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Heptamethine and nonamethine cyanine dyes: novel synthetic strategy, electronic transitions, solvatochromic and halochromic evaluation

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ABSTRACT

New polymethine cyanine dyes covering heptamethine cyanine dyes (tricarbo-cyanine dyes) and nonamethine cyanine dyes (tetracarbo-cyanine dyes) derived from the nucleus benzo[(2,3-b)benzoxazine; (2',3'-b')furo (3,2-d)pyrazole] were designed and prepared using novel synthetic strategy. Electronic transitions for all the synthesized cyanine dyes was determined and evaluated through investigating their electronic visible absorption spectra in 95% ethanol solution. The dyes were thought to be better electronic transitions when they absorb light at higher wavelength bands (bathochromic shifted and/or red shifted dyes). Consequently, the electronic transitions of the dyes decreases when they absorb light at lower wavelength bands (hypsochromic shifted and/or blue shifted dyes). Solvatochromic and/or halochromic evaluation for some selected dyes was carried out and determined through examining their electronic visible absorption spectra in 6 (six) pure solvents having different polarities [water (78.54), dimethylformamide (36.70), ethanol (24.3), chloroform (4.806), carbontetrachloride (2.238) and dioxane (2.209)] and/or in 8 (eight) aqueous universal buffer solutions owing varied pH values (1.99, 2.99, 4.30, 6.87, 7.96, 8.91, 10.55 and 12.04 units), respectively. Structural characterization and determination was carried out via elemental analysis, visible, mass, IR and ¹H-NMR spectroscopic data.

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Capsule Summary: New heptamethine and nonamethine cyanine dyes were prepared using novel synthetic strategies. The electronic transitions, solvatochromic and halochromic properties of the synthesized dyes has been evaluated.

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INTRODUCTION

Polymethine dyes (cyanine dyes) (Shindy, 2017; Shindy et al., 2018; Kurutosu et al., 2016; Shindy et al., 2016; Komljenovic et al., 2016; Matsuoka, 1990; Tyutyulkov et al., 1991; Shi et al., 2016; Qiu et al., 2017; Shindy et al., 2020; Shindy 2012; Shindy, 2015; Shindy, 2020) represent a class of organic

molecules with absorption bands that cover a broad spectral range (340-1400 nm), larger than any other class of dye system (Matsuoka, 1990; Mishra et al., 2000). These dyes are of interest for studying the correlations between the structure and the properties of molecules (Mishra et al., 2000; Ishchenko, 1994; Davidenko et al., 2005). In addition, polymethine dyes (PMD) are widely used in laser technology for creating tunable laser media in the near IR spectral range,

passive Q-switches of lasers and other devices of quantum electronics and optoelectronics (Davidenko et al., 2005; Pierce, 1991; Pittman et al., 1998). The structure of cyanine dyes composed of two terminal heterocycles containing nitrogen. One nitrogen atom of the heterocycles have lone pairs of electrons (the basic center of the dye) and the other one have a positive charge (the acidic center of the dye) connected via an electron deficient polymethine bridge that allows for a push (electron donors) and a pull (electron acceptors) system between the two heterocycles, Figure (1). The delocalization of electrons across the methine bridge causes them to exhibit two mesomeric electronic transition structures (two resonance forms), (A) and (B), Figure (2), leading to highly fluorescent and long wavelength

2013) and in biomedicine for the purposes of visualization of tissues and photodynamic therapy (PDT) (Pandey et al., 2008; James et al., 2013).

Taking in accounts and consideration the above advantages of cyanine dyes we prepared here some new photosensitizers, solvatochromic and halochromic heptamethine and nonamethine 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, and particularly (according this study) as photographic sensitizers in photographic material industry, as probes for determining solvent polarity in solution chemistry and/or as indicators in operations of acid/base titrations in analytical chemistry.

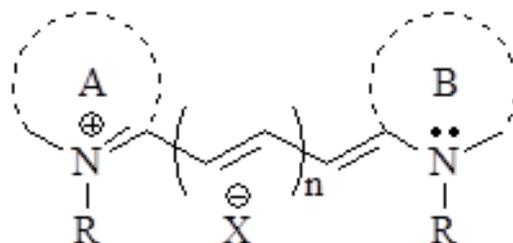


Fig. 1: General structure of cyanine dyes (Where, A, B = Heterocycles, R = CH₃, C₂H₅, X = I, Br, ClO₄, n = 1, 2, 3 ...etc.)

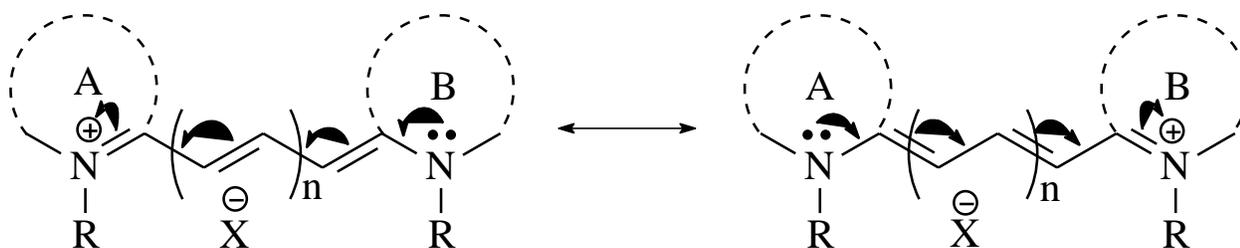


Fig. 2: General electronic transition structures of cyanine dyes (resonance forms) (Where, A, B = Heterocycles, R = CH₃, C₂H₅, X = I, Br, ClO₄, n = 1, 2, 3 ...etc.)

absorptions bands that span from the visible to the near infrared regions (Wylar, 1969; Wylar, 1969a; Musso, 1979; Reichardt, 1995). The two resonance forms (A) and (B) in Figure (2) have the reason and/or the responsibility for the intensity of the colours of cyanine dyes, where they produce a delocalized positive charge over the conjugated chromophoric group system of the cyanine dyes structures (Shindy, 2017). Due to the diversity in function associated with this class of dyes, an extensive number of cyanine dyes have been synthesized and developed for numerous applications in photographic processes and more recently as fluorescent probes for bio-molecular labeling and imaging ((Mishra et al., 2000; Pisoni et al., 2014; Wada et al., 2015; Hyun et al., 2014; Hyun et al., 2015; Njiojob et al., 2015; Hyun et al., 2015a; El-Shishtawy et al., 2010; Henary and Levitz,

MATERIAL AND METHODS

General

All the melting points of the prepared compounds are measured using Electrothermal 15V, 45W 1 A9100 melting point apparatus (Chemistry, Faculty of Science, Aswan University, Aswan, Egypt) and are uncorrected. Elemental analysis was carried out at the Microanalytical Center of Cairo University by an automatic analyzer (Vario ELIII Germany). Infrared spectra were measured with a FT-IR (4100 Jasco, Japan). ¹HNMR spectra were accomplished using Varian Gemini-300 MHz NMR Spectrometer (Cairo University). Mass Spectroscopy was recorded on Mass 1: GC2010 Shimadzu Spectrometer (Cairo University).

Table 1: Characterization of the prepared compounds (2), (3a-c) and (5a-g)

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} ($\text{mol}^{-1} \text{cm}^2$)
					C	H	N	C	H	N		
2	Brown crystals	55	165	$\text{C}_{29}\text{H}_{22}\text{N}_3\text{O}_5\text{I}$ (619)	56.22	3.55	6.79	56.17	3.52	6.66	-----	-----
3a	Violet	60	141	$\text{C}_{37}\text{H}_{31}\text{N}_4\text{O}_4\text{I}$ (722)	61.5	4.29	7.76	61.46	4.23	7.72	420, 450, 580, 460, 910	8670, 10770, 6510, 3100, 9000
3b	Deep violet	65	145	$\text{C}_{41}\text{H}_{33}\text{N}_4\text{O}_4\text{I}$ (772)	63.73	4.27	7.25	63.71	4.22	7.23	460, 500, 600, 660, 950	13710, 13430, 8570, 4280, 11000
3c	Violet	62	140	$\text{C}_{37}\text{H}_{31}\text{N}_4\text{O}_4\text{I}$ (722)	61.5	4.29	7.76	61.44	4.24	7.72	430, 460, 590, 650, 930	12220, 12460, 6680, 3320, 9500
5a	Violet	66	157	$\text{C}_{39}\text{H}_{33}\text{N}_4\text{O}_4\text{I}$ (748)	62.57	4.41	7.49	62.55	4.36	7.44	740, 820, 840, 870, 970	18540, 12800, 11700, 10000, 7020
5b	Deep violet	71	166	$\text{C}_{43}\text{H}_{35}\text{N}_4\text{O}_4\text{I}$ (798)	64.66	4.39	7.02	64.59	4.31	7.01	760, 860, 890, 990	16620, 10540, 11280, 7490
5c	Violet	67	158	$\text{C}_{39}\text{H}_{33}\text{N}_4\text{O}_4\text{I}$ (748)	62.57	4.41	7.49	62.45	4.35	7.41	650, 750, 850, 890, 980	10000, 16660, 10850, 8320, 4410
5d	Deep violet	69	163	$\text{C}_{44}\text{H}_{37}\text{N}_4\text{O}_4\text{I}$ (812)	65.02	4.56	6.90	65.01	4.51	6.88	690, 770, 860, 900, 1000	11900, 19430, 11750, 11440, 7770
5e	Deep violet	67	143	$\text{C}_{49}\text{H}_{39}\text{N}_4\text{O}_4\text{I}$ (874)	67.28	4.46	6.41	67.23	4.41	6.36	790, 860, 880, 910, 1020	19750, 12490, 13650, 13430, 10600
5f	Deep violet	63	168	$\text{C}_{50}\text{H}_{41}\text{N}_4\text{O}_5\text{I}$ (904)	66.37	4.54	6.19	66.31	4.52	6.11	800, 860, 900, 930, 1030	21370, 14520, 15240, 14550, 11870
5g	Deep violet	61	177	$\text{C}_{49}\text{H}_{38}\text{N}_5\text{O}_6\text{I}$ (919)	63.98	4.13	7.62	63.89	4.11	7.57	780, 840, 880, 910, 1010	18120, 10370, 11940, 11640, 8460

Electronic visible absorption spectra were carried out on visible spectrophotometer spectra 24 RS Labomed, INC (Chemistry Department, Faculty of Science, Aswan University, Aswan, Egypt).

Synthesis of 3-ethyl-5,12-dione-2-phenyl-4-(carbonylbutadienyl)methyl-benzo[(2,3-b)benzoxazine;(2',3'-b')furo(3,2-d)pyrazolium] iodide quaternary salt (2)

This compound was prepared through heating of 1:1 molar ratios of (1) (0.03 mol, 1.9 gm) and crotonaldehyde (0.03 mol, 25 ml) in ethanol (50 ml) containing piperidine (3-5 drops) for 4-6 hrs. The dark brown mixture was filtered off while hot to remove any impurities, concentrated and precipitated using cold water. The separated intermediate compound (2) was filtered off, washed with cold water, air dried and recrystallized from ethanol. The results are summarized in Table 1.

Synthesis of 3-ethyl-5,12-dione-2-phenyl-benzo[(2,3-b)benzoxazine;(2',3'-b')furo(3,2-d)pyrazole]-4[2(4)]-heptamethine cyanine dyes (3a-c)

Piperidine (3-5 drops) was added to a mixture of equimolar ratios of (2) (0.01mol, 0.6 gm) and N-ethyl (α -picolinium (0.01 mol, 0.25 gm), quinaldinium (0.01 mol, 0.3 gm), γ -picolinium (0.01 mol, 0.25 gm) iodide quaternary salts dissolved in ethanol (50 ml). The reaction mixture was heated under reflux for 6-8 hrs and attained violet colour (for 3a, c) and deep violet colour (for 3b) at the end of the refluxing time. It was filtered off while hot, concentrated and cooled. The precipitated products which appear on dilution with cold water were filtered off, washed with water, dried and crystallized from ethanol. The data are listed in Table 1.

Synthesis of 1-ethyl-2(4)[propenyl(2R-propenyl)]quinaldinium (pyridinium)iodide quaternary salts (4a-g)

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

Comp. No.	IR Spectrum (KBr, Cm ⁻¹)	¹ H NMR Spectrum (DMSO, δ); & (Mass data).
2	690, 755 (monosubstituted phenyl). 840, 904 (o.disubstituted phenyl). 1025, 1182 (C—O—C cyclic). 1367 (C—N). 1491 (C=N). 1602 (C=C). 1714 (C=O). 2924 (quaternary salt). 3433 (NH).	0.9-1.6 (m, 3H, CH ₃ of position 3). 1.9-2.4 (b, 4H, 2CH ₂ of positions 3 and 4). 3.3 (s, 1H, NH). 6.8-8.4 (m, 14H, aromatic + 5 —CH=). 9.7 (b, 1H, CHO). M ⁺¹ : 620.44
3b	693, 753 (monosubstituted phenyl). 834 (o.disubstituted phenyl). 1159 (C—O—C cyclic). 1366 (C—N). 1488 (C=N). 1602 (C=C). 1709 (C=O quinone). 2925, 2857 (quaternary salt). 3431 (NH).	0.9-1.4 (m, 3H, CH ₃ of position 3). 1.5-1.8 (m, 3H, CH ₃ of N-quinolinium). 3-3.6 (m, 1H, NH). 1.9-2.4 (b, 4H, 2CH ₂ of position 3 and N-quinolinium). 6.7-8.5 (m, 22H, aromatic + heterocyclic + 7 —CH=).
5b	693, 754 (monosubstituted phenyl). 834 (o.disubstituted phenyl). 1162 (C—O—C cyclic). 1362 (C—N). 1490 (C=N). 1597 (C=C). 1712 (C=O quinone). 2925, 2856 (quaternary salt). 3423 (NH).	0.9-1.3 (m, 3H, CH ₃ of position 3). 1.4-1.8 (m, 3H, CH ₃ of N-quinolinium). 1.9-2.4 (b, 4H, 2CH ₂ of position 3 and N-quinolinium). 3.4 (s, 1H, NH). 6.6-8.6 (m, 24H, aromatic + heterocyclic + 9 —CH=).

These compounds were prepared in accordance routes that described earlier (Koraïem et al., 1989).

Synthesis of 3-ethyl-5,12-dione-2-phenyl-benzo[(2,3-b)benzoxazine;(2',3'-b')furo(3,2-d)pyrazole]-4[2(4)]-nonamethine cyanine dyes (5a-g)

Piperidine (3-5 drops) was added to a mixture of equimolar ratios of (2) (0.01mol) (0.6 gm) and the compounds (4a-g) (0.01 mol) (0.27 gm for 4a, 0.32 gm for 4b, 0.27 gm for 4c, 0.34 gm for 4d, 0.4 gm for 4e, 0.43 gm for 4f, and 0.45 gm for 4g) dissolved in ethanol (50 ml). The reaction mixture was heated under reflux for 6-8 hrs and attained violet colour (for 5a, c) and deep violet colour (for 5b, 5d, 5e, 5f, 5g) at the end of the refluxing. It was filtered of while hot, concentrated and cooled. The precipitated products which appear on dilution with cold water were filtered off, washed with water, air dried and crystallized from ethanol. The data are listed in Table 1.

Spectral behaviour of the prepared cyanine dyes

The electronic visible absorption spectra of the all prepared cyanine dyes were examined in 95% ethanol solution and recorded using 1Cm Qz (Quartz) cell in visible

spectrophotometer, spectra 24 RS Labomed, INC. A stock solution (1x10⁻³ 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 halochromism

The electronic visible absorption spectra of some selected synthesized cyanine dyes were investigated in pure organic solvents of spectroscopic grade (Shindy et al., 2014; Shindy et al., 2014a) and different polarities and/or in aqueous universal buffer solutions of varying pH values and recorded using 1cm quartz cell in Vis spectrophotometer spectra 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 procedure

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

Solvent	H ₂ O		EtOH		DMF		CHCl ₃		CCl ₄		Dioxane	
	λ_{\max} (nm)	ϵ_{\max} (mole ⁻¹ cm ²)										
3b	450	12040	460	13710	410	17900	470	10770	450	12040	430	13730
	480	11710	500	13430	500	15110	480	11710	480	12870	460	13710
	590	8750	600	8570	540	15440	530	11380	610	6440	490	13180
	920	9500	660	4280	630	10970	610	6240	970	12500	520	12250
			950	11000	990	8600	960	8360			610	6240
5b	760	17570	760	16620	795	17900	760	17570	765	17590	790	17800
	830	7250	860	10540	855	9890	860	11750	850	9860	850	9860
	850	9250	890	11280	870	11090	910	9750	870	11090	890	11310
	880	8160	990	7490	920	11350	1000	4960	1005	4980	900	10560
	970	5780			1020	7000					1010	6560
											980	12800

The reaction of the compound (1) (Shindy et al., 2019) with unimolar ratio of crotonaldehyde in ethanol containing piperidine as basic catalyst led to the formation of the intermediate compound 3-ethyl-5,12-dione-2-phenyl-4-(carbonyl butadienyl)methyl-benzo[(2,3-b)benzoxazine;(2',3'-b')furo(3,2-d)pyrazolium] iodide quaternary salt (2), Scheme (1). Reaction of the intermediate compound (2) with either N-ethyl (2-picolinium, quinaldinium and/or 4-picolinium) iodide quaternary salts in equimolar ratios and in ethanol containing few drops of piperidine gave 3-ethyl-5,12-dione-2-phenyl-benzo[(2,3-b)benzoxazine;(2',3'-b')furo(3,2-d)pyrazole]-4[2(4)]-heptamethine cyanine dyes (3a-c), Scheme (1). Reaction of the intermediate compound (2) with 1-ethyl-2(4)[propenyl(2R-propenyl)] quinaldinium (pyridinium)iodide quaternary salts (4a-g) in equimolar ratios and in ethanol containing few drops of piperidine gave 3-ethyl-5,12-dione-2-phenyl-benzo[(2,3-b)benzoxazine;(2',3'-b')furo(3,2-d)pyrazole]-4[2(4)]-nonamethine cyanine dyes (5a-g), Scheme (1). The structure of the prepared compounds were characterized and identified by elemental analysis, Table 1, Visible spectra, Table 1, mass spectrometer, IR (Wade, 1999) and ¹H-NMR (Wade, 1999a) spectroscopic data, Table 2.

Electronic transitions evaluation

Electronic transitions for all the synthesized cyanine dyes was determined and evaluated through investigating their electronic visible absorption spectra in 95% ethanol solution. The dyes were thought to be better electronic transitions when they absorb light at higher wavelength bands (bathochromic shifted and/or red shifted dyes). Consequently, the electronic transitions of the dyes decreases when they absorb light at lower wavelength bands (hypsochromic shifted and/or blue shifted dyes). The electronic transitions of one dye is higher than the other one if the wavelength of the maximum absorption spectrum of the former one is longer than that of the latter one. In contrary, the electronic transitions of one dye is lower than the other one if the wavelength of the maximum absorption

spectrum of the former one is shorter than that of the latter one (Shindy, 2018). The visible electronic transitions absorption spectra of the heptamethine cyanine dyes (3a-c) in 95% ethanol solution disclose bands in the visible region 420-950 nm. The positions of these bands and their molar extinction coefficient are largely influenced by the nature of the heterocyclic quaternary residue (A) and their linkage positions. So, substituting A=1-ethyl pyridinium-2-yl salt in the heptamethine cyanine dye 3a by A = 1-ethyl quinolinium-2-yl salt to get the heptamethine cyanine dye 3b causes strong bathochromic shift by 40 nm, accompanied by intensified the absorption bands in the case of the heptamethine cyanine dye 3b, Scheme (1), Table 1. This can be attributed to increasing π -delocalization conjugation in the latter dye due to the presence of quinoline ring system in correspondance to the pyridine ring system in the former dye.

Changing the linkage positions from 2-yl salt to 4-yl salt passing from the heptamethine cyanine dye 3a to the heptamethine cyanine dye 3c resulted in a remarkable red shift by 20 nm accompanied by intensification 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 salt dye 3c due to the presence of the γ -picolinium structure system compared to the former 2-yl salt dye 3a which contain the α -picolinium structure system. In addition, the visible electronic transition absorption spectrum of the nonamethine cyanine dyes (5a-g) displays bands in the visible region (650 nm-1030 nm). The positions of these bands and their molar absorptivity are remarkably effected by the nature of the heterocyclic quaternary salt residue (A), their linkage positions and types of the penta ene side chain (R). So, substituting A=1-ethyl pyridinium-2-yl salt by A=1-ethyl quinolinium-2-yl salt, transferring from dye (5a) to dye (5b) causes strong bathochromic shifts by 20 nm. This can be illustrated according to increasing π -delocalization conjugation in the quinaldinium nucleus dye (5b) compared to α -picolinium nucleus dye (5a), Scheme (1), Table 1.

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

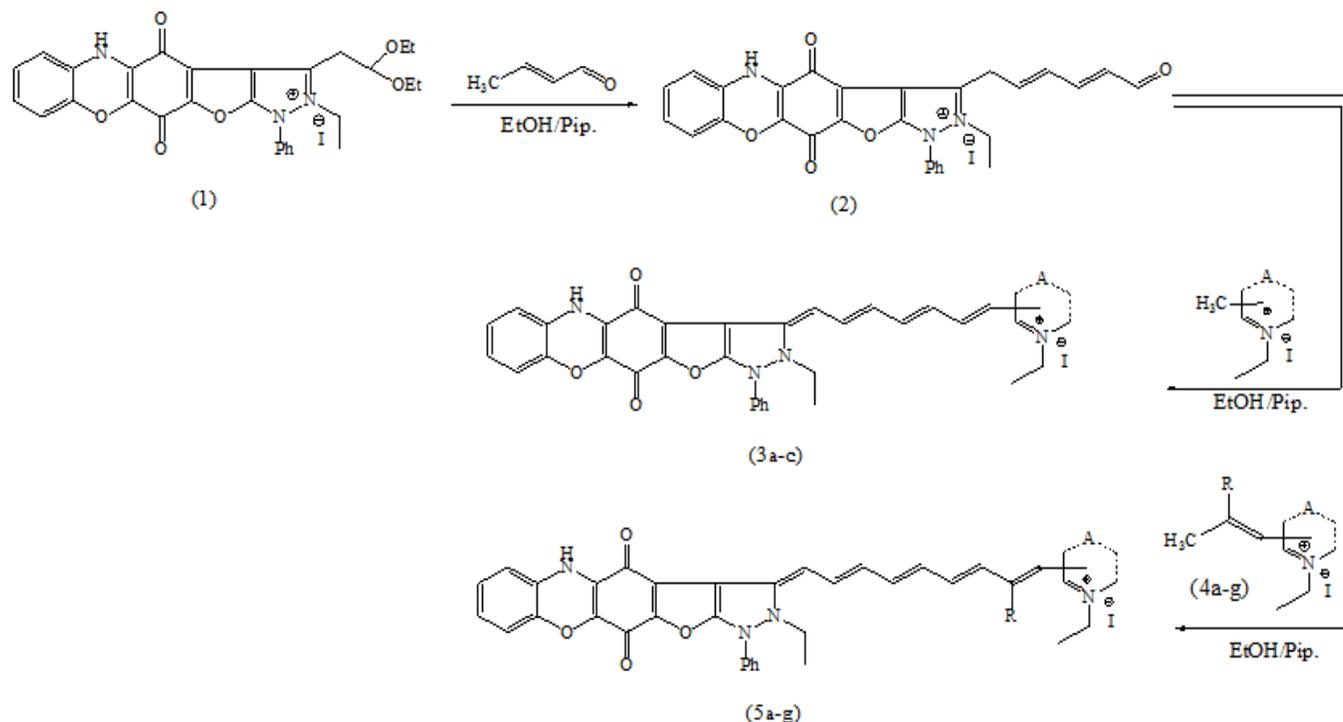
Comp.	Universal Buffers							
	1.99		2.99		4.30		6.87	
No.	λ_{\max} (nm)	ϵ_{\max} (mol ⁻¹ cm ²)						
3b	430	9020	430	9020	425	9990	425	9992
	460	9840	450	10560	455	10560	457	10562
	490	9510	490	10070	485	10790	486	10070
	560	6600	580	6910	580	7560	582	6910
	630	3240	640	3460	640	4110	642	3460
	910	8040	915	8290	920	8750	925	9010
5b	710	14140	710	16400	712	16421	715	17000
	750	13000	750	14280	752	14290	755	14500
	800	8420	760	8330	763	9000	765	9100
	820	9900	790	9530	792	9600	795	9700
	840	9090	850	9240	855	9400	860	9450
	930	5800	940	5980	950	6150	960	6200

Table 4: Continue...

Comp.	Universal Buffers							
	7.96		8.91		10.55		12.04	
No.	λ_{\max} (nm)	ϵ_{\max} (mol ⁻¹ cm ²)						
3b	425	9995	430	10840	430	13250	440	13490
	456	10580	459	11540	460	13255	470	14420
	486	10798	485	11410	490	13610	500	13780
	582	7660	583	7890	584	8160	600	10160
	641	4117	642	4119	644	4150	660	6270
	930	9180	935	10000	940	10540	950	11000
5b	717	17050	719	17070	730	17500	740	17400
	760	14551	762	14555	760	16520	770	14500
	764	9105	765	9150	800	12130	810	9150
	795	9688	797	9700	830	13190	840	9900
	860	9443	861	9445	860	12360	870	8590
	970	6150	890	6155	990	8340	1000	7000

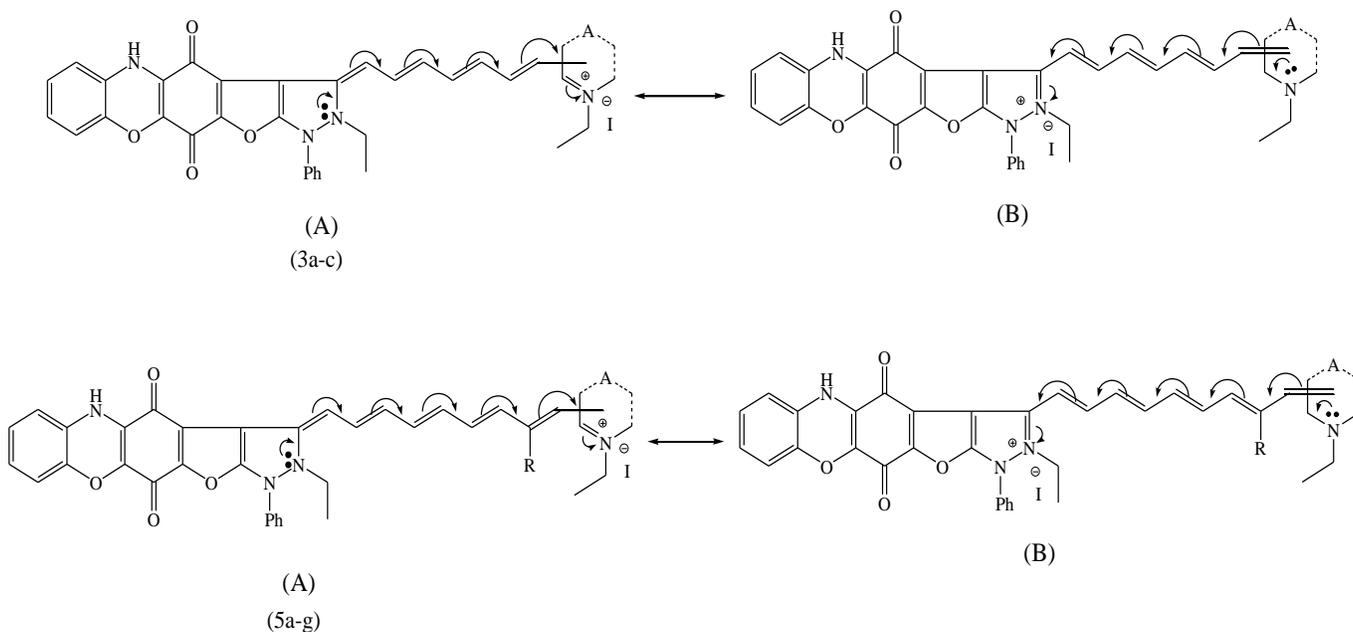
Changing the linkage position from 2-yl salt in dye (5a) to 4-yl salt to give dye (5c) produced red shifted by 10 nm. This can be explained in the light of increasing the length of the π -delocalization conjugation to the quaternary nitrogen in the γ -picolinium dye (5c) compared to the α -picolinium dye (5a), Scheme (1), Table 1. Substituting R=H in the penta ene side chain by, R = CH₃ and/or ph, transferring from dye (5b) to dyes (5d) and/or (5e) resulted in a bathochromic shifted by 10 nm and/or 30 nm for the bands in addition to increasing intensity of the bands, respectively. This can be

related to the electron donating character of CH₃ in the dye (5d) and/or increasing conjugation of phenyl ring in dye (5e), Scheme (1), Table 1. Substituting R=C₆H₅- in the penta ene side chain in dye (5e) by R = C₆H₄-p.OCH₃ and/or R = C₆H₄-p.NO₂ to obtain dyes (5f) and/or (5g) makes red shifted and intensified bands in the case of dye (5f) and/or blue shifted bands with decreasing intensity in the case of dye (5g). This is due to the electron donating character of OCH₃ in dye (5f) and/or electron attracting character of NO₂ group in dye (5g), Scheme (1), Table 1.

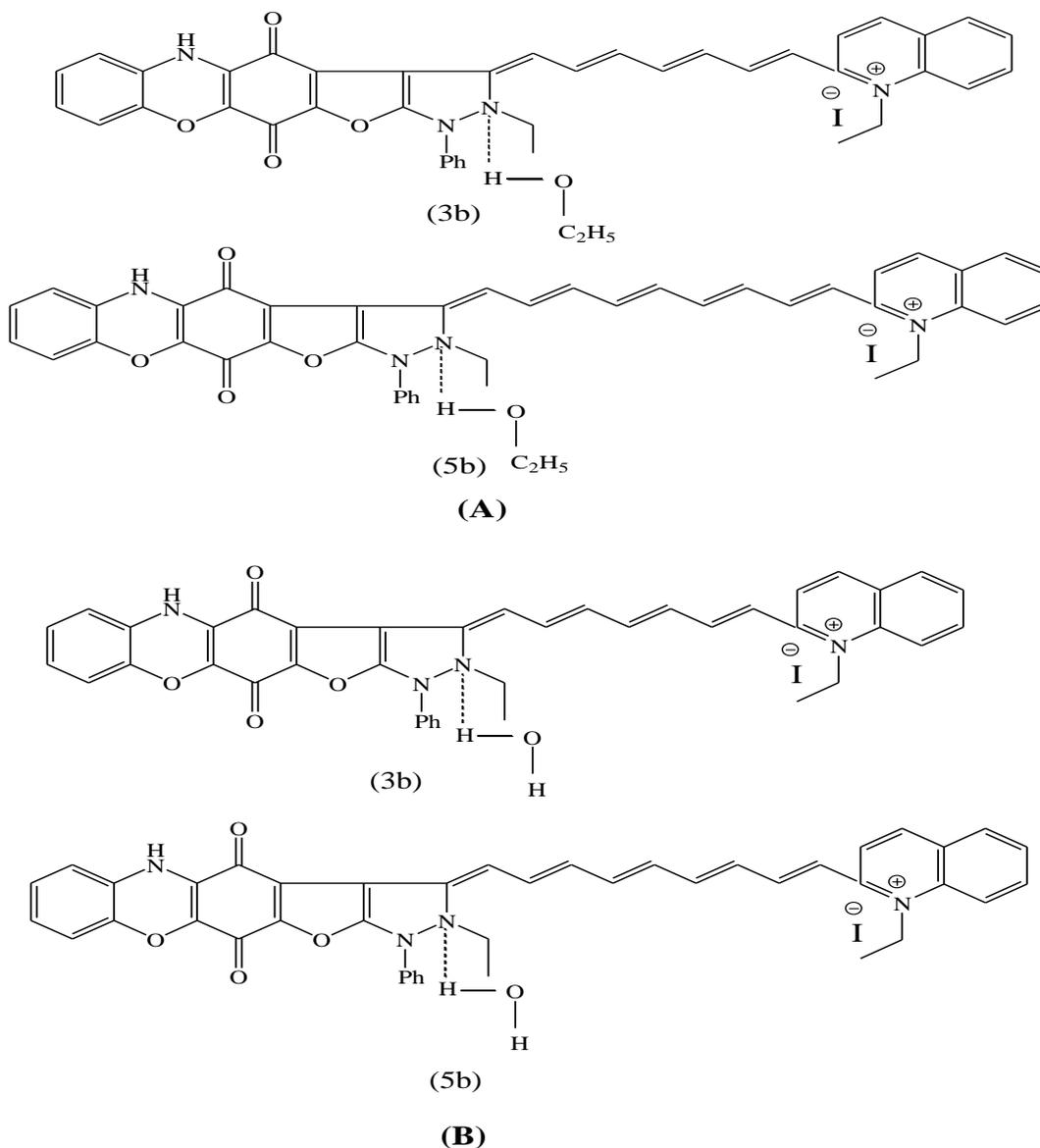


Scheme 1: Synthesis Strategy of the prepared compounds (2), (3a-c) and (5a-g).

Where, (3a-c): A = 1-ethyl pyridinium-2-yl salt (a), 1-ethyl quinolinium-2-yl salt (b), 1-ethyl pyridinium-4-yl salt (c). (5a-g): R = H, A = 1-ethyl pyridinium-2-yl salt (a), R = H, A = 1-ethyl quinolinium-2-yl salt (b), R = H, A = 1-ethyl pyridinium-4-yl salt (c), R = CH_3 , A = 1-ethyl quinolinium-2-yl salt (d), R = C_6H_5 , A = 1-ethyl quinolinium-2-yl salt (e), R = $\text{C}_6\text{H}_4\text{.p.OCH}_3$, A = 1-ethyl quinolinium-2-yl salt (f), R = $\text{C}_6\text{H}_4\text{.p.NO}_2$, A = 1-ethyl quinolinium-2-yl salt (g).



Scheme 2: Colour intensity and the electronic charge transfer pathways illustration of the synthesized heptamethine cyanine dyes (3a-c) and nonamethine cyanine dyes (5a-g).



Scheme 3: (A) Hydrogen bond formation between the heptamethine cyanine dye (3b), nonamethine cyanine dye (5b) and ethanol molecules (specific solvent effect) and (B) Hydrogen bond formation between the heptamethine cyanine dye (3b), nonamethine cyanine dye (5b) and water molecules (specific solvent effect).

Electron donating and/or pushing group likes CH₃, OCH₃ makes increasing for the intensity of the electronic charge transfer pathways to the heterocyclic quaternary nitrogen, and consequently, red shift occur. Inversely, electron attracting and/or pulling groups makes decreasing for the intensity of the electronic charge transfer pathways to the heterocyclic quaternary nitrogen, and accordingly, blue shift occurs.

Comparison the visible electronic transitions absorption spectra of the nonamethine cyanine dyes (5a-g) with those of the heptamethine cyanine dyes (3a-c) showed that the former nonamethine cyanine dyes (5a-g) have red shifted and intensified absorption bands in comparison to the latter heptamethine (3a-c) cyanine dyes,

Table 1. This can be attributed to increasing conjugation due to increasing the number of methine units in the former nonamethine cyanine dyes (5a-c) in comparison to the later heptamethine cyanine dyes (3a-c) by two methine units, Scheme (1), Table 1.

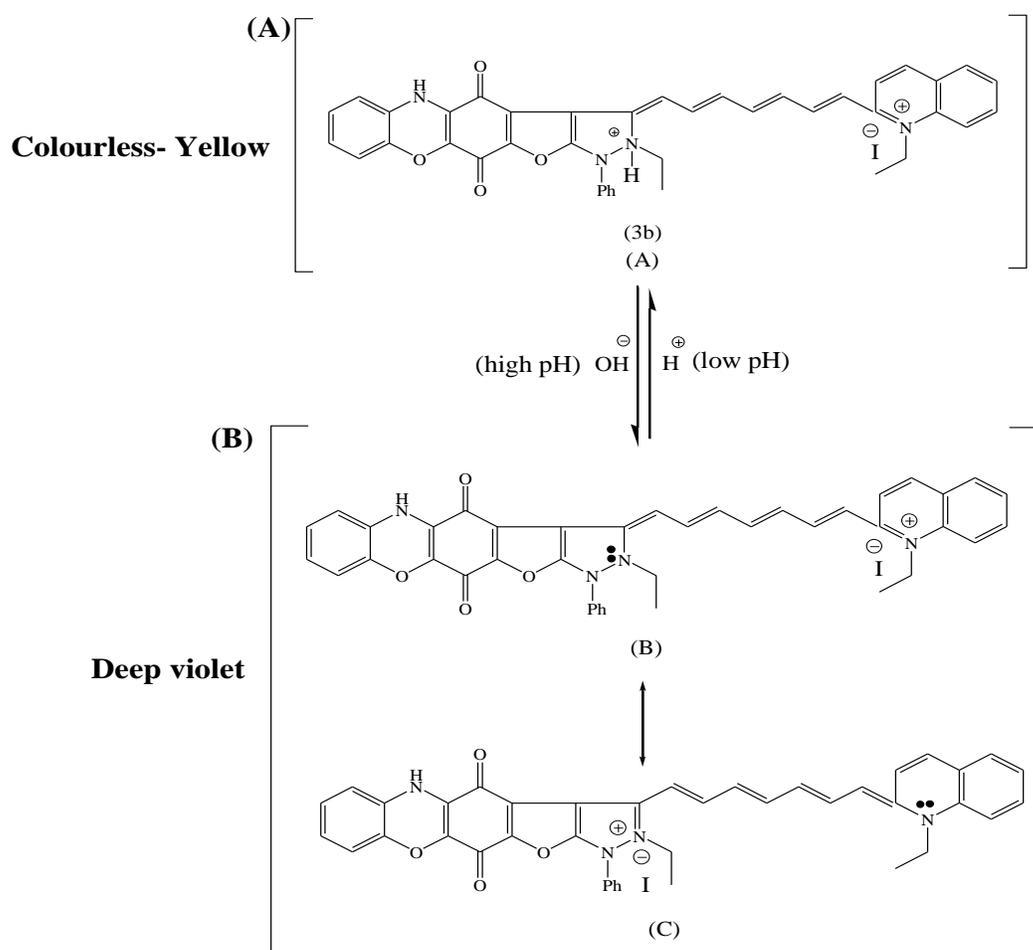
Solvatochromic evaluation

Solvatochromic evaluation for some selected synthesized cyanine dyes (3b) and (5b) was carried out via examining of their electronic visible absorption spectra in pure solvents having different polarities. The dyes were thought to be better solvatochromic dyes when they give strong positive and/or negative solvatochromism in pure solvents

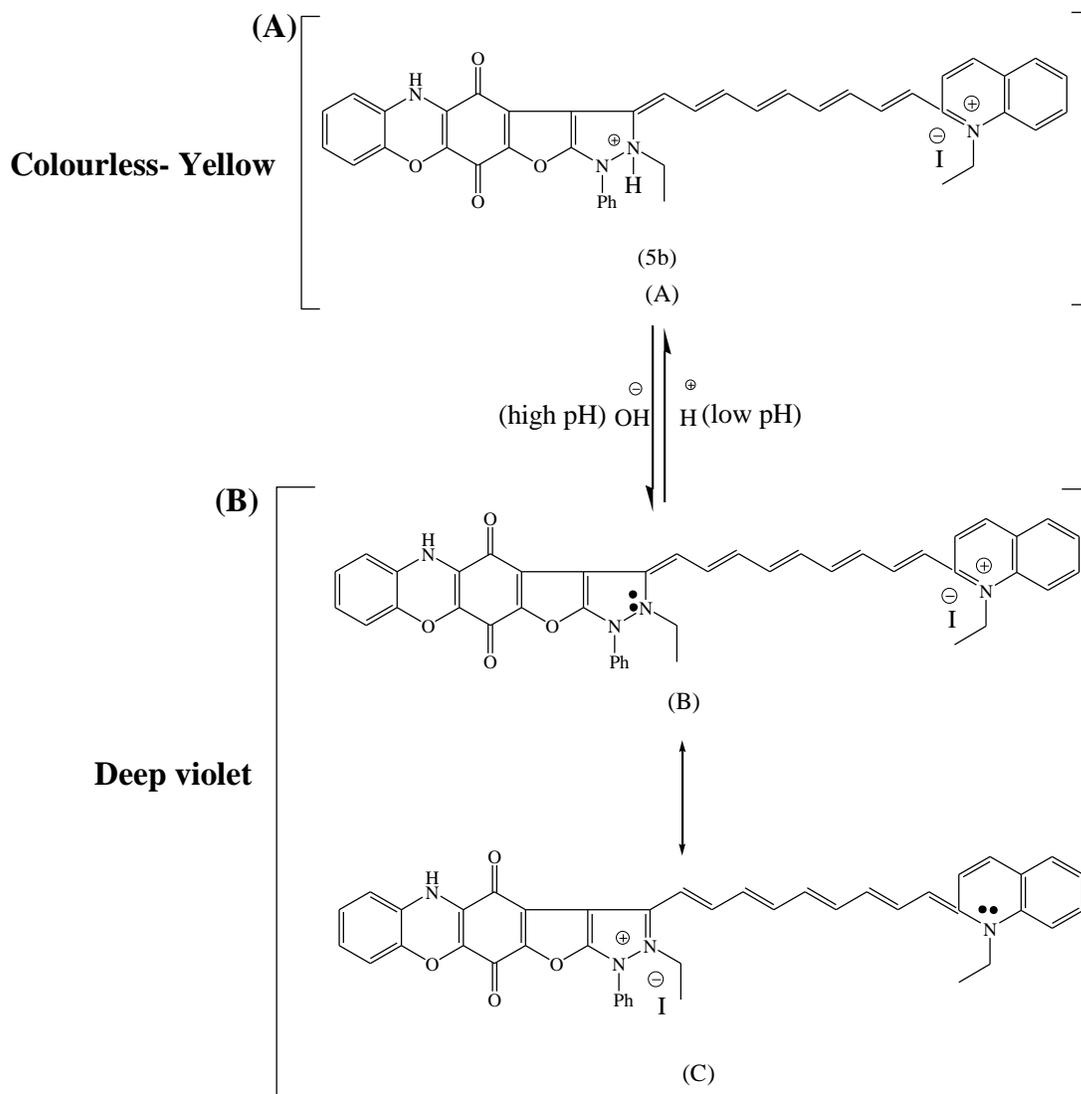
having different polarities. Consequently, the solvatochromic of the dyes decrease when they give weak positive and/or negative solvatochromism in pure solvents having different polarities. The solvatochromic of one dye is higher than the other one if the positive and/or the negative solvatochromism in pure solvents having different polarities of the former one is stronger than that of the later one. In contrary, we may say that the solvatochromic of one dye is lower than the other one if the positive and / or the negative solvatochromism in pure solvents having different polarities of the former one is weaker than that of the latter one (Shindy, 2019). Positive solvatochromism reveals bathochromic shifted (red shifted) absorption bands with increasing solvent polarity. In contrast, negative solvatochromism discloses hypsochromic shifted (blue shifted) bands with increasing solvent polarity. This study was carried out to select the best solvents to use of these dyes as photosensitizers when there are applied in photosensitive material industry. The other important purpose of this study is to evaluate the solvatochromic properties of these dyes to may be used and / or applied as

probes for determining solvent polarity, in physical, physical organic, inorganic and / or in solution chemistry.

So far, the electronic visible absorption spectra of heptamethine cyanine dye (3b) and nonamethine cyanine dye (5b) in pure solvents of different polarities (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., 2014; Shindy et al., 2014a). The λ_{\max} (wavelength) and ϵ_{\max} (molar extinction coefficient) values of the absorption bands due different electronic transitions within the solute molecule in these solvents are represented in Table 3. From Table 3, it is clear that the electronic visible absorption spectra of the cyanine dyes (3b) and (5b) in the ethanolic medium are characterized by the presence of five essential absorption bands (for the dye 3b) and four essential absorption bands (for the dye 5b). These bands can be assigned to intermolecular charge transfer transition (Shindy et al., 2014; Shindy et al., 2014a).



Scheme 4: Decolourization (protonation) and colourization (deprotonation) of the heptamethine cyanine dye (3b) in acid and base media, respectively [acido (dication)-basic (monocation)] equilibrium



Scheme 4: Continue...(Decolourization (protonation) and colourization (deprotonation) of the nonamethine cyanine dye (5b) in acid and base media, respectively [acido (dication)-basic (monocation)] equilibrium)

These charge transfer is due to transfer of lone pair of electrons from the N-ethyl pyrazole nitrogen atoms (the basic and/or the electron pushing center of the dyes) to the positively charged quaternary nitrogen atoms of the quinolinium salts residue, (the acidic and/or the electron pulling center of the dyes) and vice versa, Schemes (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 carbontetrachloride. This effect may be related to the following factors:

A) The bathochromic shifts in DMF relative to ethanol is a result of the increase in solvent polarity due to the increasing of dielectric constant of DMF relative to ethanol.

B) The hypsochromic shift occurs in ethanol relative to dioxane, chloroform and carbontetrachloride is a result of the solute solvent interaction through intermolecular hydrogen bond formation between ethanol and the lone

pair of electrons of the N-ethyl pyrazole nitrogen atoms, Scheme (3) (A). This decreases slightly the electron density on the N-ethyl pyrazole nitrogen atoms 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 consequently a hypsochromic shift occurs.

Also, from the data given in Table 3, it is observed that occurrence of unexpected hypsochromic shifts in water relative to 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 N-ethyl pyrazole nitrogen atoms, Scheme (3) (B). This makes difficult the transfer of electronic charge from the N-ethyl pyrazole nitrogen atoms to the quaternary nitrogen atoms of the heterocyclic quinolinium salt residue, and

accordingly there is observed a hypsochromic shift in water relative to ethanol and the other solvents.

Halochromic evaluation

Halochromic evaluation for some selected synthesized cyanine dyes (3b) and (5b) was carried out by investigated of their electronic visible absorption spectra in aqueous universal buffer solutions having varied pH values, Table 4. The dyes were thought to be better halochromic dyes when they give strong positive and/or negative halochromism in aqueous universal buffer solutions having varied pH values. Consequently, the halochromic of the dyes decrease when they give weak positive and/or negative halochromism in aqueous universal buffer solutions having varied pH values. So, we may say that the halochromic of one dye is higher than the other one if the positive and/or the negative halochromism of the former one in aqueous universal buffer solutions having varied pH values is stronger than that of the latter one. In contrary, we may say that the halochromic of one dye is lower than the other one if the positive and/or the negative halochromism of the former one in aqueous universal buffer solutions having varied pH values is weaker than that of the latter one (Shindy, 2019). Positive halochromism means occurrence of a bathochromic shifted (red shifted) absorption bands with changing solution pH of the buffer solution. In contrast, negative halochromism means occurrence of a hypsochromic shifted (blue shifted) absorption bands with changing the pH of the buffer solution.

The solutions of the heptamethine (3b) and nonamethine (5b) cyanine dyes behaves as halochromic compounds where, their ethanolic solutions gives 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 to study their spectral behavior in different buffer solutions to select a suitable pH 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 operations of 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 there are present in the ionic form, which has higher planarity (Shindy et al., 2014; Shindy et al., 2014a) and therefore more conjugation.

The electronic visible absorption spectra of the dyes (3b) and (5b) in aqueous universal buffer solutions of varying pH values were (1.99, 2.99, 4.30, 6.87, 7.96, 8.91, 10.55 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 bands at low pH (acidic media), Table 4. Therefore the mentioned dyes which have free lone pair of electrons on the N-ethyl pyrazole nitrogen atom undergo protonation in acidic media. This generates positive charge on the N-ethyl pyrazole nitrogen atom, and consequently the electronic charge transfere pathways from the N-ethyl pyrazole nitrogen atom to the heterocyclic quaternary nitrogen atom of the quinolinium salt residue will be greatly affected and difficult resulting in a hypsochromic shift, protonated structures (colourles), 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 N-ethyl pyrazole nitrogen atom, and accordingly the electronic charge transfer pathways to the quaternary heterocyclic nitrogen atom of the quinolinium salt residue will be easier, facilitated and more favoured resulting in a bathochromic shift, deprotonated structures (coloured), Schemes (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., 2014; Shindy et al., 2014a). The acid dissociation or protonation constants values of the dyes (3b) and (5b) are listed in Table 5.

CONCLUSIONS

1. The electronic visible absorption spectra of the heptamethine cyanine dyes (3a-c) and nonamethine cyanine dyes (5a-g) undergoes displacements to give bathochromic

Table 5: The variation of absorbance with pH at fixed λ for the dyes (3b and 5b) in aqueous universal buffer solutions

pH	Compound Number Absorbance at fixed λ	
	3b $\lambda=930$ (nm)	5b $\lambda=960$ (nm)
1.99	0.65	0.335
2.99	0.7	0.432
4.30	0.875	0.604
6.87	0.901	0.611
7.96	0.914	0.615
8.91	0.918	0.622
10.55	1	0.817
12.04	1.05	0.631
Pka	9.9	10.2
	3.8	3.7

and/or hypsochromic shifts depending upon the following factors: The nature of the heterocyclic quaternary salt residue in the order of quinaldinium dyes > α -picolinium dyes (in the heptamethine and nonamethine cyanine dyes). Linkage position of the heterocyclic quaternary salt residue in the order of γ -picolinium dyes > α -picolinium dyes (in the heptamethine and nonamethine cyanine dyes). Types of the penta ene side chain (R) in the order of, i) H-dyes < CH₃-dyes < Ph-dyes (in the nonamethine cyanine dyes), ii) C₆H₄.p.OCH₃ dyes > C₆H₅-dyes > C₆H₄.p.NO₂ dyes (in the nonamethine cyanine dyes). The number of the methine units and/or groups between the two heterocyclic ring system of the cyanine dyes molecules in the order of: nonamethine cyanine dyes > heptamethine cyanine dyes.

2. The intensity of the colour of the heptamethine cyanine dyes, and nonamethine cyanine dyes is illustrated according to the following suggested two mesomeric electronic transitions structures (A) and (B) producing a delocalized positive charges over the conjugated chromophoric group system of the dyes, Scheme (2).

3. The solvatochromism of the examined cyanine dyes (3b) and (5b) 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: Increasing and/or decreasing the polarity (the dielectric constant) of the solvent (General solvent effect). Hydrogen bond and/or molecular complex formation between the solute (dyes molecules) and the solvent used (specific solvent effect).

4. The electronic visible absorption spectra of the heptamethine (3b) and nonamethine (5b) cyanine dyes in aqueous universal buffer solutions having varied pH values underwent displacements to give hypsochromic shifted and lower intensity bands in the lower pH media (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 media (basic media) due to the deprotonated and/or coloured structures of the dyes in this media.

5. These cyanine dyes can be used as spectral sensitizers for silver halide emulsion in photographic material industry due to their spectral sensitization properties.

6. These cyanine dyes can be used as probes for determining solvent polarity in solution chemistry due to their solvatochromic properties.

7. These cyanine dyes can be used as acid-base indicators in analytical chemistry due to their halochromic properties.

8. Because cyanine dyes have multi purposes uses and applications in various fields and different research area, this research paper is recommended not only for heterocyclic and/or cyanine dyes chemists but also for other scientists in other fields like biology, biotechnology, biochemistry,

physics, engineering, pharmacology, medicine as well as environment and clinical analysis.

9. This study is recommended for all whom interested in the light absorbing systems in their research, labeling of biomolecules and/or in the synthesis and characterization of complex organic compounds.

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