323	57.31	0.02	0.074
π*(C14 - O20)	0.23861	π*(C10 - C12)	0.04323	35.50	0.03	0.072

E (2) means energy of hyper conjugative interactions.
Energy difference between donor and acceptor i and j NBO orbitals.
F(i,j) means the Fock matrix element between i and j NBO orbitals

- σ*(C1 - N7) to π*(C2 - C3) interaction which has high stabilization energy of 60.26 kJ mol^{-1} that involve in the intermolecular charge transfer within the IMF molecule.
- LP(2)O15 to π*(C9 – O17) interaction which has high stabilization energy of 56.26 kJ mol^{-1} that involve in the intermolecular charge transfer within the molecule.
- σ (C10 to H11) to σ *(C12 – H13) interaction which has low stabilization energy of 4.68 kJ mol^{-1}

Hirshfeld Surface Analysis



- Hirshfeld surface analysis visualizes the intermolecular interactions within a crystal structure. The normalized contact distance (d_{norm}) (Fig. c) is defined in terms of d_i, d_e and the van der Waals (vdW) radii of the atoms.
- In the 3D hirshfeld surface analysis d_i (Fig. a) and d_e (Fig. b) surface show the distance between the surface to the nearest nucleus internal and external to the surface.
- The shape index is hollow red and blue bump region which indicate closer contact of the molecule (Fig.d).
- Curvedness on Hirshfeld Surface (Fig. e)) shows green regions are separated by blue edges.

Conclusions

- Imidazolium Fumarate (IMF) Single Crystal was grown by Slow evaporation method.
- Cell parameter a = 7.480 Å, b = 7.765 Å, c = 8.422 Å, Crystal system - monoclinic, Space group was confirmed by Single Crystal XRD
- UV-Vis-IR Absorption spectrum the crystal will be used for optical application from 400- 1100 nm.
- Functional Groups present in IMF single crystal are confirmed by FTIR spectrum.
- The energy gap of this molecule is 4.83 eV which is calculated from HOMO-LUMO.
- In the Mulliken atomic charges, the highest positive value is noted for C9 and lowest value is for N7 atom.
- Molecular Electrostatic Potential (MEP) surface were also evaluated by using DFT.
- The bonding and antibonding are identified using Density of States (DOS).
- σ*(C1 - N7) to π*(C2 - C3) interaction which has high stabilization energy of 60.26 kJ mol^{-1} that involve in the intermolecular charge transfer within the IMF molecule
- In Hirshfeld Surface Analysis the different intermolecular interactions of the synthesized crystal has been find out.

References

1.Chengmin Ji, Tianliang Chen, Zhihua Sun, Yan Ge, Wenxiong Lin, Junhua Luo, Qian Shi and Maochun Hong, "Bulk crystal growth and characterization of imidazolium L-tartrate (IMLT): a novel organic nonlinear optical material with a high laser-induced damage threshold," CrystEngComm 15, 2157 (2013).

2.Nardelli, M. (1995). J. Appl. Cryst. 28, 65

3.Rodolfo Moreno-Fuquen, Javier Ellena and Jahyr E.Theodoro, Imidazolium fumarate, Organic compounds, Acta Crystallographica Section E.

4.A. Muthuraja and S. Kalainathan, Growth of organic benzimidazole (BMZ) single crystal by vertical bridgeman technique and its structural, spectral, thermal, optical, mechanical and dielectric properties, Opt. Mater., 2015, 47, 354–360

5.Shouwen Jin • Daqi Wang, Synthesis and Structural Characterization of Hydrazine Bridged Imidazole and its Fumarate Salt, J Chem Crystallogr (2012) 42:524–528, DOI 10.1007/s10870-011-9999-4.

6.Helen Merina Albert, Alosious Gonsago C, Synthesis, and characterization of an organic material: L-histidinium glutarate monohydrate, J. Chem. Pharm. Res. 7 (2) (2014) 87–94