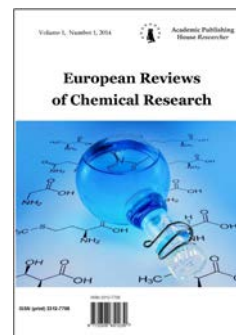


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Published in the Russian Federation
European Reviews of Chemical Research
Has been issued since 2014.
ISSN: 2312-7708
Vol. 4, Is. 2, pp. 126-140, 2015

DOI: 10.13187/ercr.2015.4.126

www.ejournal14.com

UDC 544; 547

Synthesis, Structure/Spectra Correlation and Chromism Studies of some Novel Monomethine and *bis*-Monomethine Cyanine Dyes

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Abstract

Novel methine cyanine dyes, covering monomethine and *bis*-monomethine cyanine dyes having the nucleus of benzo-[2,3-b;2',3'-b']-*bis*-furo-[2,3-d]-imidazoline-3,5,8,10-*tetra* were synthesized and their structure was investigated. The electronic visible absorption spectra of all the synthesized cyanine dyes were examined in 95% ethanol solution. Solvatochromism and/or halochromism for some selected dyes were investigated in pure solvents owing different polarities (water, dimethylformamide, ethanol, chloroform, carbon tetrachloride and dioxane) and/or in aqueous universal buffer solutions having varied *pH* values (1.45; 2.03; 3.72; 5.09; 7.57; 8.91; 10.20 and 12.04 units), respectively. The structural determination was carried out through the elemental analysis, visible electronic absorption spectroscopy, mass spectrometry, IR, and ¹H NMR spectral data.

Keywords: cyanine dyes, methine cyanine dyes, synthesis, absorption spectra, solvatochromism, halochromism.

Introduction

Cyanine dyes [1–16] were and still have been the central focus of scientists in a several fields such as chemistry, biology, physics, biotechnology, engineering, pharmacology and medicine. This is due to their multi-purpose using and applications in a diverse and a broad area. Their usage and/or applications includes photographic sensitizers, laser technology, nucleic acid and protein detection, bactericides and fungicides, intercalating dyes, data storage materials; in optical devices – as photorefractive and photovoltaic sensitive materials, fluorescent probes for bio-membrane fluidity, analytical reagents over wide *pH* values of media, indicators and/or probes for determining the solvent polarity and as inhibitors for cell growth and cell division.

Taking into consideration the above important benefits of cyanine dyes, our main goal in this research paper is the preparation of some new photosensitizers, solvatochromic and halochromic monomethine and *bis*-monomethine cyanine dyes, as new contribution for the synthesis and spectroscopic investigation in this field and/or may be used and applied in any of the wide application range of cyanine dyes, particularly as photographic sensitizers in photographic

industry, as indicators for acid/base titrations in analytical chemistry and/or as probes for determining solvent polarity in physical, physical organic and/or inorganic chemistry.

Experimental Part

1. General

All the melting points of the prepared compounds are measured using Electrothermal 15V, 45W IA9100 melting point apparatus (Electrothermal Bibby Sci. Co, UK) at Chemistry department, Faculty of Science (Aswan University), and are uncorrected. Elemental analysis was carried out at the Microanalytical Center of Cairo University by a Vario EL III Automatic Element Analyzer (Elementar Analysensysteme GmbH, Germany). Infrared spectra were measured with a JASCO FT/IR-4100 spectrometer (Jasco Analyt. Instr., Japan) at Cairo University. ¹H NMR spectra were accomplished using Varian Gemini-300 MHz NMR spectrometer (Gemini BV, Netherlands) (Cairo University). Mass spectra were recorded on Gas Chromatograph Mass Spectrometer GC-2010 (Shimadzu, Japan) at Cairo University. Electronic visible absorption spectra were carried out on Visible Spectrophotometer, Spectro 24RS (Labomed Inc., USA) at Chemistry department, Faculty of Science (Aswan University).

2. Synthesis:

2.1. Synthesis of benzo-[2,3-b;2',3'-b']-bis-furo-[2,3-d]-imidazoline-3,5,8,10-tetra one (3)

A mixture of unimolar ratio (0.01 mol) of p-chloranil (1) and bimolar ratio (0.02 mol) of hydantoin (2) was refluxed in ethanol (50 ml) containing pyridine (20 ml) for 8 hrs. The reaction mixture changed from a reddish colour to dark brown at the end of the refluxing. It was filtered while hot, concentrated, and precipitated by ice water. The products were collected, washed with water several times, dried and crystallized from ethanol. The results are listed in Table (1).

2.2. Synthesis of benzo-[2,3-b;2',3'-b']-bis-furo-[2,3-d]-imidazoline-5,8,10-tri-one-3[2(4)]-monomethine cyanine dyes (4a-c)

A mixture of the compound (3) (0.01 mol) and ethyl iodide quaternary salts of α -picoline, γ -picoline, quinaldine (0.01 mol) were dissolved in ethanol (50 ml) containing piperidine (3–5 drops). The reaction mixture was heated under reflux for 6–8 hrs and attained reddish colour for (4a–c) and violet colour for (4 b) at the end of refluxing. It was filtered off while hot, concentrated to half its volume and cooled. The precipitated dyes were filtered, washed with water, dried and crystallized from ethanol. The data are given in Table (1).

2.3. Synthesis of benzo-[2,3-b; 2',3'-b']-bis-furo-[2,3-d]-imidazoline-5,10-dione-3,8-[2(4)]-bis-monomethine cyanine dyes (5a-c)

Two different routes are employed to prepare these cyanine dyes:

Route (1): piperidine (3–5 drops) was added to an ethanolic solution (50 ml) of (3) (0.01 mol) and iodoethane quaternary salts of α -picoline, quinaldine and γ -picoline (0.02 mol). The mixture was heated under reflux for 6–8 hrs and attain deep red colour for (5a, c) and violet colour for (5b) at the end of refluxing. It was filtered off while hot, concentrated to half its volume and cooled. The precipitated dyes were filtered, washed with water, dried and crystallized from ethanol. The data are given in Table (1).

Route (2): the monomethine cyanine dyes (4a–c) (0.01 mol) and equimolar ratios of iodoethane quaternary salts of α -picoline, quinaldine and γ -picoline (0.01 mol) were dissolved in ethanol (50 ml), to which piperidine (3–5 drops) was added. The reaction mixture was refluxed for 3–5 hrs and attain deep red colour for (5a, c) and violet colour for (5b) at the end of refluxing. It was filtered off while hot, concentrated to half its volume and cooled. The precipitated dyes were filtered, washed with water, dried and crystallized from ethanol to give the same dyes obtained by Route (1), characterized by melting points, mixed melting points, same visible, IR and ¹H NMR spectral data [Table (1)].

3. Structure/Spectra Correlation

The electronic visible absorption spectra of the prepared cyanine dyes were examined in 95% ethanol solution and recorded using 1 cm Q_z cell in Visible Spectrophotometer, Spectro 24RS

(Labomed Inc., USA). A stock solution ($1 \cdot 10^{-3} M$) of the dyes was prepared and diluted to a suitable volume in order to obtain the desired lower concentrations. The spectra were recorded immediately to eliminate as much as possible the effect of time.

4. Solvatochromism and Halochromism Studies

The electronic visible absorption spectra of some selected synthesized cyanine dyes were investigated in pure organic solvents of spectroscopic grade qualities [28] with different polarities and/or in aqueous universal buffer solutions of varying *pH* values, and recorded using 1 cm Q_z cell in Visible Spectrophotometer, Spectro 24RS (Labomed Inc., USA). A stock solution ($1 \cdot 10^{-3} M$) of the dyes was prepared and diluted to a suitable volume using the suitable solvent and/or the buffer solution to obtain the required lower concentrations. The spectra were recorded immediately to eliminate as much as possible the effect of time.

Results and discussion

1. Synthesis

1:2 molar ratios of *p*-chloranil (1) and hydantoin (imidazolid-2,4-dione) (2) was reacted in ethanol containing pyridine, thus achieved benzo-[2,3-*b*;2',3'-*b'*]-*bis*-furo-[2,3-*d*]-imidazoline-3,5,8,10-*tetra* one (3) as new heterocyclic starting material [Scheme (1), Table (1)].

Equimolar reaction of (3) and iodoethane quaternary salts of α -picoline, quinaldine and/or γ -picoline in ethanol as organic solvents and piperidine as a basic catalyst gives the 3[2(4)]-monomethine cyanine dyes (4a–c) [Scheme (1), Table (1)].

Reaction of (3) and *N*-ethyl (α -picolinium, quinaldinium and/or γ -picolinium) iodide salts in 1:2 molar ratios in ethanol containing few milliliters of piperidine resulted in the 3,8[2(4)]-*bis*-monomethine cyanine dyes (5a–c) [Scheme (1), Route (1), Table (1)].

Chemical confirmations take place for the 3,8[2(4)]-*bis*-monomethine cyanine dyes (5a–c) *via* Route (2) by reactions of the previously prepared monomethine cyanine dyes (4a–c) with iodoethane quaternary salts of α -picoline, quinaldine and/or γ -picoline in equimolar ratios, in ethanol and the presence of piperidine to achieve the same 3,8[2(4)]-*bis*-monomethine cyanine dyes (5a–c) obtained by Route (1), were characterized by melting points, mixed melting points, the same visible, IR and 1H NMR spectral data [Scheme (1), Route (2), Table (1)].

The structure of the prepared compounds was confirmed by the elemental analysis (Table 1), electronic visible absorption spectra (Table 1), mass spectrometry, IR [17], and 1H NMR [18] (Table 2) spectroscopic data.

2. Structure/Spectra Correlation

The electronic visible absorption spectra of the monomethine cyanine dyes (4a–c) and *bis*-monomethine cyanine dyes (5a–c) in 95% ethanol solution disclose bands in the visible region at 370–580 nm and 370–610 nm, respectively. The positions of these bands and their molar extinction coefficients are largely influenced by the nature of the heterocyclic quaternary residue (A), their linkage positions and the number of the electronic charge transfer pathways inside the dye molecule. So, substituting A = 1-ethyl pyridinium-2-yl salts in the monomethine cyanine dye (4a) and in the *bis*-monomethine cyanine dye (5a) by A = 1-ethyl quinolinium-2-yl salts to get the monomethine cyanine dye (4b) and the *bis*-monomethine cyanine dye (5b) causes strong bathochromic shifts at 130 nm and 140 nm respectively, accompanied by increasing in the number and intensity of the absorption bands in the case of the *bis*-monomethine cyanine dye (5b) [Scheme (1), Table (1)]. This can be attributed to increasing π -delocalization conjugation in the latter dyes due to the presence of the quinoline ring system in correspondence to the pyridine ring system in the former dyes.

Changing the linkage positions from 2-yl salts to 4-yl salts passing from the monomethine cyanine dye (4a) and the *bis*-monomethine cyanine dye (5a) to the monomethine cyanine dye (4c) and the *bis*-monomethine cyanine dye (5c) resulted in a remarkable red shift by 10 nm accompanied by increasing the number and intensity of the absorption bands [Scheme (1), Table (1)]. This can be explained in the light of increasing the length of the π -delocalization conjugation in the latter 4-yl salts dyes (4c) and (5c) compared to the former 2-yl salts dyes (4a) and (5a).

Comparing the electronic visible absorption spectra of monomethine cyanine dyes (4a–c) with those of the *bis*-monomethine cyanine dyes (5a–c), we declared that the latter dyes have in their spectra bathochromically shifted bands related to the former ones. This can be attributed to the presence of two electronic charge transfer pathways inside the latter dyes molecules in correspondence to one electronic charge transfer pathways inside the former dyes molecules [Scheme (2), Table (1)].

3. Solvatochromism

Solvatochromism is the reversible colour changing induced by solvents. This often derives from changes in polarity of various solvents. This affects charge transfer mechanisms in solvatochromic compounds, causing colour changes. Cyanine dyes had been useful in studies of the colour of organic compounds [19] and today there are existed several fundamental principles that correlate origin of colour to chemical structures of the solute, as well as natures of the solvents [19–22]. Besides, this class of organic heterocyclic dyes compounds are useful in various industrial fields [23].

This encouraged us and directed our attention to study the solvachromism of some selected monomethine cyanine dyes (4b) and (5b) in pure solvents having different polarities to select the best solvents when these dyes used and/or applied as photosensitizers. Also, this study evaluates the possibility of uses and/or the applications of these dyes as probes for determining solvent polarity due to their solvatochromic properties.

The electronic visible absorption spectra of the monomethine (4b) and the *bis*-monomethine (5b) cyanine dyes in pure solvents with different dielectric constants, namely water (78.54), dimethylformamide (DMF) (36.70), ethanol (24.3), chloroform (4.806), carbon tetrachloride (2.238) and dioxane (2.209) [24], were recorded. The λ_{\max} and ε_{\max} values of the absorption bands are shown in Table (3).

From Table (3), it is clear that the electronic visible absorption spectra of the examined dyes in the ethanolic medium are characterized by the presence of four essential absorption bands. These bands can be attributed to intermolecular charge transfer [25] associated with a lone pair of electrons from the HN-imidazoline nitrogen atom migrating towards the positively charged center of the quaternary nitrogen atom of the quinolinium salt residue [Scheme (2)].

The data given in Table (3) show, that the charge transfer band exhibits a hypsochromic shift in ethanol relative to DMF, dioxane, chloroform and carbon tetrachloride. This effect may be related to the following factors:

a) The bathochromic shift in addition to the higher molar extinction coefficients in DMF relative to ethanol is a result of the increase in solvent polarity (positive solvatochromism);

b) The hypsochromic shift occurring in ethanol in addition to the lower molar extinction coefficients relative to dioxane, chloroform and carbon tetrachloride (negative solvatochromism) is a result of the solute-solvent interaction through the intermolecular hydrogen bond formation between ethanol and the lone pair of electrons of the HN-imidazoline nitrogen atom; this minimize slightly the electron density on the HN-imidazoline nitrogen atom and consequently decreases to some extent the moving and mobility of the attached π -electrons over the conjugated pathway to the positively charged quaternary nitrogen atom of the quinolinium salt residue, and accordingly a blue shift occurs in ethanol relative to dioxane, chloroform and carbon tetrachloride [Scheme (3) (A)].

Also, from the data given in Table (3) it is observed the occurrence of unexpected hypsochromic shift, as well as decreasing the number and intensity of the absorption bands in water relative ethanol and the other solvents. This can be mainly ascribed to the possible interaction of water molecules with the lone pair of electrons of the HN-imidazoline nitrogen atom forming the intermolecular hydrogen bond. This makes difficult the transfer of electronic charge from the HN-imidazoline nitrogen atom to the quaternary nitrogen atom of the heterocyclic salt residue in the quinolinium ring system, and consequently a hypsochromic shift occurs in water relative to ethanol and the other solvents [Scheme (3) (B)].

From the above discussed results we could conclude that the solvatochromism of the investigated cyanine dyes in pure solvents having different polarities underwent displacements to give positive solvatochromism (occurrence of a bathochromic shift with increasing solvent polarity) and/or negative solvatochromism (occurrence of a hypsochromic shift with increasing solvent polarity) depending upon the following factors:

- a) Increasing and/or decreasing the polarity and/or the dielectric constant of the solvent (general solvent effect);
- b) Hydrogen bond and/or molecular complex formation between the solute (dyes molecules) and the solvent used (specific solvent effect).

4. Halochromism

Halochromism means the colour change, which occurs on addition of acid or base or salt to a solution of a compound. A chemical reaction such as ion formation transforms a colourless compound into a coloured one. Halochromic compounds are compounds, which change their colour when *pH* changes occur. The term chromic is defined as a material that can change colour reversibly with the presence of a factor, and in this case the main factor is *pH*. The *pH* indicators, therefore have this property.

Solutions of the monomethine (4b) and the *bis*-monomethine (5b), cyanine dyes behave as halochromic compounds, where their ethanolic solutions gave changeable colours in acid/base media, being yellow or colourless on acidification and getting back (restore) their original permanent intense colour on basification. This encouraged us and directed our attention to study their spectral behavior in different buffer solutions having varied *pH* values to select the optimum condition and/or the suitable *pH* values for use of these dyes as photosensitizers. The other purpose of this study is to evaluate the possibility of uses and/or applications of these dyes as indicators in acid/base titrations in analytical chemistry. The acid dissociation or protonation constants of these dyes have been determined. The effect of these compounds as photosensitizers increases when they are present in the ionic form, which has higher planarity [26] and therefore more conjugation.

The electronic visible absorption spectra of the dyes (4b) and (5b) in aqueous universal buffer solutions with varying *pH* values (1.45; 2.03; 3.72; 5.09; 7.57; 8.91; 10.20 and 12.04) showed bathochromic shifts with intensification of their absorption bands at high *pH* values (alkaline media) and hypsochromic shifts with reduction in the intensity of the bands at low *pH* (acidic media) [Table (4)].

These phenomena can be explained and/or illustrated in the light of that that these dyes which have free lone pair of electrons on the HN-imidazoline nitrogen atom undergo protonation in acidic media. This generates positive charge on the HN-imidazoline nitrogen atom, and consequently the electronic charge transfer from the HN-imidazoline nitrogen atom to the heterocyclic quaternary nitrogen atom in the quinolinium salt residue will be greatly affected resulting in a hypsochromic shift, protonated and/or colourless structures [Scheme (4) (A)]. On increasing the *pH* value of the media, the absorption bands are intensified and bathochromically shifted as a result of deprotonation of the HN-imidazoline nitrogen atom, and accordingly the electronic charge transfer to the quaternary heterocyclic nitrogen atom of the quinolinium salt residue will be easier and facilitated resulting in a bathochromic shift, deprotonated and/or coloured structures [Scheme (4) (B)].

Several methods have been developed for the spectrophotometric determination of the dissociation or protonation constants of weak acids. The variation of absorbance with *pH* values can be utilized. On plotting the absorbance at fixed λ_{\max} vs *pH*, S-shaped curves are obtained. On all of the S-shaped curves obtained, the horizontal portion to the left corresponds to the acidic form of the indicator, while the upper portion to the right corresponds to the basic form, since the pK_a value is defined as the *pH* value for which one half of the indicator is in the basic form and the other half – in the acidic form. This point is determined by intersection of the curve with a horizontal line midway between the left and the right segments [27]. The acid dissociation or protonation constants values of the dyes (4b) and (5b) are listed in Table (5).

From this study we can conclude that the electronic visible absorption spectra of the monomethine (4b) and the *bis*-dimethine (5b) cyanine dyes in aqueous universal buffer solutions having varying *pH* values underwent displacements to give the hypsochromic shifted and lower intensity bands in the lower *pH* and/or acidic media due to the protonated and/or colourless structures of the dyes in these media. Inversely, the bands of these dyes are intensified and bathochromically shifted in high *pH* and/or alkaline media due to the deprotonated and/or coloured structures of the dyes in these media.

Table (1): Characterization of the prepared compounds (3), (4a-c) and (5a-c)

Comp. No	Nature of products		Molecular formula (M.Wt)	Analysis, %						Absorption spectra in 95% ethanol		
	Colour	Yield %		M.p. °C	Calculated			Found			λ_{max} (nm)	ϵ_{max} (mol ⁻¹ cm ²)
					C	H	N	C	H	N		
3	Brown crystal	60	199	48	1.33	18.67	47.99	1.31	18.65	
4a	Red	75	175	45.2	2.64	13.18	45.18	2.6	13.15	430,450	710,1550	
4b	Violet	79	179	49.57	2.75	12.05	49.54	2.73	12.02	410,450,480,580	6120,6900,6330,5280	
4c	Red	64	177	45.2	2.64	13.18	45.17	2.61	13.15	370,440,460	7070,2670,2150	
5a	Deep red	67	182	44.09	3.15	11.02	44.04	3.14	11.01	370,390,440,470	15660,14310,7170,5640	
5b	Violet	74	190	50.12	3.25	9.75	50.9	3.24	9.7	440,480,580,610	9410,8140,6630,3000	
5c	Deep red	68	188	44.09	3.15	11.02	44.03	3.13	11	390,410,460,480	21920,21530,10840,9700	

Table (2): IR and ¹H NMR (Mass) Spectral Data of the Prepared Compounds (3), (4b) and (5b)

Comp. No.	IR Spectrum (KBr, cm ⁻¹)	¹ H NMR Spectrum (DMSO, δ); & (Mass Spectrometry data)
3	1027, 1144, 1166(C-O-C cyclic) 1605 (C=C) 1627 (C=O quinone) 1750 (C=O imidazolone) 3429 (NH)	3.5 (b, 4H, 4NH) M+1 : 301
4b	828, 880, (o-disubstituted benzene) 1077, 1154 (C-O-C cyclic) 1438, 1514 (C=N) 1605 (C=C) 1750 (C=O imidazolone) 2936, 2522 (quatemary salt) 3432 (NH)	1.5 (m, 3H, CH ₃ , N-quinolinium) 3.1 (m, 2H, CH ₂ , N-quinolinium) 5 (s, 4H, 4NH) 7.9-9.2 (m, 7H, aromatic + heterocyclic + =CH-)
5b	828, 882, (o-disubstituted benzene) 1077, 1119 (C-O-C cyclic) 1437, 1517 (C=N) 1604 (C=C) 1719 (C=O quinone) 2930, 2523 (quatemary salt) 3430 (NH)	1.5 (m, 6H, 2CH ₃ , N-quinolinium) 3.1 (m, 4H, 2CH ₂ , N-quinolinium) 5 (s, 4H, 4NH) 7.8-9.2 (m, 14H, aromatic + heterocyclic + 2 =CH-)

Table (3): Solvatochromism of the dyes (4b) and (5b) in solvents having different polarities

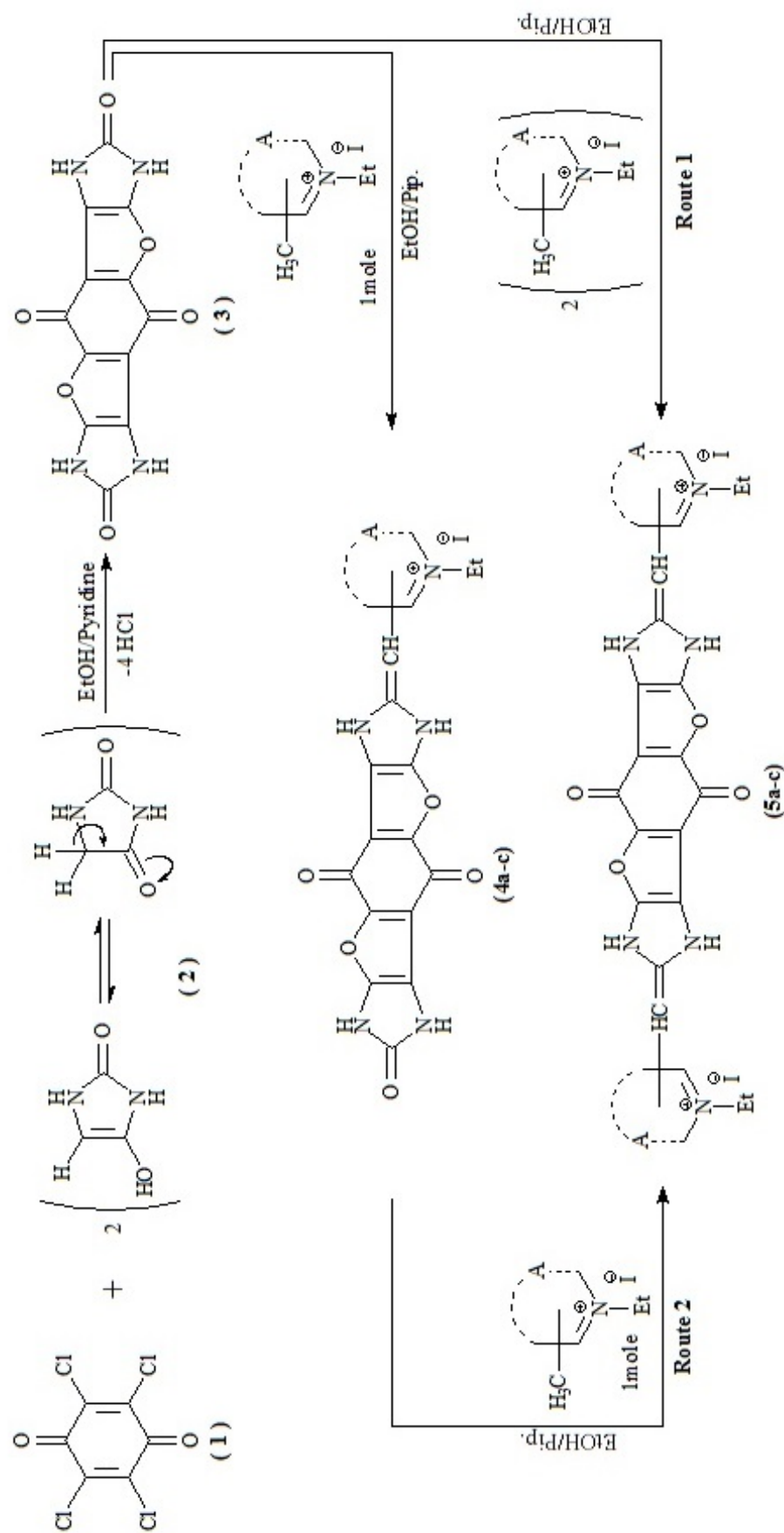
Solvent Dye No.	H ₂ O		EtOH		DMF		CHCl ₃		CCl ₄		Dioxane	
	λ_{\max} (nm)	ϵ_{\max} (mole ⁻¹ ·cm ²)	λ_{\max} (nm)	ϵ_{\max} (mole ⁻¹ ·cm ²)	λ_{\max} (nm)	ϵ_{\max} (mole ⁻¹ ·cm ²)	λ_{\max} (nm)	ϵ_{\max} (mole ⁻¹ ·cm ²)	λ_{\max} (nm)	ϵ_{\max} (mole ⁻¹ ·cm ²)	λ_{\max} (nm)	ϵ_{\max} (mole ⁻¹ ·cm ²)
4b	430	5820	410	6120	425	6890	420	8440	415	6920	410	7120
	470	5330	450	6900	440	7500	450	7360	430	8320	430	8340
	570	4280	480	6330	530	4980	550	4530	460	7150	565	5600
5b	420	8140	440	9410	460	1000	420	8480	450	10460	430	8650
	460	8070	480	8140	484	2550	442	8900	480	9480	455	9750
	560	6230	580	6630	540	5970	480	8090	588	7800	482	8280
	593	2630	610	3000	592	7800	584	6150	620	3800	589	4640
					629	5555	617	2500			624	3300

Table (4): Halochromism of the dyes (4b) and (5b) in aqueous universal buffer solutions

pH Dye No.	1.45		2.03		3.72		5.09		7.57		8.91		10.20		12.04	
	λ_{\max} (nm)	ϵ_{\max} (mol ⁻¹ ·cm ²)	λ_{\max} (nm)	ϵ_{\max} (mol ⁻¹ ·cm ²)	λ_{\max} (nm)	ϵ_{\max} (mol ⁻¹ ·cm ²)	λ_{\max} (nm)	ϵ_{\max} (mol ⁻¹ ·cm ²)	λ_{\max} (nm)	ϵ_{\max} (mol ⁻¹ ·cm ²)	λ_{\max} (nm)	ϵ_{\max} (mol ⁻¹ ·cm ²)	λ_{\max} (nm)	ϵ_{\max} (mol ⁻¹ ·cm ²)	λ_{\max} (nm)	ϵ_{\max} (mol ⁻¹ ·cm ²)
(4b)	410	2770	440	7360	442	4970	442	5100	443	5510	443	5380	420	5510	442	5400
	430	5100	470	6790	470	6390	470	6280	470	6710	470	6360	450	7070	472	6550
	460	2000	468	3680	570	4030	571	4620	573	5150	575	6000	470	6380	578	6700
	560	1740	577	6600
(5b)	440	7340	450	7340	450	6980	450	7440	450	7800	450	7940	450	8230	450	8390
	480	6800	480	6710	482	6440	482	6870	480	7330	480	7430	480	7630	480	7830
	580	4060	581	4500	583	4960	585	5520	587	6000	588	7000	580	8000	590	9000

Table (5): The variation of absorbance with *pH* at fixed λ for the cyanine dyes (4b); (5b) in different buffer solutions

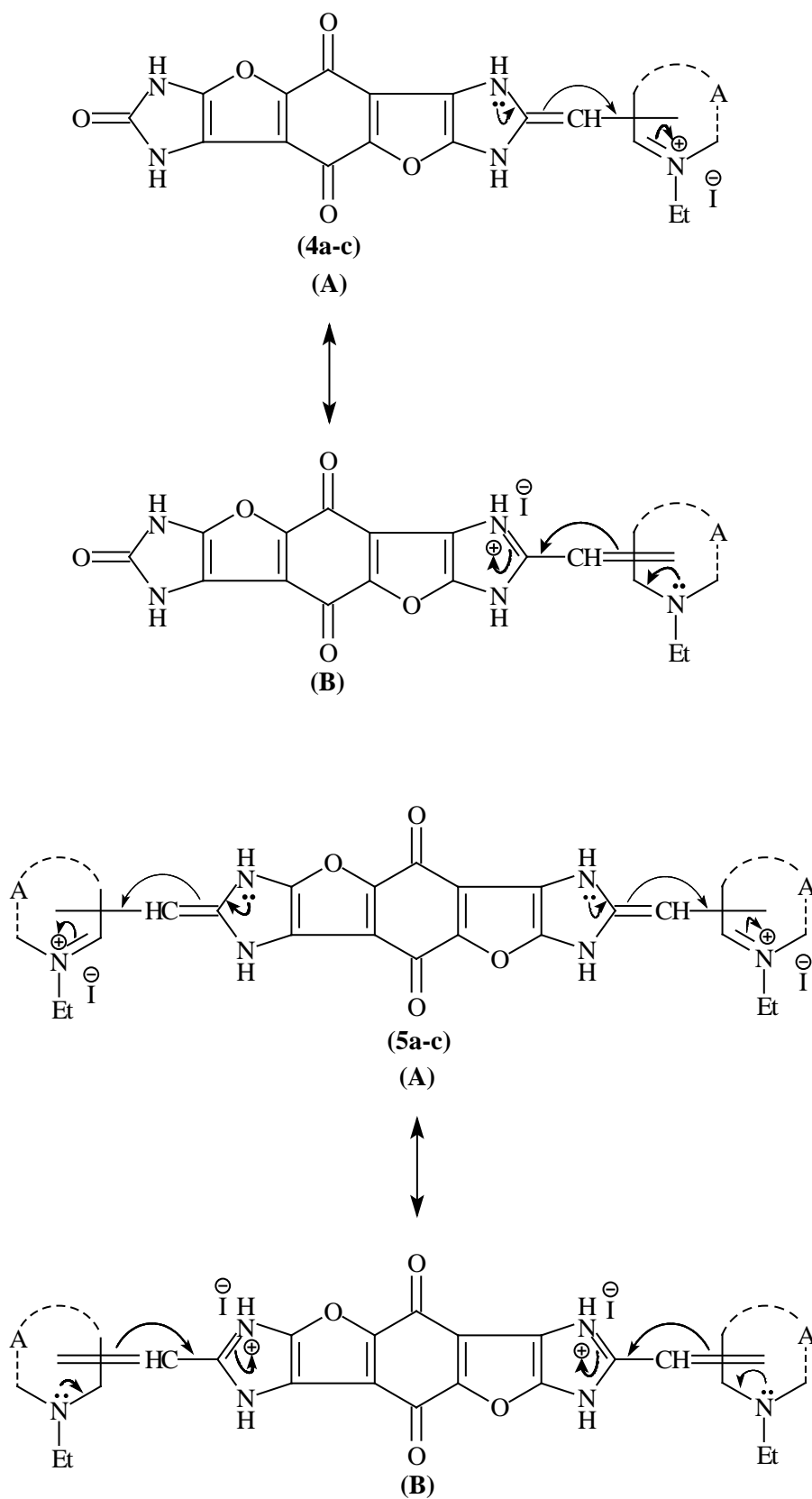
		<i>pH</i>									
		1.45	2.03	3.72	5.09	7.57	8.91	10.20	12.04		
Absorbance at fixed wavelength	(4b) λ 560 (nm)	0.2	0.39	0.4	0.44	0.45	0.59	0.6	0.64	4.8; 8.5	
	(5b) λ 580 (nm)	0.4	0.42	0.49	0.54	0.58	0.64	0.8	0.82	9.4	



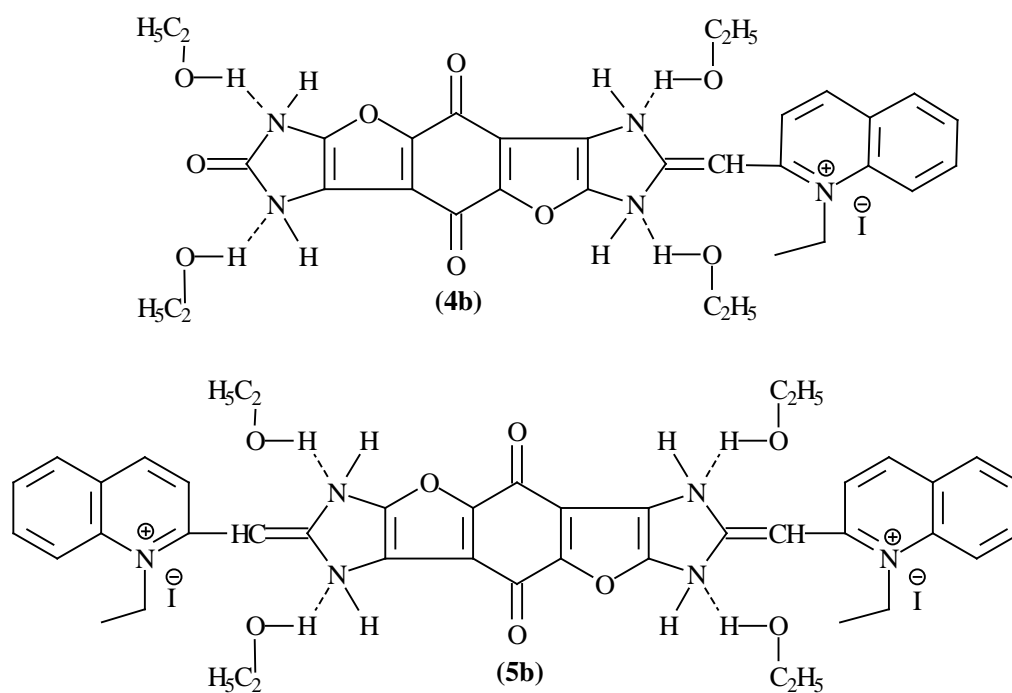
Scheme (1)

Substituents in Scheme (1):

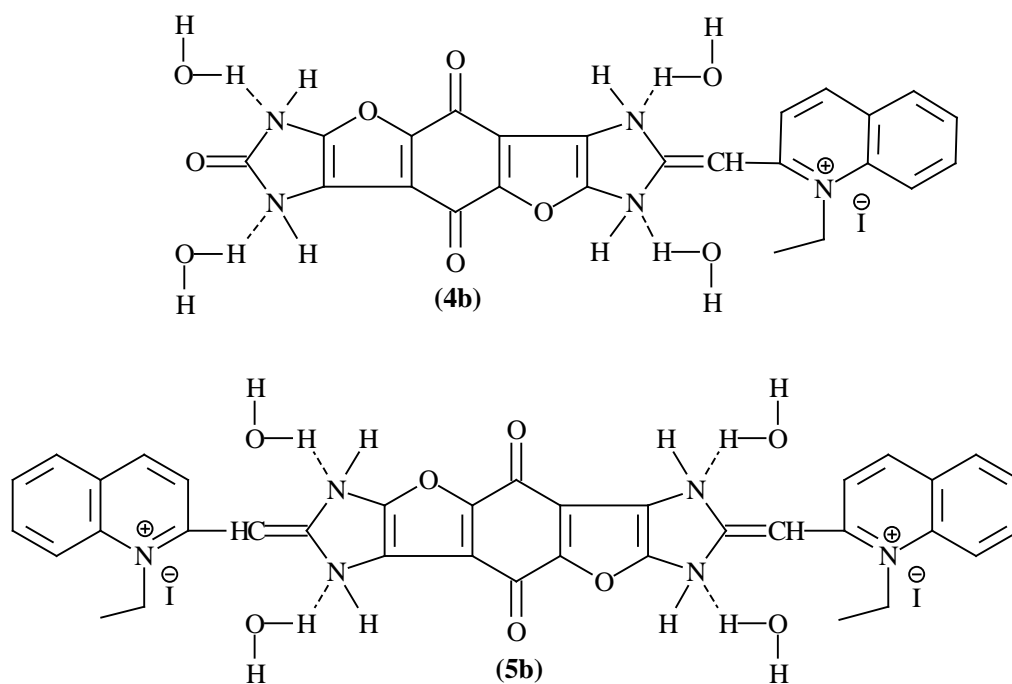
(4a-c); (5a-c): A = 1-ethyl pyridinium-2-yl salt (a); 1-ethyl quinolinium-2-yl salt (b); 1-ethyl pyridinium-4-yl salt (c).



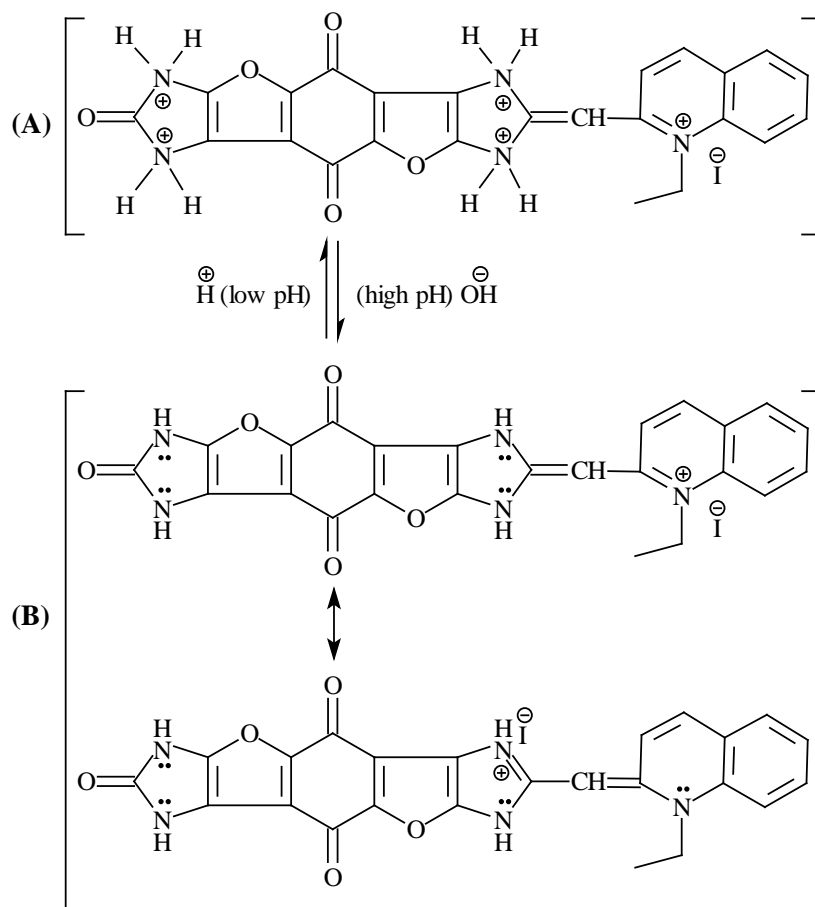
Scheme (2)



Scheme (3) (A)

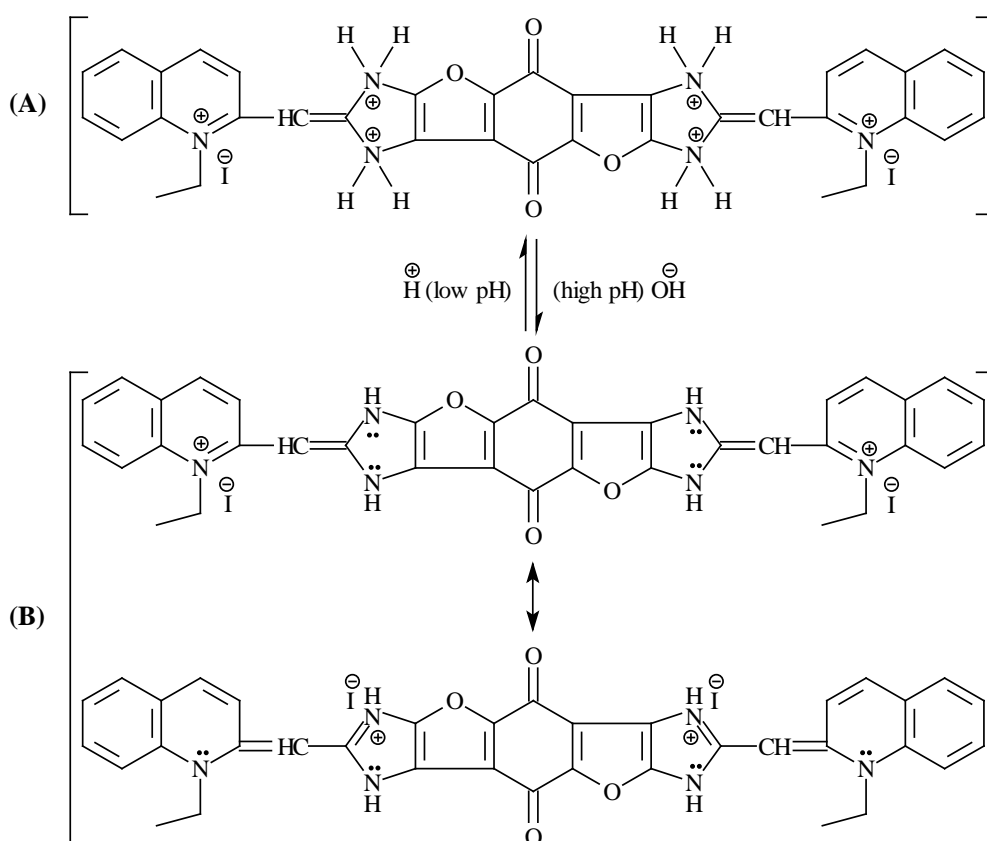


Scheme (3) (B)



Scheme (4):

Decolorization (protonation) and colorization (deprotonation) of the dye (4b) in acid/base media, respectively



Scheme (4) continue:

Decolorization (protonation) and colorization (deprotonation) of the dye (5b) in acid/base media, respectively

Conclusions

a) The electronic visible absorption spectra of the monomethine cyanine dyes (4a–c) and the *bis*-monomethine cyanine dyes (5a–c) underwent displacements to give bathochromic and/or hypsochromic shifts depending upon the following factors:

1) Type of the heterocyclic quaternary salt (A) in the order of: quinaldinium dyes > α -picolinium dyes;

2) Linkage positions of the heterocyclic quaternary salts in the order of: γ -picolinium dyes > α -picolinium dyes;

3) The number of the electronic charge transfer pathways inside the dyes molecules in the order of: two electronic charge transfer pathways dyes > one electronic charge transfer pathways dyes;

b) The intensity of the colour of the monomethine cyanine dyes (4a–c) and the *bis*-monomethine cyanine dyes (5a–c), can be attributed to two suggested mesomeric structures (A) and (B) producing a delocalized positive charge over the conjugated system [Scheme (2)].

Acknowledgements

We are thankful to the Chemistry department, Faculty of Science, Aswan University, Aswan, Egypt for supporting this work.

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