NLO Properties of 3-Styryl Coumarin Derivatives - A Computational Approach

Siddheshwar D. Jadhav

Department of Chemistry, Willingdon College, Sangli, India- 416 416
Email: *sdjchem[at]gmail.com*

Abstract: ***Coumarin-based fluorophores are known for their tunable optical characteristics. In this work, novel coumarin derivatives containing a 4-cyano group were synthesized and investigated for their nonlinear optical (NLO) properties. The presence of the cyano group enhanced intramolecular charge transfer and caused a red shift in absorption. Both experimental techniques and theoretical calculations were employed to evaluate their optical responses. First-order hyperpolarizability values were significantly high, ranging from 494 to 794 times that of urea, depending on the substituent's position. Solvent polarity was also found to influence the NLO behavior. These results highlight the potential of these compounds in future photonic and optoelectronic applications.***

Keywords: 4-Cyano coumarin, DFT, TD-DFT, NLO

1. Introduction

When Organic materials showing nonlinear optical (NLO) properties are of great interest in terms of extensive research from both experimental and computational viewpoints because of the apparent disadvantages of the widely used inorganic materials like lithium niobate in optoelectronic devices [1]. The difference lies in the fact electro-optical manifestations in the inorganic materials originate from the perturbations in geometric arrangements of the key ions within a solid-state crystalline structural framework, whereas in the organic materials the same optical properties arise on account of transfer of electronic charge across the molecule [2]. The quadratic hyperpolarizablity aspects of organic molecules make them the materials of high potential in the field of nonlinear optics (NLO) [3] for the simple reason that the origin of their polarizability is of purely electronic origin making the response times extremely fast as it is limited only by the electronic phase relaxation times of a few tens of femtoseconds. Conjugated organic molecules containing electron-donating and –accepting groups can in addition to higher response time exhibit higher second-order nonlinearity, lower dielectric constants, and higher optical thresholds than their inorganic counterparts. Their synthetic flexibility in tailoring the NLO properties makes them promising candidates to the particular needs of the specific application. Also the fact that they can be incorporated into a variety of macroscopic structures allows an easy integration with semiconductor electronics in prototype fabrications [4]. A large number of organic π-conjugated molecules during the last 3 to 4 decades have helped to establish general guidelines for the molecular design of good second-order NLO materials. Many of these molecules bear donor-acceptor groups separated by a conjugated bridge (D–π–A) with a push–pull type of arrangement [5]. Such D–π–A systems are known to perturb the pi-electron delocalization of the locally excited state (LE) attained by the absorption which can promote intra-molecular charge transfer (ICT) and such phenomena are more prominent in polar solvents. Change of molecular arrangement by substituents groups and substitution positions synthetic tools can be used as a fruitful strategy to modify the optical spectra as well as the NLO properties [6] which is possible by exploiting the synthetic methods.

The high NLO responses of push–pull organic π-systems intrinsically is related to intra-molecular charge transfer excited states [7]. In the simplified two-state model for β (Equation 1) not only the energy of this transition but also the corresponding oscillator strength f as well as the change in dipole moment μ are important factors.

$$\beta \ \propto \ \frac{\Delta E_{eg} f \Delta \mu_{ge}}{(\Delta E_{eg})^2 - (2(E_{exc})^2] \, [(\Delta E_{eg})^2 - (E_{exc})^2]} \qquad \textbf{Equation 1}$$

where ΔE_{eg} is electronic transition energy, f is oscillator strength and $\Delta\mu$ is change of dipole moment between ground and excited state, respectively. E_{exc} is the frequency of the laser used for excitation. Under the static conditions the above equation reduces to,

$$\beta \ \propto \ \frac{f \Delta \mu_{ge}}{(\Delta E_{eg})^3} \qquad \textbf{Equation 2}$$

The above equation developed by Oudar and Chemla based on the equivalent field model interprets the second-order responses and helps in understanding the trends in β by quantifying the ground state asymmetry of a π-network in a systematic fashion. It is proposed that a major portion of the second order response in π-organic chromophores could be predicted from the ground state deformation of the π-electron distribution due to the appended substituents. The perturbation of the π-cloud caused by a particular substituent which is defined as a substituent mesomeric moment (μ_R). The relationship between the π-distortion and the β is given by,

$$\beta \propto \frac{3\gamma \Delta \mu_{ge}}{\alpha} \qquad \textbf{Equation 3}$$

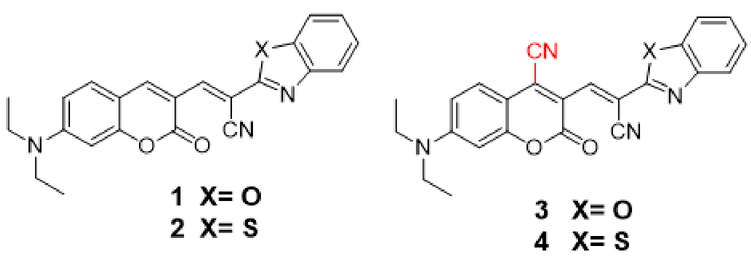
where α is polarizability, γ is second order hyperpolarizability and β is the static hyperpolarizability.

To rationalize the origin of the hyperpolarizability, β, in such systems and to guide the design of such molecules Oudar and Chemla suggested that in many systems β could be described well by a two-state model which could be used to guide the design of second-order NLO. In this model,

$$\beta \propto \frac{\mu_{ge}\Delta\mu_{ge}}{(\Delta E_{eg})^3} \qquad \text{Equation 4}$$

Where, μ_{ge} and ΔE_{eg} are the dipole matrix element and transition energy, respectively, between the ground state (0) and the first strongly allowed charge-transfer excited state (1). Physically, the introduction of a $\Delta\mu_{ge}$ term meant that as the electrons interact with the oscillating electric field of light, they show a preference to shift from one direction relative to the other. Accordingly, molecules for second-order NLO applications were based upon aromatic π-electron systems unsymmetrically endcapped with electron donating and accepting groups to impart the electronic bias. A prototypical NLO chromophore was 4-(N, N-dimethylamino)-4’- nitrostilbene (DANS) in which the two benzene rings and the double bond are the conjugated p-system and provide the polarizable electrons, and the dimethylamino group acts as the donor and the nitro group acts as the acceptor. This model guided the design of second-order NLO chromophores for quite some time and has been reviewed extensively. The maximization of β can thus be realized by increasing the product of $\mu_{ge}\Delta\mu_{ge}$ or by realizing a decrease in ΔE. So, the NIR absorbing materials are expected to give enhanced NLO properties.

Coumarin molecules though considered to be absorbing in the yellow to green regions[8,9] , the structural modification can make them absorb in red region [10–12]. The compounds considered for the study are styryl derivatives of 7-N, N-diethylamino coumarin 3-carbaldehyde and 7-N, N-diethylamino coumarin 4-cyano 3-carbaldehyde (**Figure 1**). The 2-cyanomethyl benzimidazole and 2-cyanomethyl benzthiazole were used as source of active methylene groups. The synthetic protocol was simple and is described in the previous paper [13]. The molecules **3** and **4** show 90-100 nm red shifted absorption and emissions as compared to the compounds **1** and **2.** The 4-cyano substitution has improved the quantum yield upto 10 times. In this paper we have studied the impact of the cyanation as well as the longer wavelength absorption on NLO properties of the molecules, both experimentally and computationally.



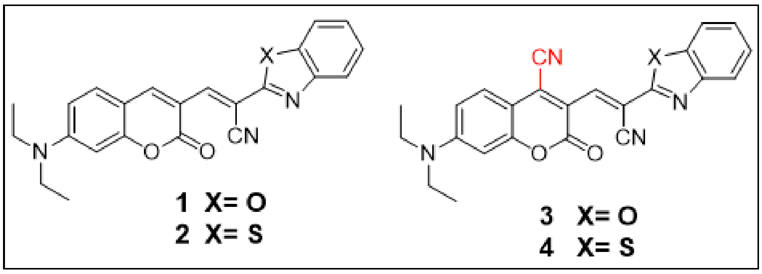


Figure 1: Coumarin compounds 1-4

2. Materials and Methods

The ground state (S_0) geometries of the compounds **1-4** were optimized in the gas phase using Density Functional Theory (DFT). The popular hybrid functional B3LYP was used, which combines Becke’s three parameter exchange functional (B3) with the nonlocal correlation functional by Lee, Yang, and Parr (LYP). All the atoms were treated with 6-31 G (d) basis set, which deems to be sufficient for the type of molecules involved[14]. The validity of the structures as local minima on potential energy surface was verified with vibrational analysis and confirmed that they are with no imaginary frequencies. The first order and second order hyperpolarizabilities were calculated using the optimized geometry. All the computations in solvents were carried out using the Polarizable Continuum Model (PCM) . Gaussian 09 program was used for all the DFT and TDDFT computations and the results were visualized with GaussView 5.0[15]. The experimental data for calculating hyperpolarizability in various solvents was used from our previous work published [13].

3. Result and Discussion

3.1 NLO properties

Coumarin molecules can be a good candidates for NLO applications and is evident from a few literature reports [16]. The non-cyanated compounds **1** and **2** has $\frac{\mu_e}{\mu_g}$ ratio less than unity and implies that the excited state is less polar for these molecules , on the contrary their 4-cyanated analogues **3** and **4** has $\frac{\mu_e}{\mu_g}$ ratio more than unity and suggests the more polar excited state.

The molecules thus are expected to show good NLO properties. The NLO properties of the molecules can be defined by parameters like α_{CT}, β_{CT}, β_0, $\langle\gamma\rangle$ and γ . Such parameters are obtained by computational and experimental methods.

3.2 Charge Transfer Charateristics

An efficient charge transfer (from between donor and acceptor) leading to a characteristic charge transfer excited state in a Donor-π-Acceptor chromophore is responsible for the manifestation of NLO properties. Within a two-level approximation the strength of electronic coupling H_{DA} between the ground and charge transfer excited states is

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related to the vertical excitation energy (ΔE_{eg}), the difference between the adiabatic dipole moments of the ground and excited states ($\Delta\mu_{eg}$), $\Delta\mu_{eg}^{D}$ is the difference in diabatic state dipole moments, and the transition dipole moment μ_{ge} by the generalised Markus-Hush (GMH) equation [17]:

$$H_{DA} = \frac{\mu_{ge}\,\Delta E_{eg}}{\Delta\mu_{eg}^{D}} = \frac{\mu_{ge}\,\Delta E_{eg}}{\left(\Delta\mu_{eg}^{2}+4\mu_{ge}^{2}\right)^{1/2}} \qquad \textbf{Equation 5}$$

The adiabatic states are assumed to be composed of these three diabatic states - a donor ground state (GS), a donor locally excited state (LE), and a charge-transfer state (CT) with the “transferring electron” localized on the acceptor. This approach has been carefully used in a few charge transfer systems[18]. For weak donor-acceptor interactions, the adiabatic states are nearly equivalent to the diabatic states, and thus it is possible to use the parameters like difference in dipole moments, transition dipole moments and the frequency of absorption obtain from the steady state absorption measurements.

$$R_{DA} = 2.06 \times 10^{-2}\,\frac{\sqrt{\nu_{max}\varepsilon_{max}\Delta\nu_{12}}}{H_{DA}} \qquad \textbf{Equation 6}$$

where ε_{max} is the molar extinction coefficient at maximum absorption, in the units of M^{-1} cm $^{-1}$, and $\Delta\nu_{12}$ is the full width at half-maximum (fwhm) of charge-transfer band. In the above equation, H_{DA}, ν_{max}, and $\Delta\nu_{12}$ are in units of wavenumber, cm^{-1}. The above equation provides a simpler method to calculate charge-transfer coupling from the characteristic values of the charge-transfer band in absorption spectra, and it is an experimental coupling value.

Table 1: Donor-Acceptor coupling value (HDA) and Donor-Acceptor coupling distance (RDA) for the dyes 1-4 in various solvent

Solvent	1		2		3		4	
	H_{DA} (cm^{-1})	R_{DA} (Å)	H_{DA} (cm^{-1})	R_{DA} (Å)	H_{DA} (cm^{-1})	R_{DA} (Å)	H_{DA} (cm^{-1})	R_{DA} (Å)
ACN	9739	3.55	9727	3.19	8285	2.02	8371	3.05
DCM	9714	4.12	9679	3.78	8168	2.25	8178	2.83
Diox	9984	3.00	9905	3.76	8859	2.30	8907	2.77
DMF	9391	3.53	9351	3.59	8397	2.84	9517	3.37
DMSO	9576	3.76	9392	3.65	8524	1.77	9409	2.80
EA	9816	3.25	9779	3.30	8710	2.41	8797	2.75
EtOH	9620	3.14	9633	3.21	8217	2.01	8302	3.16
MeOH	9739	2.70	9639	3.79	8324	1.67	8457	3.15
Toluene	9935	3.25	9836	3.31	8888	2.02	8924	3.25

The H_{DA} values calculated shows higher coupling values in non-polar solvents. The change in the coupling values is higher in compounds 3 and 4 which are based on the benzthiazole moiety. The RDA values increases for cyanated derivatives 2 and 4 in non polar solvents. The trend in non-cyanated derivatives is reverse.

3.3 Calculation of α_CT (Linear polarizability) from solvatochromic data

The linear polarizabilities α_{CT} were calculated experimentally for reported coumarins and 4-cyanocoumarins. The two-level model using UV-vis absorption/emission spectroscopy was used to determine these values. The solvatochromic method is also been utilized for determination of dipole moment of the lowest lying charge transfer excited state [19], and is also reported for the molecules under study [13].

Table 2).

The computational values of α_{CT} are almost twice higher than the experimental values. This can be attributed to the approximations exercised in computational model.

$$\alpha_{CT} = \alpha_{xx} = 2\,\frac{\mu_{ge}^{2}}{\Delta E_{eg}} = \frac{2\mu_{eg}^{2}\lambda_{eg}}{hc} \qquad \textbf{Equation 7}$$

Where,
x = direction of charge transfer, h = Planks constant, c = velocity of light in vacuum, λ_{eg} = The wavelength of transition from the ground state to excited state, μ_{ge} = The transition dipole moment, that is related to the oscillator strength *f*.

$$\mu_{ge}^{2} = \frac{3e^{2}h}{8\pi^{2}mc} \times \frac{f}{\vartheta_{max}} \qquad \textbf{Equation 8}$$

Where,
m = mass of electron, f = oscillator strength, $\vartheta_{max} = \Delta E$= Absorption frequency, e = charge on electron,

The oscillator strength can be obtained by integrated absorption coefficient. The α_{CT} are calculated by using the **Equation 7**. And all α_{CT} values are calculated for coumarins, which are compared with theoretically obtained α_{CT} or α_{xx} (

Nonetheless the trends in the solvent system coincide with experimental values. The linear polarizaility is sensitive to solvents and is evident in both the experimental and computational studies. All the compounds show higher α_{CT} values in polar solvents. The solvatochromic behaviour of the molecules is described in literature[13]. The values calculated from experimental data and those computed both highlight effect of cyanation on the α_{CT} values. There is substantial decrease of 5.2 X 10^{-30} esu to 17.1 X 10^{-30} esu experimentally and 15 X 10^{-30} esu to 16.5 X 10^{-30} esu computationally, from compound **1** to compound **3.** Similarly in the case of compound **2** to **4** there is a decrease of 3.6 X 10^{-30} esu to 22.8 X 10^{-30} esu experimentally and

17.7 X 10^{-30} esu to 19.8 X 10^{-30} esu computationally.

Table 2: Linear polarizability α_{CT} calculated by solvatochromic method and computed α_{CT} for compound 1-4.

	1		2		3		4	
	$C\ \alpha_{xx}$	$E\ \alpha_{xx}$	$C\ \alpha_{xx}$	$E\ \alpha_{xx}$	$C\ \alpha_{xx}$	$E\ \alpha_{xx}$	$C\ \alpha_{xx}$	$E\ \alpha_{xx}$
ACN	44.6	27.5	52.0	21.5	28.1	10.2	32.2	17.9
DCM	43.0	21.2	50.0	22.4	26.8	16.0	30.6	10.3
Diox	38.9	17.3	44.7	27.1	23.9	9.9	27.0	9.4
DMF	44.6	29.0	48.6	29.8	28.1	10.0	32.2	7.0
DMSO	44.7	31.9	52.1	26.4	28.2	6.9	32.3	4.9
EA	42.1	21.9	48.9	23.1	26.2	14.8	29.8	9.4
EtOH	44.3	21.0	51.7	22.2	27.9	11.8	31.9	19.5
MeOH	44.5	17.6	51.9	33.3	28.0	7.5	32.1	20.0
Tol	39.2	21.1	45.1	21.0	24.1	7.4	27.2	11.8

$E\ \alpha_{xx}$ = Experimental $C\ \alpha_{xx}$= Computational
Values are in the order of x 10^{-30} esu

The molecules are expected to show good non-linear properties. There are various experimental and theoretical methods reported to evaluate β value. Theoretical methods to evaluate β value are based on the Time-dependent perturbation theory. A common experimental method used to obtain β is to polarize the sample dissolved in a non-polar solvent with a strong electric field in order to induce molecular alignment. A laser beam is sent through this solution and the intensity of second harmonic generation (SHG) is measured. This method for evaluating the second-order molecular polarizability is the electric field induced second harmonic generation (EFISH) . The calculation of β using EFISH, the local field factors at the fundamental frequency ν, at the second harmonic frequency 2ν and at zero frequency, and also the ground state dipole moment is required. Another technique to determine β is hyper Rayleigh scattering (HRS) [20]. This involves irradiation of the sample by photons at a certain frequency ν and the detection of the scattered photons at a frequency 2ν. The HRS intensity is sensitive to the molecular environment.

The methods given above are expensive and it requires a sophisticated experimental set up. The solvatochromic method is simple to practice and cost effective.

The two level microscopic model to determine solvent dependent hyperpolarizability is based on Oudar equation [21] which in modified form can be presented as,

$$\beta_{xxx} = \beta_{CT} = \frac{3}{2h^2c^2}\frac{v_{eg}^2\,\mu_{eg}^2\,\Delta\mu_{CT}}{(v_{eg}^2 - v_L^2)\,(v_{eg}^2 - 4v_L^2)} \qquad \textbf{Equation 9}$$

Where, x is the is the direction of charge transfer, h is Planck's constant (in erg × s), c is speed of light in vacuum (in cm s^{-1}), μ_{eg} is the transition dipole moment, $v_L$is the frequency of the reference incident radiation to which the value would be referred, v_{eg} is the transition frequency and $\Delta\mu_{CT}$ is the difference between excited state and ground state dipole moment.

The hyperpolarizability calculated by this equitation is the dominant component of the hyperpolarizability tensor i.e. β_{xxx} [22] and as the formula refers to charge transfer transition the hyperpolarizability obtained often indicated as β_{CT} (charge transfer) The $\Delta\mu_{CT}$ is obtained using McRae's theory [23,24]

$$\bar{\vartheta}_{abs} - \bar{\vartheta}_{emn} = (\delta_{abs} + \delta_{emn}) + \frac{2\Delta\mu_{CT}^2}{hca^3}\left(\frac{\varepsilon-1}{\varepsilon+2} - \frac{n^2-1}{n^2+2}\right) \qquad \textbf{Equation 10}$$

Where,

$\bar{\vartheta}_{abs} - \bar{\vartheta}_{emn}$ is the Stokes shift (in cm^{-1}), λ_{abs} and λ_{emn} are the differences in the vibrational energy (in cm^{-1}) of the molecule in the excited and ground state for absorption and emission, respectively, α is the cavity radius within Onsager's model (in cm), ε is the relative dielectric constant and n is static refractive index of the solvent, α was calculated by integration of the solvent accessible surface using density functional theory optimized geometry.

Equation 10 can be written as,

$$\bar{\vartheta}_{abs} - \bar{\vartheta}_{emn} = \frac{2\Delta\mu_{CT}^2}{hca^3}\left(\frac{\varepsilon-1}{\varepsilon+2} - \frac{n^2-1}{n^2+2}\right) + (\delta_{abs} + \delta_{emn}) \qquad \textbf{Equation 11}$$

Treating this **Equation 11** as a equation of straight line,

$$y = mx + c \qquad \textbf{Equation 12}$$

Where,

$y = \bar{\vartheta}_{abs} - \bar{\vartheta}_{emn}$, $m = m = \frac{2\Delta\mu_{CT}^2}{hca^3}$, $x = \left(\frac{\varepsilon-1}{\varepsilon+2} - \frac{n^2-1}{n^2+2}\right)$ and $c = (\delta_{abs} + \delta_{emn})$

Using the value of slope m $\Delta\mu_{CT}$ was then derived, the transition dipole moment μ_{ge}^2 is related to the oscillator strength f by **Equation 8.**

The oscillator strength is obtained from integrated absorption, from the value of oscillator strength the transition dipole moment $\mu_{eg}^2$is then derived [13] , from the slope of **Equation 11** the charge transfer dipole moment is obtained, thus finally putting the values in **Equation 11** β_{CT} or β_{xxx} is obtained under static conditions when the value of $\vartheta_L = 0$

The values for first hyperpolarizability obtained using the solvatochromic method is based on several assumptions and thus allow only approximate estimate of dominant tensor of total hyperpolarizability along the direction of charge transfer which is the major contributor to the total hyperpolarizability. Although the values are approximate it has advantages over the other well-known expensive methods to understand the scenario. The calculated values are given in
Table 3.

Table 3 Experimental and computed β xxx values for compound 1-4 in various solvents.

Solvent	1		2		3		4	
	$E\ \beta_{xxx}$	$C\ \beta_{xxx}$	$E\ \beta_{xxx}$	$C\ \beta_{xxx}$	$E\ \beta_{xxx}$	$C\ \beta_{xxx}$	$E\ \beta_{xxx}$	$C\ \beta_{xxx}$
CAN	49.6	9.1	42.5	13.5	18.9	0.7	34.8	0.6
DCM	38.9	7.8	44.3	11.7	30.0	0.6	20.8	0.6
Diox	30.2	4.5	52.6	7.1	17.5	0.4	16.8	0.4
DMF	55.0	9.1	59.8	11.2	18.4	0.7	11.8	0.6
DMSO	60.5	9.2	54.2	13.7	12.1	0.7	8.4	0.6
EA	38.1	7.1	44.5	10.7	25.4	0.6	16.7	0.6
EtOH	37.6	8.9	44.7	13.2	21.9	0.7	38.3	0.6
MeOH	32.7	9.1	67.0	13.5	13.7	0.7	37.4	0.6
Tol	36.6	4.7	40.3	7.4	13.0	0.4	20.7	0.5

$E\ \beta_{xxx}$ =Experimental
$C\ \beta_{xxx}$= Computed Values are in the order of x 10^{-30} esu

The experimental and computed values of β_{xxx} for the compounds **1-4** though differ in their values, are in order of X 10^{-30} esu. The trends across the non-polar to polar solvents is well described by the computational methods. Polar solvents show higher β_{xxx} values and is reflected both in computational as well as experimental methods. The inclusion of –CN substitution at 4-position greatly impact the β_{xxx} value. The compound **1** has calculated values of 4.5 X 10^{-30} esu to 9.2 X 10^{-30} esu and experimental values from 30.2 X 10^{-30} esu to 60.5 X 10^{-30} esu across the solvents. The cyanated analogue **3** shows calculated values at 0.4 X 10^{-30} esu to 0.7 X 10^{-30} esu and experimental values at 8.4 X 10^{-30} esu to 34.8 X 10^{-30} esu. Similar effect can be seen on the other pair of compound **2** and **4.** The decrease in the β_{xxx} tensor can be attributed to the change in charge transfer direction due to –CN substitution at the 4-position. The –CN group is placed at around 60° angle to the withdrawing group in original molecule.

The value of β_0 or total first order hyperpolarizability of the molecule gives an estimate of the NLO properties of the organic molecules. This value considers all the directional tensor components of hyperpolarizability. The computed values were compared with the values obtained for urea. The comparison of the values is given below in **Error! Reference source not found.**.

Table 4: Total first order hyperpolarizability (β_o) calculated with B3LYP/6-31G (d) for compound 1-4

Solvent	1	2	3	4
	(β_o) (x 10-30)			
ACN	254.5	324.5	225.9	306.0
DCM	218.5	281.0	181.9	203.8
Diox	126.6	167.9	86.9	102.7
DMF	255.0	270.1	226.6	306.8
DMSO	257.6	328.0	230.0	310.9
EA	198.4	256.5	159.1	228.1
EtOH	248.9	317.8	218.7	297.3
MeOH	253.3	323.0	224.4	304.2
Tol	132.5	175.3	92.2	142.0
Average	216.1	271.6	182.9	244.6
Ratio with Urea (Urea: Compound)	584	734	494	661

The total hyperpolarizability calculated is 494 to 734 times greater than that of urea. The effect of the substitution of bezothiazole ring system as against benzoxazole is clear and shows a higher first order hyperpolarizability. The compound **2 and 4** shows higher (β_o) by 150 to 167 X 10^{-30} esu as compared to their benzimidazole analogues **1** and **3** respectively. The (β_o) shown by the cyanated compounds **3** and **4** is lower by 90 X 10^{-30} esu and 73 X 10^{-30} esu. The solvent effect is consistently shows higher value in polar solvents.

The second order hyperpolarizability $\langle\gamma\rangle_{SD}$ at molecular level originating from the electronic polarization in the non-resonant region can be treated by a three-level model described in literature [25]. The Quasi-two-level model in place of three level model using the density matrix formalism to a simpler **Equation 13**.

$$\langle\gamma\rangle = \frac{1}{\Delta E_{eg}^3}\mu_{eg}^2\left(\Delta\mu_{ge}{}^2 - \mu_{eg}^2\right) \qquad \textbf{Equation 13}$$

The second order hyperpolarizability can be expressed as the "solvatochromic descriptor" and the values calculated are given in **Table 5**

Table 5: Solvatochromic descriptor ⟨γ⟩ of third order hyperpolarizability of compound 1-4

Solvent	1	2	3	4
ACN	3.1	4.5	2.3	3.6
DCM	3.4	4.6	3.0	2.9
Diox	2.8	4.5	2.0	2.0
DMF	3.7	4.8	2.3	1.4
DMSO	3.5	5.3	1.6	1.1
EA	2.8	4.2	2.3	2.0

EtOH	3.2	4.8	2.6	3.8
MeOH	3.4	4.8	1.8	3.2
Tol	2.8	4.1	1.6	2.2

*Values are in the order of x 10^{-35} esu

The solvatochromic descriptor ⟨γ⟩ of second order hyperpolarizability of compounds show higher values in case of a benzimidazole ring containing molecules **2** and **4** as compared to bezoxazole containing molecules **1** and **3.** This can be understood on the basis of higher electron pulling effect of benzothiazole ring as compared to benzoxazole ring system, which helps in creating a stronger dipole and contribute to the hyperpolarizabilities.

Like β_{xxx} and β_0 the solvatochromic descriptor ⟨γ⟩ is also affected by the presence of cyano group and the values drop by 0.4 X 10^{-35} esu to 1.9 X 10^{-35} esu for compound **3** and 0.9 X 10^{-35} esu to 4.2 X 10^{-35} esu across the solvents. The solvent effect is also evident on this parameter, higher the polarity of the solvent, higher the second order hyperpolarizability.

3.4 Computational γ value (Second order static hyperpolarizability)

The individual components of the second order static hyperpolarizability γ were obtained computationally. The values are considered to be proportional to the solvatochromic descriptor ⟨γ⟩ of the second order hyperpolarizability. The values obtained are given in **Table 6**.

Table 6: Second order static hyperpolarizability obtained computationally using B3LYP/6-31G(d) for 1-4

Solvent	1	2	3	4
ACN	1886.3	1587.5	1933.8	2026.8
DCM	1264.5	1393.3	1697.9	1776.9
Diox	831.1	882.4	1061.1	1100.4
DMF	1427.0	1505.0	1937.3	2030.8
DMSO	1438.4	1603.3	1954.2	2049.9
EA	1173.7	1283.7	1313.2	1628.4
EtOH	1399.8	1557.8	1897.0	1985.4
MeOH	1419.3	1581.1	1925.7	2018.1
Tol	860.6	916.3	1103.8	1130.8
	*Values are in the order of x 10^{-35} esu.			

The values has a trend where higher polarity solvents show higher values of γ, the similar trend is followed by the solvatochromically obtained values.

4. Conclusion

In this work, we explored the nonlinear optical (NLO) behavior of red-emitting coumarin derivatives using both experimental techniques and computational analysis. Substituting a –CN group at the 4-position was found to alter the electron flow, diverting it from the primary acceptor and thereby lowering the values of the β_{xxx} and β_0 and ⟨γ⟩ values. On the other hand, incorporation of the benzothiazole ring contributed positively to NLO performance, consistent with its strong electron-withdrawing characteristics. Molecules 1-4, demonstrated remarkably high first-order hyperpolarizability—ranging from 494 to 794 times that of urea. However, the introduction of an additional –CN group in a perpendicular orientation had a diminishing effect on this property. Considering their high NLO response and straightforward molecular design, these compounds hold significant promise for use in nonlinear optical applications.

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Author Profile

Dr. Siddheshwar D. Jadhav holds a Ph.D. in Chemistry from the Institute of Chemical Technology, Mumbai, and is currently an Associate Professor at Willingdon College, Sangli. He has published extensively in international journals and authored the book "Density Functional Theory: Advances in Applications." A certified NSDC trainer and Yog-Shikshak Diploma holder, he serves on academic and administrative boards of Shivaji University, Punyashlok Ahilyadevi Holkar University, and Government ITI, Kavathemahankal.