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FT-IR, UV/Vis and Fluorescence spectra studies and Quantum Chemical Calculations on 3-Amino-5-(4-fluorophenyl)isoxazole

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Abstract

*In this investigation, the molecular structural properties of 3-Amino-5-(4-fluorophenyl) isoxazole (3AFPI) have been verified experimentally by using FT-IR (400-4000 cm^{-1}), UV-Visible (300-1100 nm) and Fluorescence spectroscopies. Furthermore, the experimentally obtained values were compared with theoretically calculated values of 3AFPI by using DFT/B3LYP/6-311++G** method. Thereafter, the least energy and more stable conformation of the investigated molecule were calculated by using potential energy surface (PES) scan method. Stabilization energy of the molecule, charge transfer within the molecule and hyperconjugative structure of the molecule was calculated by using natural bonding orbital (NBO) analysis. The non-linear optical (NLO) performance of the molecule was examined by calculating the polarizability (α), hyperpolarizability (β), and dipole moment (D) values of the titled molecule and results were compared with standard compound Urea. According to Koopman's theorem, Ionization potential and Electron affinity of the molecule was calculated by using frontier molecular orbital analysis. Molecular electrostatic potential (MEP) map analysis of the tiled compound have been calculated and analysed. All theoretical values were compared with experimental results by which a good agreement was obtained.*

Keywords: 3-Amino-5-(4-fluorophenyl) isoxazole, NBO, NLO, MEP, IP, EA.

1. Introduction

Isoxazole heterocyclic ring containing compounds and their derivatives show a significant role in the synthesis of potential medicines including anti-infective, antitumor, cardiovascular and body nervous system agents (Pevarello et al. 1999). The compound which was named as 5-methyl-N-[4-(trifluoromethyl) phenyl]-isoxazole-4-carboxamides an isoxazole containing heterocyclic compound recently recognized as the suitable medicine for the cure of active rheumatoid arthritis in USA. Isoxazoles act as an immunosuppressive, antibacterial, antifungal anticancer, antitumor. Now a day, chemists show their interest to synthesis the isoxazole derivatives due to appreciable importance in the pharmaceuticals industry and in the branch of synthetic organic chemistry. Isoxazole derivatives were also used in the branch of pesticide and medicine industry due to their biological activity. Recently scientists focus on synthesis of substituted isoxazoles due to wide applications in therapeutic usage and some part of them are highly impressive discriminatory antagonists. Moreover, isoxazoline derivatives were good proaromatic acceptors. Isoxazoline derivative nucleus with dyes of Merocyanine composed of powerful electron acceptor and donor group is the most important organic functional dyes. These compounds, which consist of conjugated donor-accepter (D-π-A) property show different type of optical properties similar to the nonlinear optical (NLO) properties. Isoxazole derivatives also includes in semisynthetic penicillin's, semisynthetic lephalosporins, antibacterial sulfonamides, anabolic steroids, monoamine oxidase inhibitor was mainly used in psychotherapy etc. In addition to that isoxazole derivatives were also used in the treatment of leprosy. Cycloserine was the isoxazole containing equivalent structure shows antitubercular and antibacterial activity.

In present days, theoretical and computational molecular models perform an important role in chemical structure analysis. Density functional theory is the most important method to calculate the molecular structure parameters due to its proficiency and accuracy. Most probably density functional theory approach was subjected to electron correlation distributions in the system containing conjugation or lone pairs. In DFT calculations, B3LYP method was proved to be one of the best methods for calculating vibrational force constants and wave numbers in cm^{-1} for organic compounds. To the best of our knowledge, there was no proper investigation on the compound 3-Amino-5-(4-fluorophenyl) isoxazole by using quantum mechanical calculations, density functional theory method in literature. So, in this article, we report quantum mechanical computations and the respective experimental results of the title compound.

2. Experimental Details

The title compound with 97% purity was bought from the Sigma-Aldrich, USA and was used as such in the following spectroscopic measurements.

2.1 FT-IR measurement

For recording FT-IR spectrum, we prepared the sample by KBr pellet method by taking sample and KBr in the ratio of 200:1. Then, this mixture was put in to disc and applying 5 tons pressure with hydraulic press and we get the disc-shaped sample. The resulting sample was used to record the FT-IR spectrum in the range 4000-400 cm^{-1} by using the Perkin Elmer RXII spectrometer equipped with MCT detector. The spectral resolution of 4 cm^{-1} was taken and kept in a cavity for 32 scans during the measurement.

2.2. UV-Visible measurement

The UV-Visible spectrum of the titled compound 3AFMI was recorded on Analytikjena, specord S600 type UV-Vis spectrophotometer in methanol as a solvent. D2E+Halogen lamp was used as a source for the absorption. The spectrum was recorded in the range from 300-1100 nm. All the data were recorded after 1 cycle, with an interval of 1 nm, slit width of 2 nm and scan speed of240nm-min^{-1} with the spectral resolution of 0.05–3.5 nm.

2.3. Fluorescence measurement

Fluorescence spectra of investigated compound recorded on JOBINYVONFLUROLOG-3-11 spectroflurimeter. The spectrum was recorded in the range from 200-700 nm. It consisted of a source light Xenon lamp 450 W with a PMT for UV & Visible (180 to 850 nm) region detector. The resolution of spectrometer was 0.2 nm maximum at specific wavelength.

3. Computational details

To investigate the structural and excited states, experimental and theoretical structural measurements of titled compound were performed. All the computations were performed using Gaussian 09 program software package and Gauss View 5.0 molecular visualization program on an i5 processor (Frisch et al. 2009); (Dennington et al. 2009). The most optimized molecular structure, vibrational wave numbers and other relevant properties of the compound have been calculated by using Becke-3-Lee Yang Parr (B3LYP)functional with 6-311++G** basis set at ground state level. All the internal coordinates and symmetry coordinates of the titled compound have been defined by following the recommendations of Pulay et al. After computations, we observed that all the frequencies were positive which confirms that the optimized structure was stable. However, the frequencies calculated at this level show some systematic errors. This systematic error can be eliminated by scaling down the experimental values using SQMFF procedure. The NLO properties of the compound which decides the SHG efficiency of the compound under investigation i.e., dipole moment, polarizability, second order hyperpolarizability have been computed using B3LYP/6-311++G** basis set. To know the charge transfer within the molecule, the NBO analysis have been done using NBO 3.1 program which is available in the Gaussian 9 program.

4. Results and discussion

4.1 PES scans studies

In order to explain the relation between the potential energy and optimized molecular geometry of the titled molecule, a Potential Energy Surface (PES) scan was carried out on the compound under investigation which reveals the all possible conformations of the molecule. A complete PES scan to the dihedral angle C1-C6-C7-C8 of the compound was carried out by using DFT/B3LYP/6-311++G** level of theory. The C1-C6-C7-C8 dihedral angle was increased by 10° from 0° to 180°, while the remaining geometrical parameters have been relaxed. Potential energy surface scan of the selected dihedral angle was represented in the Fig.1. In the Fig.1 we observed that the global minimum stabilization energy at 300° K was -631.8661945 Hartrees.

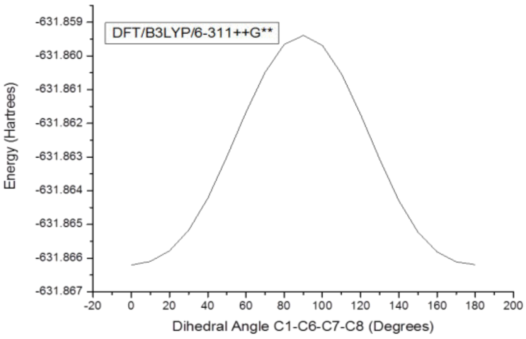

Figure-1: Potential energy surface scan for dihedral angle C1-C6-C7-C8 of 3-Amino-5-(4-fluorophenyl) isoxazole

4.2 Molecular geometry

The optimized structure of the titled compound was determined and it is observed that the compound exhibits C_1 symmetry. The optimized structure along with atom numbering scheme was represented in Fig.2. The optimized structural properties i.e., bond length; bond angle and dihedral angle values were tabulated and presented in Table 1. From the Table 1, we observed that all the geometrical parameters were almost equal in both basis sets. The values of C-C bond lengths in the phenyl ring of the tiled compound were almost equal to 1.39 Å which shows good agreement (Chandra et al. 2013) with experimental values. The bond angle C6-C7-C8 has the high value 133.34 in 6-311++G** basis set due to connection of phenyl and isoxazole rings with each other and experimentally it have value at 131.3 degrees. The bond angles of C9-N12-H19 and C9-N12-H20 in amine group of isoxazole ring have lower values at 115.25°, 113.86° in 6-311+G** whose experimental values are not known from the crystallographic structure of the similar compound. The order of dihedral angle in both basis set was C5-C4-C3-F13 > C1-C6-C7-O11 > C8-C9-N10-O11 > N10-C9-N12-H19. As geometrical properties show a good agreement, this structure was used as basis for the calculations of other properties like vibrational frequencies, NBO analysis and NLO properties.

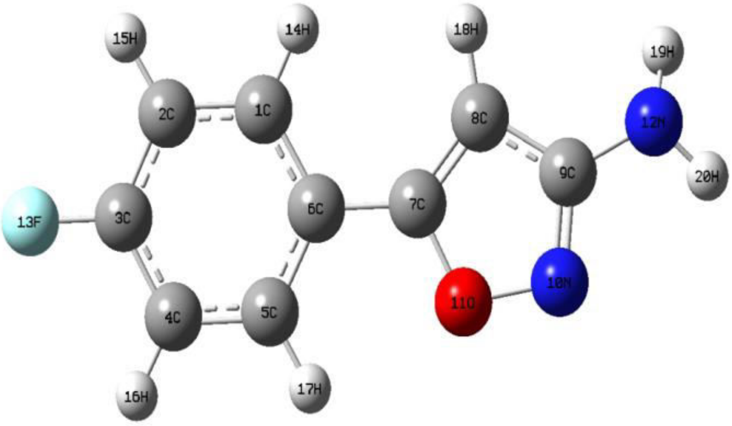

Figure-2: Molecular structures of 3-Amino-5-(4-fluorophenyl) isoxazolealong with numbering of atom.

Table-1: Optimized geometrical parameters of 3-Amino-5-(4-fluorophenyl) isoxazole obtained by B3LYP/6-311++G** density functional calculations

Bond length	**6-311++G**** (Å)	**Exp*** (Å)	**Bond Angle**	**6-311++G**** (°)	**Exp*** (°)	**Bond/ Dihedral Angle**	**6-311++G**** (°)	**Exp*** (°)
C1-C2	1.390	1.380	C1-C2-C3	118.7	120.3	C4-C5-H17	119.9	120.0
C2-C3	1.391	1.378	C2-C3-C4	121.9	119.9	C6-C5-H17	119.3	120.0
C3-C4	1.390	1.370	C3-C4-C5	118.8	120.2	C7-C8-H18	122.5	120.0
C4-C5	1.391	1.384	C4-C5-C6	120.7	119.9	C9-C8-H18	121.5	120.0
C5-C6	1.405	1.386	C5-C6-C1	118.8	119.5	C9-N12-H19	114.3	---
C6-C1	1.405	1.380	C6-C1-C2	120.8	120.0	C9-N12-H20	112.7	---
C6-C7	1.461	1.480	C1-C6-C7	120.5	121.6	C1-C2-C3-C4	0.01	-0.20
C7-C8	1.367	1.430	C5-C6-C7	120.5	--	C2-C3-C4-C5	-0.01	--
C8-C9	1.426	1.360	C8-C7-C6	133.3	131.3	C3-C4-C5-C6	-0.01	-1.60
C9-N10	1.320	1.300	O11-C7-C6	117.1	117.6	C4-C5-C6-C1	0.01	-0.10
N10-O11	1.407	1.420	C7-C8-C9	103.9	104.5	C5-C6-C1-C2	-0.01	1.60
O11-C7	1.351	1.330	C8-C9-N10	112.1	117.6	C6-C1-C2-C3	-0.01	-1.5
C9-N12	1.385	--	C9-N10-O11	104.8	109.4	C1-C6-C7-C8	-179.6	-175.2
C3-F13	1.347	--	N10-O11-C7	109.6	111.0	C1-C6-C7-O11	-180.0	-178.44
C1-H14	1.085	0.930	O11-C7-C8	109.4	109.4	C5-C6-C7-C8	-179.6	-177.36
C2-H15	1.084	0.930	C8-C9-N12	126.9	--	C5-C6-C7-O11	-54.0	-54.40
C4-H16	1.084	0.930	N10-C9-N12	120.8	--	C7-C8-C9-N10	0.49	0.45
C5-H17	1.083	0.930	C2-C3-F13	118.9	--	C8-C9-N10-O11	-0.82	-0.23
C8-H18	1.078	--	C4-C3-F13	119.1	--	C9-N10-O11-C7	0.85	0.33
N12-H19	1.011	--	C6-C1-H14	119.9	120.0	N10-O11-C7-C8	-0.57	0.45
N13-H20	1.012	--	C2-C1-H14	119.1	120.0	C8-C9-N12-H19	-39.6	--
			C1-C2-H15	121.6	120.0	C8-C9-N12-H20	-169.0	--
			C3-C2-H15	119.6	120.0	N10-C9-N12-H19	143.7	--
			C3-C4-H16	119.6	120.0	N10-C9-N12-H20	14.4	--
			C5-C4-H16	121.5	120.0	C1-C2-C3-F13	-179.9	--
						C5-C4-C3-F13	179.9	--

* [from ref- 5]

4.3 Vibrational analysis

The simulated and observed FT-IR spectrum of the titled compound was shown in Fig.3. The normal modes of 3AFPI were defined by Pulay's recommendations. The titled compound contains 19 atoms. Therefore, it has 54 vibrational wavenumbers and they are presented along with their scale factors in Table 2. The corresponding internal coordinates are presented in Supplementary material 1. These vibration modes can be distributed in to symmetrical species as following equation.

$$\Gamma 3N-6 = 37A' \text{ (in} - \text{plane)} + 17A'' \text{ (out} - \text{of} - \text{plane)} \qquad (1)$$

Table 2: Definition of local-symmetry coordinates and the values of corresponding scale factors used to correct the B3LYP/6-311++G** (refined) force field of 3-Amino-5-(4-fluorophenyl) isoxazole

No.(i)	Symbol [a]	Definition [b]	Scale factors
Stretching			
1 to 5	ν(C-H)	R1, R2, R3, R4,R5	0.970
6-13	ν(C-C)ar	R6, R7, R8, R9, R10, R11,R12,R13	0.940
14	ν(C-C)sub	R14	0.940
15	ν(C-O)ring2	R15	0.960
16	ν(N-O)ring2	R16	0.960
17	ν(C-N)sub	R17	0.960
18	ν(N-H)ss	(R18+R19)/√2	0.950
19	ν(N-H)ass	(R18-R19)/√2	0.950
20	ν(C-F)ring1	R20	0.890
21	ν(C-N)ring2	R21	0.890
In-Plane bending			
22-26	$\beta_{C\text{-}H}$	(γ22- γ23)/√2, (γ24-γ25)/√2, (γ26-γ27)/√2, (γ 28-γ29)/√2, (γ 30-γ31)/√2	0.930
27	βRtri	(γ 32-γ 33+ γ34-γ 35+ γ36-γ37)/√6	0.950
28-29	βRasy	(2γ 32-γ 33- γ34+2γ35- γ36-γ37)/√12, (a-b)(γ39- γ42) +(a+b) (γ40- γ41)	0.950,0.930
30-31	βRsym	(γ 33- γ34+ γ36-γ37)/2, γ 38+a(γ39+ γ42)-b (γ40+ γ41)	0.950, 0.930
32	$\beta_{C\text{-}C\text{-}C(ring1)}$	(γ 43- γ 44)√2	0.950
33	$\beta_{C\text{-}C\text{-}N(ring2)}$	(γ 45- γ 46)√2	0.950
34	$\beta_{C\text{-}C\text{-}C(ring2)}$	(γ 47- γ 48)√2	0.950
35	βNH$_2$sc	(2γ51-γ49- γ50)/√6	0.999
36	βNH$_2$ro	(γ50-γ51)/√2	0.999
37	βNH$_2$wa	γ 78	0.960
38	βNH$_2$tw	(γ50+γ51)/√2	0.999
39	$\beta_{C\text{-}C\text{-}F(ring1)}$	(γ52-γ53)/√2	0.960
Out of plane bending			
40-44	ωC-H	ρ 54, ρ55, ρ 56, ρ57, ρ 58	0.950
45	ωC-F	ρ 59	0.950
46	ωC-C(ring1)	ρ 60	0.980
47	ωC-C(ring2)	ρ 61	0.980
48	ωC-N(ring2	ρ 62	0.980
Torsions			0.960
49	τR1tri	(τ 63-τ64+τ65-τ66+τ67-τ68)/ √6	0.980
50	τR1asy	(τ 63-τ65+τ66-τ68)/2	0.980
51	τR2asy	b(τ69+τ73)+a(τ70+τ72)+ τ71	0.980
52	τR1sym	(-τ63-2τ64-τ65+τ66+2τ67-τ68)√12	0.980
53	τR2sym	(a-b)(τ72- τ70)+(1-a) (τ73- τ69)	0.980
54	τCCCC(sub)	(τ74- τ75)/2, (τ76- τ77)/2	0.960

Where a=cos144^0 , b=cos72^0.

Abbreviations: ν, stretching; ß, in plane bending; ω, out of plane bending; τ, torsion, ss, symmetrical stretching, ass, asymmetrical stretching, sc, scissoring, wa, wagging, tw, twisting, ro, rocking, tri, trigonal deformation, sym, symmetrical deformation, asy, asymmetric deformation, butter, butterfly, ar, aromatic, sub, substitution.

[a] These symbols are used for description of the normal modes by PED in Table 3.

[b] The internal coordinates used here are defined in table given in supplementary material 1

All the vibrational modes are active in FT-IR spectroscopy. The observed wave numbers along with computed wave number using DFT/B3LYP/6-311++G** with their potential energy distributions (PED) of the compound under study was tabulated in Table 3.

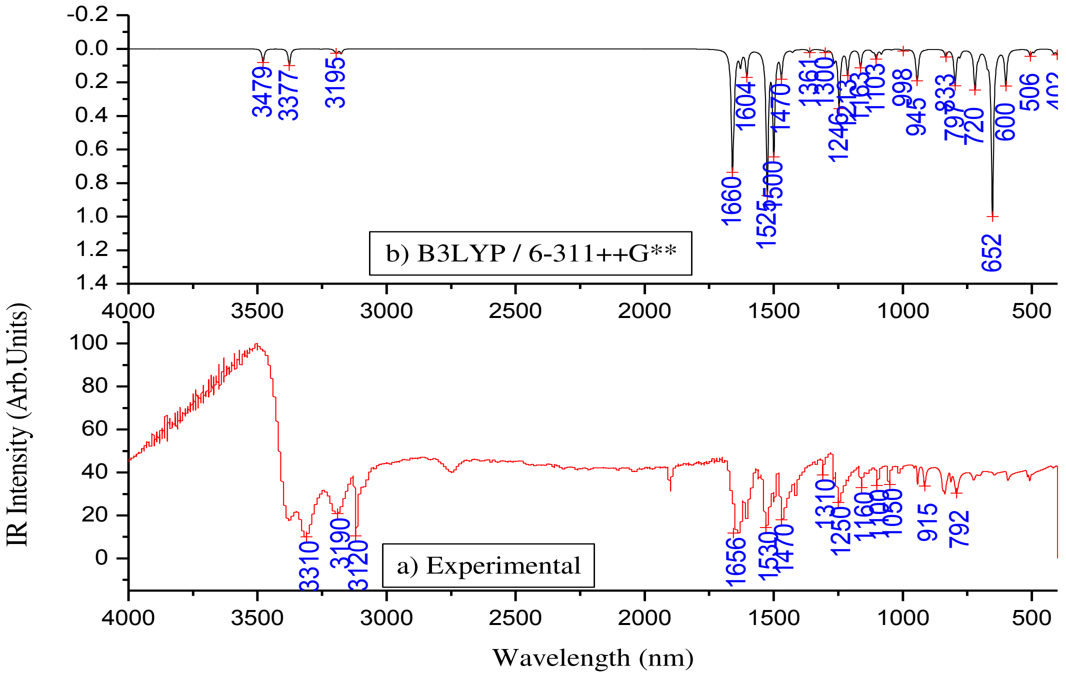

Figure-3: (a) Experimental, (b) Simulated FT-IR spectra of 3-Amino-5-(4-fluorophenyl) isoxazole.

Table-3: Detailed assignments of fundamental vibrations of 3-Amino-5-(4-fluorophenyl) isoxazole by normal mode analysis based on SQM force field calculations using B3LYP/6-311++G**

No	Experimental (cm^{-1}) FT-IR	Symmetry species	Scaled frequencies (cm^{-1})	Un-scaled frequencies (cm^{-1})	Intensity I_{IR}	Characterization of normal modes with PED (%)[b]
1	--	A'	3479	3669	1.55	υNHasy (99)
2	3377s	A'	3377	3561	0.32	υNHss (99)
3	3190s	A'	3140	3282	0.53	υCH (98)
4	3145vw	A'	3137	3230	1.02	υCH (99)
5	3132s	A'	3129	3223	10.78	υCH (99)
6	3120m	A'	3120	3216	4.88	υCH (99)
7	3117s	A'	3115	3201	5.86	υCH (99)
8	1658s	A'	1660	1674	0.29	βNH2sc(25)βNH2tw (50),βNH2tw(50) υCNsub(11)
9	--	A'	1654	1667	3.13	υCCar (59), βCH (19), βR1sym (10)

10	1636vs	A'	1629	1649	2.56	υCCar (67)
11	1605s	A'	1604	1632	0.02	υCCar (55), βCH (11), υCCsub (10)
12	1529s	A'	1525	1567	1.76	υCCar (27), βCH (36)
13	1497w	A'	1500	1530	4.04	υCCar (39), υCNsub (19), βR2sym (17)
14	1466m	A'	1470	1511	21.46	υCN(23),υCCar (18),βR2sym (15),υCO(10),βCH (10)
15	1415m	A'	1427	1455	100	υCCar (48), βCH (33)
16	1360s	A'	1361	1358	5.69	υCN (34), υCCar (26), βR2sym (10)
17	--	A'	1317	1329	0.81	υCCar (79), υCO (10)
18	1309s	A'	1299	1303	2.95	βCH (80)
19	1266s	A'	1266	1286	18.81	υNO(52), βCH (11), βR1tri (10), υCCar (10)
20	1247m	A'	1246	1237	3.66	υCF(37),βR1tri (22), υCCar (14), υNO(11),βCH (10)
21	1212w	A'	1213	1186	21.50	βCH(29),υCCar(22),υCCsub(12),υCNsub(11),υNO(10)
22	1161w	A'	1164	1143	4.30	βCH (75), υCCar (16)
23	1108w	A'	1117	1126	0.04	βNH2ro (40), υCN (20), υCCar (15), υCO (12)
24	1098m	A'	1103	1088	0.21	βCH (60), υCCar (30)
25	1053m	A'	1083	1032	7.13	βCH (29), υCCar (14), βNH2ro (12), υCO (12), βR1tri (10)
26	--	A'	1044	1025	14.48	βR1tri (30), υCcar (38), βCH (27)
27	--	A'	998	970	0.99	βR2SYM (42), υCCar (31), βCH (11), υCN (5)
28	--	A"	945	963	0.47	ωCNR2 (48), τR2sym (14), τR2asy (12)
29	942ms	A'	941	948	2.76	βR2asy (19), υCCar (28), ωCNR2 (16), βR2sym (15)
30	915w	A"	914	946	5.60	ωCH (87)
31	881m	A"	891	850	1.29	ωCH (82), τR1tri (13)
32	836m	A'	833	839	10.97	βR1sym (21), υCCar (36), υCF (20)
33	796w	A"	797	826	21.86	ωCH (69), τR1asy (10), ωCF (10)
34	785w	A"	779	779	15.13	ωCH (94)
35	--	A"	722	737	35.21	ωCH (26), τR1tri (46),
36	725m	A'	719	722	6.33	βR2asy (41), υCNsub (14)
37	--	A"	707	713	1.64	τRItri (49), ωCH (31), ωCF (10)
38	--	A'	680	668	0.24	βR1asy (58), βR1sym (19), υCCar (11)
39	--	A"	672	646	2.01	τR2sym (39), ωCCR2 (25), τR2asy (11)
40	645vw	A"	652	626	1.44	βNH2wa (36), βNH2sc (42)
41	592w	A'	601	597	15.72	βR1sym (22), υCF (15), βR2sym(13), υCCar (11)
42	507w	A"	506	522	61.06	ωCF (29), τR1asy (22), τR1sym (20), ωCCR1 (19)
43	--	A'	491	499	85.23	βCCR2 (27), βCNR2(21), βCCR1(19), βCFR1 (12)
44	--	A"	444	418	15.50	τR1sym (53), τR1asy (29), ωCH (15)
45	--	A'	415	415	8.67	βCFR1 (44), βCNR2 (24)
46		A"	402	400	18.24	τR2asy (36), ωCF (16), ωCCR2 (10)
47		A'	334	336	66.06	βCNR2 (19), τCNH2 (15), βCFR1 (13), βCCR1 (11)
48		A"	319	317	2.82	ωCCR1 (17), τR2sym (15), ωCF (13)
49		A"	297	295	1.34	τCNH2 (36), υCCsub (14), βR1sym (11)
50		A"	278	279	1.70	τCNH2 (40), βCNR2 (11)
51		A"	179	176	0.45	τR1asy (35), τR2sym (17), ωCH (13), ωCCR2 (13)
52		A'	113	115	0.28	βCCR1 (43), βCCR2 (42)
53		A"	68	70	9.99	ωCCR1 (35), ωCCR2 (30), ωCH (12), τR1asy (11)
54		A"	29	29	8.32	τCCCC (78), ωCH"(14)

[a] Abbreviations: ν, stretching; β, in plane bending; ω, out of plane bending; τ, torsion, ss, symmetrical stretching, as, asymmetrical stretching, sc, scissoring, wa, wagging, twi, twisting, ro, rocking,ipb, in-plane bending, opb, out-of -plane bending; tri, trigonal deformation, sym, symmetrical deformation, asy, asymmetric deformation, butter, butterfly, ar, aromatic, sub, substitution, vs, very strong; s, strong; ms, medium strong; w, weak; vw, very weak.
[b] Only PED contributions ≥10% are listed.

Phenyl ring Vibrations

C-H group vibrations

Generally, aromatic compounds show C-H stretching wave numbers in the region 3100-3000 cm^{-1} and also exhibit weak bands (Krishnakumar et al. 2003). In this paper, the bands observed at 3190 cm^{-1}, 3145 cm^{-1}, 3132cm^{-1}, 3120 cm^{-1}, 3117 cm^{-1} and 3117 cm^{-1} in FT-IR spectrum were assigned to the C-H stretching modes. These wave numbers were slightly higher than the expected region due to halogen substitution in the ring. The theoretically computed C-H frequency by B3LYP/6-311++G** method shows at 3140 cm^{-1}, 3137 cm^{-1}, 3129 cm^{-1}, 3120 cm^{-1} and 3115 cm^{-1} which shows a well agreement with the experimentally recorded spectra and literature. The in-plane C-H bending vibrations occurred in the region 1300-1000 cm^{-1}. In this paper, the in-plane C-H vibrations observed at 1309 cm^{-1}, 1212 cm^{-1}, 1161 cm^{-1}, 1098 cm^{-1} and 1053 cm^{-1} in FT-IR spectrum and theoretically calculated C-H in-plane bending vibrations were occurred at 1299 cm^{-1}, 1213 cm^{-1}, 1164 cm^{-1}, 1103 cm^{-1} and 1083 cm^{-1} respectively. The C-H out of plane bending vibrations lies in the region 900-650 cm^{-1}. In this paper the values 915 cm^{-1}, 881 cm^{-1}, 796 cm^{-1}, 785 cm^{-1} in FT-IR spectrum represents C-H out plane bending vibrations with corresponding theoretical values at 914, 891, 797, 779, 722 cm^{-1}. All the frequencies were in the expected region.

CC and CN group vibrations

Generally, aromatic C-C stretching vibration occurs in the region 1650-1200 cm^{-1}, this region (Bellamy, 1975) was not much affected by the substitution in the ring. In this compound, the aromatic C-C and C=C stretching frequencies observed at 1636 cm^{-1} , 1605 cm^{-1}, 1529 cm^{-1}, 1497 cm^{-1} and 1415 cm^{-1} in FT-IR spectrum show a good agreement with the scaled values. The C-N stretching frequency of hetero aromatic amine lies in the region 1386-1266 cm^{-1}. Identification of C-N stretching frequency was very difficult task because the value was lies in the convoluted region in the vibrational spectrum which is a combination of several bands. In our compound, the value at 1360 cm^{-1} in FT-IR spectrum was in good coincidence with the theoretically calculated value at 1361 cm^{-1}

C-F group vibration

Generally, the C-F stretching value of the relative compounds occurs in the wide frequency of region 1360-1000 cm^{-1} (Gunasekaran et al. 2006). The C-F band was easily affected by the neighboring atoms. In this compound, the band observed at 1247 cm^{-1} was assigned to the C-F stretching frequency. The in-plane and out of plane bending vibrations are at 415 and 506 cm^{-1} which are supported by the PED values.

NH_2 group vibration

NH_2 group gives six bands, viz., symmetric stretching, asymmetric stretching and scissoring, rocking, twisting and torsional modes. Asymmetric stretching mode has higher frequency than symmetric stretching mode. Hetero aromatic compounds containing NH_2 groups shows its frequency in the region 3500-3200 cm^{-1} (Gunasekaran et al. 1993). In this compound, the NH_2 symmetric stretching vibration is observed at 3377 cm^{-1} in FT-IR which shows an excellent agreement with the calculated value. Similarly the band e scaled at 3479 cm^{-1} was assigned to NH_2 asymmetric stretching whose counterpart was not observed in the spectrum. The strong band observed at 1658 cm^{-1} is assigned to NH_2 scissoring mode which shows an excellent agreement with the calculated value of 1660 cm^{-1}. Further, NH_2 rocking, wagging values were assigned at 1108 cm^{-1} and 648 cm^{-1} with corresponding theoretical values, 1117 cm^{-1} and 652 cm^{-1} respectively.

4.4 Natural Bond Orbital (NBO) analysis

The natural bond orbital (NBO) analysis provides significant information about the intra, inter molecular electron transfer and also furnish suitable basis for the examining the charge transfer and stabilization energy within the molecule. The NBO analysis of the second-order Fock-matrix was carried out to predict various types of donor-accepter interactions and their stabilization energy within the molecule .The donor NBO represented with (i) and acceptor NBO represented with (j), the stabilization energy $E^{(2)}$ associated with electron delocalization in between the donor and acceptor is determined as

$$E^{(2)} = -\,n_{\sigma}\frac{\langle\sigma|F|\sigma\rangle^{2}}{\varepsilon_{\sigma}^{*}-\varepsilon_{\sigma}} = -\,n_{\sigma}\frac{F_{ij}^{2}}{\Delta E} \qquad (2)$$

Where, $\langle\sigma|F|\sigma\rangle^{2}$ or F^{2}_{ij} is the Fock matrix element i and j NBO orbitals, ε_{σ}^{*} and $\varepsilon_{\sigma}$are the energies of σ and σ^{*} NBOs and n_{σ} is the population of the donor σ orbital. If the stabilization energy is more for particular transfer, then the interaction between the electron donors and electron acceptors could be intensive and greater the extent of conjugation within the molecule.

Now, coming to the present work the NBO analysis of the titled compound was carried out in the ground state energy by using NBO 3.1 program which was available in the Gaussian 09 program package at the DFT/B3LYP/6-311++G** level of theory. The results obtained from the NBO analysis has been elucidated to understand the intramolecular, conjugation of electron density and charge transfer within the molecule by using second-order perturbation theory and results were tabulated in Table 4. From the Table 4 we observed that the interaction between the Lewis bonding Donor orbital of π^{*} (C9-N10) to the Lewis anti-bonding acceptor orbital π^{*}(C7-C8) gives the stabilization energy 192.65 kcal/mol^{-1} which denotes the largest stabilization energy within the molecule which was corresponding π^{*} to π^{*} electronic transition. The hyper conjugative interaction from Lone pairs (O11) to π^{*} of C7-C8 and (N12) to π^{*} of C9-N10 show stabilization energies 35.86 kcal/mol^{-1} and 31.19 kcal/mol^{-1} respectively. The electronic transition from σ of C3-F13 to the σ^{*} of C1-C2 with a stabilization energy 1.32 kcal/mol^{-1} denotes the lowest stabilization energy within the molecule corresponding $\sigma \rightarrow \sigma^{*}$ electron transfer in the molecule. The electronic transition from π of C1-C2 to π* of C3-C4, C5-C6 with stabilization energies 22.43 and 17.28 kcal/mol^{-1} were other significant interactions with in the molecule.

Table-4: Second order perturbation theory analysis of fock matrix in NBO basis for 3-Amino-5-(4-fluorophenyl) isoxazole

Donor(i)	Type	Ed/e	Acceptor(j)	Type	Ed/e	$E^{(2)}$	E(i)-E(j)	f(i,j)
C1-C2	σ	1.97455	C1-C6	σ *	0.02144	2.93	1.27	0.054
	σ		C3-F13	σ *	0.03083	4.22	0.98	0.057
	σ		C6-C7	σ *	0.03132	3.23	1.20	0.056
C1-C2	π	1.69349	C3-C4	π *	0.37560	22.43	0.28	0.072
	π		C5-C6	π *	0.38488	17.28	0.29	0.064
C1-C6	σ	1.97310	C5-C6	σ *	0.02139	3.68	1.26	0.061
	σ		C6-C7	σ *	0.03132	2.68	1.19	0.050
C1-H14	σ	1.98104	C2-C3	σ *	0.02777	3.53	1.09	0.0555
	σ		C5-C6	σ *	0.02139	4.05	1.09	0.059
C2-C3	σ	1.98242	C3-C4	σ *	0.02777	3.23	1.28	0.058
C2-H15	σ	1.97861	C1-C6	σ *	0.02144	3.76	1.09	0.057
	σ		C3-C4	σ *	0.02777	4.06	1.09	0.060
C3-C4	σ	1.98273	C2-C3	σ *	0.02777	3.23	1.28	0.057
C3-C4	π	1.64424	C1-C2	π *	0.32618	18.40	0.29	0.066
	π		C5-C6	π *	0.38488	21.70	0.30	0.072
C4-C5	σ	1.97454	C3-F13	σ *	0.03083	4.29	0.98	0.058
	σ		C6-C7	σ *	0.03132	3.40	1.19	0.057
C4-H16	σ	1.97850	C2-C3	σ *	0.02777	4.13	1.09	0.060
	σ		C5-C6	σ *	0.02139	3.75	1.09	0.057
C5-C6	σ	1.97411	C1-C6	σ *	0.02144	3.72	1.25	0.061
C5-C6	π	1.63093	C1-C2	π *	0.32618	21.92	0.28	0.070

	π		C3-C4	π *	0.37560	19.32	0.27	0.065
	π		C7-C8	π *	0.31082	20.08	0.28	0.068
C3-F13	σ	1.99592	C1-C2	σ *	0.01308	1.32	1.59	0.041
C5-H17	σ	1.98017	C1-C6	σ *	0.02144	4.21	1.08	0.060
	σ		C3-C4	σ *	0.02777	3.59	1.08	0.056
C6-C7	σ	1.97330	C5-C6	σ *	0.02139	2.54	1.24	0.050
	σ		C7-C8	σ *	0.01817	3.29	1.28	0.058
C7-C8	σ	1.97719	C6-C7	σ *	0.03132	3.91	1.21	0.062
	σ		C9-N12	σ *	0.02204	6.62	1.17	0.079
C7-C8	π	1.80635	C5-C6	π *	0.3488	11.25	0.30	0.054
	π		C9-N10	π *	0.38725	26.92	0.29	0.083
C8-C9	σ	1.97016	C6-C7	σ *	0.03132	7.74	1.17	0.085
C8-H18	σ	1.98085	C7-C8	σ *	0.01817	2.30	1.15	0.046
	σ		C7-O11	σ *	0.03459	2.90	0.92	0.046
C9-N10	π	1.91449	C7-C8	π *	0.31082	7.58	0.34	0.048
N10-O11	σ	1.98064	C6-C7	σ *	0.03132	3.53	1.29	0.060
	σ		C9-N12	σ *	0.02204	5.78	1.25	0.076
N12-H19	σ	1.98290	C9-N10	σ *	0.02165	4.10	1.19	0.062
N12-H20	σ	1.98723	C8-C9	σ *	0.02914	5.44	1.15	0.071
N10	LP	1.95336	C7-O11	σ *	0.03459	5.22	0.80	0.058
N10	LP	1.95336	C8-C9	σ *	0.02914	5.95	0.94	0.067
O11	LP	1.72961	C7-C8	π *	0.31082	35.86	0.35	0.101
O11	LP	1.72961	C9-N10	π *	0.38725	13.06	0.34	0.061
N12	LP	1.85455	C9-N10	π *	0.38725	31.19	0.32	0.095
F13	LP	1.96794	C2-C3	σ *	0.02777	6.64	0.96	0.071
F13	LP	1.91382	C3-C4	π *	0.02777	6.62	0.96	0.071
F13	LP	1.91382	C3-C4	π *	0.37560	20.48	0.42	0.090
C9-N10	π *	0.38725	C7-C8	π *	0.31082	192.65	0.01	0.068

4.5 Frontier molecular orbital analysis:

Every organic compound contains orbitals among which the most important orbitals are frontier molecular orbitals. These are called as highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO). These two orbitals are responsible for the chemical stability in the molecule (Willard et al. 1986). The frontier molecular orbital analysis was performed on the investigated compound by using DFT/B3LYP/6-311++G** method. HOMO was characterized as a ready to donate electrons and LUMO was characterized as ready to accept electron from the HOMO. The HOMO, LUMO and HOMO-LUMO gap are responsible for the chemical reactivity, hardness, softness, Ionization Potential (I.P), Electron Affinity (E.A) in the compound. Molecular surfaces were drawn to the molecule in order to understand the bonding interactions in the molecule by taking cubes and surface models available in the Gaussian 09 view visualization program. These two molecular orbitals were represented in Fig.4. In the Fig.4, the positive and negative charges were denoted by red and green colors respectively. The calculated HOMO and LUMO and the energy gap values are in the gas phase are 6.05671, 1.18369 and 4.87301 eV respectively.

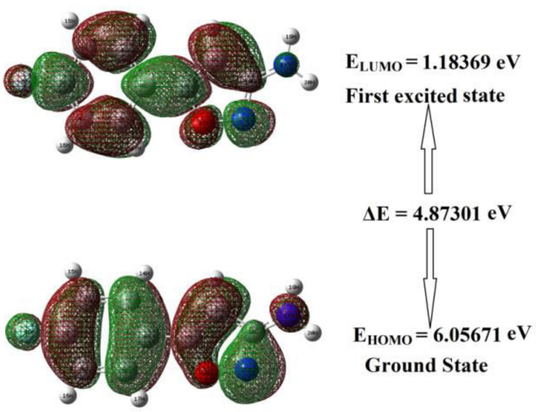

Figure-4: The atomic orbital components of the frontier molecular orbital (HOMO—MO: 46, LUMO—MO: 47) of 3-Amino-5-(4-fluorophenyl)isoxazole

4.6 Global reactivity descriptors

The energies of HOMO, LUMO, and energy gap, electronegativity (χ), chemical potential (μ), Ionization potential(I.P), Electron Affinity(E.A), Chemical hardness(η), Electrofilicity index (ω), Global Softness (σ), Total energy change(ΔE_T), Dipole moment(D)can be calculated on the basis of E_{HOMO} and E_{LUMO} values by substituting the values in the following equations. The resulting values were presented in Table 5.

Electronegativity (χ)= ½ (E_{HOMO} +E_{LUMO}), Chemical potential (μ) = $-\chi = -1/2$ (E_{HOMO} +E_{LUMO}),Global hardness (η) = ½ (E_{LUMO} - E_{HOMO}), Global softness S = $1/2\eta$ and Global electrophilicity index (ω) = $\mu^2/2\eta$.

These properties were used to understand the toxicity of different type of pollutants that is its reactivity and site selectivity of the compound. The chemical hardness and softness shows the chemical stability of the tiled molecule. Further, on could find whether the compound under investigation was Hard or Soft by using the HOMO-LUMO energy gap. Soft compounds are more polarizable and excitation is easy since they have small less energy gap. The hardness value of the titled compound was 2.436508 eV which indicates the titled compound was hard.

Table-5: The calculated quantum chemical parameters for 3-Amino-5-(4-fluorophenyl)isoxazole obtained by B3LYP/6-311++G** calculations.

Property	**3-Amino-5-(4-fluorophenyl)isoxazole**
Total energy (eV)	-17189.5301
E_{HOMO} (eV)	-6.05671319
E_{LUMO} (eV)	-1.18369586
E_{HOMO}-E_{LUMO} (eV)	4.87301733
Ionization potential(I.P) (eV)	6.05671319
Electron Affinity(E.A) (eV)	1.18369586
Chemical potential (μ) (eV)	-3.62020452
Electronegativity (χ)eV	3.62020452
Chemical hardness(η)eV	-2.43650866
Electrofilicity index (ω) eV	2.689479619
Global Softness (σ)eV	0.410423330
Total energy change(ΔE_T) eV	0.609127165
Dipole moment(D)	3.1423

4.7 UV-Visible Spectral analysis

The UV-Visible spectrum of the titled molecule, 3AFPI have been measured by taking optimized structure in the ground state energy using TD-DFT/B3LYP/6-311++G** method in the gas phase. Then the theoretical spectrum and the corresponding oscillator strengths (f), absorption wave lengths (λ) and excitation energies (E) were compared with the experimentally recorded UV-Visible spectrum. The experimental UV-Visible spectrum was recorded in taking a methanol as solvent. Simulation of UV-visible spectra has been presented in Fig.5. Experimentally the λ_{max}value was observed at 653 nm which was well coincidence with the theoretically calculated wavelength as shown in the figure. Thereafter the corresponding HOMO-LUMO contributions for absorption wavelengths were tabulated in Table 6.

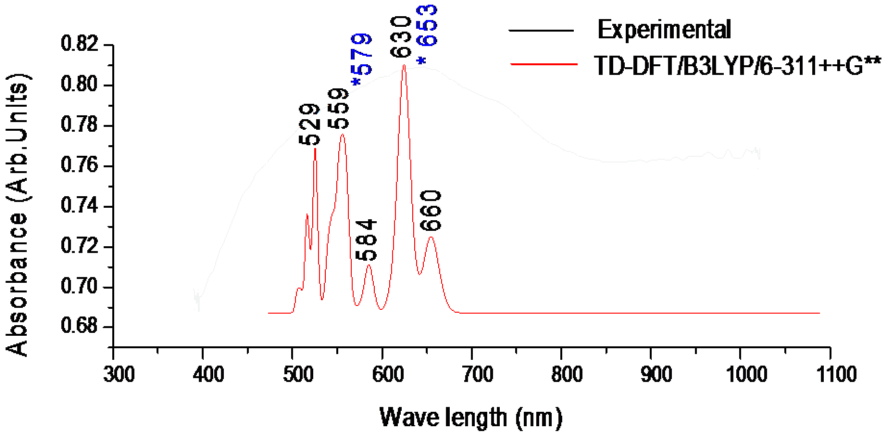

Figure-5. Theoretical and experimental UV/Vis spectra of 3-Amino-5-(4-fluorophenyl)isoxazole

Table-6: The UV–Vis excitation energy and oscillator strength for 3-Amino-5-(4-fluorophenyl)isoxazole calculated by TD-DFT/B3LYP/6-311++G** method.

No	Exp. Wavelength (nm)	Energy (cm^{-1})	Wave length (nm)	Osc. Strength	Symmetry	Major contribs
1	653	35142.383	660	0.1309	Singlet-A	H-1->LUMO (11%), HOMO->LUMO (77%)
2	--	37653.186	630	0.0065	Singlet-A	H-2->LUMO (17%), HOMO->L+1 (79%)
3	--	39367.921	584	0.4198	Singlet-A	H-1->LUMO (74%) H-1->L+1 (3%), HOMO->LUMO (7%)
4	--	41410.117493	559	0.0397	Singlet-A	H-2->LUMO (17%), H-1->L+1 (68%), HOMO->L+1 (12%)
5	--	46049.418569	529	0.0023	Singlet-A	H-4->LUMO (87%) H-3->LUMO (8%)

4.8 Fluorescence spectra analysis

Generally fluorescence spectrum was obtained from molecule containing conjugated double bonds and aromatic with a high resonance stability (Fukui, 1982). Fluorescence is very useful in the field of medical, biochemical, and chemical research for examining organic compounds. In the present compound the fluorescence spectrum at an excitation wavelength of 230 nm was recorded and presented in Fig.6.From the figure, it can be noticed that the peaks are observed at 402 and 476 nm.

Hence, this molecule can be used as a source of visible light viz., blue light which is highly useful in various scientific applications.

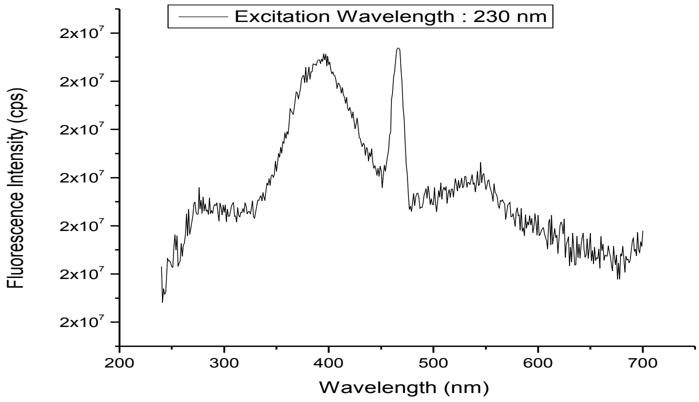

Figure-6: Fluorescence spectra of 3-Amino-5-(4-fluorophenyl)isoxazole

4.9 Nonlinear Optical (NLO) properties

Density functional theory was important tool to investigate the NLO properties of the organic compounds. The properties like dipole moment, polarizability, first order hyper polarizability of the titled compound were calculated by DFT/B3LYP/6-311++G** basis set. The calculated values were tabulated and presented in Table 7. These values are calculated using the following equations.

$$\mu = \mu^2_x + \mu^2_y + \mu^2_z \tag{3}$$

$$\alpha_o = \frac{\alpha_{xx} + \alpha_{yy} + \alpha_{zz}}{3} \tag{4}$$

$$\Delta\alpha = 2^{-1/2}[(\alpha_{xx} - \alpha_{yy})^2 + (\alpha_{yy} - \alpha_{xx})^2 + 6\alpha^2_{xx}]^{1/2} \tag{5}$$

$$\beta = (\beta^2_x + \beta^2_y + \beta^2_z)^{1/2} \tag{6}$$

$$\beta_x = \beta_{xxx} + \beta_{xyy} + \beta_{xzz} \tag{7}$$

$$\beta_y = \beta_{yyy} + \beta_{xxy} + \beta_{yzz} \tag{8}$$

$$\beta_z = \beta_{zzz} + \beta_{xxz} + \beta_{yyz} \tag{9}$$

We compared these results with Urea which is a prototypical material and used as a reference compound for comparative purposes. Generally these calculated values are in atomic units (a.u), the calculated values have been converted into electrostatic units (esu) (α: 1a.u= 0.1482 x 10^{-24} esu, β: 1 a.u = 8.6393×10^{-33} esu). The total molecular dipole moment of the molecule was 3.274070 Debye and polarizability (α) was 28.57976 x 10^{-12} esu. Further the first order hyper polarizability (β_{tot}) was 0.851179×10^{-30} esu which is greater than Urea and indicates that the compound may be treated as NLO applications material.

Table-7: Values of dipole moment, polarizability and first order hyperpolarizability of 1-(2-Aminophenyl)pyrrole by B3LYP/6-311++G** method

μ and α components	**B3LYP/6-311++G****	***β* components**	**B3LYP/6-311++G****
μ_x	-1.7219932	β_{xxx}	-39.5709252
μ_y	-0.2407611	β_{xxy}	-4.9487926
μ_z	-0.4991943	β_{xyy}	-6.972702
μ(D)	3.274070	β_{yyy}	1.2350478
α_{xx}	103.5414472	β_{xxz}	110.606968
α_{xy}	-1.5626194	β_{xyz}	-7.9300428
α_{yy}	32.7189233	β_{yyz}	7.8227532
α_{xz}	8.0036214	β_{xzz}	94.4889892
α_{yz}	0.1374093	β_{yzz}	-20.0989854
α_{zz}	157.5422896	β_{zzz}	-201.1413303
Δα			$14.51385\text{x } 10^{-24}$esu
α(esu)	$28.57976 \text{ x } 10^{-12}$ esu	βtotal (esu)	0.851179×10^{-30} esu

4.10 Molecular Electrostatic Potential (MEP) analysis

The molecular electrostatic potential (MEP) maps are related to the nuclei and electrons in the molecules at every part and surrounding space was associated with electron density. The molecular electrostatic potential map shows the significant information about the reactivity sites for the electrophilic and nucleophilic attack. It also shows a hydrogen bonding interactions with in the molecule. The external electrophile attacks the region in the molecule where the electrostatic potential value was large negative or minima because at that particular region, the electron effect is commanding. The electrostatic potential map of the compound under study was computed at DFT/B3LYP/6-311++G** level of theory and the resulting 3 dimension figure was represented in Fig.7. In Fig.7, red color indicates the negative charge region which may be attacked by positively charged species like electrophiles. Blue color indicates the positively charged region which may be attacked by negatively charged species like nucleophiles.

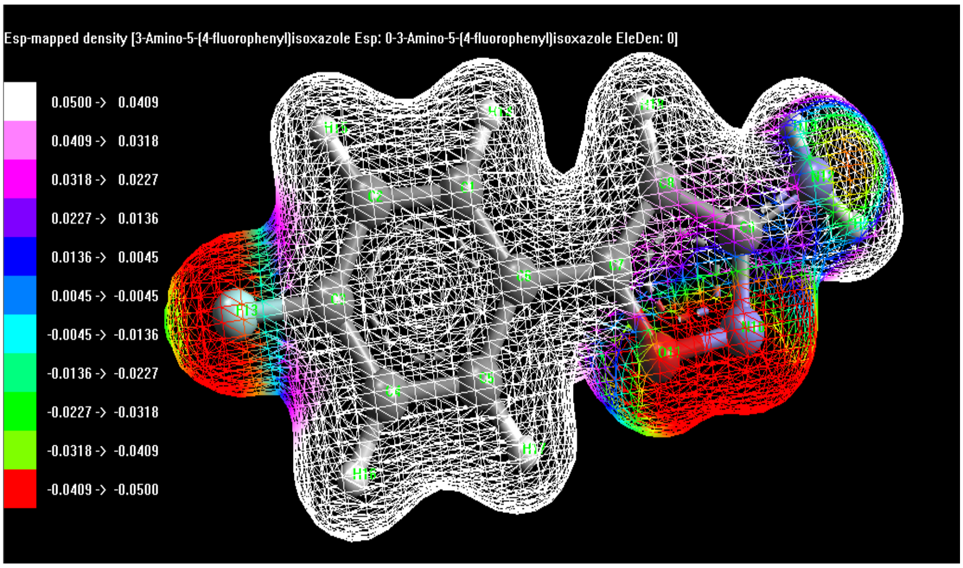

Figure-7: B3LYP/6-311++G** calculated 3D molecular electrostatic potential maps of 3-Amino-5-(4-fluorophenyl) isoxazole

5. Conclusions

In this paper, we investigated the vibrational and Structural properties of 3AFPI by using DFT/B3LYP/6-311++G** method. Potential Energy Surface scan (PES) method was used to obtain a least energy conformer which has C_1 point group symmetry and the corresponding energy was calculated. All the vibrational assignments of normal modes were predicted and compared with the observed values which yielded a good agreement. NBO analysis was carried out for the most optimized structure, in order to know the stabilization energy, charge transfer within the molecule. The energy difference in the molecule i.e. HOMO-LUMO energy difference shows that the molecule has a biological activity. Non-Linear optical property (NLO) calculations show that the molecule can be used as one of the best materials for NLO materials. The MESP shows that the Hydrogen atoms in the molecule are electrophilic and electronegative atoms in the molecule are nucleophilic.

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References

1. Pevarello, P., Amici, R., Brasca, M. G., Villa, M., and Varasi, M.1999; Recent Applications of the Isoxazole Ring in Medicinal Chemistry, In Targets in Heterocyclic Systems; Attanasi, O. A.; Spinelli, D., Eds.; Italian Society of Chemistry: Rome; Vol. 3: pp 301–339.
2. Gaussian 09, Revision C.01, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H.Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima,Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, Ö. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, and D. J. Fox,Gaussian, Inc., Wallingford CT, 2009.
3. GaussView, Version 5, Roy Dennington, Todd Keith and John Millam, SemichemInc.,Shawnee Mission KS, 2009.
4. Chandra, Raghu, K., Jayaseelan, S., Umesha, K. B., and Mahendra, M. 2013; Ethyl 5-methyl-3-phenylisoxazole-4-carboxylate, *ActaCrystallography Sect. E*, volume 69 : 0987.
5. Krishnakumar, V., and Xavier, R.J. 2003; "Normal coordinate analysis of 2-mercapto and 4, 6-dihydroxy-2-mercapto pyrimidines, Indian Journal of Pure and Applied Physics, vol. 41, pp. 597–601.
6. Bellamy, L. J. 1975; The Infrared Spectra of Complex Molecule, third ed., Wiley, New York.
7. Gunasekaran, S.,Seshadri, S.,Muthu, S. 2006; Indian J. Pure Appl. Phys. Volume no-44pp: 360–366.
8. Gunasekaran, S.,Varadhan, S. R.,Manoharan, K., 1993; Asian J. Phys. 2 (1993) 165.
9. Willard, Hobart H., Merritt jr. Lynne L., Dean, John A., and Settle jr. Frank A. 1986; Instrumental Methods of Analysis, Sixth Edition, Wadsworth Publishing Company. USA, pp.609.
10. Fukui, K. 1982; Science volume no: 218, pp: 747–754.