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Novel carbocyanine and bis-carbocyanine dyes: synthesis, visible spectra studies, solvatochromism and halochromism

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ARTICLE INFO

Article type:
Research article
Article history:
Received November 2015
Accepted December 2015
October 2016 Issue
Keywords:
Cyanine dyes
Carbocyanine cyanine dyes
Synthesis
Visible spectra
Trimethine cyanine dyes
Chromism

ABSTRACT

Novel carbocyanine dyes (trimethine cyanine dyes) and bis-carbocyanine dyes (bis-trimethine cyanine dyes) derived from the nucleus of benzo[2,3-b; 2',3'-b'] bis-furo[2,3-d]imidazoline-3,5,8,10-tetra one were synthesized. The electronic visible adsorption spectra of all the synthesized cyanine dyes were investigated in 95% ethanol solution. Solvatochromism and/or halochromism for some selected dyes were examined in pure solvents having different polarities (water, dimethylformamide, ethanol, chloroform, carbontetrachloride and dioxane) and/or in aqueous universal buffer solutions owing varied pH values (1.45, 2.03, 3.72, 5.09, 7.57, 8.91, 10.20 and 12.04 units), respectively. Structural confirmations were determined by elemental analysis, visible, mass, IR and ^{1}H NMR spectral data.

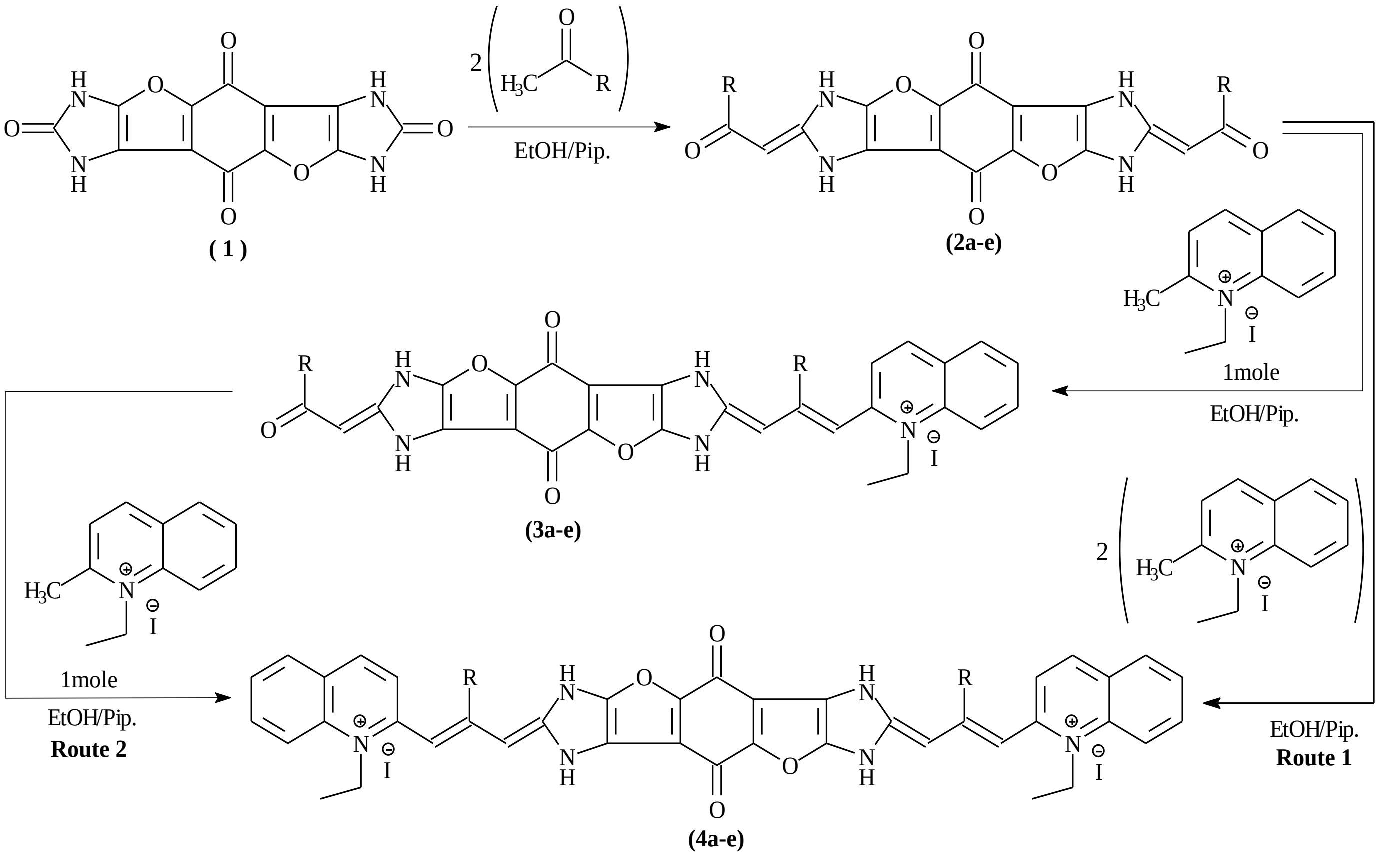
Capsule Summary: Novel carbocyanine and bis carbocyanine dyes have been prepared and their visible spectra, solvatochromic and halochromic properties were investigated.

Cite This Article As: H. A. Shindy, M. M. Goma and N. A. Harb. Novel carbocyanine and bis carbocyanine dyes: synthesis, visible spectra studies, solvatochromism and halochromism. Chemistry International 2(4) (2016) 222-231.

INTRODUCTION

Cyanine dyes are a large class of complex organic compounds which have been extensively used in a wide range of applications, from lasers and photography to diagnostic by fluorescent detection of analytics and sensitizers for photodynamic therapy, optical communication technology, laser disks materials and in textile industry (Ehret et al., 2001, Ferreira, et al., 2015, Moreira, et al., 2015, Upadhyayula, et al., 2015, Solomon, 2014, Keisar, et al., 2014, Parvathy, et al., 2015, Yi, et al., 2014, Owens, et al., 2014, Ansari, et al., 2014, Shindy, et al., 2012). In addition cyanine dyes also used in clinical chemistry, fluorescent labels in DNA, sensitizers in solar cells, anti-tumor and anti-cancer agents, lithographic printing plate precursors, in pharmaceutical industry, as probe sensors, in bio-analytical applications, as pH indicators and as probes for determining solvent polarity (Zhang, et al., 2012, Gabbutt, et al., 2012, Li, et al., 2012, Xiang, et al., 2012, Panigrahi, et al., 2012, Sun, et al., 2013, Lynch, et al., 2013; Zhao, et al., 2013, Park, et al., 2013, Park, et al., 2013).

Taking in accounts the above advantages of cyanine dyes we prepared here some new photosensitizers, solvatochromic and halochromic carbocyanine (trimethine) and bis carbocyanine (bis trimethine) cyanine dyes as new synthesis contribution and spectroscopic investigation in this field and to may be used and/or applied in any of the wide range applications of cyanine dyes, particularly as photographic sensitizers in photographic industry, as



Scheme 1: Synthesis routes of the prepared compounds

(2a-e): R = H (a); CH_3 (b); C_6H_5 (c); $C_6H_4.p.OCH_3$ (d); $C_6H_4.p.NO_2$
(3a-e); (4a-e): R = H, A = 1-ethyl quinolinium-2-yl salt (a); R = CH_3, A = 1-ethyl quinolinium-2-yl salt (b); R = C_6H_5, A = 1-ethyl quinolinium-2-yl salt (c); R = $C_6H_4.p.OCH_3$, A = 1-ethyl quinolinium-2-yl salt (d); R = $C_6H_4.p.NO_2$, A = 1-ethyl quinolinium-2-yl salt (e)

indicators in operations of acid / base titrations and/or as probes for determining solvent polarity in solution chemistry.

MATERIAL AND METHODS

General

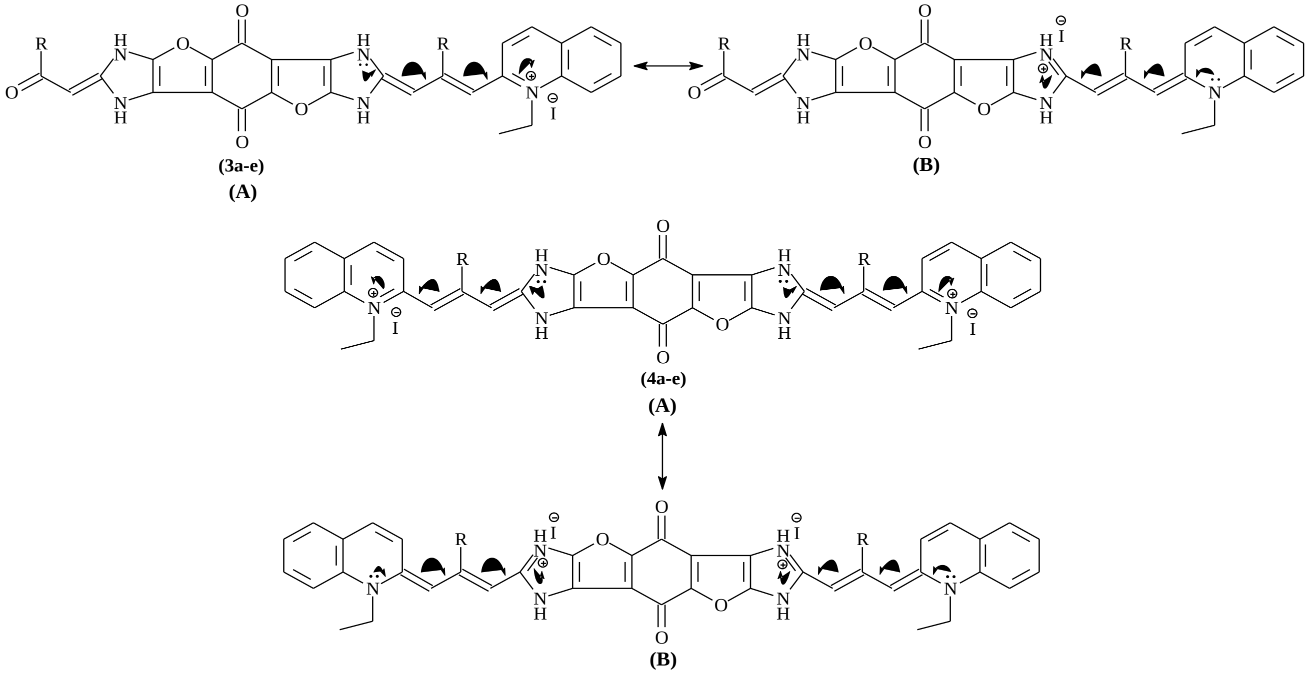
All the melting points of the prepared compounds are measured using Electrothermal 15V, 45W 1 A9100 melting point apparatus, Chemistry department, Faculty of Science, Aswan University and are uncorrected. Elemental analysis were carried out at the Microanalytical Center of Cairo University by an automatic analyzer (Vario EL III Germany). Infrared spectra were measured with a FT/IR (4100 Jasco Japan), Cairo University. ^1H NMR Spectra were accomplished using Varian Gemini-300 MHz NMR Spectrometer, Cairo University. Mass Spectroscopy was recorded on Mas 1: GC-2010 Shimadzu Spectrometer, Cairo University. Electronic visible absorption spectra were carried out on Visible Spectrophotometer, Spectro 24 RS Labomed, INC, Chemistry department, Faculty of Science, Aswan University.

Synthesis of benzo [2,3-b; 2',3'-b] bis-furo [2,3-d] imidazolinc-5,10-dione-3,8-diacylmethylideno derivatives (2a-e)

These intermediate compounds were synthesized by refluxing of the compound (1) (Shindy, et al., 2015) (0.01 mol) with acyl and/or acyl derivatives (acetaldehyde, acetone, acetophenone, p-methoxyacetophenone, p-nitroacetophenone) in 1:2 molar ratios in ethanol (50 ml) containing piperidine (3-5 drops) for 6 hrs. The brown mixture were filtered off while hot to remove any impurities, concentrated and precipitated by using cold water. The separated intermediate compounds (2a-e) were filtered, washed with water, dried and crystallized from ethanol. The results are registered in Table (1).

Synthesis of benzo [2,3-b; 2',3'-b'] bis-furo [2,3-d] imidazoline-5,10-dione-8-acylmethylideno-3(2)-trimethine cyanine dyes (3a-e)

A mixture of equimolar ratio of the intermediate compounds (2a-e) (0.01 mol) and 1-ethy quinaldinium iodide quaternary



Scheme 2: Colour intensity illustration of the synthesized cyanine dyes.

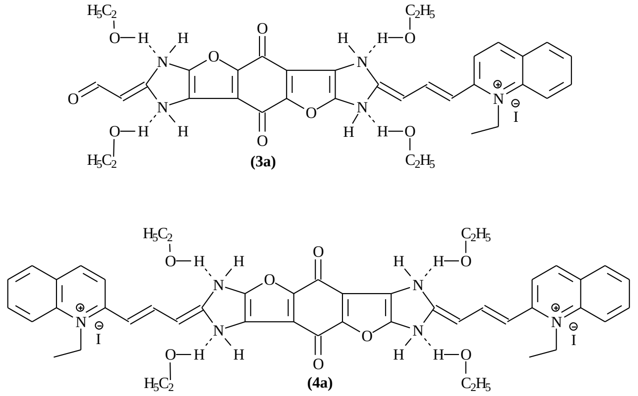
Table 1: Characterization of the prepared compounds (2a-e)

Comp. No	Nature of products			Molecular formula (M.Wt)	Analysis %					
					Calculated			Found		
	Colour	Yield %	M.p. ºC		C	H	N	C	H	N
2a	Brown	65	130	$C_{16}H_8N_4O_6$ (352)	54.55	2.27	15.90	54.54	2.25	15.80
2b	Brown	77	200	$C_{18}H_{12}N_4O_6$ (380)	56.84	3.16	14.74	56.82	3.14	14.73
2c	Brown	55	150	$C_{28}H_{16}N_4O_6$ (504)	66.67	3.17	11.11	66.61	3.15	11.90
2d	Brown	79	153	$C_{30}H_{20}N_4O_8$ (564)	63.83	3.55	9.93	63.80	3.54	9.90
2e	Brown	73	160	$C_{28}H_{14}N_6O_{10}$ (594)	56.57	2.36	14.14	56.55	2.35	14.13

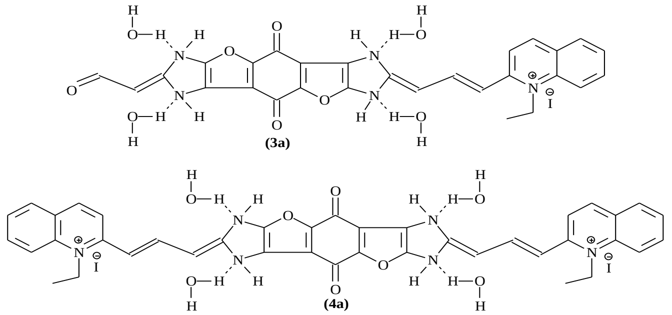
salt were heated under reflux in ethanol (50 ml) containing piperidine (3-5 drops) for 6-8 hrs. The reaction mixtures changed its colours from dark brown colour to deep violet colour at the end of the reflux. It was filtered off while hot, concentrated to half its volume and cooled. The precipitated dyes were filtered, washed with water, dried and crystallized from ethanol. The data are given in Table (2).

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

Two different routes arc employed to prepare these cyanine dyes: Route (1): was carried out by adding piperidine (3-5 drops) to an ethanolic solution (50 ml) of the intermediate compounds (2a-e) (0.01 mol) and iodoethane quaternary salt of quinaldine (0.02 mol). The reaction mixtures were heated under reflux for 6-8 hrs and changed its colours from dark brown colour to deep violet colour at the end of the reflux. It was filtered off while hot, concentrated to half its volume and cooled. The precipitated dyes were filtered off, washed with water, dried and crystallized from ethanol. The data are given in Table (2). Route (2): was accomplished through the reaction between the previously prepared trimethine cyanine dyes (3a-e) (0.01 mol) and equimolar ratios of (0.01 mol) of iodoethane quaternary salt of quinaldine in ethanol (50 ml) and presence of piperidine (3-5 drops). The reacting materials were refluxed for 6-8 hrs, and attained a permanent deep violet colour at the end of the reflux. It was filtered, concentrated, cooled, and precipitated by adding cold water. The precipitates were collected and crystallized from ethanol to give the same dyes obtained by route (1),



Scheme 3a: Hydrogen bond formation between the dyes (3a), (4a) and ethanol molecules (specific solvent effect)



Scheme 3b: Hydrogen bond formation between the dyes (3a), (4a) and water molecules (specific solvent effect).

characterized by melting points, mixed melting points, same visible, IR and ^{1}H NMR spectral data, Table (2).

Visible spectra studies

The electronic visible absorption spectra of the prepared cyanine dyes were examined in 95% ethanol solution and recorded using 1cm Qz cell in Vis Spectrophotometer, Spectro 24RS Labomed, INC. A stock solution (1 x 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.

Solvatochromism and halochromis

The electronic visible absorption spectra of some selected synthesized cyanine dyes were investigated in pure organic solvents of spectroscopic grade (Shindy, et al., 2015) and different polarities and/or in aqueous universal buffer solutions having varying pH values and recorded using 1cm quartz cell in Vis Spectrophotometer Spectro 24 RS Labomed, INC. A stock solution (1 x 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

Synthesis

Equimolar reaction of (1) (Shindy, et al., 2015) and acyl or acyl derivatives (acetaldehyde, acetone, acetophenone, p.OCH_3 acetophenone and/or p.NO_2 acetophenone) in ethanol containing piperidine gives the 3,8-diacylmethylideno derivatives (2a-e) as intermediate compounds, Scheme (1), Table (1).

Further reactions of the intermediate compounds (2a-e) with N-ethyl quinaldinium iodide quaternary salts in equimolar ratios in ethanol and presence of few drops of piperidine produced the 3(2)-trimethine cyanine dyes (3a-e), Scheme (1).

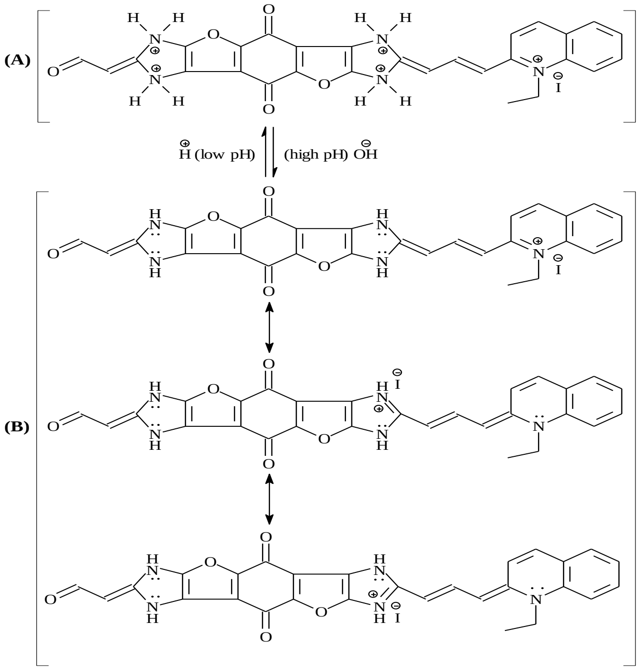
1:2 molar ratios of the intermediate compounds (2a-e) and iodoethane quaternary salts of quinaldine were reacted in ethanol and presence of piperidine and resulted the 3,8(2)-bis trimethine cyanine dyes (4a-e), Scheme (1), Route (1), Table (2).

Chemical confirmations takes place through Route (2) for the 3,8(2)-bis trimethine cyanine dyes (4a-e) by reactions of the previously prepared 3(2)-trimethine cyanine dyes (3a-e) with N-ethyl quialdinium iodide quaternary salts in equimolar ratios, in ethanol as organic solvents and piperidine as a basic catalyst to give the same 3,8(2)-bis trimethine cyanine dyes (4a-e) obtained by route (1), characterized by melting points, mixed melting points, same visible, IR and ^{1}H NMR spectral data, Scheme (1), Route (2), Table (2).

The structures of the prepared compounds was confirmed by elemental analysis (Tables 1 and 2), visible (Table 2), mass. spectrometer, IR (Wade, 1999), and ^{1}H NMR (Wade, 1999), spectral data, (Table 3).

Visible spectra studies

The electronic visible absorption spectra of the trimethine cyanine dyes and the bis-trimethine cyanine dyes (3a-e) and (4a-e) in 95% ethanol solution showed bands in the visible region 350-650 nm and 420-660 nm, respectively. The positions of these bands and their molar extinction coefficients are highly effected by the meso substituted diene side chain (R) and by the number of the electronic charge transfer pathways inside the dyes molecules. So, substituting R=H in the trimethine cyanine dye (3a) and in the bis trimethine cyanine dye (4a) by R = CH_3 to obtain dyes (3b) and (4b) resulted in a bathochromic shifts of 20 nm and 10 nm respectively, accompanied by increasing the intensity of the bands, which is due to the electron donation of the CH_3 group in the latter dyes, which facilitate and/or increase transfer of electrons to the quaternary nitrogen atom of the quinolinium salt residue, Scheme (1), Table (2). Substituting R = H in the



Scheme 4: Decolourization (protonation) and colourization (deprotonation) of the dye (3a) in acid/base media, respectively, (A) Colourless and/or yellow and (B) deep violet

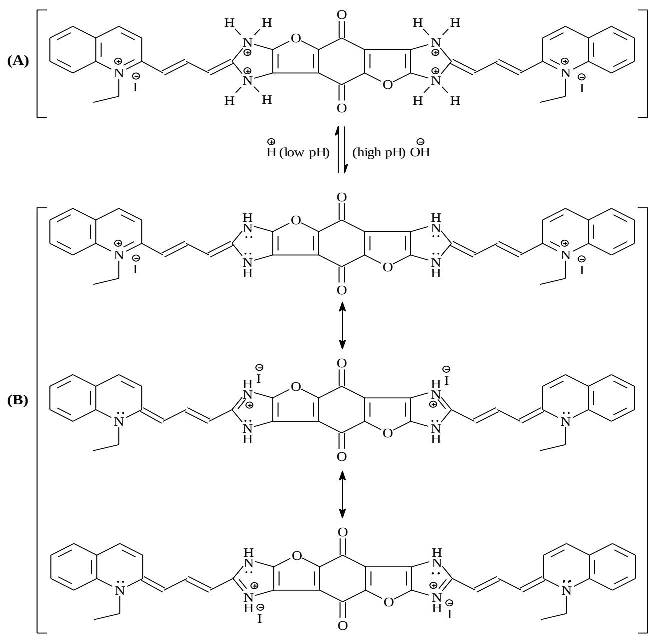
trimethine cyanine (3a) and in the bis-trimethine cyanine dyes (4a) by R = C_6H_5 to give the trimethine cyanine dye (3c) and the bis-trimethine cyanine dye (4c) resulted in a red shifts by 30 nm, which increased the intensity of the bands.

This can be explained in the light of increasing π-delocalization conjugation in the latter dyes due the presence of the phenyl ring system in their structure, Scheme (1), Table (2).

Besides, substituting R = C_6H_5 in the trimethine cyanine dyes (3c) and in the bis trimethine cyanine dyes (4c) by R=C_6H_4-p.OCH_3 to get dyes (3d) and (4d) resulted in a bathochromic shifts by 10 nm. This can be attributed to the electron pushing character of the methoxy groups in the latter dyes which facilitate and increase the intensity of the electronic charge transfer pathways to the quaternary nitrogen atom of the quinolinium salt residue and consequently red shifts occurs, Scheme (1), Table (2).

Furthermore, it is also noticed that substituting R = C_6H_5 in the trimethine cyanine dyes (3c) and in the bis trimethine cyanine dyes (4c) by R = C_6H_4.p.NO_2 to obtain dyes (3e) and (4e) caused a remarkable hypsochromic shifts for the bands by 31 nm and 30 nm, respectively. This can be related to the electron pulling character of the nitro groups in the latter dyes which minimize and/or decrease the intensity of the electronic charge transfer pathways to the quaternary nitrogen atom of the quinolinium salt residue and consequently blue shifts occurs, Scheme (1), Table (2).

Comparing the electronic visible absorption spectra of the trimethine cyanine dyes (3a-e) with those of the bis trimthine cyanine dyes (4a-e) disclosed that the latter dyes are red shifted dyes related to the former dyes. This can be related to presence of two electronic charge transfer pathways in the latter dyes molecules in correspondence to one electronic charge transfer pathways in the former dyes molecules, Scheme (2).



Scheme 4: Continue…

Solvatochromism

The electronic visible absorption spectra of the trimethine (3a) and the bis trimethine (4a) cyanine dyes in pure solvents of different dielectric constant namely water (78.54), dimethylformamide (DMF) (36.70), ethanol (24.3), chloroform (4.806), carbontetrachloride (2.238) and dioxane (2.209) (Shindy, et al., 2015), were recorded. The λ_{max} and ε_{max} values of the absorption hands are shown in Table (4).

From Table (4), it is clear that the electronic visible absorption spectra of the examined dyes in the ethanol medium are Characterized by the presence of seven essential absorption bands for the dye (3a) and eight essential absorption bands for the dye (4a). These bands can be attributed to intermolecular charge transfer (Shindy, et al., 2015) associated with a lone pair of electrons from the HN imidazoline nitrogen atom (basic center) migrating towards the positively charged of the quaternary nitrogen atom (acidic center) of the quinolinium salt residue, Scheme (2).

The data given in Table (4) shows 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:

Table 2: Characterization of the prepared compounds (3a-e) and (4a-e)

Comp. No	Color	Y[a] %	M.P. ºC	M.F[b] (M.Wt)	Analysis %						Absorption spectra in 95% ethanol	
					Calculated			Found			λ_{max} (nm)	ε_{max} (mole^{-1}cm^2)
					C	H	N	C	H	N		
3a	DV	60	160	$C_{28}H_{20}N_5O_5I$ (633)	53.08	3.16	11.06	53.07	3.14	11.03	390, 470,500,530,550, 580,610	980,3340,5000,3400,1240,3320,4590
3b	DV	65	175	$C_{30}H_{24}N_5O_5I$ (661)	54.46	3.63	10.59	54.45	3.61	10.58	370,420,450,480, 580,630	12920,6760,8380, 7580,5870,2400
3c	DV	70	190	$C_{40}H_{28}N_5O_5I$ (785)	61.15	3.57	8.92	61.11	3.54	8.90	380,420,430,460,490,510,550,580,640	5750,1790,1750, 2860,1000,4210, 2950,2960,2000
3d	DV	53	195	$C_{42}H_{32}N_5O_7I$ (845)	59.64	3.79	8.28	59.61	3.78	8.25	350,400,430,460, 560,620,650	14950,9790,10570, 10150,6590,2030, 9700
3e	DV	72	200	$C_{40}H_{26}N_7O_9I$ (875)	54.86	2.97	11.20	54.85	2.96	11.18	350,400,430,460, 560,609	11110,5750,7400, 7410,6480,1560
4a	DV	78	203	$C_{40}H_{32}N_6O_4I_2$ (914)	52.52	3.50	9.19	52.50	3.49	9.15	420,450,470,500, 520,540,600,630	1380,1740,710,2950,2950,2950,2960, 3000
4b	DV	55	209	$C_{42}H_{36}N_6O_4I_2$ (942)	53.50	3.82	8.92	53.48	3.80	8.90	420,440,480,580, 640	7480,9460,8180, 7000,3100
4c	DV	80	211	$C_{52}H_{40}N_6O_4I_2$ (1066)	58.54	3.75	7.89	58.50	3.71	7.85	425,441,482,585, 650	9620,10530,9430, 8250,3200
4d	DV	57	213	$C_{54}H_{44}N_6O_6I_2$ (1126)	57.55	3.91	7.46	57.51	3.90	7.44	426,450,483,562, 587,620,660	4190,6940,8910, 624,5700,3010,5000
4e	DV	66	217	$C_{52}H_{38}N_8O_8I_2$ (1156)	53.98	3.29	9.69	53.97	3.25	9.67	440,460,500,600, 620	800,3460,5350,3640, 3009

[a]Yield, [b]Molecular formula, DV = Deep violet

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 of DMF relative to ethanol and other solvents (positive solvatochrornism).

b) The hypsochromic shift occurring in ethanol in addition to the lower molar extinction coefficients relative to dioxane, chloroform and carbontetrachloride (negative solvatochromism) is a result of the solute-solvent interaction through 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 electrons over the conjugated pathway to the positively charged quaternary nitrogen atom of the quinolinium salt residue and accordingly a hypsochromic shift occurs in ethanol relative to the mentioned solvents, Scheme (3) (A).

Also, from the data given in Table (4) it is observed that 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 intermolecular hydrogen bond. This makes difficult the transfer of the electronic charge to the quaternary heterocyclic salt residue of the quinolinium salt residue and consequently a hypsochromic shift occur in water relative to ethanol and the other solvents, Scheme (3) (B).

Halochromism

Solutions of the trimethine (3a) and the bis trimethine (4a) cyanine dyes in ethanol gives changeable colours in acid/base media being yellow or colourless on acidification and getting back (restore) their original permanent intense colour (deep violet) on basification. This encouraged us to study their spectral behavior in different buffer solutions to select a suitable pH for uses and applications of these dyes as photosensitizers. Also, this study 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 the compounds as photosensitizers increase when they are present in the ionic form, which has higher polarity (Shindy, et al., 2015) and therefore more conjugation.

The electronic visible absorption spectra of the dyes (3a) and (4a) in aqueous universal buffer solutions of varying pH values (1.45, 2.03, 3.72, 5.09, 7.57, 8.91, 10.20 and 12.04 units) showed bathochromic shifts with intensification of their absorption bands at high pH (alkaline media) and hypsochromic shifts with reduction in the intensity of the

Table 3: IR and ^{1}H NMR (Mass) spectral data of the prepared compounds (2a), (3a) and (4a)

Comp. No	IR Spectrum (KBr, Cm^{-1})	^{1}H NMR Spectrum (DMSO, δ); & (Mass data)
2a	1080, 1146 (C-O-C cyclic). 1470, 1549 (C=N). 1616 (C=C). 1719 (C=O). 3430 (NH).	3.5 (b, 4H, 4NH). 9.455 (s, 2H, 2CHO). 7.8-9.2 (m, 2H, 2 =CH-) M$^+$: 352
3a	827, 877 (o.disubstituted benzene). 1051, 1119, 1154 (C-O-C cyclic). 1439 (C=N). 1606 (C=C). 1718 (C=O). 2927, 2520 (quaternary salt). 3429 (NH).	1.4 (m, 3H, CH_3, N-quinolinium). 3.1 (m, 2H, CH_2, N-quinolinium) 5.0 (s, 4H, 4NH). 7.18-8.8 (m, 10H, aromatic + heterocyclic + 4 =CH-). 9.18 (s, 1H, CHO).
4a	758, 826, (o.disubstituted benzene). 1151 (C-O-C cyclic). 1451, 1500 (C=N). 1604 (C=C). 2922 (quaternary salt). 3432 (NH).	1.4 (m, 6H, 2CH_3, N-quinolinium). 3.1 (m, 4H, 2CH_2, N-quinolinium) 5.0 (s, 4H, 4NH). 7.4-9.1 (m, 18H, aromatic + heterocyclic + 6 =CH-).

bands at low pH (acidic media), Table (5). Therefore the mentioned 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.

Consequently the electronic charge transfer pathways from the HN imidazoline nitrogen atom to the heterocyclic quaternary nitrogen atom of the quinolinium salt residue will be greatly difficult resulting in a hypsochromic shift, protonated and/or colourless-yellow structures, Scheme (4) (A). On increasing the pH 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 pathways to the quaternary heterocyclic nitrogen atom of the quinolinium salt residue will be easier and more favoured resulting in a bathochromic shift, deprotonated and/or coloured (deep violet) 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 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 pka 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 right segments (Shindy, et al., 2015). The acid dissociation or protonation constants values of the dyes (3a) and (4a) are listed in Table (6).

CONCLUSIONS

Following major conclusions are drawn from present investigation

a) The electronic visible absorption spectra of the trimethine cyanine dyes (3a-e) and the bis trimethine cyanine dyes (4a-e) in 95% ethanol solution underwent displacements to give bathochromic and/or hypsochromic Shifts depending upon the types of the meso substituted diene side chain (R) and the number of the electronic charge transfer pathways inside the dyes molecules, in the order of:

1) C_6H_5-dyes > CH_3-dyes > H-dyes.
2) C_6H_4.p.OCH_3 dyes > C_6H_5 dyes > C_6H_4 p.NO_2 dyes.
3) Two electronic charge transfer pathways dyes > one electronic charge transfer pathways dyes

b) The intensity of the colour of the trimethine cyanine dyes (3a-e) and/or the bis trimethine cyanine dyes (4a-e) can be illustrated according to the suggested two mesomeric structures (A) and (B) producing a delocalized positive charge over the conjugated system, Scheme (2).

c) The spectral characterization of the investigated cyanine dyes (3a) and (4a) 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:

Table 4: Solvatochromism of the cyanine dyes (3a) and (4a) in pure solvents having different polarities

Solvent→	H_2O		EtOH		DMF		$CHCl_3$		CCl_4		Dioxane	
Dye↓ No.	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)
3a	490	5000	390	980	440	7980	420	8310	430	7390	422	7260
	520	2960	470	3340	470	9340	450	9420	451	8620	455	8430
	560	3000	500	5000	500	8540	480	8810	484	7900	486	7550
	600	4000	530	3400	600	6470	586	6840	589	5700	590	4680
			550	1240	631	4000	619	2500	621	1500	628	2500
			580	3320								
			610	4590								
4a	490	2950	420	1380	430	11350	430	12190	450	11850	452	9910
	520	2950	450	1740	460	11740	560	8910	480	10380	483	8460
	580	2960	470	710	492	10460	637	3080	590	8160	589	4690
	620	3570	500	2950	590	8160			642	5000	645	2000
			520	2950	650	5000						
			540	2950								
			600	2960								
			630	3000								

Table 5: Halochromism of the cyanine dyes (3a) and (4a) in aqueous universal buffer solutions

pH→	1.45		2.03		3.72		5.09		7.57		8.91		10.20		12.04	
Dye↓ No.	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)
(3a)	450	8280	430	6400	430	6110	460	8310	450	8240	460	8600	470	8440	470	8530
	490	7090	460	7850	460	7540	490	78605	490	7930	490	8040	500	7880	500	7930
	590	4140	490	7140	490	6970	595	670	597	6260	598	7000	599	7830	600	8880
	……	……..	592	4550	593	5000	……	……..	……	……..	……	……..	……	……..	……	……..
(4a)	470	9740	470	9760	470	9980	480	10800	480	10990	480	10880	480	11040	480	12230
	500	8500	500	8720	500	8970	510	9870	510	10070	510	10110	510	9970	590	11120
	600	4820	603	5500	605	5990	609	7270	612	8300	613	9000	617	9500	620	10700

Table 6: The variation of absorbance with pH at fixed λ for the cyanine dyes (3a) and (4a) in different buffer solutions

Dyes↓	pH								
(3a) (588 nm)	0.42	0.44	0.54	0.58	0.59	0.7	0.79	0.8	9.5
(4a) (600 nm)	0.5	0.58	0.6	0.7	0.78	0.8	0.94	0.99	9.8,4.5

1) Increasing and/or decreasing the polarity and/or the dielectric constant of the solvent (general solvent effect).
2) Hydrogen bond and/or molecular complex formation between the solute (dyes molecules) and the solvent used (specific solvent effect).
d) The electronic visible absorption spectra of the trimethine (3a) and the bis trimethne (4a) cyanine dyes in aqueous universal buffer solutions having varying pH values underwent displacements to give 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 this media. Inversely, the bands of these dyes are intensified and bathochromically shifted in high pH and/or alkaline media due to the deprotonted and/or coloured structures of the dyes in this media.

ACKNOWLEDGEMENTS

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

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