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Effects of chemical structure, solvent and solution pH on the visible spectra of some new methine cyanine dyes

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ABSTRACT

Some new dimethine and *bis*-dimethine, cyanine dyes derived from benzo[2,3-b; 2`,3`-b`]*bis*-pyrazolo[4,5-*b*]-l,4-(oxa-, thia-, and pyra-)-zine-6,12-dione were synthesized. Effect of chemical structure on the electronic visible absorption spectra of all the synthesized cyanine dyes was investigated in 95% ethanol solution. Effects of solvent and/or solution pH on the electronic visible absorption spectra of some selected synthesized cyanine dyes were also examined in pure solvents having different polarities and/or in aqueous universal buffer solutions, respectively. Structural confirmations were carried out through elemental analysis, mass spectroscopy, IR and ^{1}H NMR spectra.

1. Introduction

Cyanine dyes [1-10] have a very wide range of application, especially in the so-called "high-tech" fields, science and modern technology. They are used as luminescent covalent or non-covalent probes in biological, medicinal and clinical research and assay. Well known is their utilization in optical information storage for fabrication of CD-R and DVD-R (optical recording disks), in preparation of security marks over banknotes and documents, as novel materials in non-linear optics, as highly sensitive analytical reagents, as analytical sensors, in photodynamic therapy of cancer, for single molecule fluorescence detection, as photosensitizers in photographic processes [11-13] and as photo polymerization initiators [14].

The most numerous and continuously expanding applications of cyanine dyes are in the field of biotechnology. Among those is the visualization of DNA by following different biological processes and quantification of DNA in solution. YOYO-1 (intercalating dye) labeled complexes may be employed as qualitative DNA markers in intracellular delivery studies [15].

Taking in accounts and consideration the above vital and important benefits of cyanine dyes, the aim of this research paper is synthesis of some novel photosensitizers, solvatochromic and halochromic cyanine dyes as new synthesis contribution and spectroscopic investigation in this field and/or to be used in any of the high-tech fields of cyanine dyes, particularly as photographic sensitizers, acid-base indicators and/or as probes for determining solvent polarity. In addition, because cyanine dyes have a multidisciplinary uses and applications in several fields and different areas of science, technology, engineering, pharmacology and medicine, this research paper may be very interesting to read by the many of the large heterogenous community groups of chemists, biologists, physicists, biotechnologists, pharmacologists and medical scientists.

2. Experimental

2.1. General

Melting points were recorded on a Gallenkamp melting point apparatus and are uncorrected. Elemental analyses were carried out at the Microanalytical Center at Cairo University. Infrared spectra were measured with a 1650 FT-IR instrument, and the ^{1}H NMR spectra on an EM-390 90 MHz NMR Spectrometer, and mass spectroscopy was recorded on GCMS-QP-1000 EX Spectrometer (Cairo University). The organic solvents were of spectroscopic grades and the new dyes were investigated and purified using TLC chromatographic procedures.

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Table 1. Characterization of the prepared compounds.

Compound no	Nature of products			Molecular Formula (M.Wt., g)	Analysis % Calculated (Found)			Visible absorption spectra in 95% ethanol solution	
	Color	Yield, %	M.p., °C		C	H	N	λ (nm)	ε (mol^{-1} cm^2)
2a	Dark brown crystals	63	191-193	$C_{26}H_{16}N_6O_5$ (492.12)	63.41 (63.43)	3.27 (3.83)	17.07 (17.04)	-	
2b	Dark brown crystals	43	186-188	$C_{26}H_{16}N_6O_3S_2$ (524.60)	59.53 (59.51)	3.07 (3.11)	16.02 (15.98)	-	-
2c	Pale brown crystals	59	199-201	$C_{26}H_{18}N_8O_3$ (490.50)	63.67 (63.65)	3.70 (3.67)	22.85 (22.87)	-	-
3a	Reddish brown crystals	41	202-204	$C_{26}H_{14}N_6O_6$ (506.43)	61.66 (61.63)	2.79 (2.82)	16.59 (16.62)	-	-
3b	Brown crystals	38	187-189	$C_{26}H_{14}N_6O_4S_2$ (538.55)	57.99 (57.94)	2.62 (2.59)	15.60 (15.63)	-	-
3c	Intense brown crystals	47	213-215	$C_{26}H_{16}N_8O_4$ (504.46)	61.90 (61.91)	3.20 (3.22)	22.21 (22.24)	-	-
4a	Reddish brown crystals	71	219-221	$C_{34}H_{24}N_7O_4I$ (721.09)	56.58 (56.56)	3.35 (3.31)	13.59 (13.63)	528.5	19700
4b	Reddish violet crystals	65	227-229	$C_{38}H_{28}N_7O_4I$ (773.12)	58.98 (58.95)	3.65 (3.69)	12.68 (12.65)	393.0, 445, 552.0	25310, 23150, 20970
4c	Reddish brown crystals	61	221-223	$C_{34}H_{24}N_7O_4I$ (721.09)	56.58 (56.54)	3.35 (3.37)	13.59 (13.60)	533.5	20100
4d	Pale violet crystals	36	209-211	$C_{38}H_{28}N_7O_2S_2I$ (805.08)	56.64 (56.66)	3.51 (3.53)	12.18 (12.13)	421.5, 556.0	27100, 23540
4e	Reddish violet crystals	52	217-219	$C_{38}H_{30}N_9O_2I$ (771.16)	59.13 (59.17)	3.92 (3.97)	16.34 (16.37)	461.5, 561.0	26890, 25010
5a	Dark brown crystals	68	220-222	$C_{34}H_{22}N_7O_5I$ (735.07)	55.50 (55.48)	3.02 (3.03)	13.33 (13.35)	524.5	16570
5b	Reddish violet crystals	77	231-233	$C_{38}H_{26}N_7O_5I$ (787.10)	57.93 (57.95)	3.33 (3.35)	12.45 (12.46)	381.0, 434.5, 535.0	22350, 21150, 19810
5c	Dark brown crystals	44	218-220	$C_{34}H_{22}N_7O_5I$ (735.07)	55.50 (55.53)	3.02 (3.00)	13.33 (13.31)	528.5	18970
5d	Violet crystals	49	211-213	$C_{38}H_{26}N_7O_3S_2I$ (819.06)	55.67 (55.63)	3.20 (3.18)	11.97 (12.01)	411.0, 551.0	25030, 21960
5e	Dark violet crystals	39	228-230	$C_{38}H_{28}N_9O_3I$ (785.13)	58.08 (58.11)	3.59 (3.61)	16.05 (16.01)	459.0, 557.5	26380, 25030
6a	Reddish violet crystals	60	217-219	$C_{42}H_{34}N_8O_4I_2$ (968.08)	52.06 (52.07)	3.54 (3.51)	11.57 (11.61)	543.0	24110
6b	Intense violet crystals	61	234-236	$C_{50}H_{42}N_8O_4I_2$ (1072.14)	55.96 (55.94)	3.95 (3.97)	10.45 (10.42)	411.0, 491.0, 559.5	27410, 26130, 25810
6c	Violet crystals	63	215-217	$C_{42}H_{34}N_8O_4I_2$ (968.08)	52.06 (52.10)	3.54 (3.52)	11.57 (11.56)	551.0	27110
6d	Intense violet crystals	59	224-226	$C_{50}H_{42}N_8O_2S_2I_2$ (1104.10)	54.34 (54.31)	3.83 (3.79)	10.15 (10.10)	420.0, 571.0	29830, 28630
6e	Intense violet crystals	53	237-239	$C_{50}H_{44}N_{10}O_2I_2$ (1070.14)	56.07 (56.09)	4.14 (4.11)	13.08 (13.11)	501.0, 589.5	29070, 28790

2.2. Synthesis

2.2.1. Synthesis of 4-formyl-10-methyl-2,8-diphenyl-5,ll-dihydro-benzo[2,3-b; 2`,3`-b`]bis-pyrazolo[4,5-b]-l,4-(oxa-, thia-, and pyra-)-zine-6,12-dione (2a-c)

A pure crystallized sample of compounds **1a-c** [16] was heated under reflux in equimolar ratios (0.01 mol) with selenium dioxide in dioxane (50 mL) for 16 hours. The reaction mixtures were filtered on hot to remove selenium metal and the filtrate was cooled, and then poured in ice water mixture. The precipitated products were filtered, dried, collected, and recrystallized from ethanol. The data are shown in Table 1.

2.2.2. Synthesis of 4,10-diformyl-2,8-diphenyl-5,ll-dihydro-benzo[2,3-b;2`,3`-b] bis pyrazolo[4,5-b]-l,4-(oxa-, thia-, and pyra-)-zine-6,12-dione (3a-c)

Two different routes are employed to prepare these compounds.

Route 1: This route is carried out in a way that has been described earlier [17].

Route 2: An equimolar ratios (0.01 mol) of both the 4-mono formyl derivatives (**2a-c**) and selenium dioxide were heated under reflux in dioxane (50 mL) for 16 hours. The reaction mixtures were filtered while hot to remove selenium metal, cooled, and poured in ice-water mixture. The precipitated products were filtered, dried, and recrystallized from ethanol to give the same diformyl compounds **3a-c** obtained by *Route 1* characterized by melting points, mixed melting points, same IR and ^{1}H NMR spectral data, Table 1 and 2.

2.2.3. Synthesis of 10-methyl-2,8-diphenyl-5,ll-dihydro-benzo[2,3-b; 2`,3`-b`] bis pyrazolo[4,5-b]-l,4-(oxa-, thia-, and pyra-)-zine-6,12-dione-4[2(4)] dimethine cyanine dyes (4a-e)

Reaction mixtures of equimolar ratios (0.01) of compounds **2a-c** and ethyl iodide quaternary salts of 2-picoline, quinaldine, 4-picoline were refluxed in ethanol (30 mL) containing few drops (3-5) of piperidine for 8-10 hours. During the refluxed time the colors changed from deep brown to intense violet at the end of refluxing. The reaction mixtures were filtered while hot to remove unreacted materials, concentrated by evaporation, cooled in ice bath, neutralized with glacial acetic acid and precipitated by adding cold water. The precipitates were collected, dried, and recrystallized from ethanol. The relevant data are given in Table 1 and 2.

2.2.4. Synthesis of 10-formyl-2,8-diphenyl-5,ll-dihydro-benzo[2,3-b; 2`,3`-b`] bis pyrazolo[4,5-b]-l,4-(oxa-, thia-, and pyra-)-zine-6,12-dione-4[2(4)] dimethine cyanine dyes (5a-e)

N-Ethyl-(2-picolinium, quinaldinium, 4-picolinium) iodide quaternary salts were heated under reflux in equimolar ratios (0.01 mol) with compounds **3a-c** in ethanol (30 mL) containing piperidine (3-5 drops) for 8 hours.

Table 2. IR and ^{1}H NMR spectral data of the prepared compounds.

Compound no	IR spectrum (KBr), cm^{-1}	^{1}H NMR spectrum (DMSO-d_6, δ, ppm) and Ms data
2a	674-718 (mono substituted phenyl), 1041, 1172 (C-O-C cyclic), 1284 (C-N), 1441 (C=N), 1585 (C=C), 1677(C=O quinone), 1726 (formyl group), 3424 (NH cyclic)	3.85 (s, 3H., CH_3 at C(10)), 5.85 (s, 2H, 2NH of oxazine rings), 6.80-8.00 (m, 10H, aromatic protons), 9.60 (s, 1H, -CHO group at C(4)) (*m/z* 492)
3a	626-675 (mono substituted phenyl), 1026, 1176 (C-O-C cyclic), 1326 (C-N), 1481 (ON), 1582(C=C), 1682(C=O quinone), 1737 (formyl group), 3459 (NH cyclic)	5.82 (s. 2H. 2NH of oxazinc rings), 7.00-7.82 (m. 10H, aromatic protons), 9.90 (s. 2H, 2-(CHO at C(4), C(10)) (*m/z* 506)
4b	658, 742 (mono substituted phenyl), 885, 939 (o. di substituted phenyl), 1068, 1178 (C-O-C cyclic), 1339 (C-N), 1472 (C=N), 1605 (C=C), 1680 (C=O quinone), 2919 (quaternary N), 3427 (NH cyclic)	1.30-1.70 (t, 3H, CH_3, of ethyl at N-quinoline), 3.5 (s, 3H, CH_3, at C(10)), 3.70-4.10 (q, 2H, CH_2 of ethyl at N-quinoline), 5.81 (s, 2H, 2NH of oxazine rings), 6.58-8.61 (m, 18H, aromatic, heterocyclic & -CH=)
5b	684, 743 (mono substituted phenyl), 827, 911 (o. di substituted phenyl), 1060, 1149 (C-O-C cyclic), 1273 (C-N), 1492 (C=N), 1605 (C=C), 1680 (C=O quinone), 1739 (formyl group), 2900 (quaternary N), 3380 (NH cyclic)	1.25-1.55 (t, 3H, CH_3, of ethyl at N-quinoline), 3.55-4.1 (q. 2H, CH_2 of ethyl at N-quinoline), 5.92 (s, 2H, 2NH of oxazine rings), 6.72-8.65 (m, 18H, aromatic, heterocyclic &-CH=), 9.51 (s, 1H, -CHO at C(10))
6b	693, 767 (mono substituted phenyl), 886, 955 (o. di substituted phenyl), 1068, 1186 (C-O-C cyclic), 1337 (C-N), 1477(C=N), 1596 (C=C), 1695 (C=O quinone), 2929 (quaternary N), 3437 (NH cyclic)	1.27-1.71 (t, 6H, $2CH_3$ of ethyl at N-quinoline), 3.92-4.27 (q, 4H, $2CH_2$ of ethyl at N-quinoline), 5.96 (s, 2H, 2NH of oxazine rings), 6.65-8.95 (m. 26H, aromatic, heterocyclic &-CH=)

The reaction mixtures attained dark brown color which turns pale violet at the end of the reflux. It were filtered off on hot, concentrated, neutralized with glacial acetic acid and precipitated by adding ice-water mixture. The separated cyanine dyes were filtered, washed with water, dried, and recrystallized from ethanol. The results are listed in Table 1 and 2.

2.2.5. Synthesis of 2,8-diphenyl-5,ll-dihydro-benzo[2,3-b; 2`,3`-b`] bis pyrazolo- [4,5-b]-l,4-(oxa-, thia-, and pyra-)zine-6,12-dione-4,10[2(4)] bis-dimethine cyanine dyes (6a-e)

Two different routes are employed to prepare these cyanine dyes.

Route 1: Piperidine (3-5 drops) was added to a mixture of ethanolic solution (50 mL) of compounds **3a**-**c** (0.01 mol) and 1-ethyl(2-picolinium-, -quinaldinium-, 4-picolinium-) iodide quaternary salts (0.02 mol). The reaction mixtures were heated under reflux for 10 hours and changed their colors from brown to fluorescent violet colors at the end of the reflux. It was filtered off while hot, concentrated to half its volume, cooled, poured in ice-water mixture, and neutralized with acetic acid. The precipitated dyes (**6a**-**e**) were filtered, washed with water, dried and recrystallized from ethanol. The data are given in Table 1 and 2.

Route 2: A mixture of equimolar ratios (0.01 mol) of the dimethine cyanine dyes (**5a**-**e**) and iodoethane quaternary salts of 2-methyl pyridine, 2-methyl quinoline, 4-methyl pyridine were dissolved in ethanol (30 mL), to which piperidine (3-5 drops) was added. The reaction mixtures were refluxed for 5 hours exhibiting permanent intense fluorescent violet colour at the end of refluxing. It was filtered while hot, concentrated, cooled, precipitated by adding cold water, and neutralized by acetic acid. The precipitates were collected, dried and recrystallized from ethanol to give the same dyes (**6a**-**e**) obtained by *Route 1*, characterized by melting points, mixed melting points, same IR and ^{1}H NMR spectral data, Table 1 and 2.

2.3. Visible absorption spectra

The electronic visible absorption spectra for all the prepared cyanine dyes were examined in 95% ethanol solution. Also, the spectra for some selected synthesized cyanine dyes were investigated in pure solvents of spectroscopic grade [18] and/or in aqueous universal buffer solutions of varying pH values. All the measurements recorded on a Shimadzu UV/Visible 160-A Spectrophotometer. The stock solution was about 1×10^{-3}, the lower molarities were obtained by accurate dilution.

3. Results and discussion

3.1. Synthesis

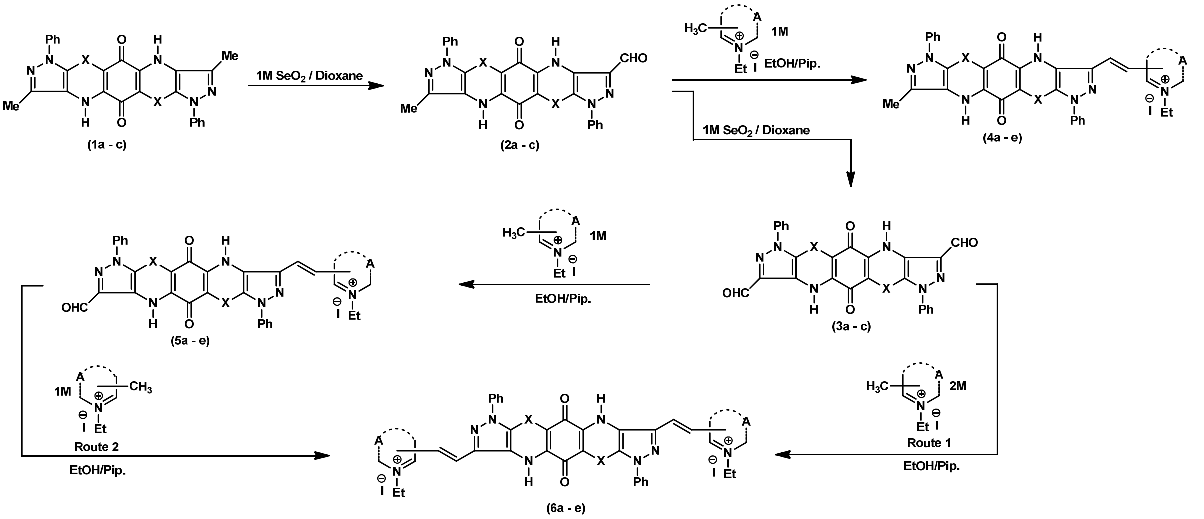
Selenium dioxide oxidation of 4,10-dimethyl-2,8-diphenyl-5,11-dihydro-benzo[2,3-b;2`,3`-b`]*bis*-pyrazolo-[4,5-b]-l,4-(oxa, thia-, and pyra-)-zine-6,12-dione (**1a**-**c**) in 1:1 molar ratios resulted the mono formyl (**2a**-**c**) compounds, Scheme 1, Table 1. Other equimolar selenium dioxide oxidation of the mono formyl compounds **2a**-**c** in dioxane as organic solvent gave the diformyl compounds (**3a**-**c**), Scheme 1, Table 1. Interaction of equimolar ratios of the 4-formyl compounds **2a**-**c** and 1-ethyl (2-picolinium, quinaldinium, 4-picolinium) iodide quaternary salts in ethanol containing piperidine gave 4[2(4)] mono cationic dimethine cyanine dyes (**4a**-**e**). Also interaction of the 4,10-diformyl compounds **3a**-**c** with equimolar and/or bimolar ratios of the iodoethane quaternary salts of 2-picoline, quinaldine and/or 4-picoline in ethanol containing piperidine yielded 4[2(4)]dimethine and/or 4,10 [2(4)] *bis*-dimethine cyanine dyes (**5a**-**e**) and/or (**6a**-**e**), respectively, Scheme 1, Table 1. Chemical confirmations take place via route 2, through reaction of the 4[2(4)] dimethine cyanine dyes (**5a**-**e**) and equimolar ratios of *N*-ethyl-(2-picolinium, quinaldinium, and/or 4-picolinium) iodide quaternary salts in ethanol catalyzed by piperidine to achieve the same 4,10[2(4)] *bis*-dimethine cyanine dyes (**6a**-**e**), characterized by same melting points, mixed melting points, same IR and ^{1}H NMR spectra, Scheme 1, Table 1 and 2.

The structures of the prepared compounds were identified by elemental analysis, Table 1, mass spectroscopy, IR [19] and ^{1}H NMR [20] spectra, Table 2.

3.2. Effect of chemical structure on the visible spectra

Effect of chemical structure on the visible spectra of all the prepared cyanine dyes were investigated by measuring their electronic visible absorption spectra in 95% ethanol solution, Table 1.

The electronic visible absorption spectra of the dimethine cyanine dyes (**4a**-**e**), (**5a**-**e**), and the *bis*-dimethine cyanine dyes (**6a**-**e**) in 95% ethanol solution showed absorption spectra bands in the visible regions, (393.0-561.0 nm), (381.0-557.5 nm), and (411.0-589.5 nm), respectively. These bands undergoes to give bathochromic and/or hypsochromic shifts depending largely on the nature of the heterocyclic quaternary salts, their linkage position and the type of the benz-*bis* biheterocyclic system present, Table 1. Thus, the absorption spectrum of the dimethine cyanine dyes **4a**, **5a**, and **6a** (X = O, A = 1-ethyl pyridinium-2-yl salt) showed bands at λ 528.5, 524.5, and 543.0 nm, respectively.



(1a-c); (2a-c);(3a-c): (a), X = O; (b), X = S; (c), X= NH. (4a-e); (5a-e) & (6a-e): (a) X = O, A = 1-ethyl pyridinium-2-yl salt; (b) X = O, A = 1-ethyl quinolinium-2-yl salt; (c) X = O, A = 1-ethyl pyridinium-4-yl salt; (d) X = S, A = 1-ethyl quinolinium-2-yl salt; (e) X = NH, A = 1-ethyl quinolinium-2-yl salt

Scheme 1

Substituting A = 1-ethyl quinolinium-2-yl salt to give dyes **4b**, **5b**, and **6b** causes a bathochromic shifts of 23.5, 10.5, and 16.5 nm with intensification of the absorption bands in addition to the appearance of new absorption bands at (393.0, 445.0 nm), (381.0, 434.5 nm) and (411.0, 491.0 nm) for the latter dyes, respectively. This is related to extra conjugation in the quinoline moiety in the latter dyes compared with the pyridine moiety in the former dyes, Scheme 1, Table 1. Also, changing the linkage position in the pyridinium residue from 2-yl salts in dyes **4a**, **5a**, and **6a**, to 4-yl salts in dyes **4c**, **5c**, and **6c**, resulted in a bathochromic shift of 5, 4, and 8 nm, respectively, accompanied by increasing the intensities of the absorption bands. This is due to increasing the π-delocalization conjugation in the latter 4-yl salt dyes compared with the former 2-yl salts, Scheme 1, Table 1. Additionally, the dimethine and *bis*-dimethine cyanine dyes **4b**, **5b**, and **6b** incurporating pyrazolo-oxazine nucleus showed hypsochromically shifted bands by (4 and 9 nm); (16.0 and 22.5 nm); and (11.5 and 30.0 nm) if compared by its analogous, dyes, (**4d**, **4e**); (**5d**, **5e**); and (**6d**, **6e**) which contain pyrazolo-thiazine and pyrazolo-pyrazine nuclei, respectively. This is due to increasing the electron attracting character of the oxazine ring in dyes **4b**, **5b**, and **6b** compared with thiazine and pyrazine rings in dyes (**4d**, **4e**), (**5d**, **5e**), and (**6d**, **6e**), respectively. This is leads to decreasing the electronic charge transfer pathways to the heterocyclic quaternary nitrogen atom of quinolinium salt residue, and consequently a hypsochromic shift is resulted in oxazine dyes. On the other side it was observed that substituting the 10-methyl group in dyes (**4a**-**e**) by 10-formyl group to give dyes (**5a**-**e**), made hypsochromic shifts in addition to decreasing the intensities of the absorption spectra bands. This could be attributed to the electron donating character of methyl group in dyes (**4a**-**e**) and electron attracting character of the formyl group in dyes (**5a**-**e**), Scheme 1, Table 1. Moreover, it is noticed that the number of electronic charge transfer pathways have a remarkable effect on the spectral behavior of these dyes, so, the *bis*-dimethine cyanine dyes (**6a**-**e**) showed absorption spectra bands which are bathochromically shifted if compared with its analogous dimethine cyanine dyes (**5a**-**e**) and/or (**4a**-**e**) with intensification of the absorption spectra bands, Table 1. This is can be explained by the presence of two electronic charge transfer pathways in the *bis*-dimethine cyanine dyes (**6a**-**e**) in correspondence to one electronic charge transfer pathways in the dimethine cyanine dyes (**5a**-**e**) and/or (**4a**-**e**), Scheme 2 (A), (B), Table 1.

3.3. Effect of solvent on the visible spectra

Effect of solvent in the visible spectra of the prepared *bis*-dimethine cyanine dye **6b** was investigated by measuring its electronic visible absorption spectra in pure solvents having different polarities, Table 3.

The electronic visible absorption spectra of the *bis*-dimethine cyanine dye **6b** in pure solvents of different dielectric constant via water (78.54), DMF (36.70), ethanol (24.3), chloroform (4.806), carbontetrachloride (2.238) and dioxane (2.209) [21] are recorded. The λ (wavelengths) and ε (molar extinction coefficients) values of the absorption bands due to different electronic transitions within the solute molecule in these solvents are represented in Table 3.

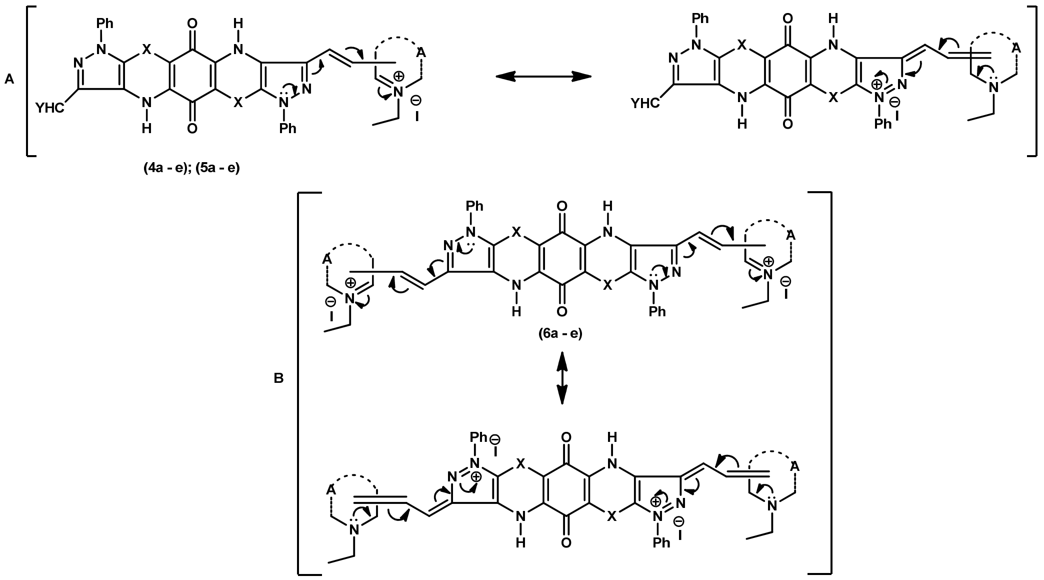
From Table 3, its clearly that, the electronic visible absorption spectra of the dye **6b** in ethanolic medium are characterized by the presence of three essential absorption bands. These bands can be assigned to intramolecular charge transfer transitions [22]. These charge transfer is due to transfer of lone pair of electrons from the N-Ph pyrazole nitrogen atom to the positively charged quaternary nitrogen atom of the quinolinium salt, Scheme 2, (B).

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 attributed to the following factors: (a) The bathochromic shift 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 occur in ethanol relative to dioxane, chloroform and carbontetracloride is a result of the solute solvent interaction through inter-molecular hydrogen bond formation between ethanol and the lone pair electrons of N-Ph pyrazole nitrogen atom, Scheme 3 (A). This decreases slightly the electron density on the N-Ph pyrazole nitrogen atom, and consequently decreases to some extent the mobility of the attached π-electrons over the conjugated pathway to the positively charged quaternary nitrogen atom of the quinolinium quaternary salt.

Table 3. Electronic visible absorption spectra of the *bis*-dimethine cyanine dye (**6b**) in pure solvents.

Solvent	**H_2O**		**EtOH**		**DMF**		**$CHCl_3$**		**CCl_4**		**Dioxane**	
Dye no	λ *	ε **	λ *	ε **	λ *	ε **	λ *	ε **	λ *	ε **	λ *	ε **
(6b)	484	20220	411	27410	503	26680	507	19200	504	18070	453	19160
	551	19220	491	26130	579	28830	569	16910	576	15160	581	14110
	-	-	559.5	25810	-	-	-	-	-	-	-	-

* Unit: nm.
** Unit: $mol^{-1}\ cm^2$.



(4a-e); X = O, Y = H2, A = 1-ethyl pyridinium-2-yl salt (a); X = O, Y = H2 A = 1-ethyl quinolinium-2-yl salt (b); X = O, Y = H2, A = 1-ethyl pyridinium-4-yl salt (c);
X = S, Y = H2, A = 1-ethyl quinolinium-2-yl salt (d); X = NH, Y = H2, A = 1-ethyl quinolinium-2-yl salt (e).
(5a-e); X = O, Y = O, A = 1-ethyl pyridinium-2-yl salt (a); X = O, Y = O, A = 1-ethyl quinolinium-2-yl salt (b); X = O, Y = O, A = 1-ethyl pyridinium-4-yl salt (c);
X = S, Y = O, A = 1-ethyl quinolinium-2-yl salt (d); X = NH, Y = O, A = 1-ethyl quinolinium-2-yl salt (e).
(6a-e); X = O, A = 1-ethyl pyridinium-2-yl salt (a); X = O, A = 1-ethyl quinolinium-2-yl salt (b); X = O, A = 1-ethyl pyridinium-4-yl salt (c);
X = S, A = 1-ethyl quinolinium-2-yl salt (d); X = NH, A = 1-ethyl quinolinium-2-yl salt (e).

Scheme 2

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 as well as decreasing the number and intensity of the absorption bands. This can be mainly ascribed to the possible interaction of water molecules with the lone pair electrons of N-Ph pyrazole nitrogen atom, Scheme 3 (A). This makes difficult the transfer of electronic charge from the N-Ph pyrazole nitrogen atom to the quaternary heterocyclic residue of the quinolinium salt, and consequently there is observed a hpsochromic shift in water relative to ethanol and the other solvents.

3.4. Effect of solution pH on the visible spectra

Effect of solution pH on the visible spectra of the synthesized *bis*-dimethine cyanine dye **6b** was investigated by measuring its spectra in aqueous universal buffer solutions.

The solutions of the *bis*-dimethine cyanine dye **6b** have a permanent cationic charge in basic media that then discharged on acidification. This prompted and encouraged us to study its spectral behavior in different buffer solutions in order to select a suitable pH for use of this dye as photosensitizers. The acid dissociation or protonation constant of this dye has been determined. The effect of the compound as photosensitizers increases when they are present in the ionic form, which has a higher planarity [23], and therefore more conjugation.

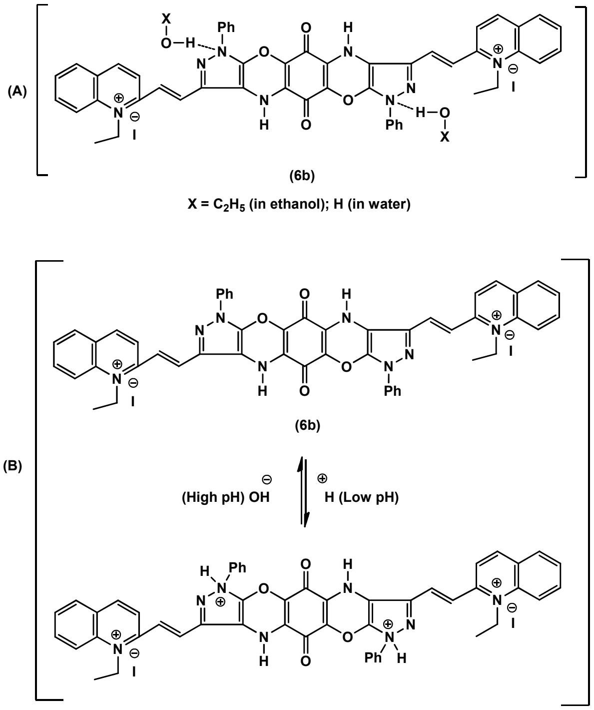
The electronic absorption spectra of the *bis*-dimethine cyanine dye **6b** in aqueous universal buffer solutions of varying pH values (1.87, 2.51, 3.92, 5.06, 6.89, 8.13, 9.56 and 11.41) showed bathochromic shifts with intensification of their absorption bands at high pH (alkaline media) and hypsochromic shifts with quenching the intensity of the bands at low pH media (acidic media). So, the mentioned dye which has lone pair of electrons on the N-Ph pyrazole nitrogen atom undergoes to protonation in low pH (acidic media). This leads to a criterion of positive charge on N-Ph pyrazole nitrogen atom, and consequently the electronic charge transfer pathways to the quaternary heterocyclic quinolinium salt will be difficult resulting a hypsochromc shift for the absorption band, Scheme 3, (B). On increasing the pH of the media, the absorption bands are intensified and bathochromically shifted due to deprotonation of the N-Ph pyrazole nitrogen atom, and consequently the electronic charge transfer pathways to the quaternary heterocyclic quinolinium salt will be easier and facilitated, Scheme 3 (B).

Several methods have developed for spectrophotometric determination of the dissociation constants of weak acids. The variation of absorbance with pH can be utilized. On plotting the absorbance at fixed λ *vs.* pH, S-shaped curves are obtained, Table 4. An 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 [24]. The acid dissociation or protonation constants values of the dye **6b** are given in Table 4.

Table 4. The variation of absorbance (λ = 550 nm) with pH at settled λ for the cyanine dye (**6b**) in different buffer solution *.

pH	1.87	2.51	3.92	5.06	6.89	8.13	9.56	11.41
Absorbance at settled wavelength	1.376	1.409	1.657	1.900	1.957	2.188	2.351	2.387

* pK_a= 4.380 and 8.235.



Scheme 3

4. Conclusion

From the results discussed in this study we can conclude that, theses cyanine dyes can be used as (i) Photographic sensitizers for silver halide emulsions in photographic industry due to their spectral and/or photosensitization properties, (ii) Indicators for solvent polarity due to their solvatochromic properties, (iii) Acid-base indicators in analytical chemistry due to their halochromic properties.

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