Nonlinear Optical Properties (NLO) study of some novel fluorescent 2-chloroimidazo[1,2-a] pyridine Derivatives

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Abstract:

2-chloroimidazo[1,2-a]pyridine-3-carbaldehyde styryl extended dyes showed bathochromic shift of 83 to 99 nm from starting aldehyde in various nine different polarity solvents. Resonance due to proper position of Styryl group with lone pair of nitrogen and electron donating hyperconjugated methyl group in imidazo[1,2-a]pyridine was responsible for enhancement of broad absorption maximum 6 to 8 nm in various solvents. Experimental trends are matching with computational absorption wavelengths. In HOMO-LUMO energy gap, nonmethylated dyes showed higher energy gap of 0.05 eV than methylated dyes. In this research work, NLO properties were computed with its fundamental limits and intrinsic values using DFT method in conjunction with 6-31G(d) basis set & vibrational NLO properties with 6-311++g(d,p) basis set. Fundamental limits and intrinsic properties of dyes were within Hamiltonian limits. The fundamental limits provide a figure of merit for studied extended styryl dyes for future optical applications.

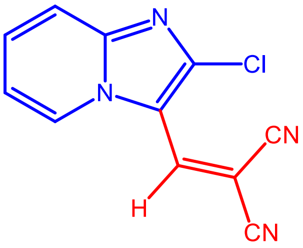
***Keywords**: Imidazo[1,2-a]pyridine, Photophysical, Solvatochromism, NLO, DFT, TDDFT.*

1. Introduction

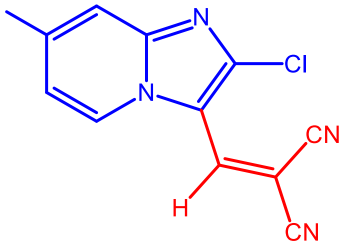
Organic molecules display nonlinear electric susceptibilities with potential applications in telecommunications, organic field effect transistors(OFETs), organic photovoltaics(OPVs), an organic light emitting diode(OLEDs), optical information & environment sensitive fluorescent sensors[1]. Indoles and azaindoles are isosters of imidazo[1,2-a]pyridine moiety and possessing electron donating properties [2]. Recently, applications of imidazo[1,2-a]pyridine derivatives have been reported as multiple fluorescent chemosensors, in an electron transport layer of an organic light emitting device, biomarker of hypoxic tumor cells, as a receptor in fluorescent high-affinity ligand in dopamine D3 due to their promising NLO (nonlinear optical properties)[3]. Styryl dyes typically employed in advanced material such as laser dyes, solar cell sensitizer, optical or electro-optical devices or sensor materials, DNA probes and voltage-sensitive dyes in cardiac tissue[4]. Intramolecular charge transfer (ICT) properties of dyes are one of the key features to reduce the energy gap between HOMO and LUMO orbital of the molecule for broadening the range of absorption properties applied in high tech applications [5].

Imidazo[1,2-a]pyridines own the highest electron-density at C3 and this is typically the site of an attack in electrophilic aromatic substitution. The second position of imidazo[1,2-a]pyridine ring doesn’t more affect by a donor-acceptor group. Attaching electron withdrawing active methylene core at the C3 position would lead to dyes with promising optical properties. Hence, easily accessible chloride is substituted at the second position of imidazo[1,2-a]pyridine. Polarisability and hyperpolarizability coefficients of organic molecules are increased by increasing extended conjugated π electrons and capacity of terminal donor and acceptor system [6]. In this context, well defined extended styryl rigid structures were studied. Intramolecular charge transfer moieties have potential applications as chromophores for nonlinear optics (NLO). Electron donor imidazopyridines and electron acceptor conjugated active malononitrile group has been used for the study. Significant, hyperconjugated electron donating effect and styryl electron withdrawing effect shown large change in nonlinear optical (NLO) properties in imidazo[1,2-a]pyridine derivatives.

Studied Dyes



4a: 2-((2-chloroimidazo[1,2-a]pyridin-3-yl)methylene)malononitrile
Chemical Formula: $C_{11}H_5ClN_4$
Exact Mass: 228.02
Molecular Weight: 228.64



4b: 2-((2-chloro-7-methylimidazo[1,2-a]pyridin-3-yl)methylene)malononitrile
Chemical Formula: $C_{12}H_7ClN_4$
Exact Mass: 242.04
Molecular Weight: 242.66

Figure 1. Molecular structures of extended 2-chloroimidazo[1,2-a]pyridine-3-carbaldehyde based styryl dyes.

2. Experimental

2.1 Materials and equipment and Computational Strategy

All the reagents were used as supplied from S. D. Fine Chemicals (India), Sigma Aldrich without any further purification. All the solvents were of the spectroscopic grade. Styryls were synthesized by using absolute ethanol & only piperidine as a catalytic amount used for the Knoevenagel condensation. Styryl dyes exhibited small fluorescence may be due to the presence of the twisting in the molecule. Styryles are soluble in common organic solvents, such as toluene, ethyl acetate (EA), acetonitrile, 1,4-dioxane (dioxane), dimethyl sulfoxide (DMSO), N,N-dimethylformamide (DMF), acetone, chloroform and dichloromethane (DCM) but are insoluble in water. The visible absorption spectra of the dyes were recorded in polar and non polar solvents on a Perkin-Elmer Lambda 25 UV-Visible spectrophotometer. All the computations were performed with Gaussian 09 package [7]. Styryls were optimized in gas phase in ground state by DFT method while TDDFT for excited state optimization was employed. The hybrid functional namely B3LYP and 6-31G(d) basis sets were used and the 6-31G(d) basis set was used in various solvent environment [8].

3. Result and Discussion

3.1 Photophysical Properties

Absorption spectra of starting material **3a:** 2-chloroimidazo[1,2-a]pyridine-3-carbaldehyde and **3b:** 2-chloro-7-methylimidazo[1,2-a]pyridine-3-carbaldehyde were shown in **Figure 2** and in various solvent medium.

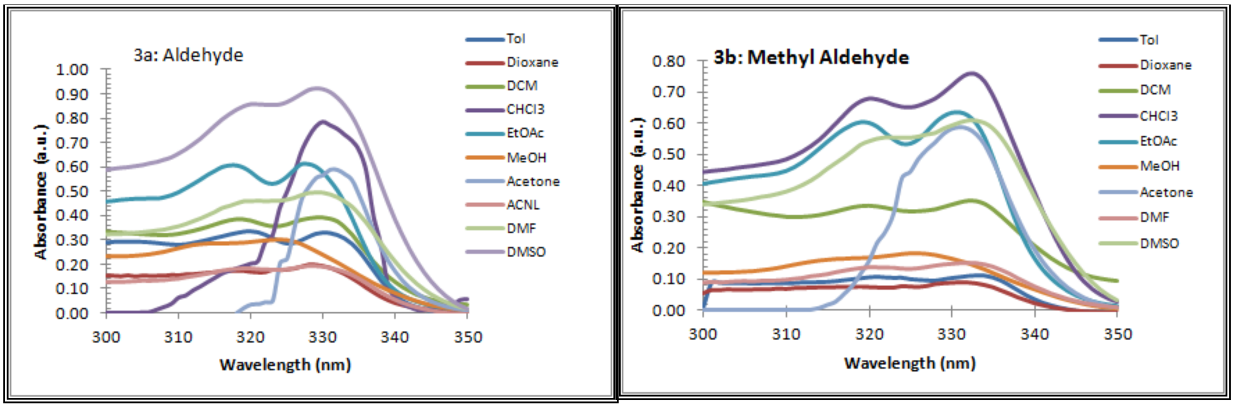


Figure 2. Effect of solvent polarity on absorption spectra starting aldehydes **3a** and **3b**.

Maximum absorption wavelength of starting aldehydes **3a:** 2-chloroimidazo[1,2-a]pyridine-3-carbaldehyde and **3b:** 2-chloro-7-methylimidazo[1,2-a]pyridine-3-carbaldehyde were in the range of 300 to 333 nm in various solvent mediums. In both aldehydes, absorption wavelengths were varying in small extend but its intensities were varied in large extend in series of polar and nonpolar solvents. Nonpolar solvents like Dioxane and Toluene shown less absorption intensities, while polar solvents ethylacetate and dimethyl sulfoxide (DMSO) shown highest absorption intensities. Which supports solvent dependent absorption behavior of both aldehydes in a wide range of nonpolar to polar environments.

Absorption spectra of extended styryl dyes (**4a and 4b**) are presented in **Figure 3** in various solvent medium.

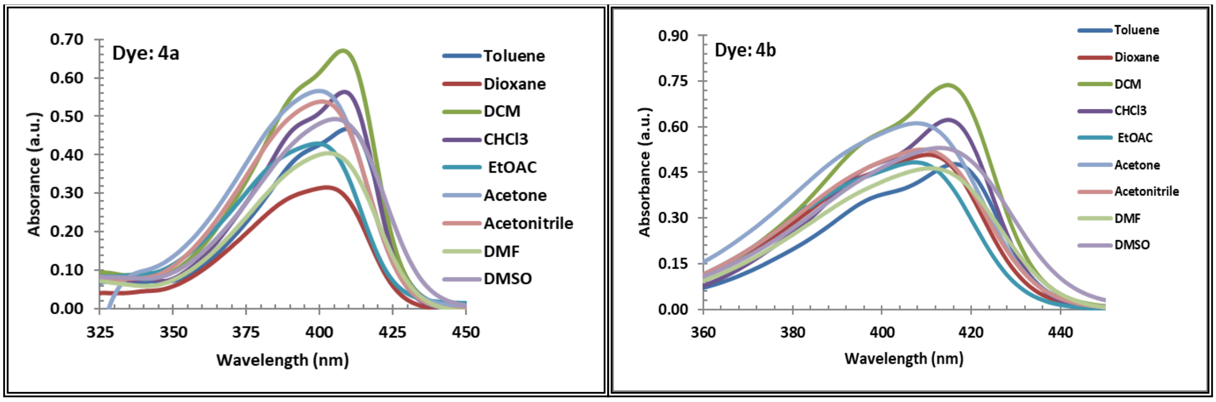


Figure 3. Effect of solvent polarity on absorption spectra of styryl dyes **4a-4b**.

The solvent polarity effect on photophysical properties like experimental absorption wavelength (in nm and in cm^{-1}), transition dipole moment (μ_{ge}), oscillator strength (*f*), molar absorptivity (ε), full width half maximum (FWHM) and computational vertical excitation in nm, oscillator strength (*f*) and orbital contribution band gap (eV) in different solvents is summarized in **Table 1**.

Table 1. Effect of solvent on photophysical properties of styryl dyes **4a-8b**.

Dyes	**Solvents**	**Experimental**						**Computed (TDDFT)**		
		$^a\lambda_{abs}$**(nm)**	$^a\lambda_{abs}$ **(cm^{-1})**	**ε Molar absorptivity (dm^{3}mo^{-1}1cm^{-1})**	f^b	**FWHM**	μ_{ge} **(Debye)**	**Vertical excitation (nm)^c**	f^b	**Orbital contribution band gap (eV)**
4a	Toluene	410	24390	10635.6	0.1596	46	3.73	385.51	0.6813	3.2161
	Dioxane	402	24876	7163.9	0.1087	48	3.05	383.46	0.6658	3.2333
	DCM	408	24510	15249.5	0.2199	44	4.37	387.14	0.6660	3.2025
	CHCl3	408	24510	12782.9	0.1809	44	3.96	386.46	0.6717	3.2082
	EtOAc	399	25063	9770.9	0.1688	49	3.79	385.06	0.6547	3.2198
	Acetone	400	25000	12872.2	0.2073	50	4.20	386.24	0.6493	3.2101
	ACN	401	24938	12249.5	0.1922	49	4.05	386.12	0.6451	3.2111
	DMF	403	24814	9206.7	0.1437	50	3.51	388.48	0.6657	3.1915
	DMSO	405	24691	11228.5	0.1863	51	4.01	388.22	0.6625	3.1937
4b	Toluene	416	24038	11581.2	0.1489	42	3.63	390.31	0.7411	3.1766
	Dioxane	410	24390	12311.6	0.1728	46	3.88	388.19	0.7255	3.1939
	DCM	415	24096	17841.3	0.2248	42	4.46	392.22	0.7290	3.1611
	CHCl3	415	24096	15038.1	0.1745	41	3.93	391.47	0.7331	3.1671
	EtOAc	407	24570	11668.3	0.1599	47	3.72	390.07	0.7171	3.1785
	Acetone	408	24510	14825.4	0.2096	49	4.27	391.28	0.7141	3.1687
	ACN	409	24450	12680.7	0.1796	48	3.96	391.14	0.7108	3.1698
	DMF	411	24331	11208.2	0.1589	49	3.73	393.57	0.7308	3.1502
	DMSO	413	24213	12865.6	0.1948	50	4.14	393.29	0.7279	3.1525

[a] Experimental absorption wavelength.
[b] Oscillator strength.
[c] Computed absorption wavelength.

In experimental results, all styryl dyes showed a large bathochromic shift in the range between 399 to 416 nm which is higher than starting aldehydes in range of 300 to 333 nm. In both dyes, toluene showed highest absorption wavelength, whereas ethylacetate, acetonitrile and acetone showed lowest absorption wavelengths. Generally, the extension of the π -systems and the strong electron withdrawing or donating ability exert an important influence on the absorption spectra. In these styryls, which may be attributed to the additional double bond in acceptor moiety with good conjugation in the acceptor-donor system. Especially due to hyperconjugation effect of the introduction of a methyl group at seventh position, **4b** dye showed red-shifted absorption wavelength in all solvents as shown in **Table 2** in comparison with its parent **4a** dye.

Table 2. Hyperconjugation methyl group effect on the wavelength of **4a-8b** styryl dyes.

Dye / Solvents	Toluene	DIOX	DCM	CHCl3	EtOAc	Acetone	ACN	DMF	DMSO
4a to 4b	6	8	7	7	8	8	8	8	8

Styryl dyes showed a large red shift in the polar solvent due to hyperconjugation effect of the methyl group. This large change maximum absorption (λ_{max}) is observed due to the increasing acceptor strength and conjugation of dyes. Transition dipole moments of the dyes ranging from 3.05 to 4.46, which indicates better charge transfer in dyes. Computational oscillator strength is ranging from 0.6451 to 0.7411 which is higher than experimental values which are ranging from 0.1087 to 0.1948.

3.2 Frontier Molecular Orbitals:

The absorption leading to the electronic excitation from the HOMO or HOMO-1 to the LUMO orbital can constitute the charge transfer from the imidazo[1,2-a]pyridine donor unit to the various acceptor unit malononitrile. In case of all the dyes, the HOMOs are mainly located on chloro-imidazole ring and π bridge while the LUMOs are located on the pyridine ring and acceptor units and represented in **Figure 4**.

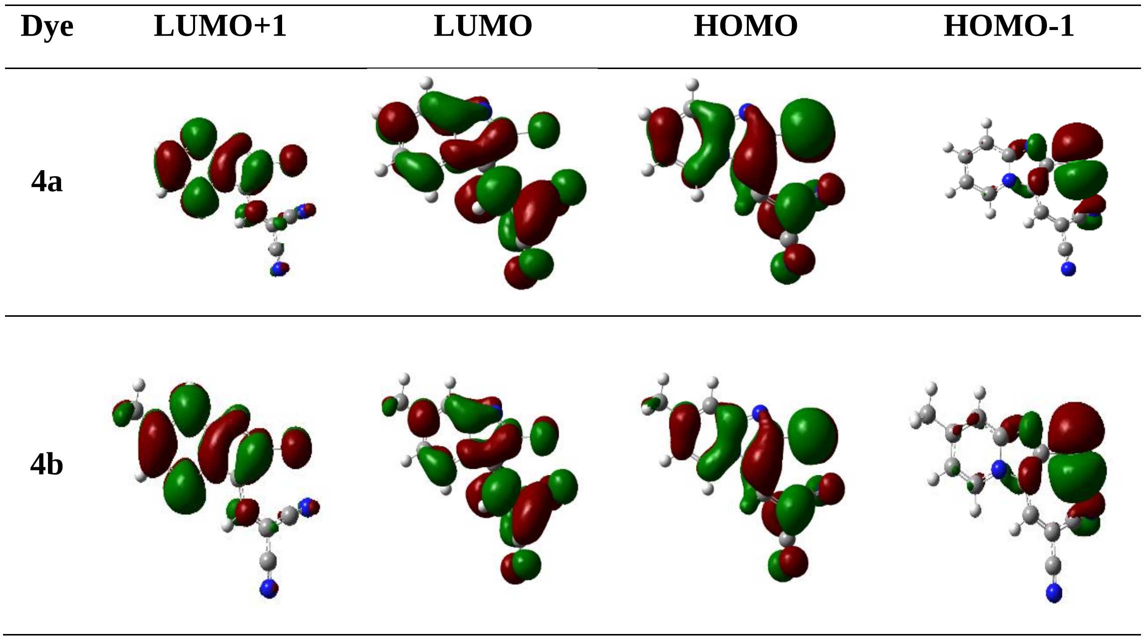


Figure 4. Frontier molecular orbitals of dyes **4a-8b** in DMSO solvent medium.

The HOMO and LUMO energy level diagram give a quantitative idea of electronic structure and excitation properties. In derivatives of malononitrile (**4a** and **4b**), HOMO-1 is located on chlroimidazole ring and small extent on cyano group and completely transferred to pyridine ring in LUMO+1. **Figure 5** tells that the calculated HOMO-LUMO energy band gap of the dyes **4a** and **8b** are 3.60 eV and 3.55 eV respectively.

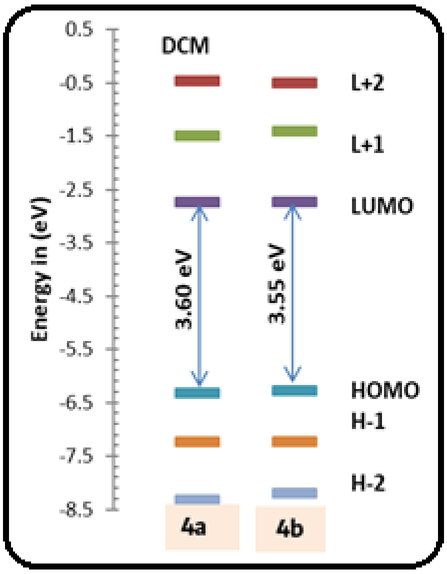


Figure 5. HOMO (H) – LUMO (L) energy level diagram of dyes **4a-4b** in DCM solvent.

As shown in **Figure 5,** Hyperconjugative effect of the methyl group in methylated dye **4b** exhibited a continuous reduction in the energy gap of 3.55 eV than nonmethylated dye **4a** 3.60.0 eV. The results reveal that lengthening of the π- systems, electron-donating and electron accepting ability of chromophore leads to dropping the HOMO-LUMO energy band gap. For dye **4b**, solvent polarity effect on HOMO-LUMO energy gap is represented in **Figure 6**.

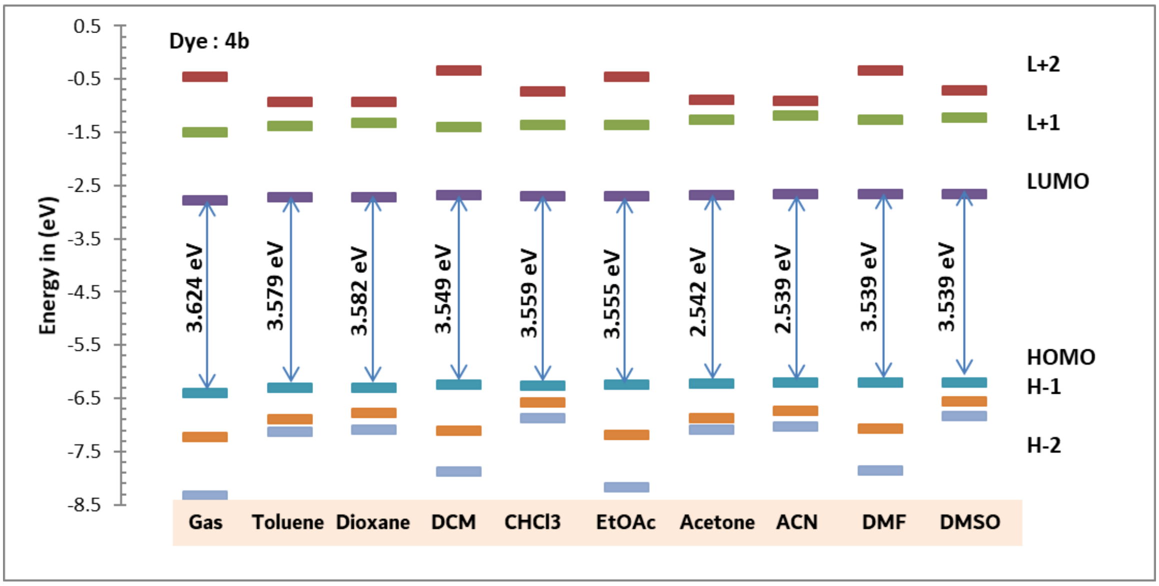


Figure 6. HOMO (H) – LUMO (L) energy level diagram of dye **4b** in various solvents.

In dye **4b**, change in HOMO-LUMO energy gap is observed in range 3.624-3.539 eV and lower in polar solvent whereas higher in the gas phase as well as in lower polarity solvent. Dyes are more stable in a polar solvent.

4. Nonlinear optical properties with its fundamental limits and intrinsic properties

Nonlinear optical properties of extended styryl dyes based on 2-chloroimidazo[1,2-a]pyridine-3-carbaldehyde in the different DCM solvent medium were evaluated using B3LYP functional with 6-311+G(d,p) basis set of the finite-field approach and solvatochromic method as well. The fundamental limit is the function of an energy difference between the ground and first excited state and number of electrons [9]. Mean polarizability (α_0), the mean first hyperpolarizability (β_0) and static second hyperpolarizability (γ) estimated and quantum sum rules applied to calculate the absolute maximum bound values of off-resonant electronic α, β and γ NLO properties allowed by nature [10]. Polarizability and hyperpolarizability with its fundamental limits and intrinsic values for dye **4a-8b** in DCM solvent by the CAM-B3LYP method represented in **Table 8**.

Table 3. Polarizability and hyperpolarizability with its fundamental limits and intrinsic values for dye **4a-8b** in DCM solvent by the CAM-B3LYP method.

Dye	μ	α_0	α_0^{max}	α_0^{int}	β_0	$\mu\beta_0$	β_0^{max}	β_0^{int}
		in 10^{-24} esu			in 10^{-30} esu			
4a	12.63	37.00	166	0.2229	34.46	435.35	1279	0.0269
4b	13.81	40.18	172	0.2336	44.01	607.64	1357	0.0324

Mean polarizability (α_0), mean first hyperpolarizability (β_0),upper limit of polarizability (α_0^{max}), upper limit of first hyperpolarizability (β_0^{max}), intrinsic polarizability (α_0^{int}) and intrinsic first hyperpolarizability (β_0^{int}).

Isophorone styryl derivatives (**6a** and **6b**) observe to show better values than all other dyes due to extended conjugation. The second-order hyperpolarizability with its maximum and minimum fundamental limits with intrinsic values for dyes **4a-8b** in DCM solvent medium by the CAM-B3LYP method are represented in **Table 9**.

Table 4. second-order hyperpolarizability with its maximum and minimum fundamental limits and intrinsic values for dyes **4a-8b** in DCM solvent medium by the CAM-B3LYP method.

Dye	$\bar{\gamma}$	$\bar{\gamma}^{min}$	$\bar{\gamma}^{max}$	$\bar{\gamma}_{int}^{min}$	$\bar{\gamma}_{int}^{max}$
4a	77.8	-5675	22702	-0.0137	0.0034
4b	89.11	-6179	24717	-0.0144	0.0036

Static second hyperpolarizability ($\bar{\gamma}$), upper negative ($\bar{\gamma}^{min}$) and positive ($\bar{\gamma}^{max}$) limit of the second hyperpolarizability, static negative intrinsic second hyperpolarizability ($\bar{\gamma}_{int}^{min}$), static positive intrinsic second hyperpolarizability ($\bar{\gamma}_{int}^{max}$).

The observed range for intrinsic polarizability is 0.2005 – 0.2676 and intrinsic first hyperpolarizability is 0.0261- 0.1015 which is within the limit of optimized range i.e. less than or equal to ($\leq$) 0.71. Observed range for negative second hyperpolarizability is -0.0137 - -0.0486 and positive second hyperpolarizability is 0.0034 - 0.0122 while optimized range is $-0.15 \leq \gamma \leq 0.6$ [11]. All the intrinsic property values are higher values for extended styryls derivatives. The fundamental limits provide a figure of merit for studied extended styryl dyes for future optical applications.

5. Vibrational Nonlinear optical properties

NLO properties can be separated into the electronic contribution and vibrational contribution on nuclear motions and the vibronic coupling. Vibrational properties play vital role in NLO properties of organic molecules[12]. The longitudinal components of vibrational and electronic polarizabilities and first hyperpolarizability as well as the ratio vibrational over electronic (α_v/α_e) and the addition of electronic and vibrational ($\alpha_e+\alpha_v$) are represented in **Table 10**.

Table 5. Longitudinal electronic and vibrational **polarizability** for dyes **4a-4b** in DCM solvent medium.

Dye	Electronic				Vibrational				α_v/α_e	$\alpha_e+\alpha_v$
	α_{xx}	α_{yy}	α_{zz}	α_e	α_{xx}	α_{yy}	α_{zz}	α_v		
4a	412.4	9.1	242.7	221.4	136.5	28.0	57.8	74.1	0.33	295.5
4b	453.1	18.9	258.3	243.4	148.7	32.5	69.5	83.5	0.34	327.0

The ratio of vibrational over electronic polarizability varies from 0.33 to 0.34. Longitudinal electronic and vibrational hyperpolarizability in atomic units for dyes **4a-4b** in the different solvent medium are summarized in **Table 11** by B3LYP functional and 6-311++g(d,p) basis set.

Table 6. Longitudinal electronic and vibrational **hyperpolarizability** for dyes **4a-8b** in DCM solvent medium.

Dye	Electronic				Vibrational				β_v/β_e	$\beta_v+\beta_e$
	β_{xx}	β_{yy}	β_{zz}	β_e	β_{xx}	β_{yy}	β_{zz}	β_v		
4a	-2198	-1779	-179	-1385	6226	732	-515	2148	-1.67	762.4
4b	-3155	-2025	-339	-1840	6728	800	-621	2302	-1.25	462.9

Vibrational properties are more significant than the electronic ones and observed ratio of vibrational over electronic first hyperpolarizability varies from 1.25 to 1.67 for studied styryls.

6. Conclusion

In conclusion, styryl dyes based on 2-chloroimidazo[1,2-a]pyridine-3-carbaldehyde showed a significant red shift in absorption wavelength. In dye **4b**, change in HOMO-LUMO energy gap is observed in range 3.624-3.539 eV and lower in polar solvent whereas higher in the gas phase as well as in lower polarity solvent. Dyes are more stable in a polar solvent. Observed range for intrinsic polarizability is 0.2229 – 0.2336 and intrinsic first hyperpolarizability is 0.0269- 0.0324 which is within the limit of optimized range i.e. less than or equal to (≤) 0.71. Observed range for negative second hyperpolarizability is -0.0137 - -0.0144 and positive second hyperpolarizability is 0.0034 - 0.0036 while optimized range is $-0.15 \leq \gamma \leq 0.6$. All the intrinsic property values are higher values for extended styryls derivatives indicating strong candidature for optical applications.

7. Acknowledgement:

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