



Spectral Characterization and Vibrational Assignments of Ethyl 4-(3-(2,3-Dihydrobenzofuran-5-Carboxamido)Phenyl)-6-Methyl-2-Oxo-1,2,3,4-Tetrahydropyrimidine-5-Carboxylate by Ab Initio Density Functional Method

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ABSTRACT

In the present investigation, then novel compound ethyl 4-(3-(2,3-dihydrobenzofuran-5carboxamido)phenyl)-1,2,3,4-tetrahydro-6-methyl-2-oxopyrimidine-5-carboxylate(DFOC) were synthesized .The synthesized compound have been characterized by using UV-visible, FT-IR, FT-Raman, ¹H-NMR and ¹³CNMR spectral studies. The harmonic vibrational frequencies, optimized molecular geometry have been carried out with the help of B3LYP density functional theory method. The stability of the molecule was analyzed by means natural bond orbital analysis and delocalized π - π^* interactions. Moreover, the frontier molecular orbital analysis, molecular electrostatic potential surface and thermodynamic properties of DFOC were investigated using DFT calculations.

Keywords: DFOC, NBO, NLO HOMO-LUMO and DFT.

INTRODUCTION

Dihydropyrimidin-2-(1H)-ones plays a vital role in natural and synthetic organic chemistry. It have wide range of biological activities ^{1,2}. Such as, anti-leishmanial³, anti-tuberculosis⁴,

analgesic, anti-inflammatory⁵⁻⁷, antimicrobial⁸, antifungal⁹anti-emetic¹⁰and antitumor properties¹¹. The nonlinear optical active molecules with π -conjugated backbones, electron donating, electron withdrawing moieties are important class of materials in modern technologies, such as telecommunication

and optoelectronics¹², multiphoton microscopy¹³, Organic light-emitting diodes (OLED)¹⁴, organic field effect transistors (OFET)¹⁵ and to achieve hierarchical self-assembly in "all-organic" photovoltaic devices¹⁶

Here, we report synthesis of a new nonlinear molecule ethyl

ethyl 4-(3-(2,3-dihydrobenzofuran-5-carboxamido)phenyl)-1,2,3,4-tetrahydro-6-methyl-2-oxopyrimidine-5-carboxylate (DFOC). The optimized molecular structure, FT-IR, FT-Raman frequencies and NMR chemical shift values were analyzed using experimental and theoretical approach. The nonlinear optical behavior of the title molecule has been calculated by the first hyperpolarizability components. The intramolecular charge transfer occurs from the donor-acceptor interactions are examined using Natural bond orbital analysis. In addition UV-Visible analysis, frontier molecular orbital energies (HOMO and LUMO), electronegativity (χ), hardness (η), Electrophilicity (Ψ) thermodynamic properties, and molecular electrostatic potential maps (MEP) are investigated.

Computational details

The theoretical calculation of DFOC were performed quantum chemical calculations of DFOC have been performed using Gaussian 03 program package utilizing DFT/6-31G(d,p) the B3LYP level of theory¹⁷⁻¹⁹. By using VEDA4 program, FT-IR, FT-Raman frequencies are on the basis of potential energy distribution.²⁰ The calculated wave number were scaled down uniformly by a factor of 0.9608 for obtaining a decent agreement with experimental results.

EXPERIMENTAL

Synthesis of ethyl 4-(3-(2,3-dihydrobenzofuran-5-carboxamido)phenyl)-1,2,3,4-tetrahydro-6-methyl-2-oxopyrimidine-5-carboxylate (I)

Ethanol mixtures of 3-nitro-benzaldehyde (0.6 mmol), ethyl acetoacetate (0.9 mmol) and urea (0.9 mmol) were stirred in Con. Hydrochloric acid in a RB. The reaction mixture was refluxed at 80°C for 12h. The thin layer chromatography was performed to check completion of the reaction. The crude content was cooled and poured into crushed ice, the obtained solid product was filtered and washed with ethanol.

The crude product was recrystallized from absolute ethanol. Yield: 73%, melting point = 218 °C.

IR (KBr): ν ~ [cm⁻¹] 3441, 3356, 3240, 3105, 2962, 1703, 1649, 1633, ¹H NMR (400 MHz, DMSO-d₆): δ = 1.1-1.08 (t, 3H, J = 7.07 Hz), 2.26 (s, 3H), 4.01-3.94 (q, 2H, J = 7.1 Hz), 5.29-5.28 (d, 1H, J = 3.01 Hz), 7.64-7.62 (d, 1H, J = 7.8 Hz, ArH), 7.67-7.66 (d, 1H, J = 7.71 Hz, ArH), 7.69-7.67 (m, 1H, ArH), 8.11-8.07 (s, 1H, ArH), 8.13 (s, 1H, NH), 9.36 (s, 1H, NH), ¹³C NMR (75 MHz, DMSO-d₆): δ = 165.0, 151.7, 149.3, 147.6, 146.9, 132.1, 130.3, 122.9, 120.9, 98.2, 59.3, 53.4, 17.0, 13.9.

Reduction of compound (I) to ethyl 1,2,3,4-tetrahydro-6-methyl-4-(3-aminophenyl)-2-oxopyrimidine-5-carboxylate (II)

The compound I is stirred with 10% Palladium on charcoal in equimolar quantity of ethanol with methanol and ethyl acetate (50%). The reaction mixture was stirred under hydrogen atmosphere for 12 h. Then the completion of reaction TLC monitoring, the reaction mixture was filtered. The filtrate was concentrated under reduced pressure resulting in a solid compound which was further purified by recrystallization. Yield: 73% melting point = 201 °C.

IR (KBr): ν ~ [cm⁻¹] 3441, 3360, 3242, 3105, 2976, 1707, 1651, 1616, ¹H NMR (400 MHz, DMSO-d₆): δ = 1.11-1.09 (t, 3H, J = 7.08 Hz), 2.21 (s, 3H), 3.97-3.95 (q, 2H, J = 7.9 Hz), 4.98-4.97 (d, 1H, J = 3.04 Hz), 5.03 (s, 2H, -NH₂), 6.39-6.37 (d, 1H, J = 7.03 Hz, ArH), 6.41-6.40 (d, 1H, J = 6.91 Hz, ArH), 6.43-6.42 (m, 1H, ArH), 6.93-6.91 (s, 1H, ArH), 7.59 (s, 1H, NH), 9.07 (s, 1H, NH), ¹³C NMR (75 MHz, DMSO-d₆): δ = 165.4, 152.1, 148.5, 147.6, 145.4, 128.6, 113.8, 112.8, 111.6, 99.4, 59.0, 54.0, 17.1, 14.0.

Ethyl 4-(3-(2,3-dihydrobenzofuran-5-carboxamido)phenyl)-1,2,3,4-tetrahydro-6-methyl-2-oxopyrimidine-5-carboxylate (III)

The compound (II) (0.01 mmol) was dissolved in DMF (10 ml) and added using O-(7-azabenzotriazol-1-yl)-N,N,N₂,N₂-tetramethyluronium hexafluorophosphate (HATU) (0.076 mmol), N,N-Diisopropyl ethylamine (DIEA) (0.11 mmol), 2,3-dihydrobenzofuran-5-carboxylic acid (0.01 mmol) added at 0°C. The reaction mixture was stirred for

8h, then it was kept at room temperature for 4h. The completion of the reaction was monitor by TLC. The product mixture diluted with water, extracted with ethyl acetate and separated the organic layer, washed with water and brine solution. The organic layer was dried over anhydrous sodium sulphate and concentrated to produce crude solid which was purified by column chromatography eluting with 30-40%ethylacetate in hexane to obtained compound(III).Yield: 71%, melting point =158°C.

IR (KBr): ν ~ [cm⁻¹] 3369, 3277, 3226, 3015, 1701, 1643, ¹H NMR (400 MHz, DMSO_d₆): δ = 1.1-1.08 (t, 3H, *J* = 7.07 Hz, C-15), 2.24 (s, 3H, C-12), 3.2 (t, 2H, C-29), 4.00-3.95 (q, 2H, *J* = 7.1 Hz, C-14), 4.63-4.59 (t, 2H, *J* = 8.72 Hz, C-30) 5.13-5.12 (d, 1H, *J* = 3.01 Hz, C-6), 6.94-6.86 (d, 1H, *J* = 8.6 Hz, ArH, C-21), 6.95-6.94 (d, 1H, *J* = 7.72 Hz, ArH, C-28), 7.27-7.23 (m, 1H, ArH, C-20), 7.84-7.63 (m, 3H, ArH, C-19, 27, 25), 7.85 (s, 1H, ArH, C-17), 7.94 (s, 1H, NH-3), 9.16 (s, 1H, NH-5), 10.01 (s, 1H, NH-2). ¹³C NMR (75 MHz, DMSO_d₆): δ = 165.3, 165.0, 162.5, 151.9, 148.2, 145.3, 139.4, 130.5, 128.6, 127.8, 124.8, 121.5, 119.6, 118.2, 108.6, 108.3, 99.4, 71.9, 59.1, 54.2, 28.5, 28.3, 17.7.

Spectral measurements

The FT-IR spectrum of the synthesized DFOC was measured in the 4000–400 cm⁻¹ region at the spectral resolution of 4 cm⁻¹ using on SHIMADZU FT-IR affinity Spectrophotometer (KBr pellet technique). The UV spectrum has been recorded with SHIMADZU- 1650 spectrophotometer (λ_{max} nm) in spectral grade methanol solvent. NMR spectral studies were carried out using Bruker 300 MHz spectrometer, using TMS as an internal standard and DMSO-d₆ as solvent and recorded at Indian Institute of Technology (IIT), Chennai.

RESULTS and DISCUSSIONS

Molecular geometry

The optimized geometrical parameters of DFOC using DFT/B3LYP6-31 G(d,p) level of theory. The optimized structure of DFOC as shown in fig(1). The geometrical parameters such as bond length, bond angle and dihedral angle are listed in table 1 and compared with available crystal data of analogous molecule²¹. The bond length of C₄-O₉, C₁₄-O₁₆, and C₃₅-O₃₇ are calculated as

1.2219, 1.2249 and 1.2271Å respectively from the B3LYP method. All the above C=O bond lengths are more or less equal one to other because they are conjugated with a phenyl group and mesomeric effect of ethoxy group in ester moiety. The C₄, C₁₄, and C₃₅ atoms are having SP² hybridization. The bond length for C₁₄-O₁₅, O₁₅-C₁₇, C₄₅-O₄₇ and C₄₈-O₄₇ are calculated about 1.3582, 1.4454, 1.3604 and 1.4535 Å. In which the bond length of C₁₄-O₁₅ is very lower value O₁₅ atoms having inductive effect dominate mesomeric effect²².

The C₄₅-O₄₇ bond length is shorter, which indicates the lonepair of oxygen atom overlapping with the π -orbitals of the phenyl ring. The bond length for C₄-N₅, C₁-N₅, C₄-N₇, C₃-N₇, C₂₇-N₃₄ and C₃₅-N₃₄ are calculated about 1.4028, 1.3832, 1.3647, 1.4644, 1.4095 and 1.3803Å. This C₃-N₇ bond length is higher value due to increasing P character of C₃ carbon atom and it also having SP₃ hybridization. The heterocyclic C=C double bond of C₁-C₂ bond length is lower value 1.3642 Å. Because it conjugated with the π^* (anti-bonding) orbital of the carbonyl ester, and the aromatic bond distance lies in the range of 1.3924- 1.4091 Å. In these present study carboxamide pyrimidine molecules, bond angle C₁-N₅-C₄, C₃-N₇-C₄ and C₂₇-N₃₄-C₃₅ are 125.03, 123.28 and 129.09° are respectively. The C₂₇-N₃₄-C₃₅ bond angle increases because N₃₄ attached with two bulkier group, they are steric hinders one to another and they have slightly distorted pyramidal structure. The deviation in the calculated bond angles for C₁₄-O₁₅-C₁₇ and C₄₅-O₄₇-C₄₈ were (115.56°-107.69°) 7.87°. The lower bond angle value of C₄₅-O₄₇-C₄₈ indicate that it have been present in the five-membered cyclic structure (i.e) benzofuran ring.

Natural bond orbital Analysis

The NBO is an efficient method to analyze the charge transfer interaction of a molecular system²³. In the present investigation the strong delocalization in the aromatic system gives rise the orbital overlap between the π (C-C)→ π^* (C-C) interactions gives the strong intra molecular interactions resulting in the π -conjugation due to the π -electron delocalization. These interactions are observed as an increase in electron density (occupancy) in (C-C) antibonding orbitals that weakens the respective bonds²⁴. In our study the strong intramolecular

interaction between $\pi C_1-C_2 \rightarrow \pi^* C_{14}-O_{16}$ since the stabilization energy of 104.56 kJ/mol. In addition, the interaction between $n(O_{15}) \rightarrow \pi^* C_{14}-O_{16}$ shows the hyperconjugation interaction energy about 192.05 kJ/mol. The highest interaction around the carboxamide, dihydropyrimidinones and the ester moiety can induce large bioactivity of the title molecule. In DFOC molecule has five oxygen atoms and the lone pair of electrons in it shows higher hyper conjugative interaction energies. The stabilizing lone pair interaction are $LP(O_9) \rightarrow \sigma^* C_4-N_5, LP(O_{15}) \rightarrow$

$\sigma^* C_{14}-O_{16}, LP(O_{16}) \rightarrow \sigma^* C_{14}-O_{15}, LP(O_{37}) \rightarrow \sigma^* N_{34}-C_{35}$ and $LP(O_{47}) \rightarrow \pi^* C_{43}-C_{45}$ shows stabilization energies of 116.48, 192.05, 136.52, 108.99 and 128.74 kJ/mol. are listed in table 2.

Table 1: The theoretical bond parameters of DFOC

Bond Length (Å)		
(C ₁ -C ₂)	1.3642	(O ₁₅ -C ₁₇ -H ₂₀) 108.89
(C ₁ -N ₅)	1.3832	(C ₃ -C ₂₄ -C ₂₅) 118.79
(C ₁ -C ₁₀)	1.5073	(C ₃ -C ₂₄ -C ₂₆) 122.27
(C ₂ -C ₃)	1.5292	(C ₂₅ -C ₂₄ -C ₂₆) 118.92
(C ₂ -C ₁₄)	1.4654	(C ₂₄ -C ₂₅ -C ₂₇) 121.26
(C ₃ -N ₇)	1.4644	(C ₂₄ -C ₂₅ -H ₂₈) 118.78
(C ₃ -C ₂₄)	1.5379	(C ₂₇ -C ₂₅ -H ₂₈) 119.94
(C ₄ -N ₅)	1.4028	(C ₂₄ -C ₂₆ -C ₂₉) 119.67
(C ₄ -N ₇)	1.3647	(C ₂₉ -C ₂₆ -H ₃₀) 119.53
(C ₄ -O ₉)	1.2219	(C ₂₅ -C ₂₇ -C ₃₁) 119.66
(N ₅ -H ₈)	1.0095	(C ₂₅ -C ₂₇ -N ₃₄) 116.69
(H ₆ -N ₇)	1.0109	(C ₃₁ -C ₂₇ -N ₃₄) 123.62
(C ₁₄ -O ₁₅)	1.3582	(C ₂₇ -N ₃₄ -C ₃₅) 129.07
(C ₁₄ -O ₁₆)	1.2249	(C ₂₇ -N ₃₄ -H ₃₆) 114.44
(O ₁₅ -C ₁₇)	1.4454	(C ₃₅ -N ₃₄ -H ₃₆) 116.18
(C ₂₇ -N ₃₄)	1.4095	(N ₃₄ -C ₃₅ -O ₃₇) 123.42
(N ₃₄ -C ₃₅)	1.3803	(N ₃₄ -C ₃₅ -C ₃₈) 115.01
(N ₃₄ -H ₃₆)	1.0090	(O ₃₇ -C ₃₅ -C ₃₈) 121.55
(C ₄₅ -O ₄₇)	1.3604	(C ₃₅ -C ₃₈ -C ₃₉) 123.75
(O ₄₇ -C ₄₈)	1.4535	(C ₄₁ -C ₄₅ -O ₄₇) 113.46
Bond Angle (°)		(C ₄₃ -C ₄₅ -O ₄₇) 124.42
(C ₂ -C ₃ -C ₂₄)	112.77	(C ₄₅ -O ₄₇ -C ₄₈) 107.69
(C ₂ -C ₃ -H ₅₀)	107.03	(O ₄₇ -C ₄₈ -C ₄₉) 107.04
(C ₂₄ -C ₃ -H ₅₀)	107.63	
(C ₁ -N ₅ -C ₄)	125.03	
(C ₃ -N ₇ -C ₄)	123.28	
(C ₃ -N ₇ -H ₆)	117.69	
(C ₄ -N ₇ -H ₆)	113.16	
(C ₂ -C ₁₄ -O ₁₅)	114.82	
(C ₂ -C ₁₄ -O ₁₆)	123.59	
(O ₁₅ -C ₁₄ -O ₁₆)	121.57	
(C ₁₄ -O ₁₅ -C ₁₇)	115.56	
(O ₁₅ -C ₁₇ -C ₁₈)	107.54	
(O ₁₅ -C ₁₇ -H ₁₉)	108.93	

The delocalization energies of $\Pi C_{26}-C_{29} \rightarrow \Pi^* C_{24}-C_{25}, \Pi^* C_{27}-C_{31}$ and $\Pi C_{27}-C_{31} \rightarrow \Pi^* C_{24}-C_{25}, \Pi^* C_{26}-C_{29}$ shows 94.56, 77.49 and 79.45, 92.27 kJ/mol respectively. The interactions between the oxygen lone pair $LP(O_{47})$ and the anti-bonding orbital $\Pi^* C_{43}-C_{45}$ which have total stabilization energies 128.74 kJ/mol. The intra-molecular hyper conjugative interaction of the $\sigma(C_{49}-H_{51})$ distribute to $\Pi^* O_{47}-C_{48}$ leading to stabilization of 6.53 kJ/mol. The magnitude of the intra-molecular interactions due to the orbital overlap of the Π (C-C) and Π^* (C-C) in benzofuran ring results in ICT causing stabilization of the whole system. The benzofuran ring has strong delocalization energies $\Pi C_{38}-C_{40} \rightarrow \Pi^* C_{39}-C_{41}, \Pi^* C_{43}-C_{45}$ and $\Pi C_{43}-C_{35} \rightarrow \Pi^* C_{38}-C_{40}, \Pi^* C_{39}-C_{41}$ exhibit 94.35, 70.85 and 102.73, 77.03 kJ/mol respectively. In our molecule, the NBO analysis of donor-acceptor interactions to providing very small resonance energy for $LP(O_9) \rightarrow \sigma^* C_4-N_5, \sigma^* C_4-N_7$ and $LP(O_{37}) \rightarrow \sigma^* C_{31}-H_{33}, \sigma^* N_{34}-C_{35}, \sigma^* C_{35}-C_{38}$ are 8.72, 11.21 and 4.94, 8.12, 9.29 kJ/mol respectively, due to increasing S-character of Oxygen lone pair.

Vibrational Assignments

The molecular structure of DFOC belongs to C₁ point group symmetry there would not be any relevant distribution. The title molecule consists of 56 atoms and expected to have 156 normal modes of vibrations (3N-6). The complete vibrational assignments along with the frequencies are presented in Table 3. The both recorded and simulated spectra of FT-IR and FT-Raman are shown in Fig (2) and Fig (3).

Ring 1

In aromatic heterocyclic compounds, the N-H stretching vibrations occur in region 3450-3250 cm^{-1} . The N-H stretching frequency observed at 3370 cm^{-1} for aryl amide analogues²⁶. In the present study the $\nu N_{34}-H_{36}$ stretching modes are observed at 3277 cm^{-1} respectively in FT-IR. The lower in frequencies in solid phase may attribute due to hyper conjugation interaction arises with the adjacent carbonyl group. The strong band observed

in the region 1715-1600 cm^{-127} . In the present work, the very strong band observed at 1701 cm^{-1} in FT-IR and also very strong band at 1700 cm^{-1} in FT-Raman are assigned for the $\nu\text{C}_{35}=\text{O}_{37}$ stretching vibration with 79% PED contribution. The scaled wave number, at 1690 cm^{-1} in B3LYP method. The C–H stretching vibrations of benzofuran appear in the region 3148-3063 cm^{-1} . In our investigated

molecule the aromatic C–H stretching vibrations observed at 3105 cm^{-1} in FT-IR and its corresponding theoretical wavenumber at 3104, 3092 and 3057 cm^{-1} respectively. In furan $\nu\text{C}_{45}-\text{O}_{47}$ stretching modes are calculated at 1239 cm^{-1} higher frequency. Because the bond angle of C–O–C have more angle strain. The bond angle in furan ($\text{C}_{45}-\text{O}_{47}-\text{C}_{48}$) 107.60 and in ester $\text{C}_{14}-\text{O}_{15}-\text{C}_{17}$ to give 115.56

Table 2: Second order perturbation theory analysis of NBO basis for DFOC

Type	Donor(i)	ED/e	Type	Acceptor(j)	ED/e	KJ/mol	^b E(j)-E(i) a.u	^c F(i,j) a.u
σ	$\text{C}_{49} - \text{H}_{51}$	1.97826	σ^*	$\text{O}_{47} - \text{C}_{48}$	0.01922	6.53	0.77	0.031
σ	$\text{N}_5 - \text{H}_8$	1.984	σ^*	$\text{C}_1 - \text{C}_2$	0.02529	13.77	1.29	0.058
σ	$\text{H}_6 - \text{N}_7$	1.98037	σ^*	$\text{C}_2 - \text{C}_3$	0.02842	8.66	1.04	0.041
π	$\text{C}_1 - \text{C}_2$	1.84038	π^*	$\text{C}_{14} - \text{O}_{16}$	0.31454	104.56	0.28	0.078
π	$\text{C}_{26} - \text{C}_{29}$	1.66896	π^*	$\text{C}_{24} - \text{C}_{25}$	0.36118	94.56	0.28	0.072
			π^*	$\text{C}_{27} - \text{C}_{31}$	0.38752	77.49	0.28	0.065
π	$\text{C}_{27} - \text{C}_{31}$	1.62498	π^*	$\text{C}_{24} - \text{C}_{25}$	0.36118	79.45	0.28	0.066
			π^*	$\text{C}_{26} - \text{C}_{29}$	0.34861	92.97	0.28	0.071
π	$\text{C}_{38} - \text{C}_{40}$	1.64133	π^*	$\text{C}_{35} - \text{O}_{37}$	0.30667	84.52	0.27	0.067
			π^*	$\text{C}_{39} - \text{C}_{41}$	0.34596	94.35	0.28	0.071
			π^*	$\text{C}_{43} - \text{C}_{45}$	0.38336	70.50	0.27	0.061
π	$\text{C}_{39} - \text{C}_{41}$	1.70578	π^*	$\text{C}_{38} - \text{C}_{40}$	0.37755	68.28	0.29	0.063
			π^*	$\text{C}_{43} - \text{C}_{45}$	0.38336	90.37	0.29	0.072
π	$\text{C}_{43} - \text{C}_{45}$	1.62427	π^*	$\text{C}_{38} - \text{C}_{40}$	0.37755	102.3	0.29	0.075
			π^*	$\text{C}_{39} - \text{C}_{41}$	0.34596	77.03	0.29	0.066
n	N_5	1.67578	π^*	$\text{C}_1 - \text{C}_2$	0.23239	169.28	0.31	0.102
			π^*	$\text{C}_4 - \text{O}_9$	0.33921	178.45	0.33	0.106
n	N_7	1.742	σ^*	$\text{C}_4 - \text{O}_9$	0.33921	192.05	0.32	0.11
n	O_9	1.84597	σ^*	$\text{C}_4 - \text{N}_5$	0.08912	116.48	0.65	0.122
			σ^*	$\text{C}_4 - \text{N}_7$	0.0735	102.68	0.71	0.12
n	O_{15}	1.80561	π^*	$\text{C}_{14} - \text{O}_{16}$	0.31454	192.05	0.33	0.113
n	O_{16}	1.852	σ^*	$\text{C}_2 - \text{C}_{14}$	0.05646	68.87	0.72	0.099
			σ^*	$\text{C}_{14} - \text{O}_{15}$	0.09845	136.52	0.63	0.129
n	N_{34}	1.66888	π^*	$\text{C}_{27} - \text{C}_{31}$	0.38752	143.72	0.3	0.092
			π^*	$\text{C}_{35} - \text{O}_{37}$	0.30667	231.58	0.29	0.113
n	O_{37}	1.86543	σ^*	$\text{N}_{34} - \text{C}_{35}$	0.07478	108.99	0.7	0.122
			σ^*	$\text{C}_{35} - \text{C}_{38}$	0.06511	80.25	0.67	0.103
n	O_{47}	1.8356	π^*	$\text{C}_{43} - \text{C}_{45}$	0.38336	128.74	0.34	0.097
n	O_9	1.97525	σ^*	$\text{C}_4 - \text{N}_5$	0.08912	8.87	1.08	0.043
			σ^*	$\text{C}_4 - \text{N}_7$	0.0735	11.42	1.14	0.05
n	O_{37}	1.97481	σ^*	$\text{C}_{31} - \text{H}_{33}$	0.01697	4.94	1.19	0.033
			σ^*	$\text{N}_{34} - \text{C}_{35}$	0.07478	8.12	1.13	0.042
			σ^*	$\text{C}_{35} - \text{C}_{38}$	0.06511	9.29	1.1	0.045

^aE⁽²⁾ means energy of hyper conjugative interaction (stabilization energy).

^bEnergy difference between donor(i) and acceptor(j) NBO orbitals.

^cF(i,j) is the fork matrix element between i and j NBO orbitals.

Ring 2

Aromatic C–H stretching vibrations are expected to be observed in the region 3115–3074 cm^{-1} .²⁹ In our molecule the aromatic C–H stretching vibrations are observed at 3067 cm^{-1} in FT-Raman spectrum. The C=C stretching vibrations of phenyl

rings are assigned in the region of 1625–1430 cm^{-1} . In the phenyl ring, the six carbon atoms undergo coupled vibrations called skeletal vibrations^{30, 31}. For our present work, the ring C=C stretching vibrations are calculated in theoretical wave number at 1597, 1582 cm^{-1} , respectively. The strong bands observed at

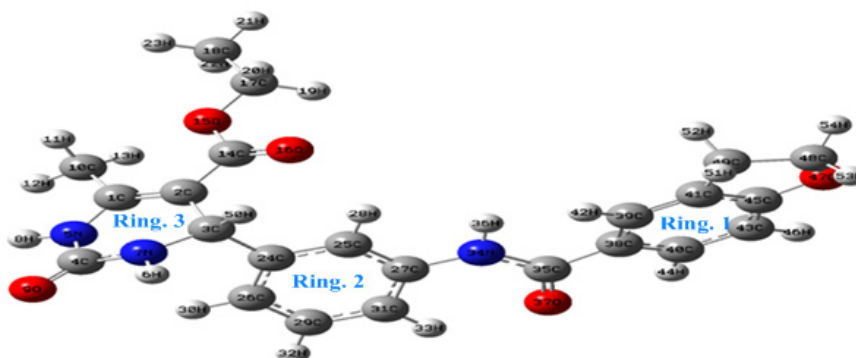


Table 3: The Fundamental vibrational assignments of DFOC

S. No	Freq.	FT-IR	Raman	Red. Masses	Frc_ Consts	IR_ Inten	Raman Activ	PED	
1	3649	3510	3369		1.08	8.46	78.58	35.88	$\nu\text{N}_5\text{H}_8(100)$
2	3641	3502	3277		1.08	8.40	12.25	34.00	$\nu\text{N}_{34}\text{H}_{36}(100)$
3	3631	3493	3226		1.08	8.36	38.95	26.95	$\nu\text{N}_7\text{H}_6(100)$
4	3270	3146			1.09	6.88	6.17	25.16	$\nu\text{C}_{31}\text{H}_{33}(99)$
5	3227	3104	3105		1.09	6.72	4.81	68.61	$\nu\text{C}_{40}\text{H}_{44}(63)+$ $\nu\text{C}_{43}\text{H}_{46}(36)$
6	3214	3092			1.09	6.65	7.35	43.03	$\nu\text{C}_{26}\text{H}_{30}(90)$
7	3214	3092			1.09	6.63	2.75	40.85	$\nu\text{C}_{40}\text{H}_{44}(36)+$ $\nu\text{C}_{43}\text{H}_{46}(63)$
8	3190	3069	3067		1.09	6.54	9.31	33.05	$\nu\text{C}_{25}\text{H}_{28}(92)$
9	3187	3066			1.09	6.51	13.82	36.68	$\nu\text{C}_{29}\text{H}_{32}(83)$
10	3178	3057			1.09	6.48	13.57	24.57	$\nu\text{C}_{39}\text{H}_{42}(100)$
11	3175	3055			1.10	6.52	3.81	16.00	$\nu\text{C}_{10}\text{H}_{13}(87)$
12	3137	3018			1.11	6.41	36.24	8.50	$\nu\text{C}_{18}\text{H}_{22}(40)+$ $\nu\text{C}_{18}\text{H}_{23}(42)$
13	3130	3011			1.10	6.36	20.30	47.74	$\nu\text{C}_{18}\text{H}_{21}(64)+$ $\nu\text{C}_{18}\text{H}_{22}(17)+$ $\nu\text{C}_{18}\text{H}_{23}(15)$
14	3129	3010			1.10	6.37	33.15	75.18	$\nu\text{C}_{48}\text{H}_{53}(13)+$ $\nu\text{C}_{48}\text{H}_{54}(82)$
15	3128	3009			1.10	6.35	16.99	35.29	$\nu\text{C}_{10}\text{H}_{11}(56)+$ $\nu\text{C}_{10}\text{H}_{12}(41)$
16	3106	2988			1.11	6.30	6.29	38.34	$\nu\text{C}_{17}\text{H}_{19}(39)+$ $\nu\text{C}_{17}\text{H}_{20}(43)$
17	3096	2978			1.10	6.20	20.35	51.69	$\nu\text{C}_{49}\text{H}_{51}(81)+$

18	3090	2973		2974	1.09	6.11	5.77	24.59	$\nu C_{49}H_{52}(12)$
19	3066	2950	2964		1.06	5.86	16.88	43.17	$\nu C_3H_{50}(100)$
20	3064	2947			1.04	5.75	17.83	88.18	$\nu C_{17}H_{19}(52)+$ $\nu C_{17}H_{20}(46)$
21	3056	2940			1.07	5.87	67.36	91.76	$\nu C_{10}H_{11}(38)+$ $\nu C_{10}H_{12}(50)+$ $\nu C_{10}H_{13}(12)$
22	3055	2939		2937	1.04	5.69	16.35	60.64	$\nu C_{48}H_{53}(86)+$ $\nu C_{48}H_{54}(11)$
23	3046	2930			1.07	5.83	23.12	70.26	$\nu C_{18}H_{21}(34)+$ $\nu C_{18}H_{22}(33)+$ $\nu C_{18}H_{23}(33)$
24	1830	1760			7.64	15.07	601.86	40.88	$\nu C_{49}H_{51}(14)+$ $\nu C_{49}H_{52}(85)$
25	1756	1690	1701	1700	9.61	17.46	190.71	576.96	$\nu C_4O_3(72)$
26	1744	1678	1643		12.01	21.52	348.81	167.90	$\nu C_{35}O_{37}(79)$
27	1676	1613		1624	7.48	12.38	160.65	167.27	$\nu C_{14}O_{16}(84)$
28	1664	1601			6.64	10.83	54.07	304.30	$\nu C_1C_2(64)$
29	1660	1597		1592	5.59	9.08	205.26	505.87	$\nu C_{39}C_{41}(24)+$ $\nu C_{43}C_{45}(11)+$ $\nu C_{40}C_{43}(14)+$ $\nu C_{39}C_{38}(12)$
30	1644	1582			5.16	8.21	4.05	83.33	$\nu C_{24}C_{25}(12)+$ $\nu C_{29}C_{26}(15)+$ $\nu C_{31}C_{29}(15)+$ $\nu C_{25}C_{27}(21)$
31	1640	1577			7.25	11.48	35.95	510.68	$\nu C_{24}C_{26}(11)+$ $\nu C_{27}C_{31}(24)$
32	1576	1516			2.06	3.01	344.24	594.41	$\nu C_{43}C_{45}(11)+$ $\nu C_{41}C_{45}(24)+$ $\nu C_{38}C_{40}(15)$
33	1542	1483	1487	1483	1.70	2.38	30.54	28.14	$\nu N_{34}C_{35}(10)+$
34	1535	1477			1.97	2.73	264.16	428.26	$\beta H_{36}N_{34}C_{27}(41)$
35	1534	1475			1.13	1.57	41.65	50.38	$\beta H_{53}C_{48}H_{54}(29)$
36	1526	1468			1.66	2.28	235.10	21.90	$\beta H_{28}C_{25}C_{27}(10)+$ $\beta H_{32}C_{29}C_{31}(18)+$ $\beta H_{53}CH_{54}(12)$
37	1513	1456			1.05	1.42	1.04	34.51	$\beta H_{19}C_{17}H_{20}(55)+$ $\beta H_{22}C_{18}H_{23}(14)$
38	1507	1449			1.15	1.53	7.99	41.28	$\beta H_{53}C_{48}H_{54}(31)+$ $\beta H_{51}C_{49}H_{52}$
39	1501	1444			1.06	1.40	7.38	60.58	$\beta H_{19}C_{17}H_{20}(14)+$ $\beta H_{22}C_{18}H_{23}(51)$
40	1501	1444	1444		1.13	1.49	5.38	54.38	$\beta H_{11}C_{10}H_{13}(16)+$ $\beta H_{12}C_{10}H_{13}(38)+$ $\Gamma C_{10}H_{11}C_1H_{13}(14)$
41	1499	1442		1441	1.89	2.50	90.77	53.26	$\beta H_{21}C_{18}H_{22}(80)+$ $\Gamma C_{18}H_{21}C_{17}H_{22}(14)$ $\beta H_{51}C_{49}H_{52}(77)$ $\nu C_4O_9(10)+$

								$\nu\text{C}_5\text{N}_5(14)+$
								$\beta\text{H}_0\text{N}_5\text{C}_4(36)+$
42	1482	1426		1.14	1.48	33.98	50.47	$\beta\text{H}_{12}\text{C}_{10}\text{H}_{13}(12)$
								$\beta\text{H}_{11}\text{C}_{10}\text{H}_{13}(11)+$
								$\beta\text{H}_{11}\text{C}_{10}\text{H}_{12}(47)+$
								$\beta\text{H}_{12}\text{C}_{10}\text{H}_{13}+$
43	1473	1417		4.69	5.99	2.12	59.00	$\Gamma\text{C}_{10}\text{H}_{11}\text{C}_1\text{H}_{12}(12)$
								$\nu\text{C}39\text{C}41(29)+$
								$\nu\text{C}40\text{C}43(24)+$
44	1468	1412		1.98	2.51	97.69	119.31	$\beta\text{H}_{44}\text{C}_{40}\text{C}_{43}(11)$
								$\beta\text{H}_6\text{N}_7\text{C}_3(13)+$
45	1448	1393	1390	2.00	2.47	101.46	51.19	$\Gamma\text{C}_3\text{C}_2\text{N}_7\text{H}_{50}(12)$
46	1438	1384		1.43	1.75	7.20	19.80	$\beta\text{H}_6\text{N}_7\text{C}_3(28)$
								$\beta\text{H}_{20}\text{C}_{17}\text{C}_{18}(10)+$
								$\beta\text{H}_{21}\text{C}_{18}\text{C}_{17}(20)+$
								$\Gamma\text{C}_{18}\text{H}_{22}\text{C}_{17}\text{H}_{23}(31)$
47	1430	1375		1.23	1.48	19.51	52.46	$\beta\text{H}_{11}\text{C}_{10}\text{H}_{13}(60)+$
								$\beta\text{H}_{11}\text{C}_{10}\text{H}_{12}(27)$
48	1408	1355		1.93	2.26	33.84	17.56	$\nu\text{C}_4\text{N}_7(10)$
49	1407	1354		1.66	1.94	98.69	16.91	$\beta\text{H}_6\text{N}_7\text{C}_3(13)$
50	1404	1351	1337	1.60	1.85	2.94	21.67	$\nu\text{C}_{45}\text{O}_{47}(10)+$
								$\beta\text{H}_{53}\text{C}_{48}\text{O}_{47}(38)+$
								$\Gamma\text{H}_{51}\text{C}_{49}\text{C}_{48}\text{H}_{54}(13)$
51	1368	1316	1323	3.29	3.63	36.45	233.80	$\nu\text{C}_{26}\text{C}_{29}(13)+$
								$\nu\text{C}_{24}\text{C}_{26}(10)+$
								$\nu\text{C}_{27}\text{C}_{31}(12)+$
								$\beta\text{H}_{28}\text{C}_{25}\text{C}_{27}(12)+$
								$\beta\text{H}_{30}\text{C}_{26}\text{C}_{29}(11)$
52	1366	1314		6.55	7.20	22.41	122.06	$\nu\text{C}_{43}\text{C}_{45}(21)+$
								$\nu\text{C}_{38}\text{C}_{40}(23)+$
								$\nu\text{C}_{38}\text{C}_{39}(19)$
53	1358	1306		1.56	1.69	160.60	114.97	$\beta\text{H}_{33}\text{C}_{31}\text{C}_{27}(14)+$
								$\beta\text{H}_{28}\text{C}_{25}\text{C}_{27}(16)+$
								$\beta\text{H}_{32}\text{C}_{29}\text{C}_{31}(12)+$
								$\Gamma\text{C}_3\text{C}_2\text{N}_7\text{H}_{50}(24)$
54	1351	1299	1289	2.60	2.80	178.93	50.18	$\nu\text{C}_2\text{C}_{14}(18)+$
								$\beta\text{H}_{50}\text{C}_3\text{C}_2(11)$
55	1324	1274		1.63	1.68	31.41	447.21	$\nu\text{N}_{34}\text{C}_{27}(11)+$
								$\Gamma\text{C}_3\text{C}_2\text{N}_7\text{H}_{50}(30)$
56	1319	1269		1.46	1.49	16.16	144.77	$\beta\text{H}_{42}\text{C}_{39}\text{C}_{38}(17)+$
								$\beta\text{H}_{44}\text{C}_{40}\text{C}_{43}(17)+$
								$\beta\text{H}_{46}\text{C}_{43}\text{C}_{45}(12)+$
								$\Gamma\text{H}_{52}\text{C}_{49}\text{C}_{41}\text{C}_{45}(11)$
57	1298	1249	1251	2.61	2.59	82.11	19.53	$\nu\text{N}_{34}\text{C}_{27}(10)+$
								$\Gamma\text{H}_{52}\text{C}_{49}\text{C}_{41}\text{C}_{45}(16)$
58	1296	1247		1.10	1.09	0.58	41.96	$\beta\text{H}_{20}\text{C}_{17}\text{C}_{18}(37)+$
								$\Gamma\text{H}_{19}\text{C}_{17}\text{O}_{15}\text{C}_{14}(24)+$
								$\Gamma\text{C}_{18}\text{H}_{21}\text{C}_{17}\text{H}_{22}(17)+$
								$\Gamma\text{C}_{14}\text{O}_{15}\text{C}_{17}\text{C}_{18}$
59	1288	1239		2.12	2.07	39.44	38.46	$\nu\text{N}_5\text{C}_1(23)+ \beta\text{H}_8\text{N}_5\text{C}_4(27)$

60	1284	1236		1236	1.89	1.84	156.18	258.43	$\beta H_{46}C_{43}C_{45}(10)+$ $\Gamma H_{52}C_{49}C_{41}C_{45}(14)$
61	1280	1231	1234		2.35	2.27	172.59	1161.76	$\nu C_{25}C_{27}(14)+$ $\nu N_{34}C_{27}(13)+$ $\beta H_{36}N_{34}C_{27}(10)$
62	1267	1219			2.13	2.01	66.96	279.05	$\nu O_{47}C_{45}(15)+$ $\nu C_{35}C_{38}(12)$
63	1264	1216			2.35	2.22	415.90	157.41	$\beta H_{50}C_3C_2(36)$
64	1236	1189			1.23	1.11	47.46	124.95	$\beta H_{42}C_{39}C_{41}(12)+$ $\Gamma H_{54}C_{48}O_{47}C_{45}(39)$
65	1213	1167	1165	1171	1.23	1.07	1.16	31.87	$\beta H_{53}C_{48}O_{47}(19)+$ $\beta H_{51}C_{49}C_{48}(40)+$ $\Gamma H_{52}C_{49}C_{41}C_{39}(17)$
66	1205	1159			1.13	0.97	1.10	82.39	$\beta H_{33}C_{31}C_{19}(19)+$ $\beta H_{30}C_{26}C_{29}(22)+$ $\beta H_{31}C_{29}C_{31}(33)$
67	1193	1147			1.97	1.65	11.42	40.76	$\nu C_{24}C_{25}(10)+$ $\nu C_3C_{24}(18)+$ $\beta H_{28}C_{25}C_{27}(18)$
68	1185	1140			1.54	1.28	3.77	6.49	$\Gamma H_{20}C_{17}O_{15}C_{14}(55)+$ $\Gamma H_{22}C_{18}C_{17}O_{15}(24)$
69	1179	1135			1.75	1.43	14.08	9.56	$\nu C_{41}C_{49}(14)+$ $\beta H_{44}C_{40}C_{43}(15)+$ $\beta H_{46}C_{43}C_{45}$
70	1149	1105		1112	2.51	1.95	19.68	8.61	$\nu N_3C_3(28)+$ $\beta H_{50}C_3C_2(12)$
71	1144	1101	1093		2.62	2.02	14.68	46.80	$\nu O_{15}C_{14}(10)+$ $\nu C_{17}C_{18}(13)+$ $\beta H_{21}C_{18}H_{23}(10)+$ $\beta C_{18}C_{17}O_{15}(12)+$ $\Gamma H_{23}C_{18}C_{17}O_{15}(19)$
72	1134	1091			2.13	1.62	114.01	44.08	$\beta H_{12}C_{10}H_{13}(13)+$ $\Gamma H_{12}C_{10}C_1N_5(68)$
73	1131	1088		1086	2.81	2.11	75.03	50.23	$\nu C_{24}C_{25}(10)+$ $\nu C_3C_{24}(18)+$ $\beta H_{28}C_{25}C_{27}(18)$
74	1123	1080			1.70	1.26	7.69	4.03	$\nu C_{26}C_{29}(22)+$ $\nu C_{29}C_{31}(21)+$ $\beta H_{33}C_{31}C_{29}(23)+$ $\beta H_{30}C_{26}C_{29}(12)$
75	1110	1067			2.58	1.87	103.62	26.14	$\nu C_{38}C_{40}(12)+$ $\beta H_{42}C_{39}H_{41}(10)$
76	1101	1060			3.08	2.20	225.64	44.00	$\nu O_{15}C_{14}(10)+$ $\nu O_{15}C_{17}(14)$
77	1079	1038	1029	1025	1.62	1.11	2.70	3.69	$\Gamma H_{53}C_{48}O_{47}C_{45}(14)+$ $\Gamma H_{51}C_{49}C_{41}C_{39}(55)$
78	1056	1016			1.54	1.01	7.53	5.18	$\beta H_{12}C_{10}H_{13}(13)+$ $\Gamma H_{12}C_{10}C_1N_5(68)$
79	1045	1005			2.47	1.59	1.77	28.73	$\nu C_{17}C_{18}(33)+$ $\nu O_{15}C_{17}(15)+$

80	1021	983	987	999	1.95	1.20	19.09	2.23	$\Gamma H_{13}C_{10}C_1N_5(14)$ $\nu C_{17}C_{18}(12)+$
81	1013	974			6.12	3.70	0.55	422.75	$\Gamma H_{13}C_{10}C_1N_5(31)$ $\nu C_{24}C_{26}(12)+$ $\beta C_{24}C_{26}C_{29}(15)+$ $\beta C_{26}C_{29}C_{31}(28)+$ $\beta C_{25}C_{24}C_{26}(23)$
82	1010	972			6.23	3.75	69.39	12.40	$\nu C_{48}C_{49}(21)+$ $\nu O_{47}C_{48}(55)$
83	994	956		950	1.28	0.74	0.60	3.31	$\Gamma H_{33}C_{31}C_{29}C_{26}(61)+$ $\Gamma H_{30}C_{26}C_{29}C_{31}(23)$
84	978	941			1.31	0.74	2.88	19.84	$\Gamma H_{44}C_{40}C_{43}C_{45}(70)+$ $\Gamma H_{46}C_{43}C_{45}C_{41}(23)$
85	967	930	937		2.77	1.52	7.48	20.22	$\nu C_{48}C_{49}(27)+$ $\nu O_{47}C_{48}(10)$
86	959	922			3.27	1.77	16.15	8.69	$\nu C_{48}C_s(23)$
87	951	915			3.76	2.00	23.86	8.85	$\nu N_5C_4(14)+$ $\nu C_1C_{10}(10)$
88	925	890			3.28	1.65	3.04	16.07	$\beta N_{34}C_{35}O_{37}(20)+$ $\beta C_{39}C_{38}C_{40}(15)+$ $\beta C_{27}N_{34}C_{35}(10)$
89	920	885			1.47	0.73	4.53	3.21	$\Gamma H_{33}C_{31}C_{29}C_{26}(22)+$ $\Gamma H_{30}C_{26}C_{29}C_{31}(57)$
90	908	874			1.52	0.74	32.03	32.79	$\Gamma H_{28}C_{25}C_{27}N_{34}(76)$
91	900	866			1.48	0.71	4.82	13.57	$\Gamma H_{42}C_{39}C_{41}C_{49}(74)$
92	889	855			2.52	1.17	3.18	81.44	$\nu O_{15}C_{17}(30)+$ $\beta H_{21}C_{18}H_{23}(18)$
93	871	837	846		3.95	1.76	2.63	15.60	$\beta N_{34}C_{35}O_{37}(20)+$ $\beta C_{39}C_{38}C_{40}(15)+$ $\beta C_{27}N_{34}C_{35}(10)$
94	856	824			2.11	0.91	18.73	8.51	$\Gamma H_{46}C_{43}C_{45}C_{41}(35)$
95	853	821			4.06	1.74	0.34	10.88	$\beta O_{15}C_{14}O_{16}(18)+$ $\beta N_5C_4N_7(10)+$ $\Gamma H_{46}C_{43}C_{45}C_{41}(11)$
96	848	815			1.84	0.78	4.83	65.50	$\Gamma H_{46}C_{43}C_{45}C_{41}(23)+$ $\Gamma H_{45}C_{48}O_{47}C_{45}(11)$
97	831	799		800	2.31	0.94	10.79	59.22	$\Gamma H_{32}C_{29}C_{31}C_{27}(36)$
98	815	784			3.10	1.21	9.29	158.91	$\nu C_{41}C_{49}(16)$
99	814	783	771		1.12	0.44	0.38	5.93	$\beta H_{20}C_{17}C_{18}(13)+$ $\Gamma H+C_{17}O_{15}C_{14}(19)+$ $\Gamma H_{20}C_{17}O_{15}C_{14}(11)+$ $\Gamma H_{22}C_{18}C_{17}O_{15}(41)$
100	796	766			2.29	0.85	34.53	78.66	$\Gamma H_{32}C_{29}C_{31}C_{27}(35)$
101	785	755		750	5.62	2.04	11.12	42.03	$\nu C_1C_{10}(10)+ \nu C_2C_{23}(17)$
102	760	731			7.17	2.44	0.83	21.46	$\Gamma O_{37}C_{38}N_{34}C_{35}(10)+$ $\Gamma O_{16}C_2O_{15}C_{14}(38)+$ $\Gamma O_9N_7N_4C_4(17)$
103	759	730			5.86	1.99	25.08	60.96	$\Gamma O_{37}C_{38}N_{34}C_{35}(44)+$ $\Gamma O^9N_7N_4C_4(11)$
104	751	723			8.35	2.78	52.34	43.12	$\Gamma O_{16}C_2O_{15}C_{14}(14)+$

105	716	689			2.41	0.73	13.52	8.39	$\Gamma O_0 N_5 N_7 C_4(60)$ $\Gamma C_{26} C_{24} C_{29} C_{31}(16)+$ $\Gamma C_{27} C_{31} C_{26} C_{29}(34)+$ $\Gamma C_{24} C_{25} C_{26} C_{29}(23)$
106	711	684	694		5.09	1.52	1.90	25.18	$\Gamma O_{37} C_{38} N_3 C_{35}(16)+$ $\Gamma C_{41} C_{43} O_{47} C_{45}(24)$
107	695	669		676	4.25	1.21	7.98	58.21	$\beta C_{40} C_{43} C_{45}(14)+$ $\beta C_{45} O_{47} C_{48}(34)$
108	684	658			4.39	1.21	0.60	35.17	$\beta C_{41} C_{49} C_{48}(19)$
109	678	652			5.16	1.40	11.68	27.12	$\beta C_{41} C_{49} C_{48}(20)$
110	648	623	623	622	4.32	1.07	6.19	28.55	$\beta C_{25} C_{24} C_{26}(12)$
111	636	612			4.62	1.10	21.04	23.97	$\beta N_5 C_4 O_9(20)+$ $\beta O_{15} C_{14} O_{16}(12)$
112	626	602		600	2.01	0.46	94.45	23.86	$\Gamma H_8 N_5 C_4 N_7(13)+$ $\Gamma H_6 N_5 C_4 N_5(19)+$ $\Gamma C_{10} C_2 N_5 C_1(14)$
113	613	589			4.00	0.88	32.81	53.81	$\beta C_{24} C_{26} C_{29}(15)$
114	588	565	561	570	2.65	0.54	23.78	61.39	$\nu C_{43} C_{45}(10)+$ $\beta C_{40} C_{43} C_{45}(17)+$ $\Gamma H_{36} N_{34} C_{35} C_{38}(23)$
115	578	556			2.31	0.45	8.69	26.03	$\Gamma H_{36} N_{34} C_{35} C_{38}(24)+$ $\Gamma N_{34} C_{27} C_{31} C_{25}(12)$
116	571	549			1.81	0.35	72.48	12.24	$\Gamma H_6 N_7 C_4 N_5(12)+$ $\Gamma H_{36} N_{34} C_{35} C_{38}(34)$
117	549	528			3.06	0.54	17.19	32.38	$\Gamma H_8 N_5 C_4 N_7(21)$
118	545	525			3.56	0.62	11.67	13.39	$\Gamma C_{38} C_{40} C_{45} C_{43}(19)$
119	537	517	516	516	1.62	0.28	3.28	51.78	$\Gamma H_8 N_5 C_4 N_7(21)+$ $\Gamma H_6 N_7 C_4 N_5(33)$
120	517	497			3.13	0.49	7.99	63.81	$\nu N_5 C_4(12)+C_1 C_{10}(11)+$ $\beta C_1 N_5 C_4(20)+$ $\Gamma H_8 N_5 C_4 N_7(25)$
121	466	449	459	457	3.51	0.45	7.99	8.60	$\Gamma C_{26} C_{24} C_{29} C_{31}(27)+$ $\Gamma N_{34} C_{27} C_{31} C(14)$
122	451	434			5.25	0.63	12.79	17.07	$\Gamma C_{38} C_{40} C_{45} C_{43}(13)+$ $\Gamma C_{43} C_{48} C_{45} O_{47}(19)$
123	447	430			5.55	0.65	9.56	14.18	$\beta N_5 C_4 O_9(20)+$ $\beta C_2 C_{14} O_{15}(20)+$ $\beta C_{18} C_{17} O_{15}(15)$
124	428	412			3.08	0.33	0.75	23.29	$\Gamma C_{38} C_{40} C_{45} C_{43}(27)+$ $\Gamma C_{38} C_{40} C_{39} C_{41}(28)+$ $\Gamma C_{43} C_{48} C_{45} O_{47}(10)$
125	416	400		393	4.83	0.49	1.77	18.03	$\beta C_{24} C_{26} C_{29}(10)+$ $\beta C_{31} C_{27} N_{34}(12)$
126	392	377			4.79	0.43	3.59	44.26	$\beta O_{15} C_{14} O_{16}(20)+$ $\beta C_{18} C_{17} O_{15}(26)$
127	387	372			5.89	0.52	11.59	81.31	$\beta C_{49} C_{48} O_{47}(12)$
128	373	359			6.11	0.50	0.05	41.54	$\beta C_2 C_3 C_{24}(13)+$ $\Gamma C_{14} C_1 C_3 C_2(19)$
129	346	333		330	3.34	0.24	7.11	14.17	$\beta C_{10} C_1 N_5(55)$
130	322	310			7.55	0.46	5.87	56.24	$\beta C_{49} C_{48} O_{47}(18)+$

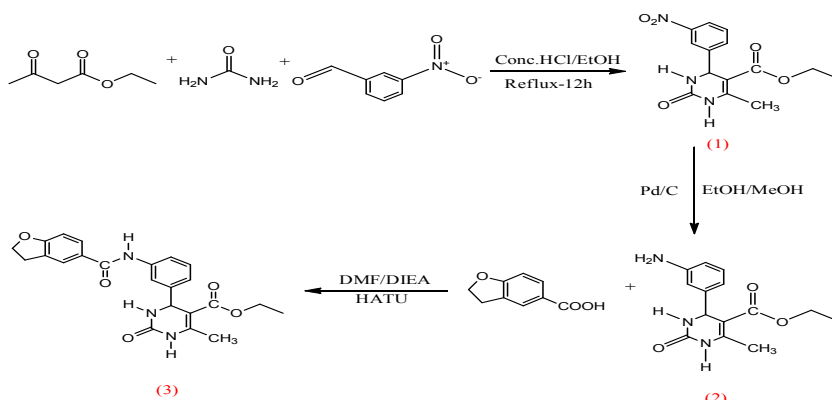
131	310	298		5.97	0.34	0.56	44.79	$\Gamma C_{35}C_{39}C_{40}C_{38}(23)$ $\Gamma N_{34}C_{27}C_{31}C_{25}(12)+$
132	301	289		4.92	0.26	10.03	37.90	$\Gamma C_{24}C_2C_3N_7(12)$ $\nu C_2C_{14}(12)+$ $\beta C_1C_2C_{14}(18)+$ $\beta C_{14}O^{15}C_{17}(28)$
133	271	261	260	1.63	0.07	1.25	10.76	$\Gamma H_{21}C_{18}C_{17}O_{15}(64)$
134	267	257		3.62	0.15	1.68	43.84	$\beta C_{35}C_{38}C_{40}(12)+$ $\Gamma H^{21}C^{18}C^{17}O_{15}(12)$
135	250	240		4.38	0.16	2.28	42.44	$\Gamma C_{26}C_{24}C_{29}C_{31}(10)$
136	244	235		4.29	0.15	5.68	54.36	$\Gamma N_{34}C_{27}C^{31}C^{25}(12)+$ $\Gamma C_{24}C_2C^3N_7(12)$
137	220	212	213	4.84	0.14	3.86	45.15	$\Gamma C_{14}C_1C_3C_2(12)+$ $\Gamma C_3C_{25}C_{26}C_{24}(12)$
138	203	195		3.19	0.08	4.46	113.42	$\beta C_{49}C_{48}O_{47}(18)+$ $\Gamma C^{43}C_{48}C_{45}O_{47}(10)+$ $\Gamma C_{45}O_{47}C^{49}C_{48}(35)$
139	193	185		6.31	0.14	2.73	93.72	$\nu C_{35}C_{38}(10)+$ $\beta C_{27}N_{34}C_{35}(21)$
140	166	160		4.27	0.07	2.88	77.98	$\Gamma C_1C_2N_5C_4(31)+$ $\Gamma N_5C_1C_4N_7(10)+$ $\Gamma C_{10}C_2N_5C_1(28)$
141	150	145		5.73	0.08	1.64	96.40	$\beta C_{35}C_{38}C_{40}(20)+$ $\beta C_3C_{24}C_{26}(16)$
142	143	138		1.71	0.02	0.89	30.25	$\Gamma H_{11}C_{10}C_1N_5(41)$
143	136	131		3.37	0.04	1.43	80.22	$\Gamma H_{11}C_{10}C_1N_5(13)+$ $\Gamma C_{35}C_{39}C_{40}C_{38}(21)$
144	122	117		2.30	0.02	2.38	3.04	$\Gamma C_2C_{14}O_{15}C_{17}(55)$
145	104	100		4.54	0.03	1.22	15.93	$\beta C_1C_{14}O_{15}(14)+$ $\beta C_1C_2C_{14}(10)+$ $\Gamma C_3C_2C_{14}O_s(18)$
146	95	91		2.60	0.01	0.87	21.34	$\beta C_2C_{14}O_{15}(16)+$ $\beta C_1C_2C_{14}(14)+$ $\beta C_{14}O_{15}C_{17}(11)+$ $\Gamma H_{11}C_{10}C_1N_5(17)$
147	86	83		2.98	0.01	1.05	66.56	$\Gamma C_3C_2C_{14}O_{15}(14)+$ $\Gamma C_{14}O_{15}C_{17}C_{18}(10)+$ $\Gamma C_{49}C_{41}C_{48}O_{47}(22)$
148	78	75	72	5.28	0.02	3.00	142.62	$\Gamma C_{31}C_{27}N_{34}C_{35}(24)+$ $\Gamma C_{39}C_{38}C_{35}N_{34}(32)$
149	71	68		4.58	0.01	0.16	148.53	$\Gamma C_3N_7N_5C_4(30)+$ $\Gamma N_5C_1C_4N_7(10)+$ $\Gamma C_{14}O_{15}C_{17}C_{18}(13)+$ $\Gamma C_{14}C_1C_3C_2(10)$
150	61	59		3.84	0.01	1.26	708.05	$\beta C_2C_3C_{24}(12)+$ $\Gamma C_3N+N_5C_4(12)+$ $\Gamma N_5C_1C_4N_7(23)$
151	55	53		3.79	0.01	0.53	528.82	$\Gamma C_3N_7N_5C_4(12)+$ $\Gamma C_{39}C_{38}C_{35}N_{34}(12)+$ $\Gamma C_{14}O_{15}C_{17}C_{18}(26)+$

152	41	39	5.57	0.01	0.20	314.84	$\Gamma C_3 C_{25} C_{26} C_{24}$ (10) $\beta C_{36} C_{35} N_{34}$ (12)+ $\beta C_{35} C_{36} C_{40}$ (11)+ $\Gamma C_{27} N_{34} C_{35} C_{38}$ (30)
153	35	33	5.01	0.00	0.29	80.35	$\beta C_{36} C_{35} N_{34}$ (11)+ $\Gamma C_3 C_2 C_{14} O^{15}$ (10)+ $\Gamma C_{27} N_{34} C_{35} C_{38}$ (13)+ $\Gamma C_{35} C_{39} C_{40} C_{38}$ (14)
154	22	22	4.17	0.00	0.08	213.64	$\Gamma C_3 C_2 C_{14} O_{15}$ (24)
155	15	14	4.36	0.00	1.23	3609.16	$\Gamma C_{31} C_{27} N_{34} C_{35}$ (43)+ $\Gamma C_{39} C_{36} C_{35} N_{34}$ (19)+ $\Gamma C^3 C_{25} C_{26} C_{24}$ (12)
156	7	7	5.63	0.00	0.45	2634.48	$\Gamma C_{27} N_{34} C_{35} C^{38}$ (12)+ $\Gamma C_2 C_3 C_{24} C_{26}$ (69)

Table 4: The Non-Linear Optical properties of DFOC

Parameters	Dipole moment (μ) Debye	Parameters	Hyperpolarisability (β_0) $\times 10^{-30}$ esu
μ_x	0.0929	β_{xxx}	-166.94
μ_y	2.5466	β_{xxy}	-288.55
μ_z	0.2333	β_{xyy}	-15.31
μ	2.5589 Debye	β_{yyy}	217.85
Parameters	Polarizability	β_{xxz}	-390.22
α_{xx}	384.08	β_{xyz}	-129.96
α_{xy}	55.88	β_{yyz}	29.35
α_{yy}	270.34	β_{xzz}	38.53
α_{xz}	0.58	β_{yzz}	-41.91
α_{yz}	30.13	β_{zzz}	74.22
α_{zz}	197.54	β_0	2.936 $\times 10^{-30}$ esu
α	6.308 $\times 10^{-30}$ esu		

Standard value for urea ($\mu=1.3732$ Debye, $\beta_0=0.3728 \times 10^{-30}$ esu): esu-electrostatic unit



Scheme1: The reaction scheme for synthesis of DFOC

1592 cm^{-1} in FT-Raman spectrum. In our present study, the bands computed at 1101, 1088 cm^{-1} are assigned to trigonal bending and breathing mode of the phenyl ring and these bands shows good agreement with experimental FT-IR bands at 1093 cm^{-1} , and FT-Raman bands at 1086 cm^{-1} .

Ring 3

In the present study, N–H stretching modes are observed at 3270, 3210 cm^{-1} for dihydropyrimidine³². The $\nu_{\text{N}_5-\text{H}_8}, \nu_{\text{N}_7-\text{H}_6}$ stretching modes are observed at 3369 and 3277 cm^{-1} respectively in FT-IR. The lower in frequencies in solid

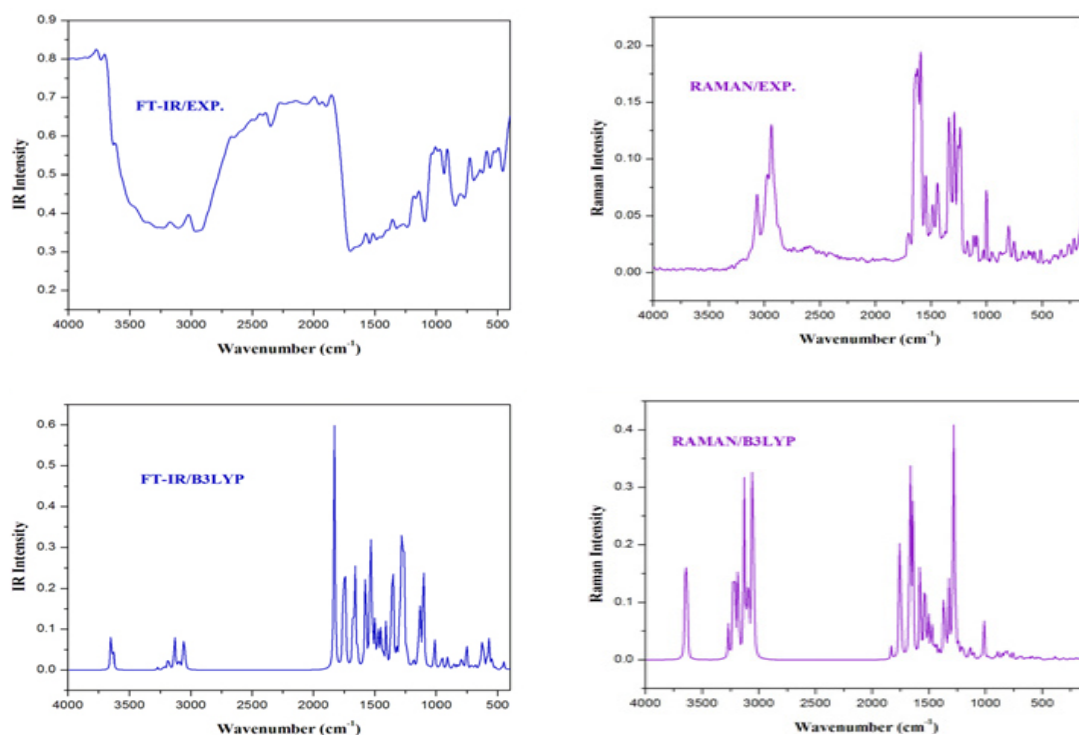


Fig. 2 & 3: The recorded and calculated FT-IR spectra of DFOC

Table 5: The global reactivity descriptors of DFOC

Molecular properties	B3LYP
6-31G(d,p)	
E HOMO (eV)	-5.7239
E LUMO (eV)	-1.1473
E (HOMO-LUMO) (eV)	4.5765
E HOMO-1(eV)	-6.0616
E LUMO+1(eV)	-0.8624
E (HOMO-1-LUMO+1) (eV)	5.1992
Ionization potential (I)	5.7239
Chemical hardness(η)	2.2882
Electronegativity(χ)	3.4356
Electron affinity(A)	1.1473
Chemical potential (μ)	-3.4356
Electrophilicity (Ψ)	2.5791

phase may attribute due to resonance delocalization of dihydropyrimidine ring. The C–N stretching absorption in the region 1382–1266 cm^{-1} 33. The C–N stretching vibration coupled with scissoring of N–H is moderately active in the region 1275 \pm 55 cm^{-1} 34. For the pyrimidine ring, the four $\nu_{\text{C-N}}$ stretching vibrations are identified with the help of PED analysis. The C–N stretching wavenumbers are calculated at 1335 and 1216 cm^{-1} . In pyrimidine molecule C=C stretching observed at 1645 cm^{-1} and 1650–1710 cm^{-1} . In our present investigation the C1=C2 stretching vibration occurs at 1544 cm^{-1} in FT-IR and 1546 cm^{-1} in FT-Raman spectrum. The magnitude of C=C stretching frequency is lower than the expected value is due to presence of carboxylate substituent in the neighbouring atom. The π electron conjugated with the carboxylate group. Generally the carbonyl groups are appeared in the region 1700-1660

Table S6: ¹H and ¹³C NMR Spectral analysis of DFOC

Position of Hydrogen atom	Observed values	Calculated values	Position of Carbon	Observed values	Calculated values
H33	7.85	9.29	C14	165.31	167.30
H44	7.84	8.26	C45	162.50	164.16
H42	7.67	7.56	C35	165.05	163.49
H28	7.67	7.52	C4	151.95	149.13
H32	7.63	7.50	C1	148.20	147.85
H30	7.25	7.14	C24	145.36	145.04
H36	10.04	7.0	C27	139.49	140.84
H46	6.86	6.94	C40	130.52	132.76
H50	5.11	5.62	C29	128.62	129.30
H8	9.16	5.29	C38	127.88	129.23
H54	4.63	4.75	C41	124.89	126.54
H53	4.61	4.61	C39	121.50	119.80
H20	4.00	4.33	C26	119.62	117.48
H19	3.98	4.22	C31	118.26	117.09
H6	7.94	4.05	C25	108.62	114.30
H52	3.31	3.41	C43	108.38	109.15
H51	3.23	3.11	C2	99.41	103.72
H13	2.24	2.75	C48	71.90	71.96
H11	2.24	2.59	C17	59.16	61.49
H23	1.11	1.47	C3	54.25	56.95
H22	1.10	1.42	C49	28.55	30.27
H21	1.08	1.16	C10	28.36	21.71
H12	2.24	1.01	C18	17.79	12.31

Table S7: The oscillator strength and excitation energies of DFOC

Orbitals	Energy gap	Theoretical	Experimental	
Excited State 1: Singlet-A		4.0339 eV	307.35 nm	f=0.0031
110 → 112	-0.13451			
111 → 112	0.6859			
Excited State 2: Singlet-A		4.3568 eV	284.57 nm	f=0.5006
107 → 113	0.12215			282.60
111 → 113	0.65147			
Excited State 3: Singlet-A		4.5507 eV	272.45 nm	f=0.0101
107 → 113	-0.47265			
110 → 112	0.34942			
110 → 113	-0.26407			
111 → 113	0.15312			

cm^{-1} ^{35, 36}. The carbonyl absorption in FT-IR is sensitive for both C and O atoms. The stretching vibration of $\nu_{\text{C}_{14}=\text{O}_{16}}$ is observed as strong band at 1643 cm^{-1} in FT-IR assured the carbonyl group of the ester. These $\nu_{\text{C}_{14}=\text{O}_{16}}$ stretching frequencies is below the expected range, because the conjugation

of the $\text{C}_{14}=\text{O}_{16}$ bond with pyrimidine ring which may increase its single bond character, resulting in lowered values of carbonyl stretching wavenumber. Generally, in esters, the intense $\nu_{\text{O}_{15}\text{C}_{14}}$ and $\nu_{\text{O}_{15}\text{C}_{17}}$ stretching vibration wavenumber appeared at 1112 and 999 cm^{-1} in FT-Raman. Because the

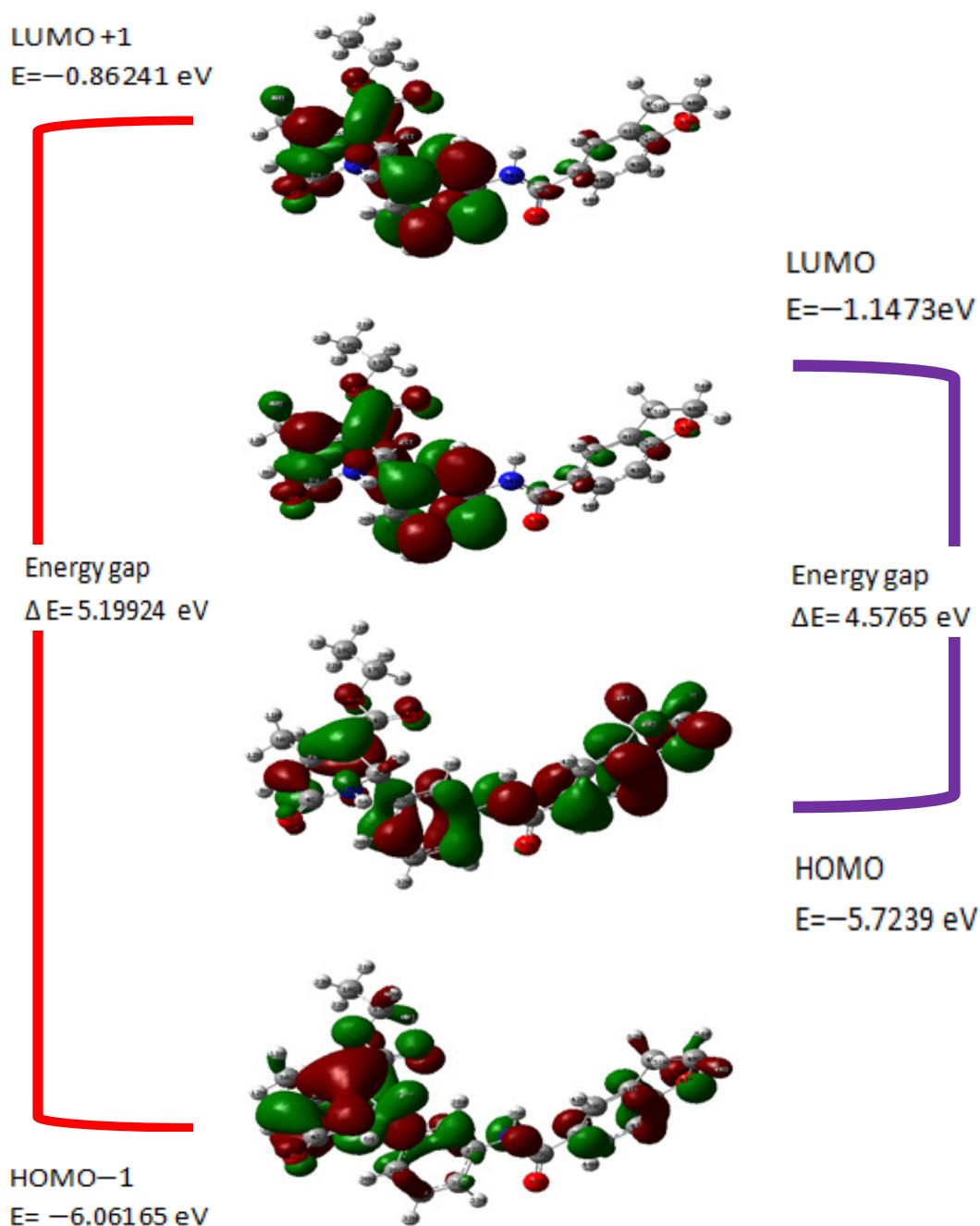


Fig. 4: The frontier molecular orbitals of DFOC

of PED contribution. The C–H stretching mode of C–H bond linked to the phenyl group because the C_3 carbon atom in SP^3 hybridization.

Nonlinear optical property

Nonlinear optical material has vast applications in the field of telecommunication, optical interconnections and optical memory for emerging technology in the area of signal processing^{40,41}. In the present study, NLO property of the title molecule has been theoretically predicted and the results are present in the Table 4. From the results, the total dipole moment of the title molecule (2.5589 Debye) is mainly attributed to an overall imbalance in charge. The first hyperpolarizability are calculated about 2.936×10^{-30} esu. The β_0 value of the title compound is six times greater than that of standard urea. Urea is one of the prototypical molecules used in the study of the NLO properties of molecular systems. Hence the investigated molecule a good nonlinear optical material.

Frontier molecular orbital analysis

The frontier molecular orbital analysis (FMOs) were mainly used to predict chemical reactivity, stability and biological implications of a molecular system⁴². predicting the most reactive position in π -electron systems and also explained several types of reactions in conjugated system⁴³. As can be seen from the figure 4 HOMO is located on dihydrobenzofuran and partially over pyrimidine ring. By contrast, LUMO is located over dihydropyrimidine with carboxylate side chain of DFOC molecule. Hence, electron delocalization mainly takes place in carboxamide moiety and is also evident from

enormous stabilization energy of -CONH from NBO analysis. The small energy gap of $\Delta E = 4.5765$ eV is corresponding to the chemical reactivity of the molecule. The globule reactivity descriptors and ΔE values of DFOC is shown in table 5.

NMR-analysis

The NMR spectroscopy is currently used for structural analysis and functional group determination of biological macromolecules. The experimental and simulate NMR chemical shifts are presented in Table 6. The observed 1H and ^{13}C NMR spectra of the title molecule are given in Fig. 6. The chemical shift of carbon atom of bond -CONH is an important indicator to identification of carboxamido group. In our study the chemical shift of C35 was observed at 165.05 ppm in experimental observation and its theoretical shift at 163.49 ppm in B3LYP level. The another carbonyl carbon atoms C14 and C4, thus its NMR signal is observed to the downfield at 165.31 and 151.95 ppm which are theoretically calculated at 167.30 and 149.13 ppm respectively. The ring formation C3 atom predicted at 56.95 ppm shows good agreement with the experimental chemical shift at 54.25 ppm. Aromatic carbons give signals in overlapped areas of the spectrum with the chemical shift value lie in the range of 100-150 ppm 44, 45. The chemical shifts of benzofuran ring carbon atoms are assigned to region 162.50-108.38 ppm respectively. In the above results reveals that the chemical shift of C45 is observed at the downfield at 162.50 ppm due to delocalization of the lone pair electron from O47 to the C45=C43 in the benzofuran ring. The four free aromatic carbons in the phenyl ring shows a chemical shift value in the region 128.62

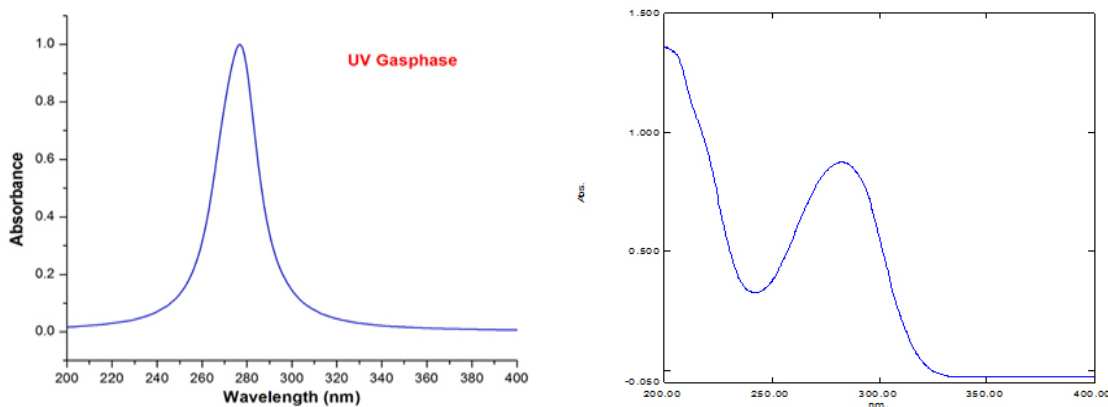


Fig. 7 : The experimental and simulated UV-spectra of DFOC molecule

-108.62 ppm from the experimental observation and 129.30 - 109.15 ppm are predicted B3LYP level. In addition, carboxamide and pyrimidine ring attached to the carbon atoms C₂₇ and C₂₄ shows signals at 145.36 and 139.49 ppm and its corresponding theoretically calculated at 145.04 and 140.84 ppm respectively.

In the above results reveals that the chemical shift of C₄₅ is observed at the downfield at 162.50 ppm due to delocalization of the lone pair electron from O₄₇ to the C₄₅=C₄₃ in the benzofuran ring. The four free aromatic carbons in the phenyl ring shows a chemical shift value in the region 128.62 - 108.62 ppm from the experimental observation and 129.30 - 109.15 ppm are predicted B3LYP level. In addition, carboxamide and pyrimidine ring attached to the carbon atoms C₂₇ and C₂₄ shows signals at 145.36 and 139.49 ppm and its corresponding theoretically δ -value calculated at 145.04 and 140.84 ppm respectively. The chemical shift of methylene carbon atoms C₄₈, C₄₉ and C₁₇ shows signals at 71.90, 28.55, and 59.16 ppm respectively. The carbon atoms C₄₈ and C₁₇ shows higher δ -value compared to the C₄₉ therefore both C₄₈ and C₁₇ carbon atoms can be attributed to the bond linked with the more electronegative oxygen atom. The least δ -value of 28.36 and 17.79 ppm observed for C₁₀ and C₁₈ atoms, because of the consequence of lower charge distribution, being favored by the part of effective atomic charges.

In the ¹H-NMR chemical shift of title molecule, a singlet at 10.04 ppm confirmed the presence of carboxamido moiety. Moreover, two singlets observed at 9.16 and 7.94 ppm are corresponding signals of two N₅-H₇₇ and N₇-H₉ protons of the dihydropyrimidinone ring. The multiples at 6.86 to 7.85 ppm for seven aromatic protons indicate the presence of benzene and benzofuran ring, which correlates to the calculated chemical shift at 6.94-9.29 ppm respectively. In addition, the singlet peak appeared at 2.24 ppm mark the methyl hydrogen in the dihydropyrimidinone ring, and another methyl proton observed at 1.16 - 1.46 ppm as triplet represents the ester group. As can be seen from Table 6, the theoretical chemical shift values are closer agreement with experimental results.

Molecular electrostatic potential

MEP is useful descriptors for determining the reactive sites and hydrogen bonding interactions of

the molecule.^{46,47} According to the calculated results the maximum positive region is localized on the N-H bonds (N₅-H₈, N₇-H₆, N₃₄-H₃₅), indicating a possible site for nucleophilic attack. The MEP map shows in fig. 5 that the negative potential sites are on electronegative carbonyl oxygen atoms (O₉, O₁₆ and O₃₇) and the positive potential sites are around the hydrogen atoms. These sites give information about the region from where the compound can have intermolecular interactions. This predicted the most reactive site for both electrophilic and nucleophilic attack.

UV analysis

In order to understand the electronic transitions of DFOC molecule were performed by TD-DFT method. From fig. 7 the absorption maximum of investigated molecule observed at 282 nm and this band is due to the $\pi \rightarrow \pi^*$ transition of the molecule. The intensity of the band is very high. The absorption maxima (284 nm) of DFOC is calculated, by TD-DFT/6-31G(d,p) level of theory. The predicted results involving the vertical excitation energies, oscillator strength (f) and wavelength are carried out and are listed in Table 7.

CONCLUSION

This work reports the synthesis and computational analysis of nonlinear molecule ethyl 4-(3-(2,3-dihydrobenzofuran-5-carboxamido)phenyl)-1,2,3,4-tetrahydro-6-methyl-2-oxopyrimidine-5-carboxylate. The structure was determined and characterized by UV-visible, FT-IR, FT-Raman and NMR spectral studies. The NBO results reveals the strong hyperconjugative interactions occurs in the molecule leads to the highest stabilization energy of of the molecular system. The investigated DFOC have small energy gap 4.5765 eV is responsible for the nonlinear optical activity. The first hyperpolarizability calculated as 2.936×10^{-30} esu, which is eight times greater than that of reference urea. The effect is even more important for nonlinear molecule with strong intramolecular charge transfer from electron donor group to electron acceptor group (D-II-A) interacting through a conjugated Π system. The UV-visible absorption analysis, mainly takes place $\Pi - \Pi^*$ transition of the title molecule. The charge sites are identified by the molecular electrostatic potential mapped surface.

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