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SPECTROSCOPIC AND VIBRATIONAL CHARACTERIZATION OF FLUORINATED PYRIMIDINE, NBO, NLO, THERMODYNAMIC FUNCTIONS, HOMO LUMO ANALYSIS BASED ON DENSITY FUNCTIONAL THEORY

Richa Sharma

Venketeshwara University,
Gajraula (Amroha) U.P,
India

neharicha1989@gmail.com

B.S.Yadav

DNPG College, Meerut U.P,
India

bijendrasyadav@gmail.com

ABSTRACT

The FT-IR and FT-Raman spectra of title compound have been made both experimentally and theoretically. Due to the importance of fluorinated pyrimidine compound, the study of molecular structure of title compound plays an important role in the relevant fields. The vibrational frequencies and intensities have been analysed with the help of Gaussian Programme using standard methods DFT/B3LYP and HF with 6-311++G(d,p) basis set with assignments. The homo and lumo analysis has been made using TD-SCF method with 6-311++G(d,p) basis set. The hyperconjugative interactions between the molecules has been evaluated by NBO analysis. The first order hyperpolarizability has been calculated under non linear optics investigation. The biomolecular activity of fluorinated compound has been discussed. The Mulliken charges and NBO charges have been evaluated and correlated.

Keywords: FTIR, FT-Raman, NBO, Hyperpolarizability, fluorinated pyrimidine.

1. INTRODUCTION

The heterocyclic compounds like pyrimidine, uracil, cytosine, thymine etc. are well known for their biological and pharmaceutical importance. These pyrimidine compounds are very important on the basis of nucleic acids. Similarly fluorinated pyrimidines and their nucleosides have been used in a wide range as biochemical tools[1] for the medication in cell biology. The fluorine atom has an atomic radius 1.35 Å as compared with that of 1.20 Å for the hydrogen atom which seems very close to physical and chemical properties of hydrogen. The substitution of fluorine for hydrogen makes fluorinated pyrimidine more stable biologically. The specific example of a rationally developed class of anticancer drugs, the fluoropyrimidines are now the very important drug used in cancer chemotherapy[2]. The vibrational analysis is the most important tool to investigate the molecular properties of compounds. The DFT studies of compounds have got considerable success in modelling structure and reactivity of chemical systems[3]. In present compound having



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fluorine atom are widely used in cancer chemotherapy as well as diagnostics for different type of cancer of colon[4], rectum, breast, stomach and pancreas. Recently, focus on cancer diagnostics research has increased all over the world. Many researchers have worked on the study of pyrimidine compounds regarded their pharmaceutical importance[5]. The chemistry of fluorinated compound has become a particular interest cause of their important roles in the treatment of gastric cancer and solid tumors[6]. Most orally active prodrugs of fluorinated uracil has been verified for the treatment of different type of disorders. The most widely used fluorinated compound is 5-fluoro uracil which is a prototype fluorinated pyrimidine which works as an antimetabolite to disrupt nucleic acid synthesis and then kill cells[7-11]. The present investigation was undertaken to study the vibrational spectra of 2,4-dihydroxy-5-fluoropyrimidine molecule to identify the molecular properties with the support of wavenumber assignments.

2. EXPERIMENTAL

Spec-pure grade of 2,4-Dihydroxy-5-Fluoropyrimidine was obtained from Aldrich Chemie U.S.A. Its purity was confirmed by elemental analysis and melting point (282°C) determination. Infrared spectrum was recorded with Perkin Elmer M-683 spectrophotometer in the region 200-4000 cm^{-1} in KBr and polythene film. The far-infrared spectrum of the above molecule was recorded on a Fourier-Far-infrared Spectrophotometer Model-20 in the region 20-180 cm^{-1} . The laser Raman Spectrum in the region 25-4000 cm^{-1} has been recorded on a spex spectrophotometer using argon laser source with exciting radiations 5145 Å.

3. COMPUTATIONAL DETAILS

The entire calculation was performed at HF and DFT level using 6-311++G(d,p) basis set using Gaussian 03 programme. The optimized structural parameters were used in the vibrational frequency calculations at the HF/6-311++G(d,p) and DFT/B3LYP/6-311++G(d,p) levels. The IR intensities, Raman intensities, reduced masses, depolarization coefficients, force constant are calculated by both HF and DFT levels. The constant scaling factors are used to fit the theoretical wavenumbers to experimental wavenumbers for both HF and DFT levels respectively. The natural bond orbital (NBO) calculations[12] were performed at DFT/B3LYP/6-311++G(d,p). The frontier molecular orbital parameters as global hardness, global softness, electrophilicity, electronegativity and chemical potential have been calculated using HOMO and LUMO analysis in both HF and DFT levels. The non linear parameters were also calculated at both levels. All the values of parameter of thermodynamics of molecule was calculated for both HF and DFT levels also. All the theoretical values are in good agreement.

4. RESULT AND DISCUSSION

The structural diagram of the compound is given in Fig1:

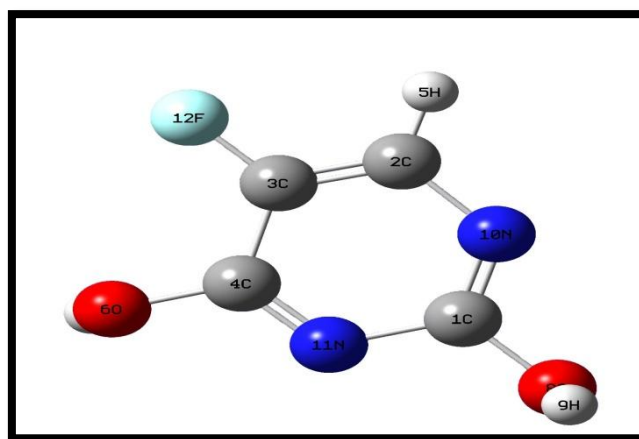


FIG:1

5. OPTIMIZED GEOMETRY

Most of the antifungal and agrochemical activity exhibit by the compound cause of the presence of fluorine group at the 12th position in the title compound. The stable optimized geometrical parameters such that bond length, bond angle and dihedral angle are shown in Table 1. As shown in table, the C-C bond length of C3-C4(1.35Å) is slightly ~0.01Å greater than C2-C3(1.34Å) due to the delocalization of electron density. The changes in the frequency or bond length of C-H bond on substitution arise due to the change in



charge distribution of carbon atom of the benzene ring[13-14]. The small molecules C-H.....O present in title compound have been considered as weak H-bonds on the basis of geometrical analysis. A long neglected stabilizing force in biopolymers[15] which is present in RNA, DNA and proteins[16] is to be caused of this type of interactions. Due to the π bond character of the former the bond angle between C3-C4-N11 and C3-C4-C6 is 121.04 and 119.79 respectively. The presence of hyperconjugative interaction is arised due to the bond angles of C3-C2-N10(122.1) and C3-C4-N11(121.24). The bond angles of C2-C3-F12 (122.20) and C4-C3-F12 (120.94) are also show the presence of hyperconjugative interaction due to the presence of fluorine group. On account of fluorine and nitro group present in the compound, the sharing of electron between neighbouring atoms occur easily which result increased C-C bond length. All experimental and theoretical data shown in Table 1 have been correlated in a good manner.

Table 1: Optimized geometrical parameters of 2,4-Dihydroxy-5-Fluoropyrimidine bond length(A°), bond angles(°), dihedral angles(°) using HF/6-311++G(d,p) and DFT/6-311++(d,p) basis sets.

Atom	Bond Length Atom			Atom	Bond Angle			Atom	Dihedral Angle	
	Exp.	HF	DFT		Exp.	HF	DFT		HF	DFT
C1-O8	1.23	1.3197	1.3424	O8-C1-N10	120	117.6527	117.9498	N10-C1-O8-H9	0.0	-0.0001
C1-N10	1.38	1.3067	1.3292	O8-C1-N11	110	115.3156	115.2046	N11-C1-O8-H9	-180.0	179.9998
C1-N11	1.37	1.3215	1.3332	N10-C1-N11	116	127.0318	126.8456	O8-C1-N10-C2	180.0001	180.0
C2-C3	1.34	1.3575	1.3755	C3-C2-H5		120.2768	120.3291	N11-C1-N10-C2	0.0001	0.0
C2-H5		1.0755	1.0852	C3-C2-N10	120	121.9213	122.1036	O8-C1-N11-C4	179.9998	180.0
C2-N10	1.33	1.3318	1.3415	H5-C2-N10		117.8019	117.5673	N10-C1-N11-C4	-0.0002	-0.0001
C3-C4	1.35	1.3956	1.4017	C2-C3-C4	119	117.4337	116.8557	H5-C2-C3-C4	179.9998	180.0
C3-F12	1.35	1.3222	1.3455	C2-C3-F12	121	121.613	122.2037	H5-C2-C3-F12	0.0	0.0
C4-O6	1.23	1.3136	1.3365	C4-C3-F12	115	120.9533	120.9407	N10-C2-C3-C4	-0.0001	0.0
C4-N11		1.3043	1.323	C3-C4-O6	112	119.797	119.517	N10-C2-C3-F12	179.9999	180.0
O6-H7		0.9459	0.9688	C3-C4-N11	126	121.0493	121.2472	C3-C2-N10-C1	0.0001	0.0001
O8-H9		0.9441	0.9669	O6-C4-N11	124	119.1537	119.2358	H5-C2-N10-C1	-180.0	-180.0
				C4-O6-H7		107.2655	108.9714	C2-C3-C4-O6	180.0	180.0
				C1-O8-H9		106.8936	108.5588	C2-C3-C4-N11	0.0	-0.0001
				C1-N10-C2		115.7711	116.0216	F12-C3-C4-O6	0.0	0.0
				C1-N11-C4	120	116.7928	116.9264	F12-C3-C4-N11	180.0	180.0
								C3-C4-O6-H7	180.0003	180.0008
								N11-C4-O6-H7	0.0003	0.0009
								C3-C4-N11-C1	0.0001	0.0001
								O6-C4-N11-C1	-179.9999	-180.0

6. VIBRATIONAL ASSIGNMENTS

The vibrational frequencies and vibration modes related with molecular structure of titled compound is find out with the help of vibrational analysis. In the titled compound, there are 12 atoms possess 30 modes of vibrations. All the internal coordinates in the molecule are apportionment with 12 stretching, 16 bending and 8 torsional coordinates. The experimental Far-Infrared spectra is shown in fig: . The experimental and theoretical Infrared and Raman Spectra in fig: and the correlation data experimental to theoretical is shown in Table 2 respectively. The theoretical calculated values of depolarization ratios, force constant and reduced masses at both HF and DFT level are shown in Table 3. All fundamentals are in good agreement and gives better result on correlation.



Table 2: IR intensities, Raman intensities, Reduced Mass, Force Constant, Depolarization Ratios(polarized (P) and unpolarized (U) for 2,4-Dihydroxy-5-Fluoropyrimidine using HF/6-311++G(d,p) and DFT/6-311++G(d,p) basis set

No.	IR Intensity		Raman Intensity		Depolar P		Depolar U		Reduces Mass		Force constant	
	HF	DFT	HF	DFT	HF	DFT	HF	DFT	HF	DFT	HF	DFT
1	0.3509	0.2612	0.3259	0.3542	0.7500	0.7500	0.8571	0.8571	9.7851	9.8437	0.1288	0.0985
2	2.8745	1.9512	0.3015	0.2337	0.7500	0.7500	0.8571	0.8571	7.5724	7.9965	0.2856	0.2485
3	2.5175	2.6121	0.3456	0.6381	0.6837	0.6898	0.8121	0.8164	9.5637	9.4672	0.5573	0.4654
4	13.0393	13.3287	0.1580	0.3167	0.7222	0.7311	0.8387	0.8446	5.5388	5.5389	0.5272	0.4399
5	0.7788	0.3681	1.9761	1.7022	0.7500	0.7500	0.8571	0.8571	6.4309	7.0143	0.6347	0.5727
6	47.3540	29.0751	0.2346	0.1165	0.7500	0.7500	0.8571	0.8571	2.6027	2.7868	0.3727	0.3359
7	2.6355	2.2918	3.5849	4.3419	0.5959	0.5548	0.7468	0.7137	11.3504	11.1315	1.9093	1.5967
8	45.0105	22.9764	1.3305	1.9773	0.7500	0.7500	0.8571	0.8571	1.1305	1.1223	0.2043	0.1869
9	178.465 1	181.1378	0.7565	0.7999	0.7500	0.7500	0.8571	0.8571	1.3231	1.2697	0.2550	0.2226
10	16.4905	15.6986	4.4424	5.9820	0.2514	0.2239	0.4018	0.3658	5.4450	5.2754	1.2015	0.9818
11	15.4088	9.6222	3.3545	4.4814	0.4636	0.4777	0.6335	0.6465	7.1639	7.6098	1.8367	1.6422
12	3.8867	1.7886	0.2092	0.2840	0.7500	0.7500	0.8571	0.8571	10.9853	10.6800	4.3043	3.2815
13	5.9927	15.8085	17.907	19.5193	0.0506	0.0630	0.0964	0.1186	6.9124	7.3701	2.9099	2.6820
14	36.9423	31.2934	2.4199	0.7537	0.1598	0.7500	0.2756	0.8571	10.1308	11.8838	4.4323	4.3933
15	63.8532	30.6350	0.7903	6.3863	0.7500	0.0758	0.8571	0.1409	11.6939	9.6835	5.5519	3.5812
16	9.7593	12.4344	1.2075	0.7162	0.7500	0.7500	0.8571	0.8571	1.4265	1.4121	0.9997	0.7543
17	23.5797	23.6202	3.6196	2.8621	0.0672	0.0767	0.1259	0.1424	4.0180	4.2811	2.9323	2.6037
18	138.789 6	253.5948	8.7739	1.0167	0.1927	0.4658	0.3231	0.6356	7.9858	2.1871	7.1523	1.7447
19	258.354 2	64.2861	0.9783	1.3701	0.5195	0.5477	0.6838	0.7071	2.0347	2.4701	1.9690	2.2118
20	51.2421	172.3914	1.1777	2.6185	0.6703	0.6369	0.8026	0.7782	2.3227	4.0299	2.5376	3.7506
21	212.800 1	78.0464	7.4424	4.6088	0.4295	0.4205	0.6009	0.5921	1.9979	1.7523	2.3126	1.7097
22	13.5648	13.4368	0.5440	0.8450	0.2959	0.2533	0.4566	0.4043	1.4796	2.0186	1.8378	2.1776
23	29.5084	77.7795	16.0433	16.2008	0.1090	0.1091	0.1966	0.1967	4.6046	4.6181	6.2285	5.2742
24	429.499 7	420.4063	1.3638	0.6166	0.4097	0.6123	0.5813	0.7595	7.5631	6.0537	11.8049	7.8964
25	652.703 1	378.1507	6.1495	3.9106	0.3131	0.3508	0.4769	0.5194	8.3363	6.9103	13.4574	9.2327
26	362.055 0	238.7891	2.1512	4.5831	0.6463	0.6085	0.7851	0.7566	6.6635	6.9327	12.9168	11.0032
27	125.676 5	60.1206	10.0348	8.8591	0.1991	0.2566	0.3321	0.4084	7.0010	6.4796	13.9808	10.5188
28	8.8155	7.3689	96.3881	116.4563	0.2920	0.2900	0.4521	0.4496	1.0953	1.0926	7.2523	6.5025
29	180.142 4	113.5009	64.9446	109.6848	0.2327	0.2306	0.3775	0.3748	1.0657	1.0646	10.6570	8.8828
30	157.069 0	109.5684	57.7755	90.5411	0.2284	0.2196	0.3719	0.3601	1.0658	1.0647	10.8059	9.0283



Table 3: Assignments of Vibrational Frequencies of 2,4-Dihydroxy-5-Fluoropyrimidine experimentally and theoretically using HF/6-311++G(d,p) and DFT/6-311++(d,p) basis set

Mode no.	Experimental Wave no.		Theoretical wave no. (Unscaled)		Scaled		Assignments
	FT-IR	FT-Raman	HF	DFT	HF	DFT	
1.	110 m	115*vs	149.45	130.34	133.01	118.60	Lattice Vibration
2.	150 m	-	253.01	229.65	225.17	208.98	Lattice Vibration
3.	330 m	340m	314.50	288.87	279.90	262.87	λ (C-OH)
4.	400 m	390vs	401.95	367.14	357.73	334.09	γ (O-H) γ (C=O) γ (C-F)
5.	420 m	420m	409.29	372.27	364.26	338.76	γ ring
6.	-	-	493.03	452.29	438.79	411.58	γ ring
7.	550 vs	555m	534.42	493.42	475.63	449.01	β ring
8.	-	-	553.87	531.61	492.94	483.76	-
9.	590 w	-	571.94	545.49	509.02	496.39	γ ring, β (C-H)
10.	-	-	611.98	562.01	544.66	511.42	γ ring, β (C-H)
11.	640 vs	650m	659.66	605.20	587.09	550.73	β (C=O), β (C-H)
12.	-	-	815.49	722.15	725.78	657.15	γ (N-H)
13.	-	-	845.28	785.91	752.29	715.17	Ring breathing
14.	-	-	861.72	792.12	766.93	720.82	β ring
15.	990 s	-	897.66	792.26	798.91	720.95	Ring breathing
16.	1060 vs	1065vs	1090.64	952.19	970.66	866.49	β ring
17.	1180 s	1175m	1112.95	1016.01	990.52	924.56	β (C-OH)
18.	1240 s	1235vs	1232.94	1163.59	1097.31	1058.86	ν (C-H), β (O-H)
19.	1280 ms	-	1281.59	1232.79	1140.61	1121.83	ν (C-F)
20.	1310 w	-	1361.72	1256.82	1211.93	1143.70	ν (C-OH)
21.	1340 w	-	1401.61	1286.85	1247.43	1171.03	ν ring
22.	1450 m	1450vs	1451.92	1353.13	1292.20	1231.34	ν ring
23.	1515 ms	1515w	1515.19	1392.26	1348.51	1266.95	ν ring
24.	1530 ms	1535m	1627.63	1487.91	1448.59	1353.99	ν ring
25.	1550 ms	-	1655.28	1505.88	1473.19	1370.35	ν ring
26.	1640 m	-	1813.85	1641.28	1614.32	1493.56	ν (C=O)
27.	1690 m	1680vs	1841.02	1659.91	1638.50	1510.51	ν (C=O)
28.	3010m	-	3352.39	3178.22	2983.62	2892.18	ν (N-H)
29.	3420m	-	4119.81	3763.12	3666.63	3424.43	ν (C-H)
30.	3550m	-	4148.26	3793.66	3691.95	3452.23	ν (O-H)

6.1. C-H Vibration

Mostly, three C-H stretching vibrations are related to a_1 species and other one is related to b_1 species in pyrimidine. The C-H stretching wavenumber appear in the range $3100-3000\text{cm}^{-1}$ in aromatic compounds[17]. This region is characterized for the confirmation of C-H stretching vibration. The heterocyclic aromatic compounds are very close to benzene results C-H stretching frequencies in benzene arises from various modes of benzene at 3073, 3096, 3060 and 3080cm^{-1} . Here the carbon atom of the ring is attached with one hydrogen atom results involvement in C-H valence oscillation in $3000-3100\text{cm}^{-1}$ region in accordance to the literature[18-20]. A weak band at 3040cm^{-1} has been assigned to C_5H stretching vibration. The C-H in plane bending has been well assigned at 650cm^{-1} relative to Raman band and 640cm^{-1} relative to infrared active band experimentally. The strong FT-IR bands at 605, 659, 722, 815cm^{-1} and C-H in plane bending harmonic vibration at 861, 785, 845, 792cm^{-1} are computed by HF and B3LYP methods. The nature of substituent does not affected to the bands.



6.2. C-C Vibrations and C-N Vibrations

Due to the interaction of closely lying vibration at 1010cm^{-1} , the frequency of ring breathing mode under reduced symmetry is lowered which correspond to the a_{1g} (999cm^{-1}) mode of benzene. The ring C=C and C-C stretching vibration usually find in the region $1400\text{--}1625\text{cm}^{-1}$. The form of substitution around the ring is actual cause for the determination of the position of three modes[21]. Usually four bands corresponding to coupled C-C, C-N stretching vibration occurs in the region $1600\text{--}1400\text{cm}^{-1}$ in the tautomers of uracil and pyrimidine. In the present case, the vibrations have been assigned to $1450, 1515, 1530, 1550\text{cm}^{-1}$ correspond to Raman active $1435, 1515, 1535\text{cm}^{-1}$ respectively. The components of vibration at 606 and 404cm^{-1} correspond to C-C in plane and out of plane deformation mode have been well identified in their respective region which support from the literature values[22-23]. The ring stretching mode is demonstrated as strong bands in Raman spectrum is found at 1304cm^{-1} . The infrared band in the compound at 750cm^{-1} has been assigned to ring breathing mode. The out of plane non-degenerate vibration is identified in the titled compound.

6.3. C-X Vibrations

The neutral form of uracil and its derivatives have three double bonds and their stretching vibration are expected to give result to three strong bands in the region $1600\text{--}1700\text{cm}^{-1}$. Susi and Ard et al. Suggested that the $\text{C}=\text{O}_2$, $\text{C}=\text{O}_4$ and $\text{C}=\text{C}$ stretching vibrations have been assigned the bands at $1695, 1662$ and 1621cm^{-1} . In the present case the bands are observed at $1690, 1640$ and 1610cm^{-1} assigned to three double bond stretching vibrations. Due to higher electronegativity of fluorine atom, the C-F stretching frequency appears in the region $1300\text{--}100\text{cm}^{-1}$ [24]. The C-F bond is expected to be polar which results a very strong infrared absorption. Goel et al [25] assigned this mode at 1250cm^{-1} in substituted absorption. The medium strong band at 1280cm^{-1} has been assigned to C-F stretching mode in the title compound. During the present study the bands observed at 550 and 400cm^{-1} in the compound have been taken to represent in plane bending and out of plane deformation modes respectively, however the Raman bands at 555cm^{-1} and 390cm^{-1} have been taken to represent this mode.

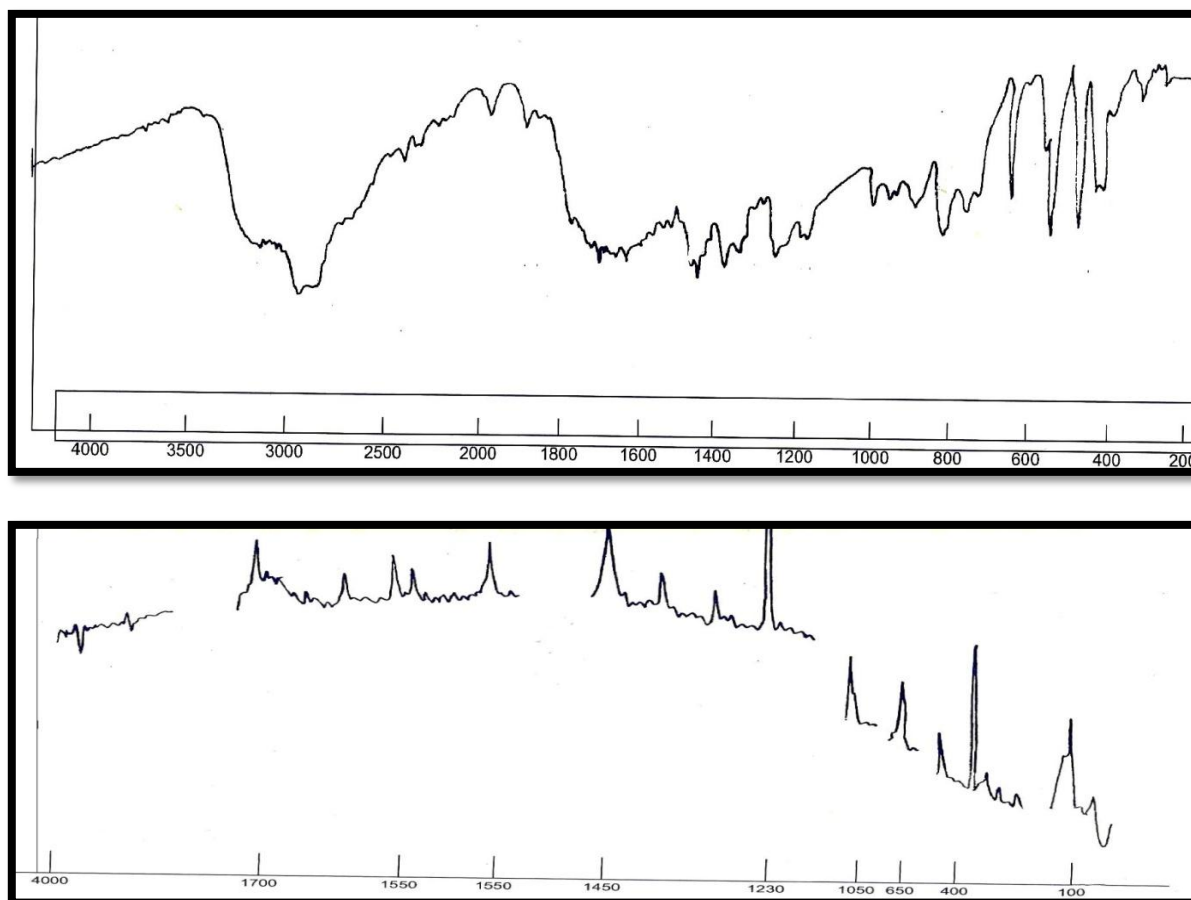
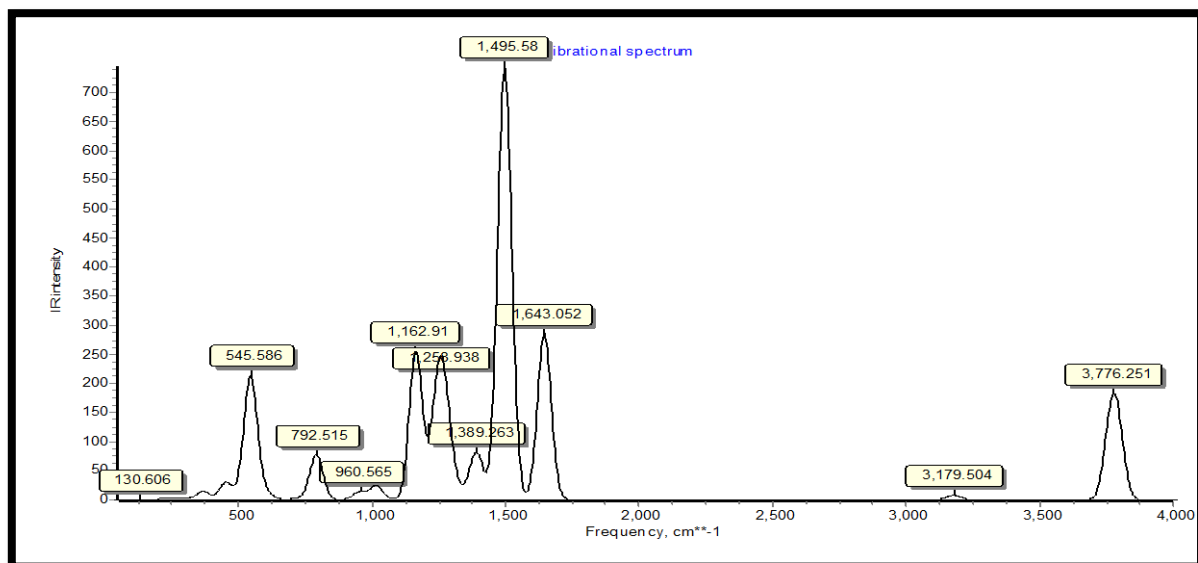


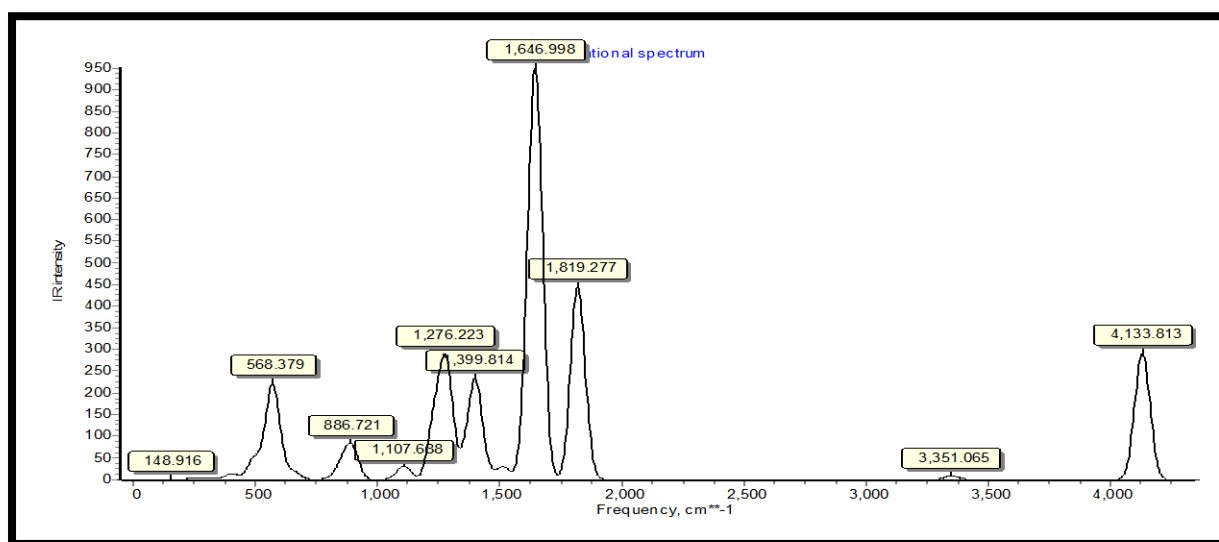
FIG 2: Experimental Infrared and Raman spectra of 2,4-dihydroxy-5-fluoropyrimidine



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(a)



(b)

FIG 3: Theoretical Infrared spectra of 2,4-dihydroxy-5-fluoropyrimidine using DFT/B3LYP/6-311++G(d,p) and HF level

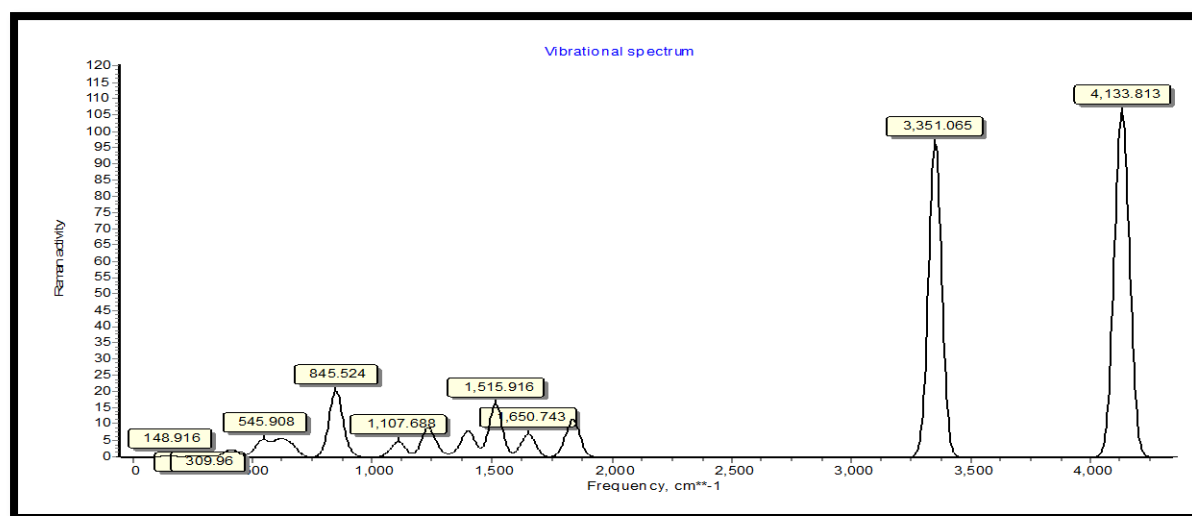
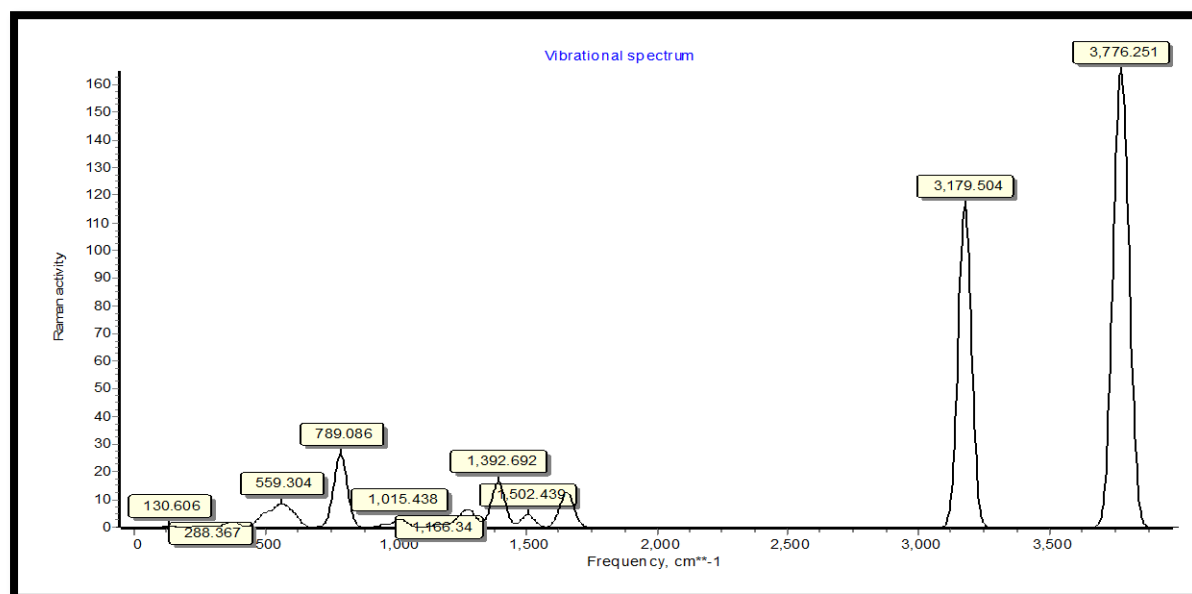


FIG 4: Theoretical Raman spectra of 2,4-dihydroxy-5-fluoropyrimidine using DFT/B3LYP/6-311++G(d,p) and HF level

7. NON-LINEAR OPTICAL PROPERTIES

Non linear optics and techniques are the most valuable method to determine the important parameters related to molecular structures[26]. This method aids from the interaction of applied electromagnetic field in various phases to produce new electromagnetic fields as frequency and other physical quantities.[27]. The first order hyperpolarizability β_0 and other consisting properties like total molecular dipole moment μ , mean polarizability α_0 and the anisotropy of polarizability $\Delta\alpha$ are calculated with the help of Gaussian programme using HF/6-311++G(d,p) and DFT/B3LYP6-311++G(d,p) on the basis of finite field approach.They are defined as:



$$\begin{aligned}\mu &= (\mu_x^2 + \mu_y^2 + \mu_z^2)^{1/2} \\ \alpha_0 &= (\alpha_{xx} + \alpha_{yy} + \alpha_{zz})/3 \\ \alpha &= (2)^{-1/2} [(\alpha_{xx} - \alpha_{yy})^2 + (\alpha_{yy} - \alpha_{zz})^2 + (\alpha_{zz} - \alpha_{xx})^2 + 6\alpha_{xx}^2]^{1/2} \\ \beta_0 &= (\beta_x^2 + \beta_y^2 + \beta_z^2)^{1/2} \\ \beta_x &= \beta_{xxx} + \beta_{xyy} + \beta_{xzz} \\ \beta_y &= \beta_{yyy} + \beta_{xyx} + \beta_{yzz} \\ \beta_z &= \beta_{zzz} + \beta_{xxz} + \beta_{yyz}\end{aligned}$$

Since we found the values of all above parameters in a.u. which can be converted to esu by multiplying some values as:

For $\alpha = 1 \text{ a.u.} = 0.1482 \times 10^{-24} \text{ esu}$

For $\beta = 1 \text{ a.u.} = 8.639 \times 10^{-33} \text{ esu}$

where a.u. = atomic unit, esu = electrostatic unit

The first order hyperpolarizability is a third rank tensor that can be described by $3 \times 3 \times 3$ matrices which component can be reduced to 10 components due to Kleinmann symmetry [28]. The total value of dipole molecular dipole moment is calculated using HF and DFT method is 0.84791 Debye and 0.4691 Debye respectively. The calculated first order hyperpolarizability are 6.166×10^{-32} and 4.182×10^{-32} respectively both using HF and DFT methods. The values show the linearity of the molecules as seen in Table 4.

Table 4: NLO properties of 2,4-dihydroxy-5-fluoropyrimidine

Parameters	HF	DFT
Dipole Moment (μ)	0.84791	0.46961
Mean Hyperpolarizability (α_0)	-49.931066	-50.103166
Anisotropy of polarizability ($\Delta\alpha$)	14.03035×10^{-33}	1.1726×10^{-19}
First order hyperpolarizability (β_0)	61.6673×10^{-33}	41.8256×10^{-33}

8. NBO (Natural Bond Orbital theory)

The detailed insight of the nature of electronic conjugation between the bonds is explained by natural bond orbital analysis. The electronic structure of molecule and the nature of bonding between molecules is predicted by NBO analysis in table 5(a). The role of intra and intermolecular interaction in the complex can also be described. It also gives all the information about interaction in both filled and unfilled orbital in molecule. The tendency of donation from electron donors to electron acceptors and conjugation of the complete system depends upon $E^{(2)}$ value [29]. For each donor NBO(j), the stabilization energy $E^{(2)}$ associated between donor and acceptor is estimated as;

$$E^{(2)} = -q_i \frac{(F_{ij})}{\epsilon_i - \epsilon_j}$$

where q_i is the orbital occupancy, ϵ_i and ϵ_j are diagonal elements and F_{ij} is the off-diagonal NBO Fock matrix element. The second order Fock matrix was carried out to evaluate donor (i)-acceptor(j) i.e. interaction between donor-level bonds and acceptor-level bonds in NBO analysis [30]. This analysis has been performed on the molecule at the DFT/B3LYP/6-311++G(d,p) level to elucidate the rehybridization, intramolecular and delocalization of electron density within the molecule [31]. According to calculation, the fluorine atom forms a single bond (sigma bond) with C3 atom having 1.99537 respectively. As seen from Table 5(b), π (C1-N10, C2-C3, C4-N11) bonds to π^* (C2-C3, C4-N11, C1-N10) having energy 29.83, 31.01, 35.03 kJ/mol respectively. The NBO interactions between the oxygen lone-pair both LP(1)-O8 and LP(2)-O8 and the antibonding π^* (C4-N11) and C1-N10 consist the stabilization energies having values 39.89 and 39.33 KJ/mol respectively.



Table 5(a): Natural Bond Analysis of 2,4-dihydroxy-5-fluoropyrimidine by natural atomic hybridization(B3LYP/6-311++G(d,p))

Bond	Occupancy	Energy	Hybridization	s%	p%	S%	P%
σ C1-O8	1.99085	-0.95754	05865sp ^{2.39} +0.8099sp ^{2.66}	29.47/27.32	70.34/72.59	34.40	65.60
σ N1-N10	1.99313	-0.87490	0.6313sp ^{1.67} +0.755sp ^{1.53}	37046/39.44	62.44/60.47	39.85	60.15
σ C1-N10	1.84968	-0.34045	0.6393sp ^{1.00} +0.7689sp ^{1.00}	0.05/0.00	99.77/99.85	40.87	59.13
σ C1-N11	1.97682	-0.87655	0.6375sp ^{1.78} +0.7704sp ^{1.84}	35.94/35.12	63.98/64.79	40.65	59.35
σ C2-C3	1.98827	-0.77115	0.7304sp ^{1.66} +0.7108sp ^{1.37}	37.56/42.15	62.38/57.80	49.97	50.53
σ C2-C3	1.79937	-0.31226	0.6973sp ^{1.00} +0.7168sp ^{1.00}	0.00/0.00	99.91/99.93	48.62	51.38
σ C2-H5	1.98181	-0.56432	0.7815sp ^{1.97} +0.6239sp ^{0.00}	33.62/99.95	66.34/0.05	61.07	38.93
σ C2-N10	1.96812	-0.85580	0.6411sp ^{2.46} +0.7674sp ^{2.43}	28.85/29.14	71.05/70.78	41.11	58.89
σ C3-C4	1.98279	-0.76347	0.7108sp ^{1.96} +0.7034sp ^{1.80}	33.80/35.71	66.15/64.23	50.52	49.48
σ C3-F12	1.99537	-1.04550	0.5279sp ^{3.18} +0.8493sp ^{2.39}	23.82/29.47	75.81/70.46	27.86	72.14
σ C4-O6	1.99530	-0.98690	0.5857sp ^{2.61} +0.8105sp ^{2.59}	27.62/27.82	72.15/72.10	34.30	65.70
σ C4-N11	1.98774	-0.8852	0.6364sp ^{1.74} +0.7713sp ^{1.48}	36.46/40.31	63.44/59.60	40.51	59.49
σ C4-N11	1.84823	-0.35006	0.6373sp ^{1.91} +0.7706sp ^{1.90}	0.04/0.01	99.77/99.84	40.61	59.39
σ O6-H7	1.97134	-0.77569	0.8620sp ^{3.98} +0.5068sp ^{0.00}	20.05/99.86	79.86/0.14	74.31	25.69
σ O8-H9	1.97260	-0.75647	0.8620sp ^{3.93} +0.5069sp ^{0.00}	20.28/99.88	79.63/0.12	74.31	25.69
LP(1)-O6	1.95324	-0.64681	sp ^{7.64}	-	-	11.57	88.38
LP(2)-O6	1.95183	-0.36294	sp ^{1.47}	-	-	40.55	59.41
LP(1)-O8	1.95463	-0.63051	sp ^{1.10}	-	-	47.56	52.40
LP(2)-O8	1.94681	-0.34192	sp ^{19.69}	-	-	4.83	95.12
LP(1)-N10	1.90809	-0.38267	sp ^{2.17}	-	-	31.53	68.39
LP(1)-N11	1.89733	-0.38554	sp ^{2.18}	-	-	31.40	68.51
LP(1)-F12	1.99065	-1.06615	sp ^{0.42}	-	-	70.56	29.49
LP(2)-F12	1.96438	-0.44442	sp ^{99.99}	-	-	0.06	99.9
LP(3)-F12	1.92297	-0.44369	sp ^{1.00}	-	-	0.00	99.97
σ^* C1-O8	0.04980	0.35301	0.8099sp ^{2.39} -0.5865sp ^{2.60}	29.47/27.32	70.34/72.59	65.60	34.40
σ^* C1-N10	0.03126	0.50397	0.7755sp ^{1.67} -0.6318sp ^{1.53}	37.46/39.44	62.44/60.47	60.15	39.85
σ^* C1-N10	0.24285	-0.03078	0.7689sp ^{1.00} -0.6393sp ^{1.00}	0.05/0.00	99.77/99.85	59.13	40.87
σ^* C1-N11	0.07197	0.49792	0.7752sp ^{2.04} -0.6317sp ^{2.51}	32.87/28.45	67.02/71.47	60.09	39.91
σ^* C2-C3	0.02345	0.53299	0.7108sp ^{1.66} -0.7034sp ^{1.37}	37.56/42.15	62.38/57.80	50.53	49.47
σ^* C2-C3	0.20048	-0.01627	0.7168sp ^{1.00} -0.6973sp ^{1.00}	0.00/0.00	99.91/99.93	51.38	48.62
σ^* C2-H5	0.01417	0.38962	0.6239sp ^{1.97} -0.7815sp ^{0.00}	33.62/99.95	66.34/0.05	38.93	61.07
σ^* C2-N10	0.01575	0.50290	0.7674sp ^{2.46} -0.6411sp ^{2.43}	28.85/29.14	71.05/70.78	58.89	41.11
σ^* C3-C4	0.07533	0.48509	0.7034sp ^{1.96} -0.7108sp ^{1.80}	33.80/35.71	66.15/64.23	49.48	50.52
σ^* C3-F12	0.03151	0.24124	0.8493sp ^{3.18} -0.5279sp ^{2.39}	23.82/29.47	75.81/70.46	27.86	72.14
σ^* C4-O6	0.05472	0.34319	0.8105sp ^{2.61} -0.5857sp ^{2.59}	27.62/27.82	72.15/72.10	65.70	34.30
σ^* C4-N11	0.02291	0.51353	0.7713sp ^{1.74} -0.6364sp ^{1.48}	36.46/40.31	63.44/59.60	59.49	40.51
σ^* C4-N11	0.23916	-0.0386	0.7706sp ^{1.91} -0.6373sp ^{1.90}	0.04/0.01	99.77/99.84	59.39	40.61
σ^* O6-H7	0.00572	0.36068	0.5068sp ^{3.98} -0.8620sp ^{0.00}	20.05/99.86	79.86/0.14	25.69	74.31
σ^* O8-H9	0.00559	0.38392	0.5069sp ^{3.93} -0.8620sp ^{0.00}	20.28/99.88	79.63/0.12	25.69	74.31



Table :5(b) Second Order perturbation theory analysis of Fock matrix on NBO basis 2,4-dihydroxy-5-fluoropyrimidine using (B3LYP/6-311++G(d,p))

Donor NBO	Type	E _i _{d/e}	Acceptor NBO	Type	E _j _{d/e}	E(2)	E _j -E _i	F(i,j)
C1-O8	σ	1.9931	C1-N10	σ*	0.0402	0.51	1.46	0.025
			C2-N10		0.0107	1.94	1.46	0.048
			C4-N11		0.0223	1.74	1.48	0.045
C1-N10	σ	1.9880	C1-N11	σ*	0.0411	2.09	1.37	0.048
			C2-H5		0.0210	2.42	1.27	0.049
			C2-N10		0.0107	0.86	1.38	0.031
C1-N10	π	1.7302	C1-N10		0.4271	1.55	0.31	0.020
			C2-C3		0.3121	29.83	0.33	0.089
			C4-N11		0.4429	7.68	0.80	0.045
C1-N11	σ	1.9822	C1-N10	σ*	0.0402	1.88	1.38	0.046
			C4-O6		0.0410	4.11	1.22	0.064
			C4-N11		0.0223	0.89	1.39	0.031
			O8-H9		0.0078	1.36	1.25	0.037
C2-C3	σ	1.9851	C2-H5	σ*	0.0210	0.90	1.16	0.029
			C2-N10		0.0107	1.16	1.27	0.034
			C3-C4		0.0475	3.22	1.26	0.057
			C4-O6		0.0410	3.50	1.12	0.056
C2-C3	π	1.7042	C1-N10	π*	0.4271	10.36	0.28	0.050
			C2-C3		0.31212	0.64	0.30	0.012
			C4-N11		0.44294	31.01	0.27	0.085
C2-H5	σ	1.9804	C1-N10	σ*	0.0402	3.70	1.07	0.056
			C3-C4		0.0475	3.13	1.05	0.052
			C3-F12		0.0276	1.04	0.81	0.026
C2-N10	σ	1.9792	C1-O8	σ*	0.0501	4.20	1.21	0.064
			C1-N10		0.0402	0.93	1.36	0.032
			C2-C3		0.0314	1.23	1.39	0.037
			C3-F12		0.0276	3.12	1.10	0.052
C3-C4	σ	1.9794	C2-C3	σ*	0.0501	3.02	1.30	0.056
			C2-H5		0.0402	2.13	1.15	0.044
			C4-O6		0.0314	0.86	1.11	0.028
			C4-N11		0.0276	1.89	1.28	0.044
			O6-H7		0.0314	1.88	1.13	0.041
C3-F12	σ	1.9953	C2-C3	σ*	0.0210	0.56	1.57	0.027
			C2-N10		0.0410	1.24	1.54	0.039
			C4-N11		0.0223	1.21	1.55	0.039
C4-O6	σ	1.9940	C1-N11	σ*	0.0110	1.55	1.48	0.043
			C2-C3		0.0314	0.89	1.52	0.033
			C4-N11		0.0107	0.84	1.50	0.032
C4-N11	σ	1.9809	C1-O8	σ*	0.0223	3.58	1.24	0.060
			C1-N11		0.0411	1.04	1.38	0.034
			C3-C4		0.0314	2.29	1.37	0.050
			C3-F12		0.0223	2.47	1.13	0.047
C4-N11	π	1.7488	C1-N10	π*	0.0501	35.03	0.32	0.099
			C2-C3		0.0411	8.41	0.34	0.048
			C4-N11		0.0475	1.41	0.31	0.020
O6-H7	σ	1.9857	C3-C4	σ*	0.0276	4.21	1.26	0.066



			C4-N11		0.4271	1.04	1.29	0.033
O8-H9	σ	1.9847	C1-N10	σ^*	0.3121	0.78	1.26	0.028
			C1-N11		0.4429	5.20	1.26	0.073
LP(1)-O6	σ	1.9766	C1-N11	σ^*	0.0475	0.52	1.14	0.022
			C3-C4		0.0223	0.65	1.13	0.024
			C4-N11		0.0402	6.03	1.16	0.075
LP(2)-O6	π	1.8317	C4-N11	π^*	0.0411	39.89	0.32	0.109
LP(1)-O8	σ	1.9770	C1-N10	σ^*	0.0411	5.73	1.14	0.072
			C1-N11		0.0475	0.90	1.13	0.029
LP(2)-O8	π	1.8403	C1-N10	π^*	0.0223	39.33	0.31	0.107
LP(1)-N10	π	1.9073	C1-O8	π^*	0.44294	5.34	0.73	0.056
			C1-N11		0.04025	12.01	0.88	0.093
			C2-C3		0.04114	7.36	0.92	0.075
			C2-H5		0.42714	2.96	0.78	0.044
			C3-F12		0.05018	0.69	0.63	0.019
			O8-H9		0.04114	0.59	0.76	0.019
LP(1)-N11	π	1.8921	C1-O8	π^*	0.03143	4.60	0.74	0.053
			C1-N10		0.02104	10.48	0.89	0.088
			C2-C4		0.02763	8.84	0.87	0.080
			C3-F12		0.00782	0.79	0.63	0.020
			C4-O6		0.05018	5.77	0.73	0.059
			O6-H7		0.04025	0.59	0.75	0.019
LP(1)-F12	σ	1.9951	C2-C3	σ^*	0.04754	1.11	1.60	0.038
			C3-C4		0.02763	0.70	1.55	0.030
LP(2)-F12	π	1.9668	C2-C3	π^*	0.04100	6.26	0.97	0.074
			C3-C4		0.01103	7.29	0.93	0.058
LP(3)-F12	π	1.9326	C2-C3	π^*	0.03143	17.41	0.42	0.082
C1-N10	π	0.4271	C2-C3	π^*	0.31212	141.39	0.02	0.073
C4-N11	π	0.4429	C2-C3	π^*	0.31212	137.44	0.02	0.082

Where $E^{(2)}$ means energy of hyper conjugative interactions,

$E(j)-E(i)$ is the energy difference between donor and acceptor i and j NBO orbitals

$F(i,j)$ is Fock matrix element

9. HOMO LUMO ANALYSIS

The frontier molecular orbital theory deals that homo acts as electron donor and lumo acts as electron acceptor. In view of energetic behaviour of title compound homo and lumo analysis is very important. The energy gap of homo lumo explains the complete charge transfer interaction within the molecule [32] which influences the biological activity [33] of the molecule. Some important parameters of molecule for quantum chemistry like chemical reactivity, kinetic stability are found with the help of homo and lumo analysis and frontier orbital gap. The electronegativity (χ), chemical potential μ , global hardness η , global softness S and global electrophilicity index ω are calculated by following equations;

$$\begin{aligned}\chi &= -\frac{1}{2}(E_{\text{LUMO}} + E_{\text{HOMO}}) \\ \mu &= -\chi = \frac{1}{2}(E_{\text{LUMO}} + E_{\text{HOMO}}) \\ \eta &= \frac{1}{2}(E_{\text{LUMO}} - E_{\text{HOMO}}) \\ S &= \frac{1}{2\eta} \\ \omega &= \mu^2/2\eta\end{aligned}$$

The global softness of the title compound has been increased as the level increased which is found as 9.97058 and 12.5636 for another level. All values are presented in Table 6. The least HOMO-LUMO gap shows the more reactivity of compound.



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Table 6: HOMO LUMO Analysis using TD-SCF/DFT/6-311++G(d,p) level

Energy	Value	Ionisation Potential	Electron Affinity	Chemical Potential	Global Hardness	Electronegativity	Global Softness	Electrophilicity Index
E_{HOMO}	-0.32083	0.32083	0.16164	0.241235	0.100295	-0.100295	9.970586	0.36556
E_{LUMO}	-0.16164							
$E_{\text{HOMO}+1}$	-0.13024	0.13024	0.33083	0.230535	0.079595	-0.079595	12.563603	0.26495
$E_{\text{LUMO}-1}$	-0.33083							

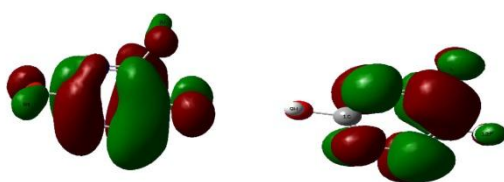


FIG 5: HOMO and LUMO images of 2,4-dihydroxy-5-fluoropyrimidine using DFT/B3LYP/6-311++G(d,p) level

10. MULLIKEN CHARGES AND NBO CHARGES

The chemical behaviour of atoms have been rationalized with the help of mulliken charges. Atomic charges play an important role in quantum chemistry[34]. In the present study carbon atom consists negative charge but 1C, 2C, 4C show positive mulliken charges which show that these carbon atoms are bonded with heavy electronegative atom like fluorine and nitrogen. The hydrogen atom 5H, 7H, 9H, shows positive NBO and Mulliken charges such that 0.21814e, 0.48474e, 0.48452e and 0.235219e, 0.282317e, 0.275590e respectively which may suggest the formation of intramolecular interaction in solid forms[35]. The NBO charges are slightly greater than mulliken charges. The fluorine atom has negative charge in both methods as -0.33189e and -0.175654e which shows the electronegativity of fluorine atom. The 2C carbon atom shows negative value in NBO as -0.02069e and 3C carbon atom shows negative value in mulliken method as -0.04302e respectively. All the NBO and Mulliken atomoc charges values have been shown in Table7 using DFT/B3LYP-6-311++G(d,p).

Table 7: Mulliken charges and NBO charges using B3LYP/DFT6-311++G(d,p)

Atoms	NBO charges	Mulliken charges
1C	0.70611	0.015512
2C	-0.02069	0.086869
3C	0.32662	-0.043024
4C	0.52542	0.087826
5H	0.21814	0.235219
6O	-0.70348	-0.245449
7H	0.48474	0.282317
8O	-0.69560	-0.228458
9H	0.48452	0.275590
10N	-0.48528	-0.136791
11N	-0.50861	-0.153957
12F	-0.33189	-0.175654

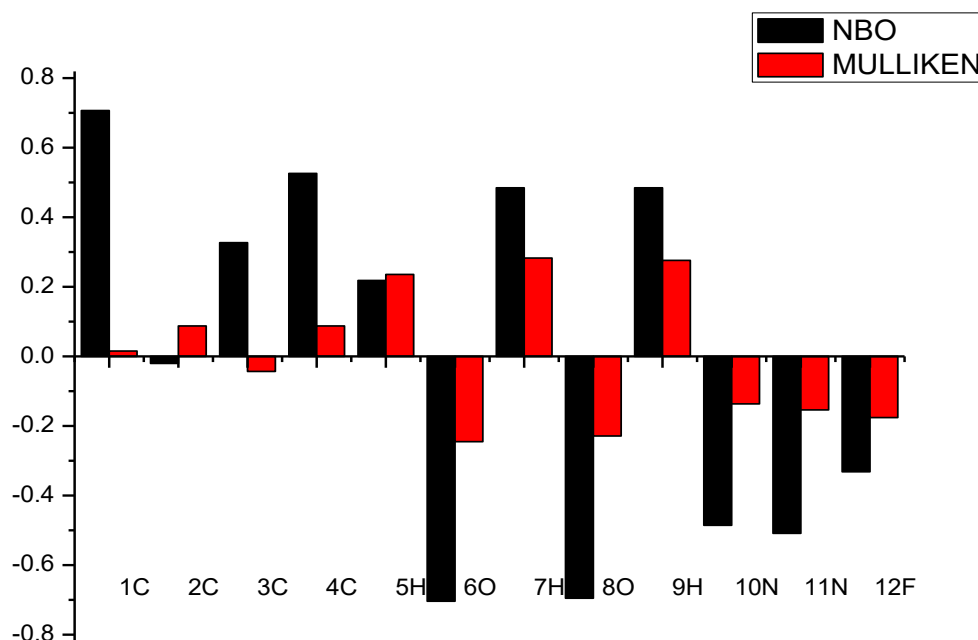


FIG 6: Graphical Representation of Mulliken and NBO charges using DFT/B3LYP/6-311++G(d,p)

11. THERMODYNAMIC PARAMETERS AND THERMODYNAMICS OF MOLECULAR PARAMETERS

The statically thermodynamic functions like heat capacity, entropy, enthalpy, Gibbs free energy are very important parameters obtained by vibrational analysis of molecule. It has been well known that molecular vibrational intensities increased with increased with temprature except Gibbs free energy. The principle of moment of inertia, molecular weight, temperature and vibrational fundamentals play an important role for the calculation of thermodynamic properties[36]. The correlation equations between heat capacity, entropy, enthalpy, Gibbs free energy and temperature were well suited by quadratic formulas which are as follows;

$$C_p = 3.434 + 0.311T - 0.009T^2 \quad (R^2 = 0.999)$$

$$(H-E)/T = 0.585 + 0.275T - 0.007T^2 \quad (R^2 = 0.999)$$

$$(G-E)/T = -66.67 - 0.135T - 0.007T^2 \quad (R^2 = 0.999)$$

$$S = 57.18 + 0.292T - 0.005T^2 \quad (R^2 = 1.000)$$

Where R^2 is the filling factor for equations.

All the values of thermodynamic parameters listed in Table 8 for temperature range 100-1500 K. The value of zero point vibration energy is higher in HF than DFT. The potential barrier and thermal energy with increasing temperature of titled compound also have been shown in Table 9. The other important parameters like zero point vibrational energy, specific heat capacity, thermal energy, rotational temperature and entropy have been shown in Table10 .



Table 8: Thermodynamic Functions (in Cal/mole-°K) of 2,4-Dihydroxy-5-Fluoropyrimidine

Temperature(°K)	$\frac{H^\circ - E^\circ}{T}$	$\frac{F^\circ - E^\circ}{T}$	S°	C_p°
200	13.53	56.84	70.37	19.45
273	15.57	61.67	77.24	22.76
300	16.27	63.26	79.53	23.91
400	18.68	68.56	87.25	27.87
500	20.87	73.19	94.07	31.29
600	22.85	77.36	100.21	34.08
700	24.62	81.17	105.79	36.30
800	26.19	84.70	110.89	38.06
900	27.59	87.98	115.58	39.46
1000	28.84	91.06	119.90	40.59
1100	29.95	93.95	123.91	41.51
1200	30.94	96.69	127.64	42.27
1300	31.84	99.28	131.13	42.91
1400	32.65	101.75	134.40	43.44
1500	33.38	104.09	137.48	43.89

Table 9: Potential Barrier and Thermal Energy with Temperature of 2,4-Dihydroxy-5-Fluoropyrimidine

Temperature(°K)	Potential Barrier	Thermal Energy
200	11.620	0.4761
273	8.512	0.4075
300	7.746	0.3887
400	5.810	0.3366
500	4.648	0.3011
600	3.873	0.2749
700	3.320	0.2545
800	2.905	0.2380
900	2.582	0.2244
1000	2.324	0.2129
1100	2.112	0.2030
1200	1.936	0.1943
1300	1.787	0.1867
1400	1.660	0.1799
1500	1.549	0.1738

Table 10: Thermal Properties of 2,4-dihydroxy-5-fluoropyrimidine

Parameters	HF	DFT
Zero point correction	0.085158	0.078112
Thermal correction to energy	0.091571	0.085041
Thermal correction to enthalpy	0.092515	0.085986
Thermal energy to Gibbs free energy	0.054163	0.046693
Sum of electronic and zero point energy	-511.343956	-514.1005
Sum of electronic and thermal energies	-511.337543	-514.0936
Sum of electronic and thermal	-511.336598	-514.0927



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enthalpies		
Sum of electronic and free energies	-511.374951	-514.13199
Zero point vibrational energy (Joules/mol)	223581.8	205082.1
Zero point vibrational energy (kcal/mol)	53.43734	49.01581
Rotational Tempratures (Kelvin)		
A	0.15840	0.15840
B	0.06982	0.06832
C	0.04846	0.04727
Rotational Constants(GHz)		
A	3.30056	3.19728
B	1.45485	1.42359
C	1.00976	0.98501
Thermal Energy (Kcal/mol)		
Translational	0.889	0.889
Rotational	0.889	0.889
Vibrational	56.684	51.587
Molar Capacity at constant volume (cal/mol-Kelvin)		
Translational	2.981	2.981
Rotational	2.981	2.981
Vibrational	18.483	20.512
Entropy Total (cal/mol-kelvin)		
Translational	40.501	40.501
Rotational	28.663	28.585
Vibrational	13.535	11.634

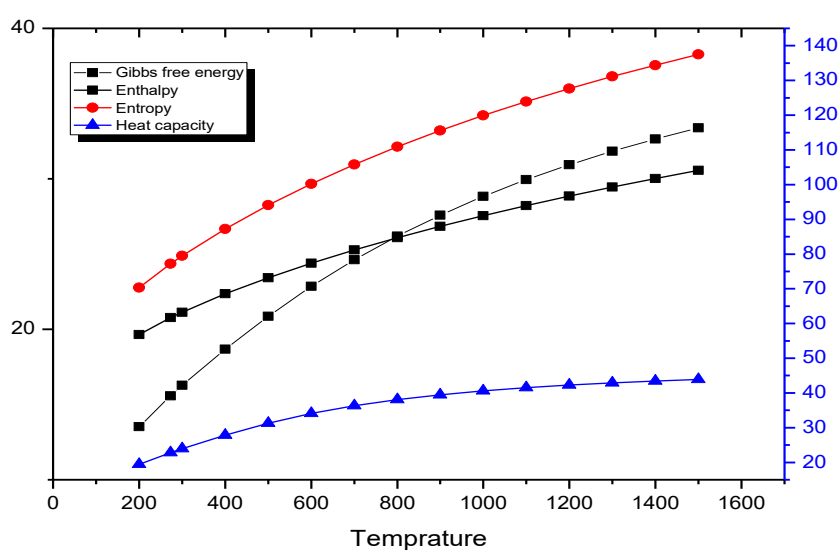


FIG 7: Graphical representation of thermodynamic parameters on the effect of temperature of 2,4-dihydroxy-5-fluoropyrimidine



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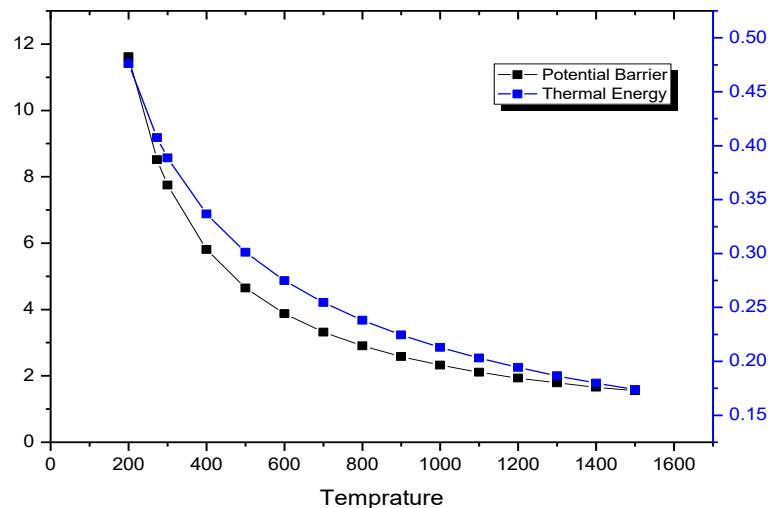


FIG 8: Graphical representation of potential barrier and thermal energy on the effect of temperature of 2,4-dihydroxy-5-fluoropyrimidine

12. CONCLUSION

All the attempts have been made in present study using HF and DFT levels and all the results are seen in good agreement with experimental and theoretical calculation. The increased global hardness has been found which shows the stability of compound. The experimental absorption spectrum has been well produced using TD-DFT approach. The natural bond orbital analysis has been made in good agreement which shows the molecular orbital hybridization very well. The occupancy and unoccupancy of molecules have been found at DFT/B3LYP/6-311++G(d,p) levels. The thermodynamic parameters and the thermodynamics of molecules are calculated which clarify the various properties of compound. The mulliken and natural bond orbital charges are also show each molecule consisting charge within compound.

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