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Iodinated 4(3IP)BC Coumarin Derivative Dipole Moments by a Solvatochromic Shift Method and DFT Approach

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Abstract

Iodinated coumarin derivative 4(3-Iodo-phenoxymethyl)-benzo[h]-chromen-2-one [4(3IP)BC] molecule, which is biologically active in anticancer and anti-tuberculosis properties, was synthesized to study the photophysical properties and the effect of the molecule in polar and nonpolar solvents at room temperature. Experimentally, the dipole moments of the ground state and excited state were estimated by the solvatochromic shift method using three independent Lippert's, Bakhshiev's, and Kawaski-Chamma-Viallet's equations. It was found that as the solvent polarity increases, the bathochromic shift occurs, which is a considerable red shift, and the excited state dipole moment was greater than that of the ground state dipole moment. The change of dipole moment was 2.43D by the solvatochromic method and 1.49D by the Reichardt microscopic solvent polarity parameter. The solvent effect on spectral characteristics was studied using the Kamlet and Catalan multiple linear regression method. The interactions of the dielectric of the solvent have more influence than hydrogen bonding operations, and polarizability, dipolarity and acidity have more influence than basicity. A theoretical computational study was performed with the Gaussian 16W program using the DFT/B3LYP approach. The HOMO-LUMO energies, ESP maps, Mulliken atomic charges, and nonlinear optical properties of the molecule were investigated **using an optimized geometry.**

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The UV-visible spectra with solvents were estimated using TD-DFT, and the change in dipole moments was **confirmed** with experimental values.

Keywords: Coumarin derivatives, Dipole moment, Stokes shift, Density Function Theory (DFT), Nonlinear optical properties (NLO)

1. Introduction

Among the oxygen heterocycles, coumarin derivatives are important motifs that widely **occur** in various natural products belonging to the benzopyrone family. They are recognized for biological activities like anticancer, antituberculosis, anti-inflammation, antioxidant, antimalarial, anti-HIV and antimicrobial properties [1-2]. In modern times, cancer has become a leading cause of death and an incurable illness that impacts various organs within the human body. Coumarin derivatives play a major role in medicinal chemistry **due to** their diverse biological activities, chemical versatility, and favourable pharmacokinetic properties. The significance of coumarin derivatives is that they are key molecular frameworks in medicinal chemistry due to their broad pharmacological spectrum, ease of chemical modification, potential as drug leads or scaffolds and compatibility with modern drug design approaches. They continue to inspire the development of next-generation therapeutics targeting a diverse **range** of diseases, **including** cardiovascular disorders, cancer, and neurodegenerative conditions. In the biologically active iodinated coumarin derivatives, iodine acts as a heavy halogen atom that can enhance the lipophilicity of the molecule. This leads to **improved** drug absorption and **enhanced** binding affinity for the hydrophobic regions of enzymes and receptors, without activating them, which demonstrates significant anticancer and anti-tuberculosis activity.

In the realm of scientific research, it pertains to investigating the photophysical properties of recently synthesized iodinated coumarin derivatives. In syntheses of a series of iodinated-4-aryloxymethyl coumarin, the author **studied** the 4(3-Iodo-phenoxymethyl)-benzo[h]-chromen-2-one (4(3IP)BC) molecule. The dipole moment of a molecule was evaluated by the solvatochromic shift method. Molecular absorption and emission spectra are useful tools for **investigating** Stokes shifts, **which reveal** how the electron distribution in molecules changes between the ground and excited states. These shifts are influenced by solvent polarity, hydrogen bonding capacity, electrostatic and non-electrostatic interactions. A bathochromic (red) shift indicates positive solvatochromism, while a hypsochromic (blue) shift indicates negative solvatochromism, depending on how the solute interacts with the solvent. When the solute molecule enters a cavity within the solvent, its ground state becomes more stable. When the solute's dipole moment increases as a result of an electron transition, it creates an excited

state within the cavity of **the** solvent and is partially surrounded by dipoles of **the** solvent. The increase in solvent polarity leads to a bathochromic (red) shift, where the stability of the excited state of the molecule is **greater** than **that** of the **ground state**. Compared to the ground state, the excited state is more polar. When the solute dipole moment decreases during the transition of an electron, the efficient stabilization of the excited state is hindered by an affected solvent cavity with improperly aligned dipoles. As the polarity of a solvent increases, a hypsochromic shift takes place, causing the ground state's energy to decrease more than the excited states, resulting in the ground state having a larger dipolar effect than the excited state [3-4].

In the present work, the ground and excited state dipole moment of 4(3IP)BC was studied using the Lippert, Bakhshiev and Kawaski-Chamma-Viallet equations using polar and nonpolar solvents experimentally. A theoretical quantum computational study was **conducted** using the Gaussian 16 software. The dipole moment, Mulliken charges, HOMO and LUMO molecular orbital energies, the electrostatic potential map (ESP) and nonlinear optical properties of the molecule were studied with optimized geometry using density function theory. The UV-visible spectra using TD-DFT in solvents were estimated theoretically.

2. Materials and Methods

The molecule of coumarin derivative, 4(3-Iodo-phenoxymethyl)-benzo [h]-chromen-2-one [4(3IP)BC], was synthesized by following the method outlined in reference [5]. Solutions are prepared by keeping the solute concentrations fixed at 10^{-6} M/L using a semi-microbalance (Sartorious CP 2245). Its molecular structure is presented in Figure 1. Various polar and nonpolar solvents, including methanol, ethanol, propanol, butanol, diethyl ether, tetrahydrofuran (THF), ethyl acetate (EAC), acetone, dimethylformamide (DMF), dimethyl sulfoxide (DMSO), acetonitrile, cyclohexane, toluene, 1-4 dioxane, and others, were used directly without purification to prepare samples, ensuring low concentration to reduce the self-absorption effects. UV-visible absorption spectra were measured using a Model T90+ spectrometer (PG Instruments Ltd.), and emission spectra were recorded using the Hitachi F7000 fluorescence spectrometer.

For theoretical computational **studies,** Gaussian 16W software supports simulations ranging from small molecules to complex macromolecules using various methods. Among all methods, the TD-DFT method, particularly the most efficient for excited-state geometry, was used. The key molecular properties, such as dipole moment, energies of HOMO and LUMO, atomic charges by the analysis of Mulliken population, electron density, distribution of charges in electrostatic potential maps, and NLO properties of the molecule, were also studied using the DFT/B3LYP/3-21G [6-9].

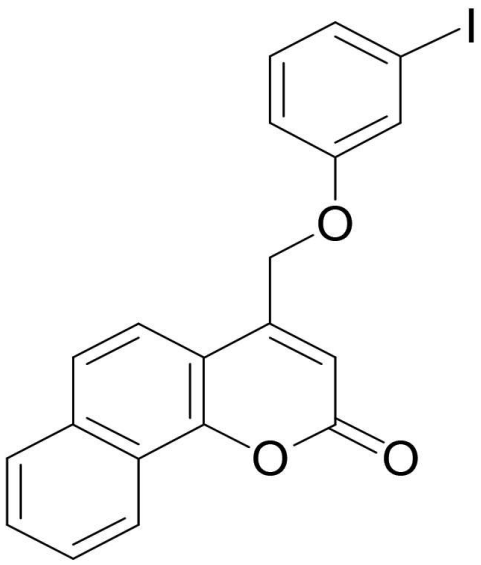

Figure 1: The structure of molecule 4(3IP)BC

2.1 The solvatochromic approach:

The solvatochromic approach of the 4(3IP)BC molecule in different solvents with changing 'n,' the refractive index, and 'ϵ,' the constant of dielectric, is utilized to estimate the dipole moments of the ground state and after excitation with three independent equations.

- Lippert's equation [10]

$$\overline{\nu_a} - \overline{\nu_f} = m_1 F_1(\epsilon, n) + constant \quad (1)$$

Bakhshiev's equation [11]

$$\overline{\nu_a} - \overline{\nu_f} = m_2 F_2(\epsilon, n) + constant \quad (2)$$

Kawaski-Chamma-Viallet's equation [12-13]

$$\frac{\overline{\nu_a} + \overline{\nu_f}}{2} = -m_3 F_3(\epsilon, n) + constant \quad (3)$$

where **the** maximum values of wave numbers for absorbing and emitting fluorescence are expressed in $cm^{-1}$and are denoted by $\overline{\nu_a}$ and $\overline{\nu_f}$ respectively. The variable 'n' is the refractive index of different solvents, and the respective 'ϵ' is the dielectric constant. The polarity parameters of the three equations are denoted as F_1 (ϵ,*n*), F_2 (ϵ,*n*) and F_3 (ϵ,*n*) and are given in equations (4), (5) and (6) respectively.

$$F_1(\epsilon, n) = \left[\frac{\epsilon - 1}{2\epsilon - 1} - \frac{n^2 - 1}{2n^2 + 1}\right] \quad (4)$$

$$F_2(\epsilon,n) = \left[\frac{\epsilon-1}{\epsilon+2} - \frac{n^2-1}{n^2+2}\right]\frac{(2n^2+1)}{(n^2+2)} \quad (5)$$

$$F_3(\epsilon,n) = \frac{(2n^2+1)}{2\,(n^2+2)}\left[\frac{\epsilon-1}{\epsilon+2} - \frac{n^2-1}{n^2+2}\right] + \frac{3\,(n^4-1)}{2\,(n^2+2)^2} \quad (6)$$

From equations (1), (2), and (3), linear graphs of ($\overline{\nu_a} - \overline{\nu_f}$) versus $F_1(\epsilon,n)$, ($\overline{\nu_a} - \overline{\nu_f}$) versus $F_2(\epsilon,n)$ and ($\overline{\nu_a} + \overline{\nu_f}$)/2 versus $F_3(\epsilon,n)$ provide slopes m_1, m_2, and m_3 in that proportion. They are listed below.

$$m_1 = \frac{2\,(\mu_e - \mu_g)^2}{\mathrm{h}ca^3} \quad (7)$$

$$m_2 = \frac{2\,(\mu_e - \mu_g)^2}{\mathrm{h}ca^3} \quad (8)$$

$$m_3 = \frac{2\,({\mu_e}^2 - {\mu_g}^2)}{\mathrm{h}ca^3} \quad (9)$$

where μ_g & μ_e represents ground and excited state dipole moments, respectively. The symbol 'a' represents Onsager's cavity of 4(3IP)BC molecule radius, 'c' represents the light speed in vacuum, and 'h' stands for **Planck's** constant. The value of 'a' is determined by the J.T. Edwards atomic increment method [14]. Generally, the dipole moments μ_e of the excited state and μ_g of the ground states are typically not in parallel to one another and have a very tiny angle Φ between them [15], which may be found using the equation (10**) below.**

$$\cos\,\Phi = \frac{1}{2\mu_g\mu_e}\left[\left(\mu_g^2 + \mu_e^2\right) - \frac{m_2}{m_3}\left(\mu_e^2 - \mu_g^2\right)\right] \quad (10)$$

Assume μ_e and μ_g are almost parallel to one another and **give** the following equations (11) and (12) derived from equations (8) and (9).

$$\mu_g = \frac{m_3 - m_2}{2}\left[\frac{\mathrm{h}ca^3}{2m_2}\right]^{1/2} \quad \mathrm{For}(m_3 > m_2) \quad (11)$$

$$\mu_e = \frac{m_3 + m_2}{2}\left[\frac{\mathrm{h}ca^3}{2m_2}\right]^{1/2} \quad (12)$$

The theoretical calculations exhibit a greater correlation with the molecular

microscopic solvent polarity E_T^N than with bulk functions of polarity using 'ϵ', the dielectric constant & 'n', the refractive index. Reichardt presented **the** Stokes shift with **the** parameter of E_T^N [16], which Ravi et al. refined. [17]

$$\overline{\nu_a} - \overline{\nu_f} = 11307.6 \times E_T^N \left[\left(\frac{\Delta\mu}{\Delta\mu_B} \right)^2 \left(\frac{a_B}{a} \right)^2 \right] + constant \qquad (13)$$

where a_B=6.2Å and $\Delta\mu_B$=9D are the respective Onsager cavity radius of the Betadine dye molecule and dipole moment change upon excitation [18], and the quantities a and Δμ are the same for the 4(3IP)BC coumarin molecule of our present interest. The E_T^N is given below.

$$E_T^N = \frac{E_T(Solvent) - 30.7}{32.4} \qquad (14)$$

The negatively solvatochromic Betadine dye, pyridinium N-phenolate, is the basis for E_T *(Solvent)* values [19]. The value of E_T for various solvents is given below.

$$E_T \text{ (Solvent)} = 28.591/(\lambda_{max}) \qquad (15)$$

where λ_{max} is the absorption maximum wavelength in the spectrum of pyridinium-N-phenolatebetaine dye.

The solvent effect on **the** spectral characteristics of molecule 4(3IP)BC was studied using the Kamlet and Catalan method. According to Eq.(16), **the** solvent polarizability index for measuring dipole through comprehensive interactions (π*) of dielectric, HBD-the strength of hydrogen bond donor (α), and HBA-the strength of hydrogen-bond acceptor (β), **is** based on the Kamlet approach of the multiple linear regression method. [20]

$$y = y_0 + a\alpha + b\beta + c\pi^* \qquad (16)$$

where y_0 and y are the spectroscopic properties in the gas phase and of interest, respectively. The coefficients a & b are the respective solvent abilities of HBD and HBA. The comprehensive dielectric interaction of **the** solvent is c.

Four empirical scales—specifically SA, the solvent acidity; SB, the solvent basicity; SP, the polarizability of the solvent; and SdP, the solvent dipolarity — were proposed **by Catalan using different methods** based on an equation (17).

$$y = y_{0+} a_{SA} SA + b_{SB} SB + c_{SP} SP + d_{SdP} SdP \qquad (17)$$

where a_{SA}, b_{SB}, c_{SP}, and d_{SdP} are the measurements of solvents SA, SB, SP, and SdP, respectively, and y and y_0 have their normal implications. The

contributions of the medium's acidity, **basicity**, polarizability and dipolarity can be isolated using this method [21].

2.2 Molecular Orbital:

The nature of an electron or electronic pair in a molecule is provided by the frontier molecular orbital (FMO). The HOMO (Highest Occupied Molecular Orbital) and LUMO (Lowest Unoccupied Molecular Orbital) identify the boundary between occupied and unoccupied electronic states in a molecule. From basic theory, ionization potential gives HOMO energy ($Z= E_{HOMO}$) and the electron affinity gives LUMO energy ($E= E_{LUMO}$). The electronic parameter, electronegativity (χ), gives **an** uneven distribution of electron density, with the average value of energy and the electronic chemical potential (μ) **giving** the propensity of escaping electrons from the system in equilibrium. The chemical hardness (η) understands the chemical stability of a molecule, the chemical softness (σ) indicates a high capacity to be easily polarized and the electrophilicity (ω) gives a decrease in total energy while electron sharing. These were calculated through HOMO and LUMO energies with the **following** equations [22-23].

Electronegativity	**Chemical potential**	**Chemical hardness**	**Chemical softness**	**Electrophilicity**
$\chi = \frac{Z+E}{2}$	$\mu = -\frac{Z+E}{2}$	$\eta = \frac{Z-E}{2}$	$\sigma = \frac{1}{2\eta}$	$\omega = \frac{\mu^2}{2\eta}$

2.3 Nonlinear Optical (NLO) Properties:

Nonlinear optical characteristics are connected with the nonlinear behaviour of the charge distribution of polarization caused by a substance's interaction with electromagnetic radiation. These properties are characterized by the electric dipole moment (μ), polarizability (α), hyperpolarizability of first order (β) and hyperpolarizability of the second order (γ). These describe the properties of optical non-linearity within an electric field of a single molecule. Specifically, the entire dipole moment μ_{tot}, polarizability in static (α_0)**, isotropic** polarizability and static hyperpolarizability of first-order (β0) are extracted from the Taylor series expansion and given from equations (18) to (21)[24-25].

$$\mu = \sqrt{\mu_x^2 + \mu_y^2 + \mu_z^2} \quad (18)$$

$$\alpha_0 = \frac{[\ \alpha_{xx} + \alpha_{yy} + \alpha_{zz}]}{3} \quad (19)$$

$$\Delta\alpha = \sqrt{\frac{[\alpha_{xx}-\alpha_{yy}]^2 + [\alpha_{yy}-\alpha_{zz}]^2 + [\alpha_{zz}-\alpha_{xx}]^2 + 6\alpha_{xz}^2}{2}} \quad (20)$$

$$\beta_o = \sqrt{[\beta_{xxx}+\beta_{xyy}+\beta_{xzz}]^2 + [\beta_{yyy}+\beta_{yxx}+\beta_{yzz}]^2 + [\beta_{zzz}+\beta_{zxx}+\beta_{zyy}]^2} \quad (21)$$

3. Results and Analysis

3.1. Experimental Studies

The spectroscopic study of the 4(3IP)BC molecule involved recording spectra of absorption and emission in a normalized state, which are shown in Figures 2 and 3. The peak of absorption is observed at 330 to 350 nm, while the emission occurs in the range of 400 to 440 nm in polar and nonpolar solvents. Table 1 presents the maximum wavelengths of absorption and emission spectra, Stokes shifts, and average **wavenumbers** in various solvents. Table 2 presents solvent functions of polarity parameters derived from Lippert's, Bakhshiev's, and Kawaski-Chamma-Viallet's equations (4), (5), (6) and equation (14) in the solvents used. In the absorption spectra, there is not much difference in spectral band shift except for nonpolar cyclohexane, which shows a nearly 20 nm band shift with polar solvents. In the emission spectra, when the solvent was changed from nonpolar cyclohexane to the polar protic solvent methanol, there was a spectral band shift of 36 nm, whereas it was 61 nm for the aprotic solvent acetone. The fluorescence spectra shift towards longer wavelengths in the presence of solvents. The Stokes shift was more in polar solvents compared to nonpolar solvents. The Stokes shift value is 3447 cm^{-1} in nonpolar cyclohexane, 6233 cm^{-1} in the polar protic solvent methanol, and 6705 cm^{-1} in the aprotic solvent acetone. Figures 4 and 5 illustrate correlations between polarity functions F_1 and F_2 with Stokes shifts and Figure 6 gives the correlation of F_3 with the average value of wave numbers. The slopes of these plots were used to calculate the excited (μe) and ground (μg) state dipole moments. Figure 7 shows **that** the Stokes shift increases with the microscopic polarity of the solvent. Table 3 displays the respective dipole moments in statistical treatment with the Onsager radius of the molecule. The molecule 4(3IP)BC has a 0.27D dipole moment in the ground state and 2.7D in the excited state. The Lippert, Bakhshiev's and Kawaski-Chamma-Viallet equations have μ_e values of 4.5D, 2.7D and 2.7D**,** respectively. The change of dipole moment is 2.43D from the solvatochromic method**,** and from E_T^Nit is 1.49D. This shows the dipole moment in the excited state is more than in the ground state. The bathochromic shift occurs as the solvent polarity increases, which confirms a π → π* transition with intramolecular charge transfer (ICT) and is a considerable red shift. **This is confirmed** by the solvatochromic shift method and solvent polarity parameters, indicating that the molecule is more polar in the excited state than in the ground state [26-27].

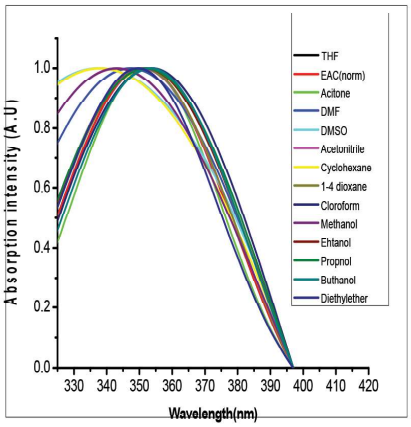

Figure 2: Spectra of absorption of 4(3IP)BC

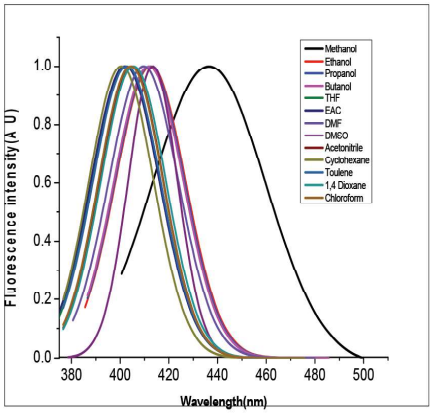

Figure 3: Fluorescent spectra of 4(3IP)BC

Table 1: Parameters of spectra of absorption and fluorescence of 4(3IP)BC molecule.

Solvents	λ_a [nm]	λ_f [nm]	$\overline{\nu_a}$ [$_{cm}^{-1}$]	$\overline{\nu_f}$ [$_{cm}^{-1}$]	$\overline{\nu_a} - \overline{\nu_f}$ [$_{cm}^{-1}$]	$(\overline{\nu_a} + \overline{\nu_f})/2$ [$_{cm}^{-1}$]
Water	351	402	28474	24900	3573	26687
Dimethyl sulfoxide	338	414	29586	24178	5408	26882
Dimethylfarmamide	348	410	28769	24414	4355	26591
Acitonitrile	351	405	28531	24716	3815	26623
Methanol	343	437	29138	22904	6233	26021
Ethanol	352	413	28409	24237	4173	26323
Acetone	353	462	28369	21664	6705	25016
Propanol	352	413	28409	24237	4173	26323
Butanol	354	412	28289	24295	3993	26292
Tetrahydrofuran	351	403	28474	24839	3635	26656
Ethylacetate	351	402	28474	24900	3573	26687
Chloroform	354	405	28257	24716	3541	26486
Diethylether	350	408	28588	24534	4054	26561
Toulene	352	403	28409	24839	3635	26656
1-4 Dioxane	351	406	28474	24655	3602	26456
Cyclohexane	338	401	29586	24963	3447	26686

Table 2. Solvents polarity functions of parameters

Solvents	ε	n	F_1 (ε, n)	F_2 (ε, n)	F_3 (ε, n)	E_T^N
Water	80.0	1.333	0.320	0.914	0.684	1
Dimethylsulfoxide	47.0	1.479	0.260	0.841	0.699	0.44
Dimethylfarmamide	38.2	1.430	0.275	0.839	0.711	0.386
Acitonitrile	36.6	1.344	0.305	0.861	0.665	0.460
Methanol	32.7	1.329	0.308	0.855	0.652	0.762
Ethanol	24.6	1.361	0.289	0.830	0.652	0.654
Acetone	20.7	1.359	0.284	0.790	0.640	0.355
Propanol	20.6	1.385	0.274	0.781	0.653	0.617
Butanol	17.4	1.399	0.263	0.749	0.646	0.586
Tetrahydrofuran	7.58	1.407	0.210	0.549	0.551	0.207
Ethylacetate	6.08	1.372	0.201	0.493	0.499	0.228
Chloroform	4.81	1.446	0.148	0.371	0.494	0.259
Diethylether	4.26	1.353	0.164	0.370	0.439	0.117
Toulene	2.38	1.497	0.013	0.029	0.035	0.099
1-4 Dioxane	2.22	1.422	0.022	0.044	0.308	0.164
Cyclohexane	2.02	1.426	0.001	0.002	0.289	0.006

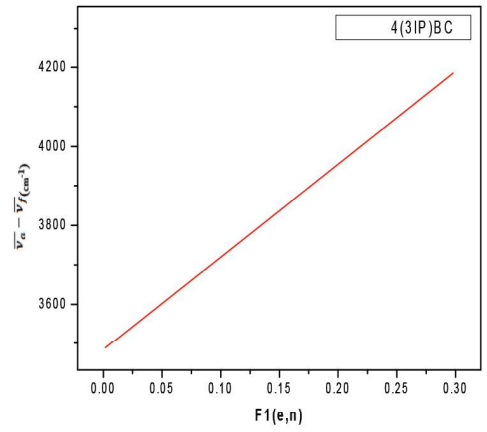

Figure 4: Stokes shift ($\overline{\nu_a} - \overline{\nu_f}$) variation with Lippert's polarity function.

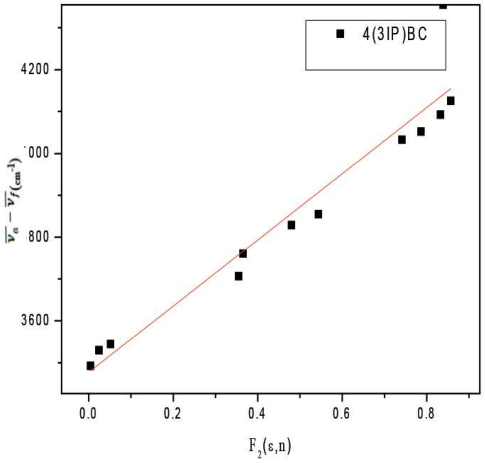

Figure 5: Stokes Shift ($\overline{\nu_a} - \overline{\nu_f}$)variation with Bakhshiev's polarity function.

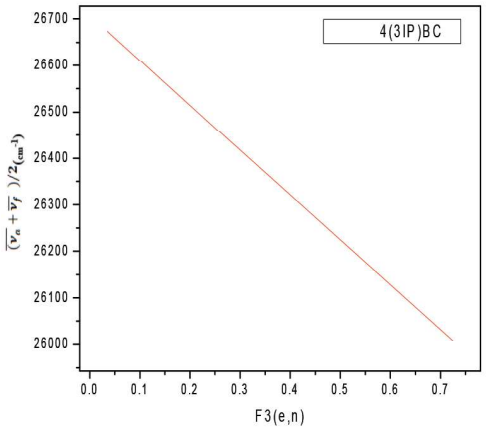

Figure 6: Variation arithmetic mean with Kawaski-Chamma-Viallet's polarity function.

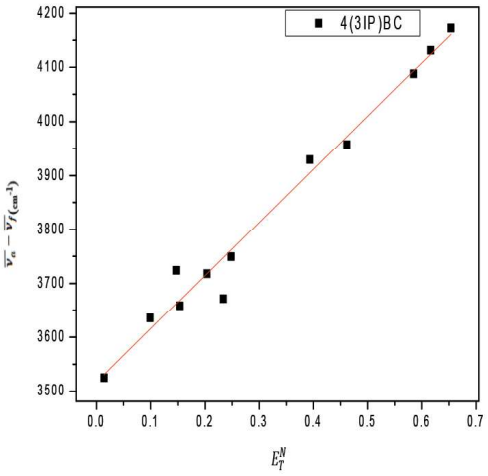

Figure 7: Stokes shift($\overline{\nu_a} - \overline{\nu_f}$) variationwith E_T^Nparameter of 4(3IP)BC molecule.

Table 3. Onsager radius, statistical treatment, dipole moments (μ_e and μ_g) of the 4(3IP)BC molecule.

Coumarin	Onsager Radius a (Å)	Statistical relations			μ-Dipole Moments							
		Slope (cm^{-1})	R square	n	μ_g^a (D)	μ_g^b (D)	μ_e^c (D)	μ_e^d (D)	μ_e^e (D)	μ_e^f (D)	$\Delta\mu^g$ (D)	$\Delta\mu^h$ (D)
4(3IP)BC	4.22	m_1 =2353	0.9172	10	5.9	0.27	2.7	4.5	2.7	2.7	2.43	1.49
		m_2=790	0.9189	10								
		m_3=-966	0.9136	11								
		m=984	0.9738	12								

The correlation coefficient is R^2, number of points n and 1 Debye=3.34×10^{-30}cm=10^{-18}esu.cm

[a]From DFT optimization geometry- μ_g.

[b]From equation(11)- Dipole moment of ground state μ_g.

[c]Calculated dipole moment of excited state μ_e from equation(12)

[d]Lippert's equation (7) dipole moment of excited state.

[e]Bakhshiev's equation(8) dipole moment of excited state.

[f]Kawaski-Chamma-Viallet's equation.(9) dipole moment of excited state.

[g]Dipole moment change from equations (11) and (12)

[h]E_T^N **Equation (14),** the dipole moment change is calculated.

3.2. Kamlet and Catalan parameters:

The spectroscopic properties of a molecule 4(3IP)BC, using the multiple linear regression method, the benefaction of solvent HBD (hydrogen bond donor) and HBA (hydrogen bond acceptor), and solvent polarizability for measuring dipole through comprehensive interactions of dielectric with Kamlet solvatochromic parameters α, β, and π* and Catalan parameters—solvent acidity, basicity, polarizability, and dipolarity—are listed in Table 4. The results of **the** spectroscopic properties **obtained using** the multiple regression method and correlation coefficients are given in equations (22) and (23).

$\overline{\nu_a}$ (cm^{-1})=28022 + 533α -513β + 1169 π* r = 0.9104

$\overline{\nu_f}$ (cm^{-1})=22028 -1396α -1649β + 3202 π* r = 0.9282 (22)

$\overline{\Delta\nu}$ (cm^{-1})=6614 +1550α -4078β – 1416 π* r = 0.9504

It is clear from the above Kamlet equations that the interactions of the dielectric (π*) of the solvent have more influence on the 4(3IP)BC molecule. The HBD and HBA parameter contributions cannot be ignored.

$\overline{\nu_a}$ (cm^{-1})= 29107 + 1287 SA + 294 SB -1612 SP + 372 SdP r=0.9227

$\overline{\nu_f}$ (cm^{-1})= 25871+ 182 SA + 63 SB -8404 SP + 5660 SdP r=0.9274 (23)

$\overline{\Delta\nu}$ (cm^{-1})=4186 + 464 SA -2739 SB +5345 SP -3263 SdP r=0.9568

It is observed from the above Catalan equations that the solvent has more influence on SP-polarizability and SdP-dipolarity. The SA-solvent acidity influences more than the SB-solvent basicity.

Table 4: Empirical solvent scale of Kamlet and Catalan parameters

Solvents	α	β	π*	SA	SB	SP	SdP
Water	1.17	0.47	1.09	1.062	0.025	0.681	0.997
Dimethyl sulfoxide	0.00	0.76	1.00	0.072	0.647	0.830	1.000
Dimethylfarmamide	0.00	0.69	0.88	0.000	0.475	0.651	0.907
Acitonitrile	0.19	0.31	0.75	0.044	0.286	0.645	0.974
Methanol	0.98	0.66	0.60	0.605	0.545	0.608	0.904
Ethanol	0.86	0.75	0.54	0.400	0.658	0.633	0.783
Acetone	0.08	0.48	0.71	0.031	0.613	0.759	0.977
Propanol	0.84	0.90	0.52	0.367	0.782	0.658	0.748
Butanol	0.84	0.84	0.47	0.341	0.809	0.674	0.655
Tetrahydrofuran	0.00	0.55	0.58	0.000	0.591	0.714	0.634
Ethylacetate	0.00	0.45	0.55	0.000	0.542	0.656	0.603
Chloroform	0.20	0.10	0.53	0.047	0.071	0.783	0.786
Diethylether	0.00	0.49	0.27	0.000	0.562	0.616	0.694
Toulene	0.00	0.11	0.54	0.000	0.128	0.782	0.284
1-4 Dioxane	0.00	0.37	0.55	0.000	0.444	0.717	0.312
Cyclohexane	0.00	0.00	0.00	0.000	0.482	0.766	0.745

3.3 Computational Study:

3.3.1 HOMO-LUMO and ESP

The geometry of optimization of the 4(3IP)BC molecule was computed using the Gaussian 16W program with the DFT/ B3LYP/3-21G basis set[28]. The resulting ground-state dipole moment is 5.9 Debye, with its directional vector depicted in Figure 9. Figures 10 and 11 show the molecular orbital surfaces for HOMO (Highest Occupied Molecular Orbital) and LUMO (Lowest Unoccupied Molecular Orbital). These orbitals play an important role in determining the chemical reactivity and stability of a molecule. A narrower HOMO-LUMO gap indicates greater molecular stability and easier electronic transitions. Compared to the ground state, the excitation of an electron from HOMO to LUMO changes the dipole moment of the molecule, reflecting the redistribution of electronic density. The chemical quantities calculated in the gas phase are tabulated in Table 5. The HOMO-LUMO energy of the molecule in the gas phase is -0.0729 eV and -0.2243 eV. The energy gap is 0.1513 eV. The chemical hardness and softness are 0.0756 eV and 6.6076 eV. The molecule has a small energy gap and a large chemical softness, indicating that it is soft and highly polarizable. **Electronegativity results** in an uneven distribution of electron density, and the chemical potential describes the tendency of electrons to escape from the system in equilibrium with a lower electrophilicity.

Electrostatic potential (ESP) maps provide insight into charge distribution in relation to various colors. The blue regions indicate positive potential (favorable for nucleophilic attack), and red regions show negative potential

(favorable for electrophilic attack). The maximum red has -6.248 a.u., and the maximum blue has +6.248 a.u. The different values of electrostatic potential **are displayed** in different colours, with increased potential in the order of red, orange, yellow, green, and blue. These are visualized in Figure 13. The total electron density in Figure 12 and molecular contour surfaces for HOMO and LUMO are shown in Figures 14 and 15, displaying the probable regions for electron transitions and reactivity sites with red (positive phase) and green (negative phase) contours. [29-30].

Figure 8: 4(3IP)BC of Optimized geometry

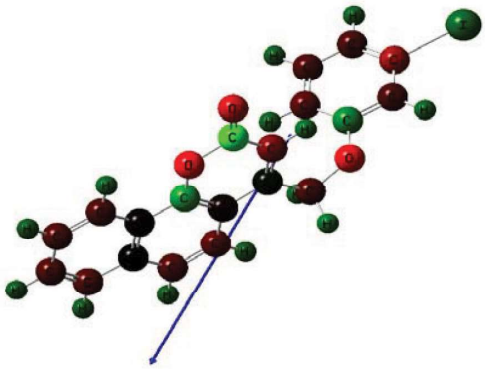

Figure 9: Vector of Dipole moment

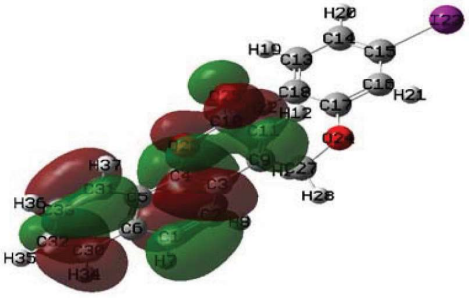

Figure 10: Molecule structure of HOMO

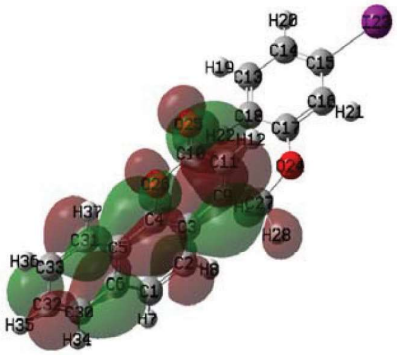

Figure 11: Molecule structure of LUMO

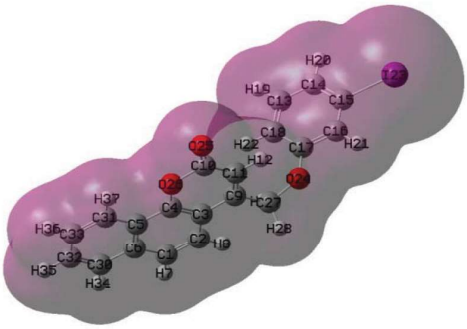

Figure 12: Total density structure

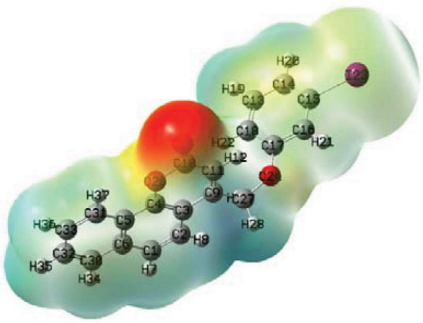

Figure 13: Electrostatic potential map(ESP)

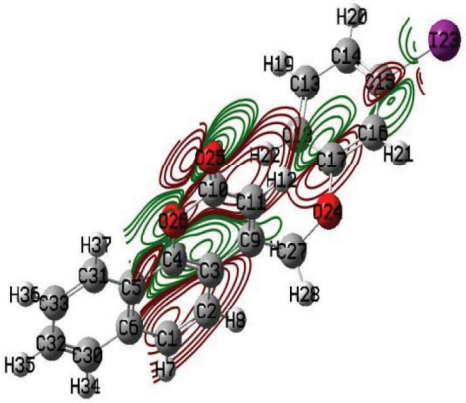

Figure 14: Contour map HOMO

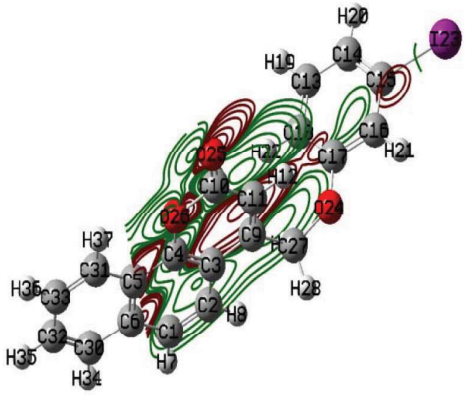

Figure 15: Contour map LUMO

Table 5: Molecular orbital parameters of 4(3IP)BC from DFT in gas phase.

Coumarin molecule	4(3IP)BC
μ_g -Ground dipole moment	5.9 D
Z-HOMOenergy in eV	-0.0729
E-LUMO energy in eV	-0.2243
ΔE -Energy gap in eV	0.1513
χ -Electro negativity in eV	-0.1486
μ- Chemical Potential in eV	0.1486
η- Global hardness in eV	0.0756
S-Global Softness in eV	6.6076
ω-Electrophilicity in eV	0.0016

3.3.2. UV-Visible Spectra

The UV-Visible spectra of the 4(3IP)BC molecule were studied using the TD-DFT/B3LYP/3-21G computational method with solvent effects modelled via the IEFPCM approach. This allowed for the evaluation of key parameters, such as absorption maxima (λmax), oscillatory strength (f), excited-state energy, and dipole moments, across different solvents, **as listed** in Table 6. Alcohols (propanol, butanol) and general solvents (diethylether, THF, acetonitrile, cyclohexane, chloroform) showed theoretical λ_{max} values that aligned well with experimental ones. Oscillatory strength (f) reflects the transition probability between energy states. High values of (f) denote strong absorption, and zero implies forbidden transitions. Excited state energies are inversely related to absorption strength. Lowering the excited energy leads to stronger absorption (higher f). Dipole Moments: The excited state has exceeded dipole moments in all solvents compared to the ground-state dipole moment, i.e. 5.9 D, suggesting significant redistribution of electron density upon excitation [31]. The change in dipole moments with solvents was nearly 2.0 D, which is confirmed by the experimental value.

Table 6. Computational UV-Visible Spectral parameters of 4(3IP)BC

Solvent	λ_{max}-Maximum absorption λ (nm)			f-Oscillator strength			E-Excited state energy (eV)			μ_e-Dipole moment (D)
	λ_1	λ_2	λ_3	f_1	f_2	f_3	E_1	E_2	E_3	μ_e
Propanol	345	317	294	0.2582	0.0014	0.0123	3.5903	3.9163	4.2083	7.6616
Butanol	345	317	295	0.2562	0.0014	0.0122	3.5922	3.9163	4.2085	7.6315
Diethylether	370	343	317	0.2318	0.1730	0.0101	3.3495	3.6101	3.9054	7.2855
Tetrahydrofuran	372	344	317	0.2471	0.0205	0.0151	3.3370	3.6088	3.9168	7.5509
Acitonitrile	373	344	316	0.2655	0.0251	0.0261	3.3206	3.3606	3.9227	7.8819
Cyclohexane	368	343	321	0.1993	0.0119	0.0096	3.3720	3.6101	3.8654	6.7449
Chloroform	370	343	317	0.2352	0.0180	0.0109	3.3468	3.3609	3.9085	7.3439

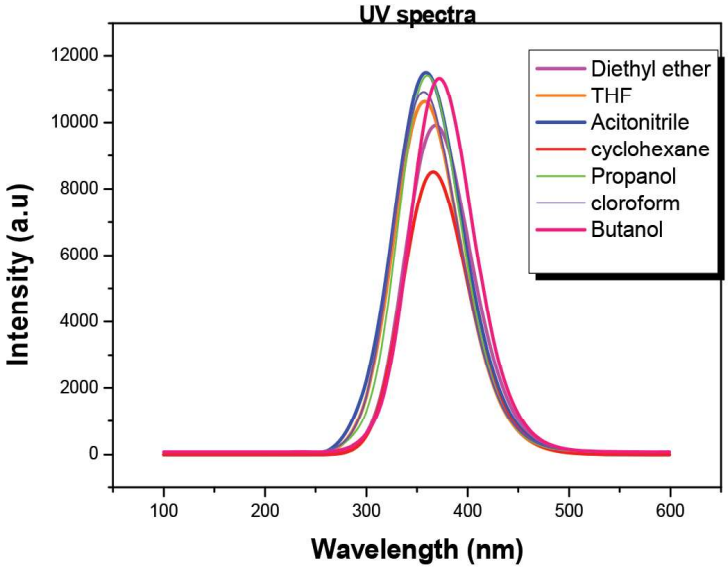

Figure 16: Computational UV-Visible spectra

3.3.3. Mulliken Charges

Mulliken atomic charges of 4(3IP)BC in the gas phase and butanol and DMSO in DFT/B3LYP are given in Table 7. From optimized geometry, on each atom the individual charges of the molecule were studied. Using charges of atoms, the chemical composition of the molecule is predicted. In **the** atomic charge distribution, the molecule consists of iodine, carbon, hydrogen, and oxygen atoms. Hydrogen atoms are positive due to electron sharing with neighbouring atoms. Carbon atom 3C is negative in butanol but becomes positive in DMSO and the gas phase, indicating the solvent-dependent charge behaviour. The carbon atom 9C exhibits opposing charges to 3C across phases. Atoms 4C, 10C, and 17C **consistently exhibit** positive charges. Atoms 1C, 2C, 5C, 6C, 11C, 16C, 18C, 27C, 30C, 31C, 32C, 33C, and all oxygen atoms are negative. Iodine atom 23I maintains a positive charge

across all environments. The data is visually summarized in Figure 17, offering a clear view of charge distribution patterns across solvents [32].

Table 7: Mulliken Charges of 4(3IP)BC in Gas phase, Butanol and DMSO

Atom	Gas Phase	Butanol	DMSO	Atom	Gas Phase	Butanol	DMSO
1 C	-0.1807	-0.1864	-0.1900	17 C	0.2360	0.3015	0.2302
2 C	-0.2075	-0.2138	-0.2208	18 C	-0.2110	-0.2188	-0.2169
3 C	0.0099	-0.0336	0.0007	19 H	0.2132	0.2227	0.2371
4 C	0.2500	0.3510	0.2415	20 H	0.2165	0.2226	0.2340
5 C	-0.0102	-0.0229	-0.0201	21 H	0.2325	0.2325	0.2454
6 C	-0.0182	-0.0189	-0.0354	22 H	0.2441	0.2264	0.2554
7 H	0.1970	0.2152	0.2265	23 I	0.2921	0.2166	0.2856
8 H	0.1960	0.2171	0.2271	24 O	-0.4982	-0.5512	-0.5028
9 C	-0.0811	0.0354	-0.0776	25 O	-0.4684	-0.5073	-0.5149
10 C	0.6148	0.6464	0.6078	26 O	-0.5311	-0.5982	-0.5428
11 C	-0.2661	-0.2926	-0.2864	27 C	-0.2968	-0.1839	-0.3390
12 H	0.2557	0.2404	0.2659	28 H	0.3188	0.2725	0.3685
13 C	-0.1852	-0.1941	-0.1933	29 H	0.3237	0.2393	0.3699
14 C	-0.1529	-0.1774	-0.1621	30 C	-0.1870	-0.1961	-0.1990
15 C	-0.3998	-0.3667	-0.4106	31 C	-0.1712	-0.1777	-0.1878
16 C	-0.1750	-0.1787	-0.1801				

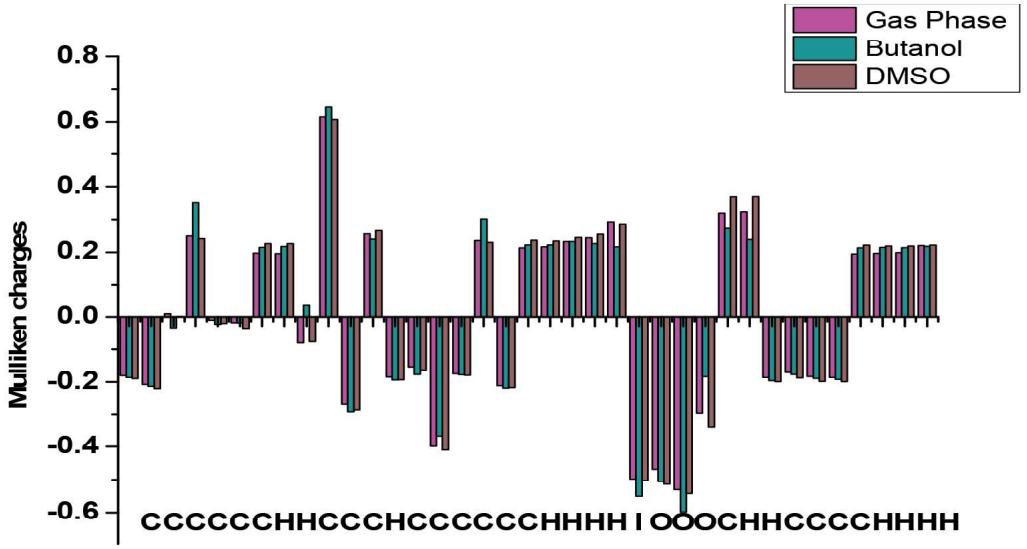

Figure 17: Mulliken atomic charges in gas phase, Butanol and DMSO

3.3.4. Nonlinear optical (NLO) properties

The NLO parameters of molecule 4(3IP)BC were calculated using optimized molecule in DFT/B3LYP and are given in Table 8. The key results include Dipole moment (μ_{tot}): 4(3IP)BC: 5.872 D, Urea (standard NLO reference): 4.259 D. Molecular polarizability (α_0):4(3IP)BC: 34.766 × 10^{-24} esu, Urea:

3.749 × 10^{-24} esu. First-order hyperpolarizability (β_0):4(3IP)BC: 7.119 × 10^{-30} esu, Urea: 0.557 × 10^{-30} esu. These values indicate that 4(3IP)BC exhibits significantly enhanced NLO behaviour compared to urea. The much higher values of polarizability and hyperpolarizability confirm its strong ability to respond to electric fields, making it a promising nonlinear optical material for applications in advanced imaging techniques [33-35].

Table 8: NLO properties of 4(3IP)BC

Parameter	Atomic unit (a.u)	Dipole moment D	Parameter	a.u	esu(10^{-24})	Parameter	a.u	esu(10^{-30})
μ_x	-1.717	-4.364	α_{xx}	384.77	57.01	β_{xxx}	511.60	4.419
μ_y	-1.358	-3.452	α_{xy}	-11.08	-1.642	β_{yxx}	-90.89	-0.7852
μ_z	0.738	1.876	α_{yy}	155.47	23.038	β_{xyy}	14.39	0.1243
μ_{tot}	**2.310**	**5.872**	α_{xz}	42.56	6.306	β_{yyy}	-127.12	-1.0983
			α_{yz}	-35.86	-5.315	β_{zxx}	24.32	0.2101
			α_{zz}	163.64	24.25	β_{xyz}	146.71	1.2675
			α_0	**234.63**	**34.766**	β_{zyy}	-32.38	-0.2797
			$\Delta\alpha$	**237.08**	**35.124**	β_{xzz}	-65.44	-0.5654
						β_{yzz}	-4.65	-4.0207
						β_{zzz}	12.77	0.1104
						β	**511.57**	**7.119**

4. Conclusion

The dipole moments of the ground state and excited state of the iodinated coumarin derivative of molecule 4(3IP)BC were studied using polar and nonpolar solvents. From the experimental and theoretical methods, it has been observed that the excited state dipole moment is greater than the ground state dipole moment. The change in dipole moment was obtained as 2.43D by the solvatochromic method, 1.49D from the microscopic solvent polarity parameter and nearly 2.0D from the computational method. The bathochromic shift that occurs as the solvent polarity increases indicates positive solvatochromism. The polar solvents stabilize the charge transfer excited state, **resulting** in red-shifted emission, and induce a strong π to π* transition. The Kamlet and Catalan multiple linear regression method has been employed in various solvents. The interactions of the dielectric (π*) of the solvent have **a greater** influence on dipole-dipole interactions than hydrogen bonding operations, and polarizability, dipolarity, and acidity have **a greater** influence than basicity. In a computational study **using** TD-DFT, the UV-visible spectra **indicate** that the dipole moments in the excited state **are greater** than **those** in the ground state, particularly **in the presence** of solvents. The small energy gap **between** the HOMO and LUMO levels indicates an easier electron transfer from the HOMO to LUMO, and the

molecule's chemical softness suggests that it is soft and highly polarizable. The electrostatic potential contour surface shows intermolecular charge transfer. In NLO parameters, the electric dipole moment, polarizability, and hyperpolarizability have high values compared to urea, **confirming** that the molecule has a strong ability to respond to electric fields, making it a promising nonlinear optical material for applications in advanced imaging techniques.

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Author Contribution: All authors contributed **to the study** conception and design, data collection, material preparation, and analysis were performed by Manjula Katageri, Srinath, Shivaleela B, Sulochana Devar and S.M. Hanagodimath. The manuscript preparation by the first author, Manjula Katageri, and all authors **has been** read and approved.

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