# Nonlinear Optical Properties (NLO) Study of Some Novel Fluorescent 2-Chloroimidazo [1,2-A] Pyridine Derivatives

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*Abstract:*

*Extended styryl dyes based on 2-chloroimidazo[1,2-a]pyridine-3-carbaldehyde showed alarge bathochromic shift in the range between 399 to 416 nm from starting aldehydes in range of 300 to 333 nm. Hyperconjugated electron donating methyl group and alone pair of nitrogen are in proper resonance with electron acceptor styryl group. These methylated dyes displayed 6 to 8 nm enhancement in broad absorption maximum in various nine solvents. Computational absorption wavelengths trends are matching with the experimental trends.*

*In HOMO-LUMO energy gap, methylated dyes showed a consistent decrease in the energy gap of 0.05 eV than nonmethylated dyes.Dyeswere studied using various solvent polarity scales and multilinear regression analysis using Kamlet-Taft and Catalan scales.NBO analysis, a large number of stabilization energy E(2) entries were observed higher than 20 k J/ mol in both dyes indicating sufficient delocalization in donor-acceptor sites. In this research work,dipole moment (μ), electronic polarizability (α), mean first hyperpolarizability (β₀) and second hyperpolarizability (γ)are computed with its fundamental limits and intrinsic values using density functional theory method in conjunction with 6-31G(d) basis set and vibrational NLO properties with 6-311++g(d,p) basis set.The dyes have fundamental limits and intrinsic properties 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 displaynonlinear electric susceptibilitieswith potential applications in telecommunications[1], organic field effect transistors(OFETs)[2],organic photovoltaics(OPVs)[3], anorganic light emitting diode(OLEDs)[4], optical information & environment sensitive fluorescent sensors[5].Indoles and azaindoles are isosters of imidazo[1,2-a]pyridine moiety and possessing electron donating properties [6]. 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 influorescent high-affinity ligand in dopamine D3 [7] due to their promising NLO (nonlinearoptical properties)[8]. Styryl dyes typically employed in advanced material such as laser dyes, solar cell sensitizer,  optical or electro-optical devices or sensor materials [9], DNA probes and voltage-sensitive dyes in cardiac tissue[10–13]. 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[14].

Imidazo[1,2-a]pyridines own the highest electron-density at C3 and this is typically the site of anattack in electrophilic aromatic substitution. Thesecond position of imidazo[1,2-a]pyridine ring doesn't more affect by adonor-acceptor group[15]. Attaching electron withdrawing active methylene core at theC3 position would lead to dyes with promising optical properties. Hence, easily accessible chloride is substituted at thesecond position of imidazo[1,2-a]pyridine. Polarisability and hyperpolarizability coefficients of organic molecules are increased by increasing extended conjugated $\pi$ electrons and capacity of terminal donor and acceptor system [16]. In this context, well defined extended styryl rigid structureswere studied. Intramolecular charge transfer moieties have potential applications as chromophores for nonlinear optics (NLO)[17]. The NLO properties of the molecules like mean polarizability ($\alpha_0$), intrinsic polarizability ($\alpha_0^{int}$), upper limit of polarizability ($\alpha_0^{max}$), mean first hyperpolarizability ($\beta_0$), upper limit of first hyperpolarizability ($\beta_0^{max}$), intrinsic first hyperpolarizability ($\beta_0^{int}$), static second hyperpolarizability ($\bar{\gamma}$), upper negative ($\bar{\gamma}^{min}$) and positive ($\bar{\gamma}^{max}$) limit of second hyperpolarizability, static negative intrinsic second hyperpolarizability ($\bar{\gamma}_{int}^{min}$), static positive intrinsic second hyperpolarizability ($\bar{\gamma}_{int}^{max}$) were estimated and correlated with the structures of styryl dyes. 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.
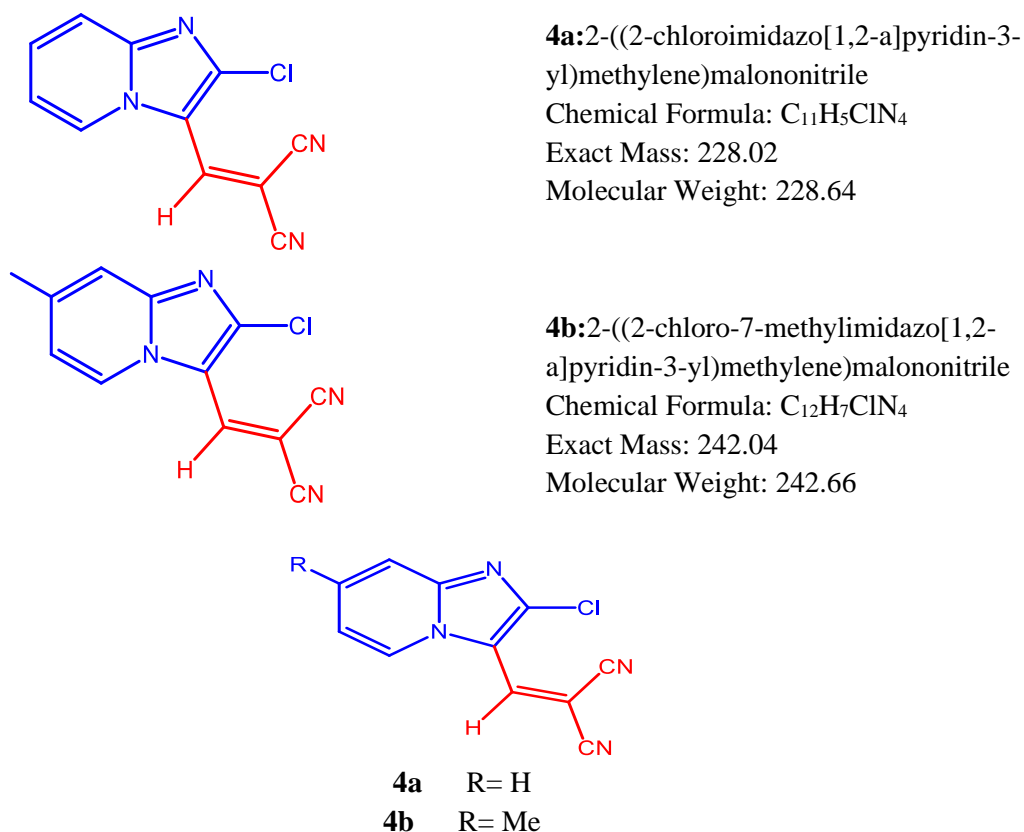
**Studied Dyes**



**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

**4a**     R= H
**4b**     R= Me

**Figure1.**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 exhibitedsmall fluorescencemay be due to the presence of the twisting in the molecule. Styrylesare soluble in common organic solvents, such astoluene, 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 [18]. 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[19–22].

## 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-carbaldehydewere shown in **Figure 2** and in various solvent medium.
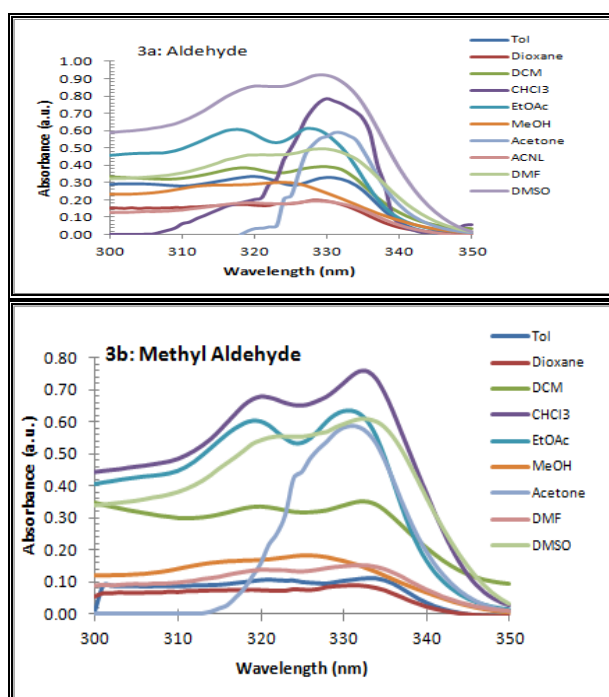


**Figure2.**Effect of solvent polarity on absorption spectra starting aldehydes **3a** and **3b**.

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-carbaldehydewere 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.
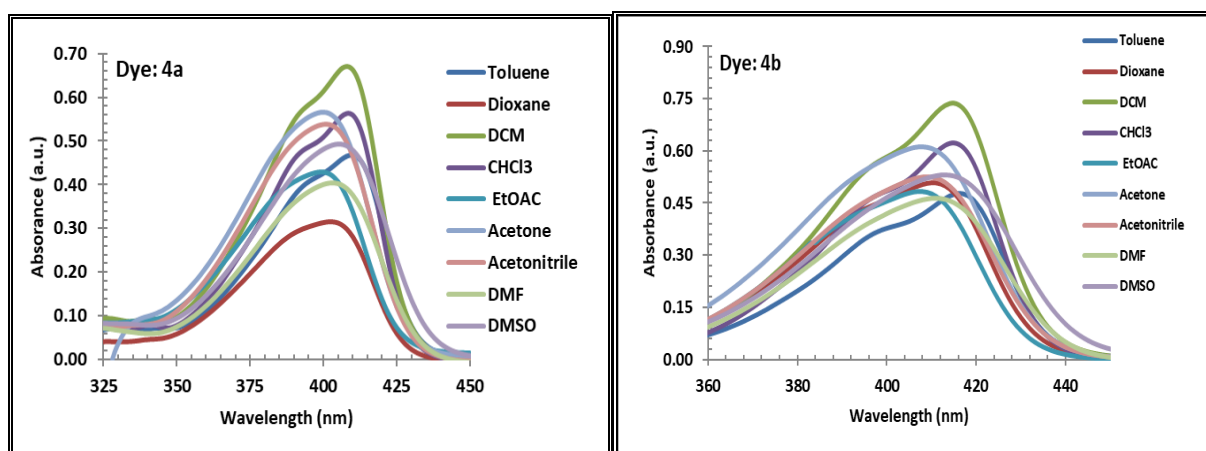


**Figure3.** Effect of solvent polarity on absorption spectra of styryl dyes **4a-4b**.

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

**Table1.** Effect of solvent on photophysical properties of styryl dyes **4a-8b**.

| Dyes | Solvents | $^a\lambda_{abs}$(nm) | $^a\lambda_{abs}$ (cm$^{-1}$) | Ɛ Molar absorptivity (dm³mo⁻¹cm⁻¹) | $f^b$ | FWHM | $\mu_{ge}$(Debye) | Vertical excitation (nm)$^c$ | $f^b$ | Orbital contribution band gap (eV) |
|------|----------|------|------|------|------|------|------|------|------|------|
| | | | | **Experimental** | | | | **Computed (TDDFT)** | | |
| **4a** | Tolue | 410 | 2439 | 10635.6 | 0.159 | 46 | 3.73 | 385.51 | 0.681 | 3.2161 |
| | Dioxa | 402 | 2487 | 7163.9 | 0.108 | 48 | 3.05 | 383.46 | 0.665 | 3.2333 |
| | DCM | 408 | 2451 | 15249.5 | 0.219 | 44 | 4.37 | 387.14 | 0.666 | 3.2025 |
| | CHCl | 408 | 2451 | 12782.9 | 0.180 | 44 | 3.96 | 386.46 | 0.671 | 3.2082 |
| | EtOA | 399 | 2506 | 9770.9 | 0.168 | 49 | 3.79 | 385.06 | 0.654 | 3.2198 |
| | Aceto | 400 | 2500 | 12872.2 | 0.207 | 50 | 4.20 | 386.24 | 0.649 | 3.2101 |
| | ACN | 401 | 2493 | 12249.5 | 0.192 | 49 | 4.05 | 386.12 | 0.645 | 3.2111 |
| | DMF | 403 | 2481 | 9206.7 | 0.143 | 50 | 3.51 | 388.48 | 0.665 | 3.1915 |
| | DMS | 405 | 2469 | 11228.5 | 0.186 | 51 | 4.01 | 388.22 | 0.662 | 3.1937 |
| **4b** | Tolue | 416 | 2403 | 11581.2 | 0.148 | 42 | 3.63 | 390.31 | 0.741 | 3.1766 |
| | Dioxa | 410 | 2439 | 12311.6 | 0.172 | 46 | 3.88 | 388.19 | 0.725 | 3.1939 |
| | DCM | 415 | 2409 | 17841.3 | 0.224 | 42 | 4.46 | 392.22 | 0.729 | 3.1611 |
| | CHCl | 415 | 2409 | 15038.1 | 0.174 | 41 | 3.93 | 391.47 | 0.733 | 3.1671 |
| | EtOA | 407 | 2457 | 11668.3 | 0.159 | 47 | 3.72 | 390.07 | 0.717 | 3.1785 |

| Aceto | 408 | 2451 | 14825.4 | 0.209 | 49 | 4.27 | 391.28 | 0.714 | 3.1687 |
| ACN | 409 | 2445 | 12680.7 | 0.179 | 48 | 3.96 | 391.14 | 0.710 | 3.1698 |
| DMF | 411 | 2433 | 11208.2 | 0.158 | 49 | 3.73 | 393.57 | 0.730 | 3.1502 |
| DMS | 413 | 2421 | 12865.6 | 0.194 | 50 | 4.14 | 393.29 | 0.727 | 3.1525 |

[a]Experimental absorption wavelength.

[b]Oscillator strength.

[c]Computed absorption wavelength.

In experimental results, all styryl dyes showed alarge 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 $\pi$ -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.

**Table2.** Hyperconjugation methyl group effect on the wavelengthof **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 ($\lambda_{max}$) 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 $\pi$ bridge while the LUMOs are located on the pyridine ring and acceptor units and represented in **Figure 4**.

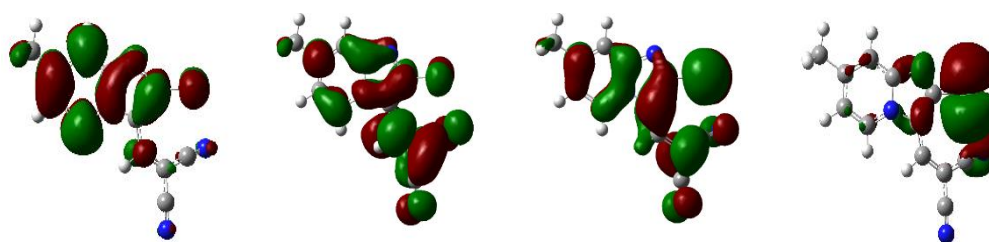| Dye | LUMO+1 | LUMO | HOMO | HOMO-1 |
|---|---|---|---|---|
| **4a** | | | | |
| **4b** | | | | |
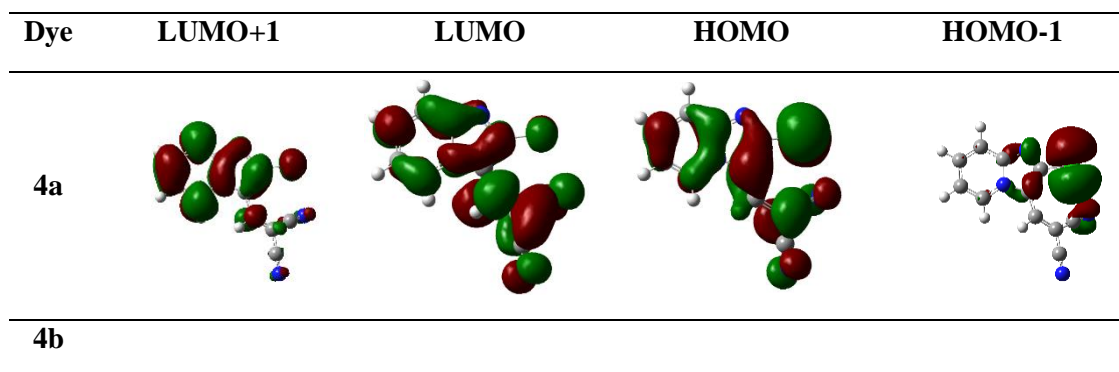
**Figure 4.** Frontier molecular orbitals of dyes **4a-8b** in DMSO solvent medium.

The HOMO and LUMO energy level diagram give aquantitative 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.
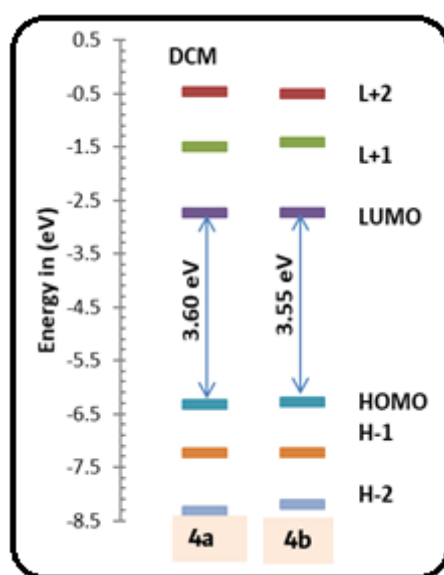


## 3.3 Natural Bond Order (NBO) Analysis

Natural charges molecule enabled to know the interactions and intramolecular charge circulation. Acceptor fragment carries a positive charge while donor carries a negative charge. In nitrogen atom, acceptor nitrogen carries negative charge while donor nitrogen atom carries a positive charge[23].Optimised Structural diagram of dye **4a** and **4b** in DCM shown in **Figure 7.**
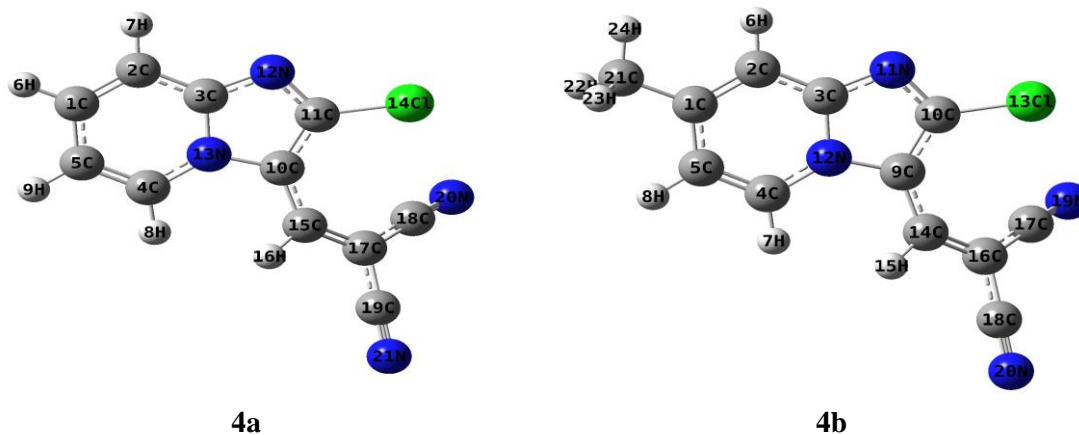


**4a**                                                                      **4b**

**Figure 5.**Optimised Structural diagram of dye **4a** and **4b** in DCM.

The Natural charges on atoms except forhydrogen in dye **4a** and **4b** have been shown in **Table 3**.
**Table 3.** Natural charges on atoms of dyes **4a** and **4b**except for hydrogen atoms in DCM.

| 4a | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| **Atom No** | **Charges** | | **Atom No** | **Charges** | | **Atom No** | **Charges** | |
| C | 1 | -0.0156 | C | 11 | 0.1820 | C | 17 | -0.3112 |
| C | 2 | -0.2126 | N | 12 | -0.5188 | C | 18 | 0.3107 |
| C | 3 | 0.3911 | N | 13 | -0.3376 | C | 19 | 0.3189 |
| C | 4 | 0.0599 | Cl | 14 | 0.0745 | N | 20 | -0.3449 |
| C | 5 | -0.2303 | C | 15 | -0.0585 | N | 21 | -0.3598 |
| C | 10 | 0.0119 | | | | | | |
| **4b** | | | | | | | | |
| C | 1 | 0.0269 | C | 10 | 0.1831 | C | 17 | 0.3114 |
| C | 2 | -0.2226 | N | 11 | -0.5218 | C | 18 | 0.3195 |
| C | 3 | 0.3996 | N | 12 | -0.3417 | N | 19 | -0.3491 |
| C | 4 | 0.0652 | Cl | 13 | 0.0727 | N | 20 | -0.3642 |
| C | 5 | -0.2266 | C | 14 | -0.0595 | C | 21 | -0.5994 |
| C | 9 | 0.0096 | C | 16 | -0.3167 | | | |

The delocalization energy E(2) describes the donor(i)- acceptor(j) interactions and given by

$$E\ (2) = q_i \frac{F(i,j)^2}{\Box_j - \Box_i}$$

Where,$q_i$ is the occupation number of the donor orbital, $\Box_j$and $\Box_i$are diagonal elements and equal to the orbital energies. Hence, F $(i, j)$ is the off-diagonal of Fock matrix[23].The donor-acceptor interactions and stability of imidazo[1,2-a]pyridine styryl dyes were investigated by the second order Fock matrix using B3LYP/6-311+G(d,p). Intermolecular charge transfer and stabilization energies of dye **4a** and **4b** were represented in **Table 4**.

**Table 4.** Second-order perturbation energies E(2) (Donor→Acceptor interactions) of dye **4a** and **4b**in DCM medium.

| Donor(i) | [a]ED(e) | Acceptor (j) | [a]ED(e) | [b]E(2) kJ/mol | [c]E(j)-E(i) a.u. | [d]F(i,j) a.u. |
|---|---|---|---|---|---|---|
| **Dye 4a** | | | | | | |
| LP(1)(N13) | 1.4739 | π*(C03-N12) | 0.5472 | 49.96 | 0.25 | 0.080 |
| | | π*(C04-C05) | 0.2338 | 33.43 | 0.30 | 0.097 |
| | | π*(C10-C11) | 0.4987 | 28.39 | 0.27 | 0.079 |
| π(C01-C02) | 1.707 | π*(C03-N12) | 0.5472 | 28.06 | 0.25 | 0.080 |
| π(C03-N12) | 1.707 | π*(C10-C11) | 0.4987 | 34.84 | 0.29 | 0.095 |
| π(C10-C11) | 1.682 | π*(C15-C17) | 0.2880 | 22.44 | 0.29 | 0.073 |
| **Dye 4b** | | | | | | |
| LP(1)(N12) | 1.4820 | π*(C04-C05) | 0.2241 | 33.52 | 0.30 | 0.224 |
| | | π*(C09-C10) | 0.5008 | 28.25 | 0.27 | 0.080 |
| π(C01-C02) | 1.6910 | π*(C03-N11) | 0.5489 | 30.15 | 0.24 | 0.080 |

| | | | | | | |
|---|---|---|---|---|---|---|
| π(C03-N11) | 1.6977 | π*(C09-C10) | 0.5008 | 35.35 | 0.29 | 0.100 |
| π(C09-C10) | 1.6821 | π*(C14-C16) | 0.2983 | 23.24 | 0.29 | 0.070 |
| π(C14-C16) | 1.7982 | π*(C17-N19) | 0.1015 | 20.79 | 0.38 | 0.080 |
| π(C14-C16) | 1.7982 | π*(C18-N20) | 0.1055 | 22.18 | 0.38 | 0.080 |

Where, [a]ED is the electron density, [b]E(2) means the energy of hyperconjugative interactions (stabilization energy), [c] Energy difference between donor and acceptor i and j NBO orbitals, [d]F(i, j) is the Fock matrix element between i and j NBO orbitals

A large number of stabilization energy E(2) entries were observed higher than 20 k J/ mol in both dyes indicating sufficient delocalization in donor-acceptor sites. In **dye 4a,** lone pair (N13) interacted with C03-N12, C04-C05 and C10-C11 with E(2) energy higher than 28.39 kJ/mol. At the same time pi interaction in C01-C02 to C03-N12, C03-N12 to C10-C11 and C10-C11 to C15-C17 with E(2) energy higher than 22.44 kJ/mol. Clearly, this direction of flow of electron is from pyridine to pyrrole and then pyrrole to styryl group means in acceptor direction. Similarly in **dye 4b,** thedirection of delocalizations C01-C02 to C03-N11, C03-N11 to C09-C10, C09-C10 to C14-C16, C14-C16 to C17-N19 and C14-C16 to C18-N20 were clearly from pyridine bonds to pyrrole, pyrrole to styryl unit then styryl unit to both cyano acceptor groups.

**3.4 Correlation with multiparameter solvent polarity scales:** Understanding the effect of microenvironmenton the spectroscopic properties of imidazo[1,2-a]pyridine dyeslooks to be very importantfor a better considerate the solute-solvent interactions. Theoretical explanation of the solute-solvent interactions hasbeen given by many scientists [24]. One of the most powerful and popular model, proposed by Kamlet and Taft[25], assumes that thesolute-solvent interactions are frequently of two kinds: non-specific(dipolarity/polarizability) and specific (hydrogen bond donor andhydrogen bond acceptor complexing) interactions[26,27]. Multiple parameters are arranged in order to characterize the solute-solvent interactions, in the term of Eq. (4.1)

$$y = y_0 + a_\alpha \alpha + b_\beta \beta + c_{\pi*}\pi* \text{ (Kamlet-Taft)} \tag{4.1}$$

where y signifies the solvent dependent physiochemical property in a given solvent, $y_0$ represents the statistical quantity conforming to the value of property in gas phase., $\alpha$ signifies the effect of acidity (hydrogen-bond donatingability) of solvent, $\beta$ signifieseffect of basicity (hydrogen-bond accepting ability) of solvent and $\pi*$ signifies the collective effectof solvent polarity (also known as dipolarity) and polarizability and $a_\alpha$, $b_\beta$, $c_{\pi*}$ are susceptibility of constants. Butif acidity or basicity of solvents is not affecting on the value of y,then among polarity and polarizability, it is difficult to sort outwhich factor is exactly influencing the studied physiochemical property y. Hence, polarity scale ($\pi*$) proposed by Kamlet andTaft has been further separated by Catalán into two independentparameters: solvent polarizability (SP) and dipolarity (SdP) scales and proposed another expression equation (2) [28,29] …

$$y = y_0 + a_{SA}SA + b_{SB}SB + c_{SP}SP + d_{SDP}Sdp \text{ (Catalan)} \tag{4.2}$$

Where SA denotessolvent acidity/solvents hydrogen bond donor strength,SB denotes solvent basicity/hydrogen bond acceptor strength, SP denotes solvent polarizability and SdP denotes solventdipolarity. The multi-linear analysis is carried out to study our red-shiftedabsorption spectra for all imidazo[1,2-a]pyridine styryl derivatives in nine polar and nonpolar solvents. we used both, the well-established Kamlet-Taft as well as itsimproved version by Catalan simultaneously to understand exactly which factor i.e. solvent basicity, acidity, polarizability or dipolarity is mainly affecting the altered

photophysical properties of these styryl derivatives in solvents of different polarities.Estimated coefficients for all dyes by Kamlet-Taft and Catalan method are represented in **Table 7** for **4a-8b** dyes.

**Table 5.**Estimated ($y_0$, a, b, c, d) their standard errors and correlation for the multi-linear analysis of absorption of dyes **4a-8b** as a function of Kamlet-Taft and Catalan solvents scales.

| Kamlet-Taft | $y_0 \times 10^3$ | $a_\alpha$ | $b_\beta$ | $c_{\pi*}$ | $r$ |
|---|---|---|---|---|---|
| **4a** | $25.04 \pm 0.40$ | $0.74 \pm 0.65$ | $1.10 \pm 0.49$ | $-1.04 \pm 0.65$ | 0.51 |
| **4b** | $24.62 \pm 0.33$ | $0.51 \pm 0.53$ | $0.86 \pm 0.40$ | $-0.94 \pm 0.53$ | 0.50 |

| Catalan | $y_0 \times 10^3$ | $a_{SA}$ | $b_{SB}$ | CSdP | $d_{SP}$ | r |
|---|---|---|---|---|---|---|
| **4a** | $27.00 \pm 0.39$ | $3.09 \pm 1.64$ | $0.79 \pm 0.12$ | $-0.29 \pm 0.15$ | $-3.29 \pm 0.48$ | 0.97 |
| **4b** | $26.18 \pm 0.25$ | $1.94 \pm 1.07$ | $0.59 \pm 0.08$ | $-0.22 \pm 0.10$ | $-2.71 \pm 0.32$ | 0.98 |

Where α or SA = solvent acidity, β or SB = solvent basicity, $\pi*$ =collective parameter of solvent dipolarilty and polarizability according to Kamlet-Taft equation, SdP and SP = solvent dipolarity and polarizability respectively according to Catalan equation.

In all dyes, Catalan parameters show better correlation coefficient (r =0.81-0.99) than Kamlet-Taft parameters (0.49-0.80). Large standard errors observed on both Kamlet-Taft and Catalan parameters for solvent acidity and basicity, factors suggest that mainly solvent dipolarity or polarizability are accountable for the slightly red-shifted absorption spectra.

Dicyanovinylene (**4a** and **4b**)derivatives showed negative valuesfor solvent dipolarilty and polarizability ($\pi*$) by Kamlet-Taft analysis and solvent polarizability (SdP) by Catalan analysis supports absorption.

## 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 thedifferent 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 [30]. Mean polarizability ($\alpha_0$), the mean first hyperpolarizability ($\beta_0$) and static secondhyperpolarizability ($\gamma$) estimated and quantum sum rules applied to calculate the absolute maximum bound values of off-resonant electronic$\alpha$,$\beta$ and $\gamma$ NLO properties allowed by nature[30–34].

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**.

## 5. Conclusion

In conclusion, styryl dyes based on 2-chloroimidazo[1,2-a]pyridine-3-carbaldehyde showed asignificant 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. In both dyes,the negative value observed for all three solvent parameters like basicity, dipolarityand polarizability both by Kamlet-Taft and Catalan analysis supports red-shifted absorption. NBO analysis for the dye **4a**, lone pair (N13) interacted with C03-N12, C04-C05 and C10-C11 with E(2) energy higher than 28.39 kJ/mol. At the same time pi interaction in C01-C02 to C03-N12, C03-N12 to C10-C11 and C10-C11 to C15-C17 with E(2) energy

higher than 22.44 kJ/mol. Clearly, this direction of flow of electron is from pyridine to pyrrole and then pyrrole to styryl group means in acceptor direction.

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 ($\leq$) 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.

## References

[1]     Brédas JL. Molecular Geometry and Nonlinear Optics. Science (80- ) 1994;263:487–8. doi:10.1126/science.263.5146.487.

[2]     Katsuta S, Miyagi D, Yamada H, Okujima T, Mori S, Nakayama K, et al. Synthesis, Properties, and Ambipolar Organic Field-Effect Transistor Performances of Symmetrically Cyanated Pentacene and Naphthacene as Air-Stable Acene Derivatives. Org Lett 2011;13:1454–7. doi:10.1021/ol200145r.

[3]     Sukeguchi D, Singh SP, Reddy MR, Yoshiyama H, Afre RA, Hayashi Y, et al. New diarylmethanofullerene derivatives and their properties for organic thin-film solar cells. Beilstein J Org Chem 2009;5:7. doi:10.3762/bjoc.5.7.

[4]     Fu H, Wu H, Hou X, Xiao F, Shao B. N -Aryl carbazole derivatives for non-doped red OLEDs 2006;156:809–14. doi:10.1016/j.synthmet.2006.04.013.

[5]     Sarma M, Chatterjee T, Ghanta S, Das SK. D-pi-A-A-pi-D prototype 2,2-bipyridine dyads exhibiting large structure and environment-sensitive fluorescence: Synthesis, photophysics, and computation. J Org Chem 2012;77:432–44. doi:10.1021/jo202015m.

[6]     Jianliang Z, Jianchao L, Qiyuan C. Advances in Synthesis of Imidazopyridine Derivatives. Chinese J Org Chem 2009;29:1708–18.

[7]      Leopoldo M, Lacivita E, Passafiume E, Contino M, Colabufo NA, Berardi F. High-Affinity Dopamine D 3 Receptor Ligands as Potential Probes for Receptor Visualization. J Med Chem 2007;50:5043–7.

[8]     Tomoda H, Hirano T, Saito S, Mutai T, Araki K. Substituent Effects on Fluorescent Properties of Imidazo(1,2-a)pyridine-Based Compounds. Bull Chem Soc Jpn 1999;72:1327–34. doi:10.1246/bcsj.72.1327.

[9]     Gromov SP, Ushakov EN, Fedorova OA, Baskin II, Buevich A V, Andryukhina EN, et al. Novel photoswitchable receptors: Synthesis and cation-induced self-assembly into dimeric complexes leading to stereospecific [2+2]-photocycloaddition of styryl dyes containing a 15-crown-5 ether unit. J Org Chem 2003;68:6115–25. doi:10.1021/jo034460x.

[10]   Matiukas A, Mitrea BG, Pertsov AM, Wuskell JP, Wei M-D, Watras J, et al. New near-infrared optical probes of cardiac electrical activity. Am J Physiol - Hear Circ Physiol 2006;290:H2633–43. doi:10.1152/ajpheart.00884.2005.

[11]   Kovalska VB, Losytskyy MY, Kryvorotenko D V, Balanda AO, Tokar VP, Yarmoluk SM. Synthesis of novel fluorescent styryl dyes based on the imidazo[1,2-a]pyridinium chromophore and their spectral-fluorescent properties in the presence of nucleic acids and proteins. Dye Pigment 2006;68:39–45. doi:10.1016/j.dyepig.2004.12.010.

[12]    Aranda AI, Achelle S, Hammerer F, Mahuteau-Betzer F, Teulade-Fichou M-P. Vinyl-diazine triphenylamines and their N-methylated derivatives: Synthesis, photophysical properties and application for staining DNA. Dye Pigment 2012;95:400–7. doi:10.1016/j.dyepig.2012.04.009.

[13]    Dna Q, Xie X, Choi B, Largy E, Guillot R, Granzhan A. Asymmetric Distyrylpyridinium Dyes as Red-Emitting Fluorescent Probes. Chem - A Eur J 2013;19:1214–26. doi:10.1002/chem.201203710.

[14]    Walker B, Kim C, Nguyen T-Q. Small Molecule Solution-Processed Bulk Heterojunction Solar Cells. Chem Mater 2011;23:470–82. doi:10.1021/cm102189g.

[15]    Firmansyah D, Ciuciu AI, Hugues V, Blanchard-Desce M, Flamigni L, Gryko DT. Bright, fluorescent dyes based on imidazo[1,2-a]pyridines that are capable of two-photon absorption. Chem - An Asian J 2013;8:1279–94. doi:10.1002/asia.201300058.

[16]    Electron transfer in flexible molecules and molecular ions . Pure Appl Chem  1993;65:1751. doi:10.1351/pac199365081751.

[17]    Xia Z-Y, Zhang Z-Y, Su J-H, Zhang Q, Fung K-M, Lam M-K, et al. Robust and highly efficient blue light-emitting hosts based on indene-substituted anthracene. J Mater Chem 2010;20:3768–74. doi:10.1039/C000092B.

[18]    Frisch MJ, Trucks GW, Schlegel HB, Scuseria GE, Robb MA, Cheeseman JR, et al. Gaussian 09, Revision C.01. Gaussian 09, Revis B01, Gaussian, Inc, Wallingford CT 2009.

[19]    Stephens PJ, Devlin FJ, Chabalowski CF, Frisch MJ. Ab initio calculation of vibrational absorption and circular dichroism spectra using density functional force fields. J Phys Chem 1994;98:11623–7. doi:10.1021/j100096a001.

[20]    Becke AD. A new mixing of Hartree–Fock and local density functional theories. J Chem Phys 1993;98:1372–7.

[21]    Lee C, Yang W, Parr RG. Development of the Colle-Salvetti correlation-energy formula into a functional of the electron density. Phys Rev B 1988;37:785–9. doi:10.1103/PhysRevB.37.78