

# N-Bridge Head Indolizin (Benzindolizin)-ium Iodide as Privileged Precursor in Heterocyclic Cyanine Dye Synthesis

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**Abstract:** 3-Methyl-1-phenyl-pyrazolin-5-imino-4(2)-indolizine (benzindolizine)-zero-3(4)-methine (27). 3-methyl-1-phenyl-pyrazolin-5-imino-4(2)-indolizine (benzo-indolizine)-B-substituted di-1-[2(4)] methine cyanine dyes (28a-d). 3-methyl-1-phenyl-pyrazolin-5-imino-4(2)-indolizine (benzo-indolizine)-β (δ) disubstituted- bis-di- [2(4)] methine cyanine dyes (30a-f) were synthesised based on 4-acetyl-1,5-dimethyl-3-phenyl-3,4-di[H]pyrazolo [4',3':5,6]pyrido[4,3-b]indolizin-6-ium iodide & 4-Acetyl-1,5-dimethyl-3-phenyl-3,4-di[H]Pyrazolo [4',3':5,6] pyrido[4,3-b]indolizin-6-ium-iodide(26a,b) & 1,5-dimethyl-3-phenyl-3,4-di[H] pyrazolo[4',3':5,6]pyrido[4,3-b]indolizin-6-ium-iodide-4-β-substituted-α,β-unsaturated carbonyl derivatives (29a-f). The new synthesized cyanine dyes were identified by elemental & spectral analyses. The UV-visible absorption spectra of some selected dyes were investigated in pure organic solvents and in aqueous universal buffer solutions.

**Keywords:** Indolizine (Benzindolizine) Cyanine Dye Synthesis, Solvato-(Media)-chromic Behaviour

## 1. Introduction

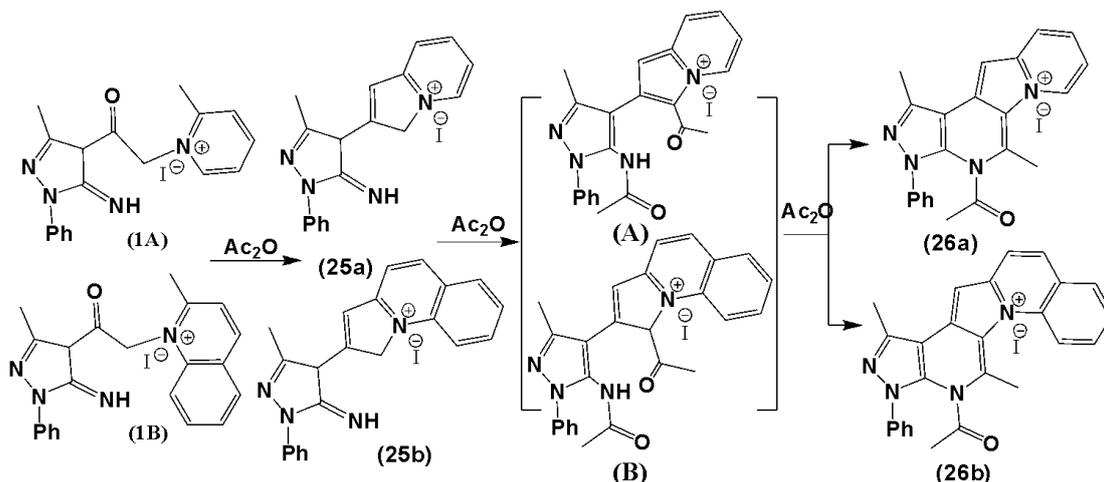
Cyanine dyes are among the most versatile functional dyes [1]. Besides their use as colorants [2], they have considerable potential for application in energy conversion [3], as laser dyes [4] and as optoelectronic and photonic devices [5]. Moreover, some cyanine and related dyes show strong interactions with nucleic acids with efficient interaction and photodamage of DNA [6, 7]. The application of these dyes as potential fluorescence sensors [8] or as electro-, chemo-, and photoluminescent devices [9] is limited. A variety of heterocyclic cyanine dyes incorporating N-bridge head bridgehead heterocyclic moieties have been reported. These have many vital general applications such as their use as photosensitizers in photographic processes, photographic material showing good antihalation or antiradiation effect [10], high sensitivity and low fogging [11], information recording media of high reflectivity and carrier-to-noise ratio, laser disc media, laser-sensitive optical recording material. Besides their use as colorants [12] they have considerable potential for application in energy conversion, [11]. N-bridge head bridgehead heterocyclic cyanine dyes were used as antimicrobial agents [13, 14a, b], useful for preparing superconducting polymers [15].

## 2. Results & Discussion

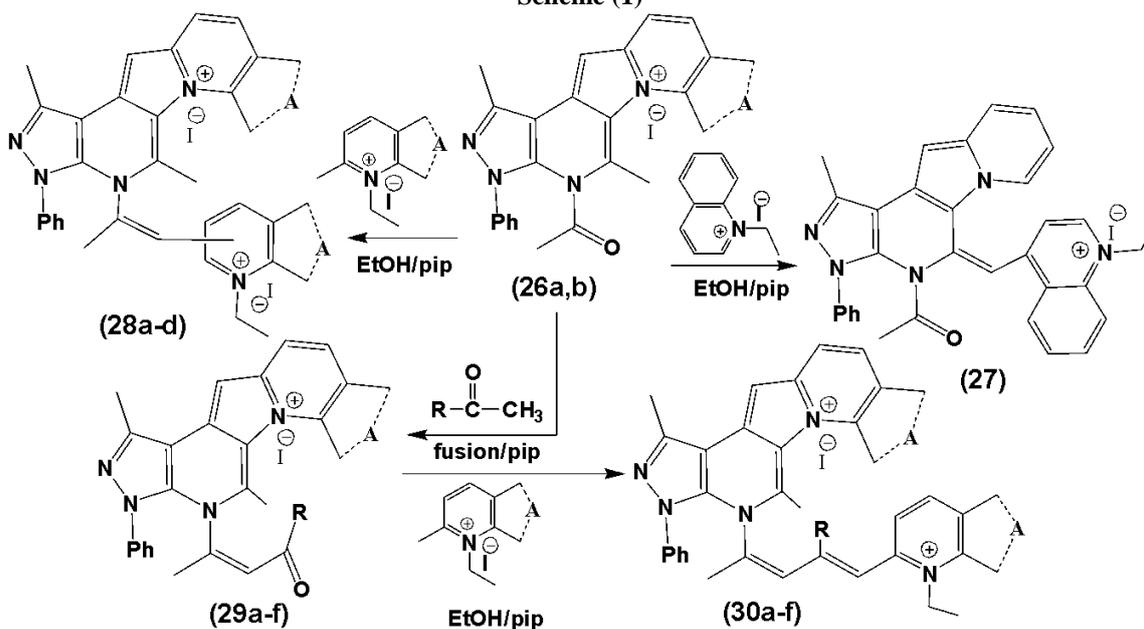
### 2.1 Synthesis

The synthesis of the desired N-bridgehead heterocyclic cyanine dyes was started by the preparation of 4-acetyl-1,5-dimethyl-3-phenyl-3,4-di[H]pyrazolo [4',3':5,6]pyrido[4,3-b]indolizin-6-ium iodide & 4-Acetyl-1,5-dimethyl-3-phenyl-3,4-di[H]pyrazolo[4',3':5,6]pyrido[4,3-b]indolizin-6-ium-

iodide (26a,b). Such preparation was conducted by a reaction of 4-acetyl-3-methyl-5-imino-1-phenyl pyrazol (1), iodine and 2-methyl pyridine (quinoline), in equimolar ratios, absolute ethanol to give 3-methyl-5-imino-1-phenyl pyrazolo 4-(N-acetyl-pyridin (quinolin)-1-ium iodide) (25a,b) [18] which under thermal acetic anhydride condition achieved the key reaction intermediates (26a, b), Scheme 1. On treatment of (26a,b), with conc. H<sub>2</sub>SO<sub>4</sub> resulted in no liberation of iodine vapors on warming. The reaction of (26a) with N-methyl (quinolinium) iodide, in equimolar ratios, under thermal piperidine catalysis afforded 4-Acetyl-1-methyl-3-phenyl-3,4-di[H]-5H-pyrazolo [4',3':5,6]pyrido[4,3-b]indolizin-3-methyl-mono-5[4]methine cyanine dye (27). On the other hand, Reaction of (26a,b) with 2(4)-methyl-pyridin(quinolin)-2(4)-ium ethyl iodide salts, in equimolar ratios, under piperidine catalysis afforded 3-methyl-1-phenyl-pyrazolin-5-imino-4(2)-indolizine (benzo indolizine)-B-substituted di-1-[2(4)] methine cyanine dyes (28a-d), Scheme (2). Our approaches are extended to the synthesis 1,5-dimethyl-3-phenyl-3,4-di[H]Pyrazolo [4',3':5,6]pyrido[4,3-b] indolizin-6-ium iodide-4-β-substituted-α,β-unsaturated carbonyl derivatives (29a-f) through the reaction of 4-acetyl-1,5-dimethyl-3-phenyl-3,4-di[H] pyrazolo [4',3':5,6]pyrido [4,3-b]indolizin-6-ium iodide & 4-acetyl-1,5-dimethyl-3-phenyl-3,4-di[H]Pyrazolo[4',3':5,6]pyrido[4,3-b]indolizin-6-ium-iodide (26a,b) with acetaldehyde, acetone and /or acetophenone derivatives, in equimolar ratios, under thermal piperidine catalysis to give (29a-f). Further reaction of the latter intermediates (29a-f) with 2(4)-methyl heterocyclic quaternary salts, in equimolar ratios, achieved 1,5-dimethyl-3-phenyl-3,4-di[H]Pyrazolo [4',3':5,6] pyrido[4,3-b]indolizin-(benzindolizin)-6-ium- bisdi-4[4]methine cyanine dye (30a-f), Scheme (2).



Scheme (1)



Scheme (2)

**Scheme (1,2) substitution:**

(28a-d): A = indolizine, A<sup>-</sup> = pyridin-2-ium ethiodide (a); A = indolizine, A<sup>-</sup> = quinolin-2-ium ethiodide (b); A = indolizine, A<sup>-</sup> = pyridin-4-ium ethiodide (c); A = benzoindolizine, A<sup>-</sup> = quinolin-2-ium ethiodide (d); (29a-f), R=H, A= indolizinium, (a); R = CH<sub>3</sub>, A = indolizinium, (b); R = phenyl, A = indolizinium, (c); R = p-methoxy benzaldehyde, A = indolizinium, (d); R = p-Nitro benzaldehyde, A = indolizinium, (e); R = phenyl, A= benzoindolizinium, (f); (30a-f): R = H, A = indolizinium, A<sup>-</sup> = quinolin-2-ium ethiodide (a); R = CH<sub>3</sub>, A = indolizinium, A<sup>-</sup> = quinolin-2-ium ethiodide (b); R = phenyl, A = indolizinium, A<sup>-</sup> = quinolin-2-ium ethiodide (c); R = p-methoxy benzaldehyde, A = indolizinium, A<sup>-</sup> = quinolin-2-ium ethiodide (d); R = p-Nitro- benzaldehyde, A = indolizinium, A<sup>-</sup> = quinolin-2-ium ethiodide (e); R = phenyl, A= benzoindolizinium, A<sup>-</sup> = quinolin-2-ium ethiodide (f);

The structure of (26b, 28b, c, 29a & 30a, d, e) was characterized and identified by elemental analysis, IR and <sup>1</sup>H-NMR spectral data. IR ( $\nu^{KBr}$  cm<sup>-1</sup>) of (28b, c) showed in addition to the general absorption bands at 1497 cm<sup>-1</sup> (C=N), 1592 cm<sup>-1</sup> (C=C), 1704 cm<sup>-1</sup> (C=O), well defined absorption band at 3058-3060 cm<sup>-1</sup> (stretching CH) and 2923 cm<sup>-1</sup>

(heterocyclic quaternary salt) [19], IR ( $\nu^{KBr}$  cm<sup>-1</sup>) of (29a) showed in addition to the general absorption bands at 1497 cm<sup>-1</sup> (C=N), 1592 cm<sup>-1</sup> (C=C), 1704 cm<sup>-1</sup> (C=O), well defined absorption band at 3058-3060 cm<sup>-1</sup> (stretching CH) and 2923 cm<sup>-1</sup> ((heterocyclic quaternary salt) for compounds (30a, d, e), [19]. <sup>1</sup>H-NMR (CD<sub>3</sub>OD, 250 MHz) spectra of (29a & 30a, d, e) showed in addition to the general single and multiple signals at  $\delta$  1.19-1.29 (s, CH<sub>3</sub>, of pyrazol), 3.1(s, 3H, CH<sub>3</sub> of  $\delta$ -substituted), 7.20-8.00 (m, 6H, Ar + Het+ =CH+ NH) for (29a), 2.8 (s, 3H, CH<sub>3</sub> of heterocyclic quaternary salt), 3.05 (s, 3H, CH<sub>2</sub>N), 7.20-8.00 (m, 6H, Ar + Het+ =CH+ NH) for (30a, e), 2.74-3.71 (s, 3H, OCH<sub>3</sub>) for (30d) [20]. Mass spectra of (29a) reveals a molecular ion 508, peaks at m/z =330, and base peak at m/z =54 for (29a) [21].

**2.2. Colour & Spectral Behaviour**

1,5-dimethyl-3-phenyl-3,4-di[H]pyrazolo[4',3':5,6]pyrido[4,3-b] indolizin-6-ium-4[4]-dimethine cyanine dyes (27) and 4-Acetyl-1-methyl-3-phenyl-3,4-di[H]-5H-pyrazolo[4',3':5,6]pyrido[4,3-b] indolizin-3-methyl-mono-5[4]methine cyanine dye (28a-d) and are highly coloured compounds. Their colour in

ethanolic solution are ranging from brownish-violet to intense reddish-violet, easily (partially) soluble in polar (non) organic solvents exhibiting coloured solutions (red/violet) concomitant with slight or intense greenish-red fluorescence depending upon the solvent used. They are soluble in concentrated H<sub>2</sub>SO<sub>4</sub> acid liberating iodine vapour on warming. Their ethanolic solutions gave permanent colours in basic media which reversibly discharged on acidification. They possess interconvertible coloured solution (brownish-violet/intense violet → yellow) in basic and acidic medium, **Table (3,4)**. 1,5-dimethyl-3-phenyl-3,4-di[H]Pyrazolo[4',3':5,6]pyrido[4,3-b]indolizin(benzo-indolizin)-6-ium-bis-di-4[4]methine cyanine dye (**30a-f**) are highly coloured compounds (brownish violet-intense violet). They are partially (easily) soluble in most nonpolar (polar) organic solvents exhibited coloured solutions (red/violet) accompanied with pale/ intense green fluorescence depending upon the solvent used. They are soluble in conc. H<sub>2</sub>SO<sub>4</sub> acid liberating iodine vapour on warming. Their ethanolic solutions gave permanent colour in basic medium changed to yellow or become colourless on acidification. The absorption spectra of 1,5-dimethyl-3-phenyl-3,4-di[H]Pyrazolo [4',3':5,6] pyrido[4,3-b] indolizin-6-ium-4[4]-dimethine cyanine dye (**27**) and 4-acetyl-1-methyl-3-phenyl-3,4-di[H]-5H-pyrazolo[4',3':5,6]pyrido[4,3-b] indolizin-3-methyl-mono-5[4]methine cyanine dye (**28a-d**) in 95% ethanol showed absorption bands batho underwent (hypso) chromically shifted depending upon the nature of heterocyclic A; heterocyclic quaternary residue A' and their linkage position. Thus, the visible absorb-maximum of dye **28a** (A = indolizine, A' = pyridine-2-ium methiodide) showed  $\lambda_{\max} = 480$  nm. Substitution of (A' = pyridine-2-ium methiodide) in dye **28a** by (A' = quinoline-2-ium methiodide) in dye **27b** resulted in bathochromic shift of  $\Delta \lambda_{\max} = 80$  nm concomitant with the increasing number of absorption bands in the case of compound **28b**. This is due to the more extensive  $\pi$ - delocalization and extra conjugation in the quinoline ring. Additionally, changing the linkage position of pyridinium from 2-ium salt in (**28a**) to the 4-ium analogue salt in compound **28c** causes bathochromic shift by  $\Delta \lambda_{\max} = 34$  nm. This is due to the extended of  $\pi$ -delocalization within pyridine-4-ium methiodide in **28c**. Also, substituting of heterocyclic (A= indolizine) in dye (**28b**) by (A = benzoindolizine) in dye **28d** causes bathochromic shift of the appearance of new shoulder of band at 556 nm. This is due to the more extensive  $\pi$ -delocalization within phenyl ring of benzoindolizine in dye (**28d**), **Table (3,4)**. On comparison between the electronic absorption spectra of both dyes (**28b** and **27**), it was obvious that the latter dye (**28**) showed absorption band is more hypsochromic shift by  $\Delta \lambda_{\max} = 10$  nm relative to that band of dye (**28b**). This may due to the linkage position of heterocyclic of dye **27** resulted in a decrease of  $\pi$ -delocalization. The absorption spectra of 1,5-dimethyl-3-phenyl-3,4-di[H]Pyrazolo [4',3':5,6] pyrido[4,3-b]indolizin(benzo-indolizin)-6-ium-bis-di-4[4]methine cyanine dye (**30a-f**) in 95% ethanol solution showed absorption bands undergo batho (hypso) chromically shifted depending upon the nature of heterocyclic (A) ; aryl substituents (R); heterocyclic quaternary residue A' and their linkage position. Thus, the visible absorption maxima of **30a** [A = indolizine, R = H, A' = quinolin-2-ium ethiodide] exhibited  $\lambda_{\max} = 406$  (521, 564) nm, **Tables (4)**.

Substitution of [R = H] in dye (**30a**) by [R = CH<sub>3</sub>] in dye (**30b**) causes bathochromic shift of  $\Delta \lambda_{\max} = 8$  nm concomitant with the appearance of new shorter absorption band located at  $\lambda_{\max} = 390$  (519-556)nm for dye (**30b**) (hypsochromic shift of the shorter (longer) wavelength. This is due to the more electron donating character of the methyl group. Substitution of (R = CH<sub>3</sub>) in dye **30b** by (R = phenyl) in dye (**30c**) causes bathochromic shift of  $\Delta \lambda_{\max} = 4$  nm concomitant with the appearance of new shorter absorption band located at  $\lambda_{\max} = 561$  nm for dye (**30c**) (hypsochromic shift of the shorter (longer) wavelength. This is due to the more electron donating character of the phenyl group. Also, Substitution of (R = phenyl) in dye (**30c**) by (R = p-methoxy benzaldehyde) in dye (**30d**) causes bathochromic shift concomitant with the appearance of new shorter absorption band located at  $\lambda_{\max} = 406$  (521, 562) nm for dye (**30d**) (hypsochromic shift of the shorter (longer) wavelength. This is due to the more electron donating character of the methoxy group. Additionally, substitution of (R= p-methoxy benzaldehyde) in dye (**30d**) by (R=p-Nitro benzaldehyde) in dye (**30e**) resulted in hypsochromic shift of the longer wavelength concomitant with the disappearance of the other bands. This is due to the electron withdrawing character of NO<sub>2</sub> group for dye (**30e**) bathochromic shift of the shorter (longer) wavelength concomitant with the appearance of new absorption bands located at  $\lambda_{\max} = 519$  and 560 nm. This may be attributed to the partial mixing of the lone pair orbitals of nitrogen with  $\pi$  system of the heterocyclic ring leading to a modified set of energy levels and this moves the band to the longer wavelength. On the other hand, substitution of (A= indolizine, R = phenyl) in dye (**30c**) by [A = benzoindolizine, R = phenyl] in dye (**30f**) resulted in bathochromic shift of  $\Delta \lambda_{\max} = 8$  nm of the shorter (longer) of, due to the more extensive  $\pi$ -conjugation within the extra phenyl ring in dye (**30f**), **Table (4)**.

### 2.3 Solvatochromic Behaviour

Cyanine dyes had been useful in studying the colour of organic substances **Ficken, G. E., (1971)** and there are several fundamental principles exist that correlate origin of colour to chemical structures of the solute as well as natures of the solvents [41]; [23; 24a,b] Moreover, these classes of heterocyclic compounds are useful in various industrial fields [25]. The colour changes of cyanine dyes with solvents (solvatochromism) was previously discussed by [15a,b, 16, 27] and extended [28a,b] and his coworkers [29] to correlate the effect of structure on molecular orbital energy levels. It is clear that the type of substituents and the solvent polarity change the electron densities of cyanine dyes. Solvatochromic dyes generally exhibit steady bathochromic (positive solvatochromism) or hypsochromic (negative solvatochromism) shifts in solvents of various polarities. Cyanine dyes are also ascribed a large change in dipole moment upon excitation due to the relative contribution of both dipolar zwitterionic benzenoid and neutral quinoid forms [30, 32, 33]. Therefore, these dyes have been used by various workers to establish empirical relationships of solvent polarity. The solvatochromism is caused by differential solvation of the ground and Franck-Condon excited state, due to the absorption of electromagnetic radiation in the UV-vis region. If the ground state is more stabilized than the excited state due to

solvation by solvents of increasing polarity, negative solvatochromism is exhibited and vice versa. According to the Franck-Condon principle [42] the time required for molecules to be excited is much smaller than that required to execute vibration or rotation. Therefore, the first excited state of the molecule in solution, called the Franck-Condon excited state, has the same solvation pattern as in the corresponding ground state, called the equilibrium ground state. The first Franck-Condon excited state is much more dipolar than the ground state due to intramolecular charge transfer upon excitation. Stabilization of the Franck-Condon excited state before and after relaxation to the equilibrium ground state and the destabilization of the Franck-Condon ground state relative to the equilibrium ground state by differential solvation leads to the positive solvatochromism. Positive solvatochromism is more sensitive to changes in solvent polarity than the corresponding absorption band in suitable cases. From these findings of view, the visible absorption spectra of some selected of newly synthesized cyanine dyes is discussed. Such dyes are 1,5-dimethyl-3-phenyl-3,4-di[H]pyrazolo [4',3':5,6] pyrido[4,3-b]indolizin-6-ium-4[4]-dimethine cyanine dyes (27) and 4-acetyl-1-methyl-3-phenyl-3,4-di[H]-5H-Pyrazolo [4',3':5,6] pyrido[4,3-b] indolizin-3-methyl-mono-5[4]methine cyanine dye (28a-d), 1,5-dimethyl-3-phenyl-3,4-di[H]Pyrazolo [4',3':5,6]pyrido[4,3-b] indolizin (benzo-indolizin)-6-ium-bis-di-4[4]methine cyanine dye (30b,d,e). The absorption spectra of (28a, b, d & 30b,d,e) in the wavelength range 350-700 nm, have been studied in different organic solvents (H<sub>2</sub>O, DMF, EtOH, MeOH, acetone, CCl<sub>4</sub>, CHCl<sub>3</sub>, and C<sub>6</sub>H<sub>6</sub>) [35b] respectively. The colour changes of such dyes with solvents having different polarities are presented in Table (1). This is constructed with the intention to illustrate the solvatochromic behaviour of these dyes ( $\lambda_{\max}$  and  $\epsilon_{\max}$ ) values of the intramolecular charge transfer bands are given in Tables (1). These dyes are showed positive solvatochromism with increased solvent polarity, which depend on the structure and the type of dye. This indicates that the polar excited states of these cyanine dyes are stabilized by polarization interaction forces as the polarizability of the solvent is increased. This behaviour occurs as a result of electrostatic interactions of the distributed cationic charges with the dipoles of the solvated molecules which lead to formation of specific solvated forms of dyes. The absorption spectra of the dyes in ethanol are characterized by the presence of one or two essential bands which reflect the presence of intermolecular charge transfer [34]. This intermolecular charge transfer had arisen from transferring the electron lone pair of the nitrogen atoms of the heterocyclic ring system towards the positively charged residue along the conjugated chain between both. The relevant data in Table (1) as well as the representing graphs disclosed that these electronic charge transfer bands exhibit a hypsochromic shifts in ethanol relative to DMF, CHCl<sub>3</sub>, and CCl<sub>4</sub>. These shifts can be attributed to the following factors: The bathochromic shift occurred in DMF relative to ethanol is mainly a result of the increase in solvent polarity due to increasing the dielectric constant of the former, Table (1). The hypsochromic shifts appeared in ethanol relative to CHCl<sub>3</sub>, and CCl<sub>4</sub> is generated from the solute-solvent interaction through intermolecular hydrogen bonding between ethanol and the lone pair of electrons within the heterocyclic ring system. Otherwise, this

decreases the mobility of the electron cloud over the conjugated pathway towards the positively charged center, Table (1). It was worth mentioning that the intermolecular hydrogen bonding between CHCl<sub>3</sub> molecules and the lone pair of electrons of nitrogen atoms of the heterocyclic ring system is difficult due to the steric hindrance of the three bulk chlorines. Moreover, the solute solvent interactions in cases of CHCl<sub>3</sub>, & CCl<sub>4</sub> generated a residual negative charge on the nitrogen atoms of the heterocyclic ring system which intern facilitated the electronic charge transfer to the positively charged center and this explain the bathochromic shifts in these solvents relative to ethanol, Table (1). The unexpected hypsochromic shifts in the absorption spectral maxima in water relative to ethanol and its lower extinction coefficients were mainly ascribed to the ease of interactions of water molecules, through intermolecular hydrogen bonding, with the lone pair of electrons of the nitrogen atoms of the heterocyclic ring system, through intermolecular hydrogen bonding, which intern preclude the charge transfer from the heterocyclic ring system to the positively charged residue along the conjugated bridge, Table (1). In point view of light absorption, it was obvious that most of the previous selected cyanine dyes, (27a,b,d, 28 & 30b,d,e) are absorbed the fundamental light absorption (violet-red) as they have got absorption values in the range 350-660 nm Table (1) in accordance with the literature's observations [44 & 35a]. The selected cyanine dyes might be suggested to be used as photosensitizers in most polar and non-polar organic solvents in the (violet-red). Thus, it was obvious that (28a, b, d, 30b, d, e) absorbed near violet light in EtOH, benzene, CHCl<sub>3</sub>, CCl<sub>4</sub> and MeOH  $\lambda_{\max}$  = 360-420 nm extended and improved to the absorption of green light in DMF and acetone  $\lambda_{\max}$  = 520-575 nm. Dye (27) absorbed blue light in EtOH, benzene, CHCl<sub>3</sub>, CCl<sub>4</sub> and MeOH  $\lambda_{\max}$  = 450-470 nm extended and improved to the absorption of blue-green light in DMF and acetone  $\lambda_{\max}$  = 500 nm.

#### 2.4. Mediachromic Behaviour

The ethanolic solution of some selected newly synthesized 4-acetyl-1-methyl-3-phenyl-3,4-di[H]-5H-pyrazolo[4',3':5,6]pyrido[4,3-b] indolizin-3-methyl-mono-5[4]methine cyanine dye (28b,d), 1,5-dimethyl-3-phenyl-3,4-di[H]Pyrazolo [4',3':5,6]pyrido[4,3-b]indolizin (benzoindolizin)-6-ium-bis-di-4[4]methine cyanine dyes (30b,d,e) give a permanent colour in basic medium which is discharged on acidification. This promoted us to study their spectral behaviour in different aqueous universal buffer solution in order to ensure optimal pH in the application of these dyes as photosensitizers and determine their pK<sub>a</sub> values too. The effectiveness of such compounds as photosensitizers increases when they are present in the ionic forms (non-protonated form) which have higher planarity [36]. The ethanolic absorption spectra of the selected cyanine dyes (28b,d & 30b,d,e) in aqueous universal buffer solution of different values of pH (2.09,4.10,6.09,7.8,36, 10.38,11.98) show regular changes with increasing the pH of the medium especially in the n- $\pi^*$  and CT bands Tables (2,3). Also, the absorption spectra of the selected cyanine dyes in aqueous universal buffer solutions of varying pH values showed bathochromic shifts with intensification of the absorption bands at high pH values (alkaline media),

otherwise, hypsochromic shifts with quenching the intensity of the absorption bands at low pH values (acidic media) were recorded. Moreover, increasing the pH values of the medium intensified the electronic charge transfer due to deprotonation which intern support the lone pairs of electrons of the heterocyclic ring system and increase its mobility. In the other hand, decreasing pH values of the medium interrupted the charge transfer due to protonation and intermolecular hydrogen bonding which intern preclude the availability of the lone pairs of the heterocyclic ring system. Several methods had been adopted for spectrophotometric estimation of the dissociation constants of weak acids; the variation of absorbance at settled wavelength could be utilized. Thus, on plotting the absorbance at settled wave number versus pH values, S-shaped curves were obtained. For all S-shaped curves, the horizontal portion to the left corresponded to the acidic form of the indicator, while the upper portion to the right corresponded to the basic form. Since the pKa value was defined as the pH value for which one half of the indicator (dye) is in the basic form and the other half in the acidic form. This point, (pKa value), was determined by the intersection of the S-curve with horizontal line midway between the left and right segments [43] and Tables (2,3). The spectral behaviour of (28a, b, d & 30b,d,e) in 95% ethanol and/or in aqueous universal buffer solution showed that these compounds absorbed the blue light  $\lambda_{\max} = 360-420$  nm and the near violet light extended to the green light  $\lambda_{\max} = 520-575$  nm. Such dyes in aqueous universal buffer solution reveal absorption of the violet light at pH = 2.09 with hypsochromic and bathochromic shifted in the absorption of blue light and blue-green light at pH  $\geq 7.0$  relative to ethanol. The hypsochromic shift of the violet light at pH = 2.09 is due to the presence of quinolin-4-ium methiodide as strong inductively group which increase to some extent the indolizine type resonance causes the protonation of indolizine nitrogen atom in such solution of low pH value and therefore the interaction is inhibited and the protonated form does not absorb energy in the visible region. On the other hand, the resulted bathochromic shift as the pH of the medium increases is due to the fact that the protonated compound becomes deprotonated and therefore its mesomeric interaction with the rest of the molecule becomes high and consequently the CT interaction within the free base is facilitated. The determination of pKa values of (27a, b, d & 30b,d,e) were listed in Table (2). The results showed that the pKa values of these compounds depend upon the nature of such cyanine dye type which contains quinolinium heterocyclic quaternary residue in position-3-reveals pKa. These results were suggested that these dyes are more sensitive as photosensitizers in both acidic and basic mediums.

### 3. Experimental

All melting points are uncorrected. Elemental analysis was carried out at the Micro analytical center (Cairo-University). The IR ( $\nu_{\text{KBr}}$ ) spectra were determined with Perkin Elmer Infrared 127B spectrophotometer (Cairo-University).  $^1\text{H-NMR}$  spectra were recorded with a Bruker AMX-250 spectrometer. Mass spectra were recorded on a HpMs 6988 spectrometer (Cairo University). The absorption spectra were recorded within the wavelength range (350-700) on

6405 UV/Visible recording spectrophotometer, Faculty of Science, Aswan. 4-Acetyl-3-methyl-1-phenyl pyrazol-5-(one)-pyridin (quinolin)-1-ium-iodide salts (**1A,B**) was carried out according to [38], (**1A,B**), (**1a**): m. p. = 130 °C, yield = 85 %, colour = brown, Molecular formula =  $\text{C}_{18}\text{H}_{19}\text{N}_4\text{OI}$ , M.wt = 434, Analysis % calculated (found) = C = 49.77 (49.81), H = 4.37 (4.41), N = 12.90 (12.94), (**1b**): m.p.= 180°C, yield = 89 %, colour = Deep reddish brown, Molecular formula =  $\text{C}_{22}\text{H}_{21}\text{N}_4\text{OI}$ , M.wt = 484, Analysis % calculated (found)= C = 54.54 (54.58), H = 4.33 (4.37), N = 11.57(11.59)

#### Synthesis of 2-(3-methyl-1-phenyl-4,5-dif[H]-1H-pyrazol-5-imino--4-yl)-3H-indolizin-4-ium iodide (25a) & 1H-pyrrolo[1,2-a]quinolin-10-ium iodide (25a)

Mixture of (**1A,B**, 0.005 mol) with acetic anhydride (10 ml).The reaction mixture was refluxed for 3 hours, and filtered, concentrated and cooled, the solid product was collected and crystallized from ethanol to give (**25a,b**), **25a**: m. p. = 165°C, yield = 85 % colour = black, Chemical Formula:  $\text{C}_{18}\text{H}_{17}\text{IN}_4$ , Molecular Weight: 416.27, Analysis % calculated (found) N, = C = 51.94 (51.86), H = 4.12 (4.25), N = 13.46 (13.22), (**25b**): m.p.= 120°C, yield = 70 %, colour = yellowish brown, Chemical Formula:  $\text{C}_{22}\text{H}_{19}\text{IN}_4$ , Molecular Weight: 466.33, , Analysis % calculated (found):: C, 56.66(56.78),; H, 4.11(4.19); N, 12.01(12.69), IR ( $\nu_{\text{KBr}}$   $\text{cm}^{-1}$ ) of (**25b**) showed in addition to the general absorption bands at 1497  $\text{cm}^{-1}$  (C=N), 1592  $\text{cm}^{-1}$  (C=C), 1705  $\text{cm}^{-1}$  (C=O) [19].  $^1\text{H-NMR}$  ( $\text{CD}_3\text{OD}$ , 250 MHz) spectra of (**25b**) showed in addition to the general single and multiple signals at  $\delta$  1.19-1.29 (s,  $\text{CH}_3$ , of pyrazol), 3.1(s, 6H,  $\text{CH}_3$  of Acetyl substituted), 7.20-8.00 (m, 6H, Ar + Het+ =CH), [20]. Mass spectra of (**25b**) reveals a molecular ion 482, peaks at  $m/z = 420$  and base peak at  $m/z = 145$  for (**25b**) [21].

#### Synthesis of 4-acetyl-1,5-dimethyl-3-phenyl-3,4-dif[H]Pyrazolo[4',3':5,6]pyrido[4,3-b]indolizin[3,4-dif[H]pyrazolo[4'',3'':5',6']pyrido[4',3':4,5]1H-pyrrolo[1,2-a]quinolin-10-ium]-6-ium-iodide (26a,b)

Mixture of (**25A,B**, 0.005 mol) with acetic anhydride (10 ml).The reaction mixture was refluxed for 3 hours, and filtered, concentrated and cooled, the solid product was collected and crystallized from ethanol to give (**26a,b**), (**26a**): m. p. = 165°C, yield = 85 % colour = black, Chemical Formula:  $\text{C}_{22}\text{H}_{19}\text{IN}_4\text{O}$ , Molecular Weight: 482.33, Analysis % calculated (found) C, 54.78 (54.86); H, 3.97(4.25); N, 11.62; (11.22), (**26b**): m.p. = 120°C, yield = 70 %, colour = yellowish brown, Chemical Formula:  $\text{C}_{26}\text{H}_{21}\text{IN}_4\text{O}$ , Molecular Weight: 532.39, Analysis % calculated (found): C, 58.66(58.78), H, 3.98 (4.19); N, 10.52(12.69), IR ( $\nu_{\text{KBr}}$   $\text{cm}^{-1}$ ) of (**26b**) showed in addition to the general absorption bands at 1497  $\text{cm}^{-1}$  (C=N), 1592  $\text{cm}^{-1}$  (C=C), 1705  $\text{cm}^{-1}$  (C=O) [19].  $^1\text{H-NMR}$  ( $\text{CD}_3\text{OD}$ , 250 MHz) spectra of (**26b**) showed in addition to the general single and multiple signals at  $\delta$  1.19-1.29 (s,  $\text{CH}_3$ , of pyrazol), 3.1(s, 6H,  $\text{CH}_3$  of Acetyl substituted), 7.20-8.00 (m, 6H, Ar + Het+ =CH), [20]. Mass spectra of (**26b**) reveals a molecular ion 482, peaks at  $m/z = 420$  and base peak at  $m/z = 145$  for (**26b**) [21].

**Synthesis of 3-methyl-1-phenyl-pyrazolin-5-imin-4(2)-indolizine (benzoindolizine)- zero -3(4)- methine cyanine dyes (27).**

Mixture of (26a, b) (0.001 mol) and quinolin-4-ium iodide (0.001 mol) was dissolved in ethanol (50 ml) and few drops of piperidine were added. The reaction mixture was refluxed for 6 hours, filtered hot, and cooled. The precipitated solid product was acidified, diluted, collected and crystallized from ethanol to give (27), m. p. = 230 °C yield = 43 % colour = violet, Chemical Formula:  $C_{33}H_{28}IN_5O$ , Molecular Weight: 637.53, Analysis % calculated (found): C= 62.17 (62.35) H = 4.43 (4.78) N = 10.99 (10.76).

**Synthesis of 1,5-dimethyl-3-phenyl-3,4-di[H]pyrazolo[4',3':5,6]pyrido[4,3-b]indolizin(benzoindolizine)-6-ium-4[4]-dimethine cyanine dyes (28a-d)**

Mixture of (26a,b, 0.001 mol) and 2(4)-methylpyridin(quinolin)-2(4)-ium ethyl iodide (0.001 mol) was dissolved in ethanol (50 ml) and few drops of piperidine were added. The reaction mixture was refluxed for 6 hours, filtered hot, and cooled. The precipitated solid product was acidified, diluted, collected and crystallized from ethanol to give (28a-d), Table (4).

**Synthesis of 1,5-dimethyl-3-phenyl-3,4-di[H]Pyrazolo [4',3':5,6] pyrido [4,3-b]indolizin(benzoindolizine)-6-ium-iodide-4-β-substituted-α,β-unsaturated carbonyl derivatives (29a-f).**

Mixture of (26a, b, 0.01 mol) with acetaldehyde, acetone and /or acetophenone derivatives were dissolved in ethanol (30 ml) and few drops of piperidine were added. The reaction mixture was refluxed for 4 hours, filtered hot and cooled. The solid products were acidified, diluted, collected and crystallized from ethanol to give (29a-f), Table (5).

**Synthesis of 1,5-dimethyl-3-phenyl-3,4-di[H]Pyrazolo[4',3':5,6] pyrido [4,3-b]indolizin(benzoindolizine)-6-ium- bis-di-4[4]methine cyanine dyes (30a-f).**

Mixture of (29a-f, 0.001 mol) with 2(4)-methylpyridin(quinolin)-2(4)-ium ethyl iodide (0.001 mol) was dissolved in ethanol (30 ml) and few drops of piperidine were added. The reaction mixture was refluxed for 4 hours, filtered. the solid products were acidified, diluted, collected and crystallized from ethanol to give (30a-f), Table (6).

**Solvatochromic and Acid -Base Properties**

The organic solvents were used of spectroscopic grade of purified according to the recommended methods [39]. The electronic absorption spectra of the studied dyes in different organic solvents were recorded within the wavelength (350-700 nm) on 6405 UV/Visible recording spectrophotometer using 1 cm cell. The stock solution of the dye was of the order  $10^{-3}$  M. Solution of low molarities used in spectral measurements was obtained by accurate dilution.

**I-preparation of dyes solution**

1-For studying the effect of pure solvents in the UV and visible range: Accurate volumes of the stock solution of the dyes were diluted to appropriate volume in order to obtain the required concentrations. The spectra were recorded immediately after mixing in order to eliminate as much as

possible the effect of time. 2- For studying the spectral behaviour in mixed solvents in the visible region: An accurate volume of the stock solution ( $10^{-3}$  M in ethanol) of the dyes were placed in 10 ml measuring flask containing the required volume of ethanol, then completed to the mark with the other solvent.

3- For studying the spectral behaviour in aqueous universal buffer solutions:

An accurate volume of the stock solution was added to 5 ml of the buffer solution in 10 ml measuring flask, then completed to the mark with redistilled water. The pH of such solution was checked before spectral measurements.

**2-Preparation of Universal Buffer Solution:**

A modified buffer series derived in prospective reference [40] was prepared for use in the present investigation. The constituents are as follows: A solution of 0.4 M of each phosphoric and acetic acid was prepared by accurate dilution of A. R. concentrated stock. A solution of 0.4 M of boric acid was obtained by dissolving the appropriate weight of the recrystallized acid in redistilled water.

a-A stock acid mixture was prepared by mixing equal volumes of three acids in large bottle. The total molarity of the acid was thus maintained at 0.4 M A series of buffer solutions with pH values ranging from (2.09-11.98) was prepared as recommended by [40]. This was done by mixing 150 ml of the acid mixture in a 250 ml measuring flask with the appropriate volume of 1.0 M NaOH and completed to the mark with redistilled water. This modification was performed in order to keep the ionic strength constant at all pH's mixed with different proportions of organic solvents used. The pH's of the buffer solutions were checked using Orion pH-meter model (60, A), accurate to  $\pm 0.005$  pH units, at 25 °C.

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**Table 1:** Values of absorption (nm) and extinction coefficients ( $\text{mol}^{-1}\text{cm}^{-1}$ ) of (27, 28b,d, 30b,d,e) in pure organic solvents

| Comp | Water                  |                         | DMF                    |                         | C <sub>6</sub> H <sub>6</sub> |                         | CHCl <sub>3</sub>      |                         | CCl <sub>4</sub>       |                         | Acetone                |                         | MeOH                   |                         | EtOH                   |                         |
|------|------------------------|-------------------------|------------------------|-------------------------|-------------------------------|-------------------------|------------------------|-------------------------|------------------------|-------------------------|------------------------|-------------------------|------------------------|-------------------------|------------------------|-------------------------|
|      | $\lambda_{\text{max}}$ | $\epsilon_{\text{max}}$ | $\lambda_{\text{max}}$ | $\epsilon_{\text{max}}$ | $\lambda_{\text{max}}$        | $\epsilon_{\text{max}}$ | $\lambda_{\text{max}}$ | $\epsilon_{\text{max}}$ | $\lambda_{\text{max}}$ | $\epsilon_{\text{max}}$ | $\lambda_{\text{max}}$ | $\epsilon_{\text{max}}$ | $\lambda_{\text{max}}$ | $\epsilon_{\text{max}}$ | $\lambda_{\text{max}}$ | $\epsilon_{\text{max}}$ |
| 27   | 450                    | 15531                   | 500                    | 13435                   | 475                           | 11345                   | 455                    | 12183                   | 450                    | 12266                   | 460                    | 12661                   | 450                    | 11461                   | 470                    | 11435                   |
| 28b  | 556                    | 17628                   | 412                    | 8564                    | 409                           | 9864                    | 406                    | 13549                   | 409                    | 6299                    | 554                    | 10619                   | 396                    | 17990                   | 401                    | 29199                   |
|      | 511                    | 16993                   | 562                    | 12643                   | 567                           | 12794                   | 564                    | 18141                   | 560                    | 7175                    | 516                    | 9984                    | 556                    | 17507                   | 560                    | 28323                   |
|      | -                      | -                       | 519                    | 9984                    | 524                           | 10619                   | 521                    | 15211                   | 519                    | 6299                    | -                      | -                       | 513                    | 16722                   | 516                    | 35815                   |
| 28d  | 497                    | 5664                    | 524                    | 3368                    | 521                           | 3368                    | 519                    | 4879                    | 516                    | 4516                    | 519                    | 6148                    | 554                    | 5151                    | 556                    | 14063                   |
|      | 551                    | 5271                    | 560                    | 4516                    | 562                           | 4003                    | 562                    | 4758                    | 560                    | 4244                    | 556                    | 6419                    | 513                    | 5171                    | 516                    | 12280                   |
|      | -                      | -                       | 444                    | 2975                    | 444                           | 3096                    | 442                    | 3882                    | 438                    | 4637                    | 438                    | 5785                    | 438                    | 5785                    | 440                    | 10619                   |
| 30b  | 519                    | 9783                    | 521                    | 7485                    | 524                           | 6755                    | 560                    | 11362                   | 521                    | 7487                    | 514                    | 6885                    | 554                    | 12453                   | 556                    | 5679                    |
|      | 554                    | 12711                   | 560                    | 9783                    | 564                           | 8463                    | 524                    | 8090                    | 562                    | 9324                    | 556                    | 8693                    | 516                    | 9181                    | 519                    | 4703                    |
|      | -                      | -                       | 406                    | 5450                    | 412                           | 5306                    | 404                    | 5450                    | 409                    | 5450                    | 409                    | 4962                    | 388                    | 7487                    | 390                    | 3383                    |
| 30d  | 519                    | 8564                    | 524                    | 4879                    | 529                           | 4516                    | 521                    | 4516                    | 516                    | 4879                    | 519                    | 6782                    | 519                    | 6933                    | 521                    | 11012                   |
|      | 556                    | 10740                   | 564                    | 6540                    | 567                           | 5271                    | 562                    | 5392                    | 564                    | 6419                    | 560                    | 9229                    | 560                    | 8957                    | 562                    | 1572                    |
|      | 401                    | 8202                    | 406                    | 4122                    | 414                           | 3731                    | 409                    | 4003                    | 409                    | 4123                    | 409                    | 5785                    | 401                    | 5513                    | 406                    | 9591                    |
| 30e  | 554                    | 8693                    | 519                    | 7000                    | 513                           | 5679                    | 521                    | 6540                    | 513                    | 7487                    | 519                    | 5938                    | 508                    | 7631                    | 519                    | 25512                   |
|      | -                      | -                       | 564                    | 6282                    | 564                           | 6770                    | 567                    | 8348                    | 562                    | 8463                    | 560                    | 6655                    | 562                    | 9554                    | 560                    | 27341                   |

**Table 2:** Values of absorption (nm) and extinction coefficients ( $\text{mol}^{-1}\text{cm}^{-1}$ ) of (27b,d, 30b,d,e) in aqueous universal buffer solution

| Comp No. | Universal buffer       |                         |                        |                         |                        |                         |                        |                         |                        |                         |                        |                         |                        |                         |
|----------|------------------------|-------------------------|------------------------|-------------------------|------------------------|-------------------------|------------------------|-------------------------|------------------------|-------------------------|------------------------|-------------------------|------------------------|-------------------------|
|          | 2.09                   |                         | 4.10                   |                         | 6.09                   |                         | 7                      |                         | 8.36                   |                         | 10.38                  |                         | 11.98                  |                         |
|          | $\lambda_{\text{max}}$ | $\epsilon_{\text{max}}$ |
| 28b      | 479                    | 6093                    | 211                    | 40000                   | 511                    | 6741                    | 216                    | 39133                   | 556                    | 10462                   | 240                    | 32155                   | 514                    | 7677                    |
|          | 294                    | 24082                   | 487                    | 4166                    | 556                    | 5522                    | 513                    | 8965                    | 514                    | 9640                    | 516                    | 7291                    | 562                    | 7752                    |
|          | 243                    | 39131                   | 291                    | 14681                   | 246                    | 21283                   | 554                    | 9145                    | 288                    | 26351                   | 560                    | 7411                    | 294                    | 22284                   |
|          | -                      | -                       | 237                    | 30684                   | 214                    | 39557                   | 294                    | 22550                   | -                      | -                       | 246                    | 19311                   | 224                    | 40000                   |
| 28d      | 484                    | 3671                    | 484                    | 4112                    | 551                    | 3354                    | 556                    | 3089                    | 554                    | 6811                    | 560                    | 5011                    | 564                    | 3776                    |
|          | 224                    | 40000                   | 294                    | 12486                   | 487                    | 3982                    | 205                    | 36122                   | 513                    | 6564                    | 516                    | 5164                    | 514                    | 3991                    |
|          | 291                    | 13682                   | 320                    | 9233                    | 211                    | 39331                   | -                      | -                       | 235                    | 37633                   | 211                    | 40000                   | 213                    | 39571                   |
|          | 323                    | 9861                    | 208                    | 39132                   | -                      | -                       | -                      | -                       | -                      | -                       | -                      | -                       | -                      | -                       |
| 30b      | 320                    | 11663                   | 318                    | 10171                   | 556                    | 8564                    | 554                    | 5251                    | 558                    | 7701                    | 560                    | 7931                    | 562                    | 6111                    |
|          | 294                    | 12550                   | 296                    | 11193                   | 513                    | 7362                    | 511                    | 4463                    | 516                    | 6483                    | 514                    | 6952                    | 521                    | 5471                    |
|          | -                      | -                       | 237                    | 28172                   | 291                    | 17961                   | 291                    | 10841                   | 211                    | 40000                   | 216                    | 39131                   | 213                    | 40000                   |
|          | -                      | -                       | 208                    | 38775                   | -                      | -                       | 205                    | 39131                   | -                      | -                       | -                      | -                       | -                      | -                       |
| 30d      | 320                    | 13732                   | 323                    | 16493                   | 560                    | 7922                    | 562                    | 7033                    | 564                    | 9631                    | 554                    | 7871                    | 556                    | 9201                    |
|          | -                      | -                       | 556                    | 6062                    | -                      | -                       | 208                    | 40000                   | 224                    | 39574                   | 216                    | 39557                   | 219                    | 40000                   |
| 30e      | 318                    | 17042                   | 320                    | 18010                   | 564                    | 10311                   | 560                    | 9487                    | 562                    | 1263                    | 564                    | 5283                    | 554                    | 14066                   |
|          | -                      | -                       | 572                    | 7732                    | -                      | -                       | 219                    | 40000                   | 237                    | 39574                   | 208                    | 39755                   | 256                    | 35246                   |

**Table 3:** The variation of absorbance in  $\lambda_{\text{max}}$  characteristic for each selected (27b,27d, 30b, d, e) in different buffer solutions

| Comp. No. | 27b             | 27d             | 30b             | 30d             | 30e             |
|-----------|-----------------|-----------------|-----------------|-----------------|-----------------|
| pH        | $\lambda_{580}$ | $\lambda_{600}$ | $\lambda_{590}$ | $\lambda_{610}$ | $\lambda_{600}$ |
| 2.09      | 0.216           | 0.129           | 0.239           | 0.187           | 0.315           |
| 4.10      | 0.207           | 0.212           | 0.251           | 0.469           | 0.653           |
| 6.09      | 0.403           | 0.224           | 0.443           | 0.469           | 0.77            |
| 7         | 0.558           | 0.164           | 0.277           | 0.395           | 0.672           |
| 8.36      | 0.63            | 0.328           | 0.389           | 0.554           | 0.871           |
| 10.38     | 0.519           | 0.324           | 0.434           | 0.443           | 0.393           |
| 11.98     | 0.552           | 0.224           | 0.335           | 0.529           | 0.982           |
| pKa       | 6.1             | 8.0             | 7.8             | 6.9             | 4.0             |
|           |                 | 11.9            | 11.8            | -               | 9.3             |

**Table 4:** Characterization data of indolizine (benzoindolizine) - mono- [2(4)] substituted di methine cyanine dyes (28a-d)

| Comp. No. | M.p. °C | Yield % | Colour      | Mol. Formula (Mol.wt)                                     | Calcd.% (Found)% |             |             | Absorption spectra in EtOH  |   |
|-----------|---------|---------|-------------|---|------------------|-------------|-------------|-----------------------------|---|
|           |         |         |             |   | C                | H           | N           | $\lambda_{\text{max}}$ (nm) | $\epsilon_{\text{max}}$ ( $\text{cm}^2 \text{mol}^{-1}$ ) |
| 28a       | 210     | 67      | Deep Brown  | $\text{C}_{31}\text{H}_{32}\text{I}_2\text{N}_5$ (728.44) | 51.11 (51.87)    | 4.43 (4.98) | 9.61 (9.49) | 480                         | 36178   |
| 28b       | 150     | 62      | Violet      | $\text{C}_{34}\text{H}_{31}\text{I}_2\text{N}_5$ (763.47) | 53.49 (53.88)    | 4.09 (4.36) | 9.17 (9.48) | 401                         | 29199   |
|           |         |         |             |   |                  |             |             | 560                         | 28323   |
|           |         |         |             |   |                  |             |             | 516                         | 35815   |
| 28c       | 190     | 61      | Brown       | $\text{C}_{31}\text{H}_{32}\text{I}_2\text{N}_5$ (728.44) | 51.11 (51.87)    | 4.43 (4.68) | 9.61 (9.49) | 412                         | 39661   |
|           |         |         |             |   |                  |             |             | 446                         | 38226   |
| 28d       | 200     | 71      | Deep Violet | $\text{C}_{38}\text{H}_{33}\text{I}_2\text{N}_5$ (813.53) | 56.10 (56.39)    | 4.09 (4.36) | 8.61 (8.57) | 556                         | 14063   |
|           |         |         |             |   |                  |             |             | 516                         | 12280   |
|           |         |         |             |   |                  |             |             | 440                         | 10619   |

**Table 5:** Characterization data of 1,5-dimethyl-3-phenyl-3,4-di[H]Pyrazolo [4',3':5,6] pyrido [4,3-b]indolizine(benzoindolizine)-6-ium-iodide-4- $\beta$ -substituted- $\alpha$ , $\beta$ -unsaturated carbonyl derivatives (29a-f)

| Comp. No. | M.P. °C | Yield % | Colour        | Mol. Formula (Mol.wt)                                      | Calcd.% (Found)% |             |               |
|-----------|---------|---------|---------------|--|------------------|-------------|---------------|
|           |         |         |               |  | C                | H           | N             |
| 29a       | 240     | 66      | Brown         | $\text{C}_{24}\text{H}_{21}\text{IN}_4\text{O}$ (508.36)   | 56.70 (56.18)    | 4.16 (4.46) | 11.02 (11.77) |
| 29b       | 220-225 | 65      | Deep Brown    | $\text{C}_{25}\text{H}_{23}\text{IN}_4\text{O}$ (522.39)   | 57.48 (57.57)    | 4.44 (4.98) | 10.73 (10.17) |
| 29c       | 220     | 66.3    | Deep Brown    | $\text{C}_{30}\text{H}_{25}\text{IN}_4\text{O}$ (584.46)   | 61.65 (61.79)    | 4.31 (4.57) | 9.59 (9.98)   |
| 29d       | 230     | 67      | reddish brown | $\text{C}_{31}\text{H}_{27}\text{IN}_4\text{O}_2$ (614.49) | 60.59 (60.35)    | 4.43 (4.66) | 9.12 (9.14)   |
| 29e       | 110-120 | 65      | brown         | $\text{C}_{30}\text{H}_{24}\text{IN}_5\text{O}_3$ (629.46) | 57.24 (57.48)    | 3.84 (3.94) | 11.13 (11.85) |
| 29f       | 170     | 61      | Deep Brown    | $\text{C}_{34}\text{H}_{27}\text{IN}_4\text{O}$ (634.52)   | 64.36; (64.72)   | 4.29 (4.41) | 8.83 (8.64)   |

**Table 6:** Characterization data of 1,5-dimethyl-3-phenyl-3,4-di[H]Pyrazolo [4',3':5,6]pyrido[4,3-]indolizin(benzoindolizine)-6-ium-bis-di-4[4]methine cyanine dyes (**30a-f**)

| Comp No.   | M.P.<br>°C | Yield<br>% | Colour            | Mol.Formula<br>(Mol.wt)   | % Calcd (Found)% |                |                  | Absorption spectra in EtOH |  |
|------------|------------|------------|-------------------|---|------------------|----------------|------------------|----------------------------|--|
|            |            |            |                   |   | C                | H              | N                | $\lambda_{\max}$<br>(nm)   | $\epsilon_{\max}$<br>( $\text{cm}^2 \text{mol}^{-1}$ ) |
| <b>30a</b> | 160        | 71.3       | Violet            | <b>C<sub>36</sub>H<sub>33</sub>N<sub>5</sub></b><br>(662.60)              | 65.26<br>(65.39) | 5.02<br>(5.06) | 10.57<br>(10.98) | 406<br>521<br>564          | 18625<br>33277<br>28323                                |
| <b>30b</b> | 140        | 65         | Violet            | <b>C<sub>37</sub>H<sub>35</sub>N<sub>5</sub></b><br>(676.63)              | 65.68<br>(65.56) | 5.21<br>(5.24) | 10.35<br>(10.76) | 556<br>519<br>390          | 5679<br>4703<br>3383                                   |
| <b>30c</b> | 180        | 57         | Reddish<br>Violet | <b>C<sub>42</sub>H<sub>37</sub>N<sub>5</sub></b><br>(738.70)              | 68.29<br>(68.36) | 5.05<br>(5.08) | 9.48 (9.87)      | 561                        | 14577  |
| <b>30d</b> | 260        | 64         | Deep<br>Violet    | <b>C<sub>43</sub>H<sub>39</sub>N<sub>5</sub>O</b><br>(768.72)             | 67.19<br>(67.24) | 5.11<br>(5.16) | 9.11<br>(9.45)   | 521<br>562<br>406          | 11012<br>1572<br>9591                                  |
| <b>30e</b> | 220        | 59         | Deep<br>Violet    | <b>C<sub>42</sub>H<sub>36</sub>N<sub>6</sub>O<sub>2</sub></b><br>(656.79) | 76.81<br>(76.37) | 5.53<br>(5.66) | 12.80<br>(12.92) | 519<br>560                 | 25512<br>27341   |
| <b>30f</b> | 200        | 68         | Deep<br>Violet    | <b>C<sub>46</sub>H<sub>39</sub>N<sub>5</sub></b><br>(788.76)              | 70.05<br>(69.98) | 4.98<br>(4.99) | 8.88 (9.10)      | 363<br>516<br>556          | 10105<br>10347<br>13177                                |