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Dyes and Pigments 75 (2007) 344–350
DYES and PIGMENTS
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Synthesis, characterization and visible spectral behaviour of some novel methine, styryl and aza-styryl cyanine dyes

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Received 24 May 2006; received in revised form 6 June 2006; accepted 8 June 2006

Abstract

Novel monomethine, dimethine, trimethine, styryl and aza-styryl cyanine dyes having naphthfuro [3,2-*d*]pyrazole nucleus were prepared. The visible spectral behaviour of the synthesized cyanines was examined in 95% ethanol. Structural determinations were carried out via elemental analysis, IR and ^{1}H NMR spectral data.

Keywords: Cyanine dyes; Synthesis; Spectral behaviour

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1. Introduction

Cyanine dyes have found various applications in different fields, such as photosensitizers for silver halide emulsion [1–6], analytical reagents over a wide pH range [7], laser dyes [8], textile dyes [9], bactericidal agents [10], potential probes for the detection of nucleic acids and proteins [11] and in biomedical techniques [12–15].

2. Results and discussion

2.1. Synthesis

2,3-Dichloro-1,4-naphthoquinone (**1**) was reacted with 3-methyl-1-phenyl-5-pyrazolone (**2**) in equimolar ratios in ethanol containing pyridine and achieved 4-methyl-2-phenylnaphthfuro[3,2-*d*]pyrazole-5,10-dione (**3**) as new heterocyclic starting material, Scheme 1.

Quaternization of **3** using iodoethane resulted in the corresponding 3-iodoethane quaternary salt (**4**). Interaction of **4** and iodomethane quaternary salts of pyridine, quinoline, isoquinoline in equimolar ratios in ethanol containing a few drops of piperidine afforded the 4[4(1)]-monomethine cyanine dyes (**5a–c**), Scheme 1.

Selenium dioxide oxidation of the starting material (**3**) in dioxane resulted in the 4-carbaldehyde compound (**6**). Further reaction of **6** and iodomethane quaternary salts of α-picoline, quinaldine, γ-picoline in equimolar ratios, in ethanol and the presence of a few drops of piperidine achieved the 4[2(4)]-dimethine cyanine dyes (**7a–c**), Scheme 1.

Equimolar interaction of the quaternized compound (**4**) and triethylorthoformate in ethanol and piperidine gave the intermediate compound (**8**). Subsequent reaction of the intermediate (**8**) with 2(4)-methyl quaternary salts of α-picoline, quinaldine, γ-picoline in ethanol containing piperidine resulted in the 4[2(4)]-trimethine cyanine dyes (**9a–c**), Scheme 1.

4(1)-Styryl cyanine dyes (**10a–f**) were prepared through interaction of equimolar ratios of the quaternized compound (**4**) and an aromatic aldehyde (such as benzaldehyde, *p*-OH benzaldehyde, *p*-OCH_3 benzaldehyde, *p*-$N(CH_3)_2$ benzaldehyde, *p*-NO_2 benzaldehyde, *p*-Cl benzaldehyde) in ethanol as organic solvent and piperidine as basic catalyst, Scheme 1.

4[2(1)]-Aza-styryl cyanine dyes (**11a–c**) were prepared via equimolar interaction of the quaternized compound (**4**) with nitroso compounds (such as *p*-nitroso phenol, α-nitroso-β-naphthol, β-nitroso-α-naphthol) in ethanol and the presence of piperidine, Scheme 1.

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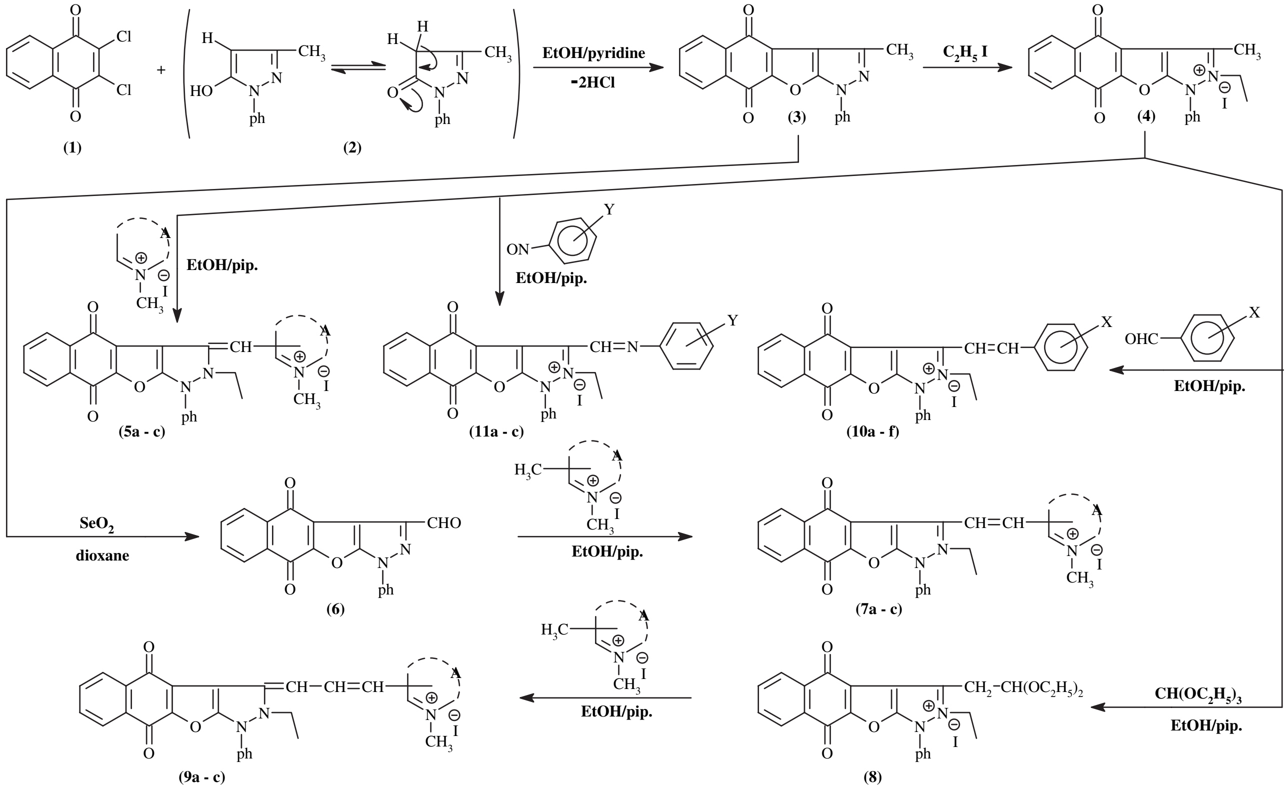
doi:10.1016/j.dyepig.2006.06.008



Scheme (1)

Substituents in Scheme (1)

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

(7a – c), (9a – c): A = 1-methyl pyridinium-2-yl salt (a);
A = 1-methyl quinolinium-2-yl salt (b);
A = 1-methyl pyridinium-4-yl salt (c).

(10a – f): X = H (a); OH (b); OCH$_3$ (c); N(CH$_3$)$_2$ (d); NO$_2$ (e) Cl (f).

(11a – c): Y = 4.OH (a);
Y = 2.OH, 5,6-benzosubstituent (b);
Y = 2.OH, 3,4-benzosubstituent (c).

Scheme 1.

2.2. Characterization

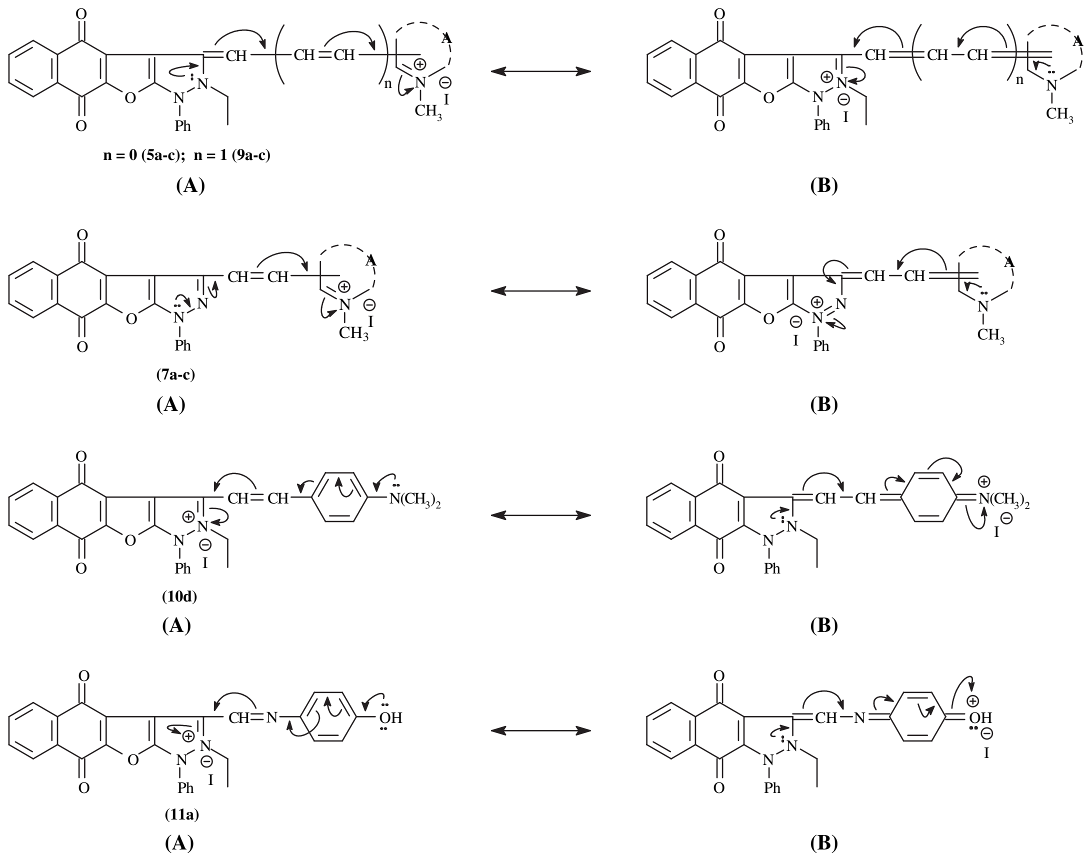
The newly prepared cyanine dyes are highly coloured compounds, partially soluble in nonpolar organic solvents and readily soluble in polar organic solvents giving coloured solutions, accompanied in many cases by pale to intense fluorescence. The intensity and colour of the fluorescence depend upon the type of dye and solvent used. The dyes are soluble in concentrated H_2SO_4 liberating iodine vapour on warming. They are also pH-sensitive dyes, and hence their ethanolic solutions give changeable colours in acid/base media being yellow or colourless on acidification and getting back their intense colour on basification. They exhibit general solute–solvent interaction depending on the dielectric constant of the solvent used, as well as specific solute–solvent interaction, this includes hydrogen bonding and molecular complex. The intensity of the colours of these dyes was illustrated according to the two suggested mesomeric structures (A) and (B), producing a delocalized positive charge over the conjugated system, Scheme 2.

The structure of the prepared compounds was confirmed by elemental analysis (Tables 1 and 2), IR [16] (Table 3) and ^{1}H NMR [17] (Table 3) spectral data.

2.3. Visible spectral behaviour

The electronic visible absorption spectra of the monomethine cyanine dyes (**5a–c**) in 95% ethanol displayed absorption bands in the visible region (360–560 nm), the positions of which, together with their molar extinction coefficients are influenced by the type of the heterocyclic quaternary salt and their linkage positions. Thus, substituting 1-methyl pyridinium-4-yl salt in dye (**5a**) by 1-methyl quinolinium-4-yl salt and/or 2-methyl isoquinolinium 1-yl salt to obtain dyes **5b** and **5c** discloses bathochromic shifts for the absorption bands accompanied by intensification of the absorption bands, Table 1. This can be explained by the increasing π-delocalization conjugation in quinoline and/or isoquinoline dyes (**5b** and **5c**) than their analogous pyridine dye (**5a**). Changing the linkage position, moving from the quinoline dye (**5b**) to the isoquinoline dye (**5c**), caused a hypsochromic shift in the absorption bands accompanied by quenching of the intensity of the absorption bands, Table 1. This is due to the decreasing π-delocalization conjugation in the heterocyclic quaternary residue in the latter dye (**5c**).

In addition, the electronic visible absorption spectra of the dimethine (trimethine) cyanine dyes **7a–c** (**9a–c**) in 95%



Scheme 2.

ethanol reveal absorption bands in the visible region of 380–565 nm (380–570 nm), the positions of which and their molar extinction coefficients are effected by the type of the heterocyclic quaternary residue (A) and their linkage positions. So, substituting 1-methyl pyridinium-2-yl salt in dyes **7a** (**9a**) by 1-methyl quinolinium-2-yl salt to give dyes **7b** (**9b**) resulted in bathochromic shifts of the absorption bands accompanied by increases in the intensity of the absorption bands, Table 1. This is due to greater conjugation in the quinoline ring than in the analogous pyridine ring. Changing the linkage position from 2-yl salts in dyes **7a** (**9a**) to 4-yl salts in dyes **7c** (**9c**) resulted in red shifted and intensified absorption bands, Table 1. This is due to the increasing conjugation in the latter dyes.

Generally, it is noticed that, the electronic visible adsorption spectra of the trimethine cyanine dyes (**9a**–**c**) changed to give bathochromically shifted bands compared with those of the dimethine cyanine dyes (**7a**–**c**) and/or the monomethine cyanine dyes (**5a**–**c**), Table 1. Also, the dimethine cyanine dyes (**7a**–**c**) displayed red-shifted bands compared with those of the monomethine cyanine dyes (**5a**–**c**), Table 1. This can be attributed to the increasing number of methine groups in these dyes in the order of trimethine > dimethine > monomethine, Scheme 1.

On the other side, the styryl cyanine dyes (**10a**–**f**) showed visible absorption spectral bands in the region 350–505 nm, the positions of which and their molar extinction coefficients are influenced by the types of benzo substituted X. Hence, substituting X = H in dye **10a** by X = *p*-OH, *p*-OCH_3, and *p*-$N(CH_3)_2$ to give dyes **10b**, **10c**, and **10d**, respectively, imparted bathochromic shifts in the absorption bands accompanied by increasing intensity of the absorption bands, Table 2. This can be attributed to the electron donating character of the latter dyes which leads to increasing electron charge transfer to the quaternary pyrazolium salt. On the other hand, substituting X = H in dye **10a** by X = *p*-NO_2 and *p*-Cl to obtain dyes **10e** and **10f**, respectively, resulted in red shifts and quenching of the absorption bands, Table 2. This is due to the electron attracting character of the latter dyes which leads to decreasing electron charge transfer to the quaternary pyrazolium salt.

Additionally, the aza-styryl cyanine dyes (**11a**–**c**) showed visible absorption spectral bands in 95% ethanol in the region 380–525 nm. The positions of these bands and their molar extinction coefficients were influenced by the type of the nitroso compounds. Thus, substituting A = H by A = 5,6-benz and/or 3,4-benz transferring from dye **11a** to dyes **11b** and **11c** imparted a bathochromic shift and intensification of the absorption bands, Table 2. This is due to the increasing conjugation in the latter dyes (**11b** and **11c**) due to the presence of additional benzene ring. Otherwise, substituting A = 5,6-benz in dye **11b** by A = 3,4-benz to give dye (**11c**) caused a red shift in the absorption bands accompanied by increasing intensity of the absorption bands, Table 2. This may be attributed to the higher planarity of the latter dye (**11c**).

Table 1
Characterization of the prepared compounds (**3**–**9**)

Comp. no.	Nature of products			Molecular formula (mol mass)	Analysis (%)						Absorption spectra in 95% ethanol	
	Colour	Yield (%)	Mp (°C)		Calculated			Found			λ_{max} (nm)	ε_{max} (cm^2 mol^{-1})
					C	H	N	C	H	N		
3	Deep red crystals	85	160	$C_{20}H_{12}O_3N_2$ (328)	73.17	3.65	8.53	73.14	3.61	8.50	–	–
4	Deep brown crystals	90	220	$C_{22}H_{17}O_3N_2I$ (484)	54.54	3.51	5.78	54.49	3.48	5.75	–	–
5a	Reddish violet crystals	65	200	$C_{28}H_{22}O_3N_3I$ (575)	58.43	3.82	7.30	58.38	3.76	7.22	510, 455, 360	26 100, 23 620, 19 000
5b	Deep reddish violet crystals	75	240	$C_{32}H_{24}O_3N_3I$ (625)	61.44	3.84	6.72	61.40	3.81	6.66	560, 465, 385	30 000, 25 200, 21 810
5c	Reddish violet crystals	67	190	$C_{32}H_{24}O_3N_3I$ (625)	61.44	3.84	6.72	61.39	3.80	6.63	545, 460, 380	20 600, 24 690, 20 030
6	Red crystals	82	210	$C_{20}H_{10}O_4N_2$ (342)	70.17	2.92	8.18	70.12	2.88	8.15	–	–
7a	Violet crystals	56	190	$C_{27}H_{18}O_3N_3I$ (559)	57.96	3.22	7.51	57.90	3.16	7.42	520, 405, 380	26 020, 18 870, 16 530
7b	Blue crystals	67	230	$C_{31}H_{20}O_3N_3I$ (609)	61.08	3.28	6.89	61.00	3.21	6.85	565, 470, 410	30 000, 25 030, 20 220
7c	Violet crystals	55	220	$C_{27}H_{18}O_3N_3I$ (559)	57.96	3.22	7.51	57.92	3.18	7.45	525, 455, 405	26 230, 22 810, 16 700
8	Reddish violet crystals	63	200	$C_{27}H_{27}O_5N_2I$ (586)	55.29	4.60	4.77	55.22	4.53	4.71	–	–
9a	Violet crystals	72	190	$C_{30}H_{24}O_3N_3I$ (601)	59.90	3.99	6.98	59.85	3.92	6.94	525, 410, 380	27 560, 20 240, 19 640
9b	Deep violet crystals	84	220	$C_{34}H_{26}O_3N_3I$ (651)	62.67	3.99	6.45	62.61	3.95	6.39	570, 475, 410	28 820, 25 400, 20 520
9c	Violet crystals	54	240	$C_{30}H_{24}O_3N_3I$ (601)	59.90	3.99	6.98	59.84	3.93	6.95	530, 415, 385	26 520, 29 800, 19 230

Table 2
Characterization of the prepared compounds (**10**, **11**)

Comp. no.	Nature of products			Molecular formula (mol mass)	Analysis (%)						Absorption spectra in 95% ethanol	
	Colour	Yield (%)	Mp (°C)		Calculated			Found			λ_{max} (nm)	ε_{max} (cm^2 mol^{-1})
					C	H	N	C	H	N		
10a	Violet crystals	56	185	$C_{29}H_{21}O_3N_2I$ (572)	60.83	3.67	4.89	60.75	3.60	4.81	450, 380, 350	20 010, 14 670, 22 100
10b	Violet crystals	59	165	$C_{29}H_{21}O_4N_2I$ (588)	59.18	3.57	4.76	59.12	3.52	4.72	455, 410, 380	21 480, 16 510, 17 270
10c	Violet crystals	57	235	$C_{30}H_{23}O_4N_2I$ (602)	59.80	3.82	4.65	59.75	3.76	4.58	475, 410, 385	24 230, 19 330, 17 770
10d	Violet crystals	58	198	$C_{31}H_{26}O_3N_3I$ (615)	60.48	4.22	6.82	60.42	4.17	6.77	505, 450, 410	26 220, 22 660, 19 210
10e	Violet crystals	55	245	$C_{29}H_{20}O_5N_3I$ (617)	56.40	3.24	6.80	56.35	3.18	6.78	410, 405, 380	19 420, 18 940, 19 070
10f	Violet crystals	54	175	$C_{29}H_{20}O_3N_2ClI$ (606.5)	57.37	3.29	4.61	57.32	3.24	4.54	410, 380, 360	19 570, 19 040, 19 040
11a	Brown	55	165	$C_{28}H_{20}O_4N_3I$ (589)	57.04	3.39	7.13	57.00	3.35	7.10	510, 410, 380	26 540, 20 070, 19 650
11b	Brownish violet crystals	58	195	$C_{32}H_{22}O_4N_3I$ (639)	60.09	3.44	6.57	60.02	3.40	6.51	515, 410, 380	26 710, 20 070, 19 600
11c	Brownish violet crystals	56	215	$C_{32}H_{22}O_4N_3I$ (639)	60.09	3.44	6.57	60.01	3.41	6.52	525, 410, 380	29 500, 22 250, 21 090

Table 3
IR and ^{1}H NMR spectral data of the prepared compounds

Comp. no.	IR (KBr, cm^{-1})	^{1}H NMR ($CDCl_3$, δ)
3	685, 752 (Monosubstituted benzene); 687, 754 (*o*-disubstituted benzene); 1051, 1153 (C–O–C cyclic); 1364 (C–N); 1490 (C=N); 1591 (C=C); 1631 (C=O quinone); 3358 (=N–N)	1.3 (s, 3H, CH_3); 7.2–8.8 (m, 9H, aromatic)
4	676, 749 (Monosubstituted benzene); 925, 998 (*o*-disubstituted benzene); 1053, 1155 (C–O–C cyclic); 1366 (C–N); 1489 (C=N); 1593 (C=C); 1633 (C=O quinone); 2917 (quaternary salt); 3384 (=N–N)	0.85 (t, 3H, CH_3 of position 3); 4.1 (q, 2H, CH_2 of position 3); 1.2 (s, 3H, CH_3 of position 4); 7.3–8.5 (m, 9H, aromatic)
5b	707, 753 (Monosubstituted benzene); 871, 935 (*o*-disubstituted benzene); 1056, 1149 (C–O–C cyclic); 1307, 1378 (C–N); 1487 (C=N); 1594 (C=C); 1621 (C=O quinone); 2917 (quaternary salt)	0.87 (t, 3H, CH_3 of position 3); 4.1 (q, 2H, CH_2 of position 3); 1.25 (s, 3H, CH_3 of quinolinium); 6.5–8.75 (m, 16H, aromatic + heterocyclic + –CH=)
6	710, 753 (Monosubstituted benzene); 871, 925 (*o*-disubstituted benzene); 1062, 1157 (C–O–C cyclic); 1387 (C–N); 1492 (C=N); 1604 (C=C); 1631 (C=O quinone); 1718 (C=O aldehydic); 2851 (C–H aldehydic); 3386 (=N–N)	9.7 (s, 1H, CHO); 7.1–8.5 (m, 9H, aromatic)
7b	698, 751 (Monosubstituted benzene); 857, 923 (*o*-disubstituted benzene); 1052, 1147 (C–O–C cyclic); 1357 (C–N); 1483 (C=N); 1595 (C=C); 1630 (C=O quinone); 2920 (quaternary salt); 3398 (=N–N)	1.3 (s, 3H, CH_3 of quinolinium); 6.5–8.7 (m, 17H, aromatic + heterocyclic + –CH=)
8	701, 754 (Monosubstituted benzene); 860, 926 (*o*-disubstituted benzene); 1018, 1155 (C–O–C cyclic); 1227 (C–O ether); 1387 (C–N); 1490 (C=N); 1591 (C=C); 1634 (C=O quinone); 2919 (quaternary salt); 3363 (=N–N)	0.87 (t, 3H, CH_3 of position 3); 4.15 (q, 2H, CH_2 of position 3); 1.25 (t, 6H, $2CH_3$ of diethoxy ethyl); 3.85 (q, 4H, $2CH_2$ of diethoxy ethyl); 4.65 (t, 1H, CH of diethoxy ethyl); 3.65 (d, 2H, CH_2 of diethoxy ethyl); 7.15–8.5 (m, 9H, aromatic)
9b	700, 753 (Monosubstituted benzene); 859, 925 (*o*-disubstituted benzene); 1052, 1151 (C–O–C cyclic); 1359 (C–N); 1488 (C=N); 1595 (C=C); 1632 (C=O quinone); 2917 (quaternary salt)	0.88 (t, 3H, CH_3 of position 3); 4.25 (q, 2H, CH_2 of position 3); 1.3 (s, 3H, CH_3 of quinolinium); 6.5–8.9 (m, 18H, aromatic + heterocyclic + –CH=)
10c	709, 753 (Monosubstituted benzene); 863, 923 (*o*-disubstituted benzene); 1023, 1161 (C–O–C cyclic); 1228 (OCH_3 stretching); 1309, 1389 (C–N); 1490 (C=N); 1590 (C=C); 1630 (C=O quinone); 2919 (quaternary salt); 3368 (=N–N)	0.9 (t, 3H, CH_3 of position 3); 4.3 (q, 2H, CH_2 of position 3); 3.85 (s, 3H, CH_3 of OCH_3); 6.6–8.9 (m, 15H, aromatic + –CH=)
10e	710, 756 (Monosubstituted benzene); 869, 926 (*o*-disubstituted benzene); 1013, 1154 (C–O–C cyclic); 1380 (C–N); 1486 (C=N); 1593 (C=C); 1625 (C=O quinone); 2923 (quaternary salt); 3359 (=N–N)	0.87 (t, 3H, CH_3 of position 3); 4.15 (q, 2H, CH_2 of position 3); 6.75–8.75 (m, 14H, aromatic + –CH=)
11b	709, 754 (Monosubstituted benzene); 868, 925 (*o*-disubstituted benzene); 1016, 1154 (C–O–C cyclic); 1383 (C–N); 1489 (C=N); 1592 (C=C); 1628 (C=O quinone); 2920 (quaternary salt); 3356 (=N–N); 3373 (OH)	0.88 (t, 3H, CH_3 of position 3); 4.10 (q, 2H, CH_2 of position 3); 6.4–8.7 (m, 16H, aromatic + OH + –CH=)

It is also interesting to notice that substituting the dimethine group (CH=CH) in the styryl cyanine dye (**10b**) by the aza-methine group (–CH=N–) to give the aza-styryl cyanine dye (**11a**) makes bathochromic shifts of the absorption bands accompanied with intensification of the bands, Table 2, Scheme 1. This may be attributed to the increasing electron releasing character in the aza-styryl cyanine dye (**11a**) by the nitrogen lone pair electrons of the aza-methine group $(CH{=}\ddot{N})$, Scheme 1, Table 2.

2.4. Conclusions

It appears that the electronic visible absorption spectral bands of the prepared cyanine dyes underwent bathochromic and/or hypsochromic shifts according to the following factors:

(I) increasing and/or decreasing conjugation in the dye molecule;
(II) increasing and/or decreasing the number of methine group;
(III) the presence of either electron donating and/or accepting groups;
(IV) higher and/or lower planarity of the dye molecule;
(V) the presence of either methine and/or aza-methine groups, Scheme 1.

3. Experimental

3.1. General

All melting points are uncorrected. Elemental analysis was carried out at the microanalytical center of Cairo University by an automatic analyzer (Heraeus). IR (KBr pellets) spectra were determined on a Perkin Elmer Infrared 127 spectrophotometer (Cairo University) and the ^{1}H NMR spectra were obtained using a Varian Gemini NMR 300 MHz spectrometer (Cairo University). Electronic visible absorption spectra were carried out on U.V. spectrophotometer (South Valley University, Faculty of Science, Aswan).

3.2. Synthesis

3.2.1. Synthesis of 4-methyl-2-phenyl-naphthfuro-[3,2-d]pyrazole-5,10-dione (**3**)

An equimolar ratio (0.01 mol) of 2,3-dichloro-1,4-naphthoquinone (**1**) and 3-methyl-1-phenyl-5-pyrazolone (**2**) was refluxed in ethanol (50 ml) containing pyridine (20 ml) for 8–10 h. The reaction mixture, which had attained a deep red colour at the end of refluxing was filtered while hot, concentrated to half its volume, cooled and neutralized with hydrochloric acid. The precipitated product, which appeared upon dilution with ice/water mixture, was filtered off, washed several times with water, dried and crystallized from ethanol. The results are listed in Table 1.

3.2.2. Synthesis of 3-ethyl-4-methyl-2-phenyl-naphthfuro-[3,2-d]pyrazolium iodide salt-5,10-dione (**4**)

The starting material (**3**) (0.01 mol) was suspended in an excess of ethyl iodide and heated gently on a water bath for 2–3 h. The reaction mixture was crystallized from ethanol to give the quaternized compound (**4**). The results are summarized in Table 1.

3.2.3. Synthesis of 3-ethyl-2-phenyl-naphthfuro[3,2-d]-pyrazole-5,10-dione-4[4(1)]-monomethine cyanine dyes (**5a–c**)

An equimolar ratio (0.01 mol) of **4** and the iodomethane quaternary salts of pyridine, quinoline, and isoquinoline was dissolved in ethanol (50 ml) and a few drops of piperidine were added. The reaction mixture was heated under reflux for 7–9 h at the end of which it attained a reddish violet colour. The mixture was filtered while hot, concentrated to half its volume, neutralized by glacial acetic acid and precipitated by the addition of cold water and stirring. The precipitated products were filtered off, washed several times with water, dried and crystallized from ethanol. The results are given in Table 1.

3.2.4. Synthesis of 4-formyl-2-phenyl-naphthfuro[3,2-d]-pyrazole-5,10-dione (**6**)

Selenium dioxide (0.01 mol) and the starting material (**3**) (0.01 mol) were refluxed in dioxane (50 ml) for 16–18 h. The ensuing product was filtered while hot to remove selenium metal, concentrated and cooled. The precipitated products were collected and crystallized from ethanol. The results are shown in Table 1.

3.2.5. Synthesis of 2-phenyl-naphthfuro[3,2-d]pyrazole-5,10-dione-4[2(4)]-dimethine cyanine dyes (**7a–c**)

A mixture of an equimolar ratio (0.01 mol) of **6** and 1,2(4)-dimethyl (pyridinium, quinolinium) iodide salts was heated under reflux in ethanol (50 ml) containing piperidine (1–2 ml) for 3–5 h, after which it attained a violet/blue colour. The reaction mixture was filtered while hot, concentrated, cooled and neutralized by glacial acetic acid. The precipitated products, which appeared upon dilution with water, were filtered off, washed with water and crystallized from ethanol. The results are listed in Table 1.

3.2.6. Synthesis of 3-ethyl-2-phenyl-4(1,1′-diethoxy ethyl)-naphthfuro[3,2-d]pyrazolium iodide salt-5,10-dione (**8**)

Piperidine (1–2 ml) was added to a mixture of an equimolar ratio (0.01 mol) of **4** and triethylorthoformate in ethanol (50 ml). The reaction mixture was refluxed for 6–8 h, after which it attained a reddish violet colour; it was filtered while hot, concentrated, cooled and neutralized by glacial acetic acid. The precipitated products were collected and crystallized from ethanol. The results are summarized in Table 1.

3.2.7. Synthesis of 3-ethyl-2-phenyl-naphthfuro[3,2-d]-pyrazole-5,10-dione-4[2(4)]-trimethine cyanine dyes (**9a–c**)

Equimolar ratios (0.01 mol) of **8** and 1,2(4)-dimethyl pyridinium iodide salts, 1,2-dimethyl quinolinium iodide salt were dissolved in ethanol (50 ml) and then piperidine (1–2 ml) was added. The reaction mixture was heated under reflux for 5–7 h, after which it attained violet/deep violet colour. The product was filtered while hot, concentrated to half its volume, cooled and neutralized by glacial acetic acid. The precipitated product, which resulted from dilution with cold water, was filtered off, washed with water several times, dried and crystallized from ethanol. The results are given in Table 1.

3.2.8. Synthesis of 3-ethyl-2-phenyl-naphthfuro[3,2-d]-pyrazolium iodide salt-5,10-dione-4(1)-styryl cyanine dyes (**10a–f**)

Equimolar ratios (0.01 mol) of **4** and aromatic aldehyde (benzaldehyde, *p*-OCH_3 benzaldehyde, *p*-$N(CH_3)_2$ benzaldehyde, *p*-NO_2 benzaldehyde, *p*-Cl benzaldehyde) were dissolved in ethanol (50 ml), and then piperidine (1–2 ml) was added. The reaction mixture was refluxed for 8–10 h and a violet to deep violet colour was attained at the end of refluxing. It was filtered while hot, concentrated, neutralized by glacial acetic acid and precipitated by addition of ice/water mixture. The precipitated products were filtered off, washed several times with water, dried and crystallized from ethanol. The results are listed in Table 2.

3.2.9. Synthesis of 3-ethyl-2-phenyl-naphthfuro[3,2-d]-pyrazolium iodide salt-5,10-dione-4[2(1)]-aza-styryl cyanine dyes (**11a–c**)

A mixture of equimolar ratios (0.01 mol) of **4** and nitroso compounds (*p*-nitroso phenol, α-nitroso-β-naphthol, β-nitroso-α-naphthol) was heated under reflux for 7–9 h in ethanol (50 ml) containing piperidine (1–2 ml). The reaction mixture attained brown to brownish violet colour at the end of refluxing, it was filtered while hot, concentrated, cooled, neutralized by glacial acetic acid, and precipitated by the addition of cold water. The precipitated products were collected and crystallized from ethanol. The results are shown in Table 2.

3.3. Spectral behaviour studies

The electronic visible absorption spectra of the dyes in 95% ethanol were recorded on a U.V. recording spectrophotometer using 1 cm quartz cells. The stock solution was about 1×10^{-3} M. Lower molarities were obtained by accurate dilution. The spectra were recorded immediately to eliminate as much as possible the effect of time.

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