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Pyrazolo quinone heterocyclic compounds and metal complex derivatives in the synthesis of cyanine dyes

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Abstract

This work describes the synthesis of new pyrazolo quinone heterocyclic derivatives, their metal complexes and relative cyanine dyes. Electronic absorption spectra in ethanol, water and different pH aqueous solutions are reported and commented. The synthesized new cyanine dyes and relative intermediates were identified and structurally characterized by elemental analysis, IR, ^{1}H-NMR spectroscopies and mass spectrometry. The synthetic approach allowed to tune the physical properties of dyes and provided chromophores useful for analytical chemistry.

Keywords: Synthesis; Pyrazole; Quinone; Metal complex; Absorption spectra; Alochromic behaviour; Acid–base properties

1. Introduction

Ongoing research by our group was directed to synthesis of heterocyclic systems to prepare and study methine cyanine dyes [1–5]. Little attention has been focused on the use of condensed bi-heterocyclic quinone in the synthesis of methine cyanine dyes. The cyanine dyes are a remarkable class of strong light absorbers, widely used in sensitizing the silver halide microcrystals in photographic films [6]. They are used in laser technologies [7], as optical recording material [8], photoinitiators in photopolymerization [9], probes for the physical state and membrane potential of liposomes and synthetic bilayers [10], as well as potential sensitizers for photodynamic therapy [11].

2. Experimental

Melting points were recorded on a Galenkanp melting point apparatus and are uncorrected. Elemental analyses were carried out at the Micro Analytical Center (Cairo University). The IR spectra (KBr) were determined on Perkin–Elmer 127B spectrophotometer. ^{1}H-NMR spectra were recorded with a Bruker AMX-250 spectrometer. Mass spectra were recorded on a HpMs 6988 spectrometer and electron-impact (EI). The electronic absorption spectra were recorded immediately after preparation of the solutions within the wavelength range (350–700 nm) on a 6405 UV/Visible recording spectrophotometer, Science Faculty of

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Aswan at 27 °C. Ethanol (95%, ethanol–water 95:5 v/v) was used. pH was measured on a Radelkis OP-208 pH-meter with universal buffer solution. The concentration of the stock solution was about 1×10^{-3} and the lower molarities were obtained by accurate dilution. Synthesis of 4-acetyl-3-methyl-1-phenyl pyrazol-5-one (**1**) was carried out according to reference [12].

*2.1. Synthesis of 3-methyl-5-oxo-(1-phenyl-4,5-dihydro-1H-pyrazol-4-yl)-oxo-acetaldehyde (**2**)*

Mixture of compound **1** (2.16 g, 0.01 mol) and selenium dioxide (1.11 g, 0.01 mol) was dissolved in 1,4-dioxane (20 ml). The reaction mixture was refluxed for 18 h and filtered hot. The process of refluxing and filtration was repeated 3 times, then filtered hot and cooled. The precipitated solid, after dilution with water, was collected and crystallized from ethanol to give a deep yellow crystalline product, m.p. 113–115 °C, yield = 75%.

Analytical data for $C_{12}H_{10}N_2O_3$ (mol. wt. 230): Calcd %: C = 62.60, H = 4.35, N = 12.17; Found %: C = 62.54, H = 4.25, N = 12.10; IR (ν^{KBr}, cm^{-1}): 1497 cm^{-1} (C=N), 1594 cm^{-1} (C=C) and 1711 cm^{-1} (CHO).

*2.2. Synthesis of 3-methyl-1-phenylpyrazol-5-one-(oxo-but-2-ene aldehyde) (**3**)*

Mixture of compound **2** (2.3 g, 0.01 mol) and acetaldehyde (0.44 g, 0.01 mol) was dissolved in AcOH (20 ml). The reaction mixture was refluxed for 5 h, filtered hot and cooled. The precipitated solid, after dilution with water, was collected and crystallized from ethanol to give a deep yellow crystalline product, m.p. 110–113 °C, yield = 60%.

Analytical data for $C_{14}H_{12}N_2O_3$ (mol. wt. 256): Calcd %: C = 65.63, H = 4.69, N = 10.94; Found %: C = 65.62, H = 4.67, N = 10.95; IR (ν^{KBr}, cm^{-1}): 1497 cm^{-1} (C=N), 1592 cm^{-1} (C=C) and 1690 cm^{-1} (CH=CH–CHO).

*2.3. Synthesis of 3-methyl-1-phenyl-benzo[4,5–b]pyrazolo-4,7-dione (**4**)*

Compound **3** (2.56 g, 0.01 mol) was heated on a sand bath without solvent in the presence of catalytic amount of piperidine for 30 min and then cooled. The semisolid product was dissolved in ethanol, refluxed for 1 h, filtered hot, concentrated and cooled. The precipitated solid, after dilution with water, was collected and crystallized from methanol to give a brownish red powder product, m.p. 115–117 °C, yield = 60%.

Analytical data for $C_{14}H_{10}N_2O_2$ (mol. wt. 238): Calcd %: C = 70.58, H = 4.20, N = 11.76; Found %: C = 70.59, H = 4.18, N = 11.75; IR (ν^{KBr}, cm^{-1}): 1498 cm^{-1} (C=N) and 1670 cm^{-1} (quinone ring); ^{1}H-NMR (CDCl$_3$, 250 MHz) δ (ppm): 1.31 (s, 3H, CH$_3$) and 7.20–7.85 (m, 7H, Ar-H).

*2.4. Synthesis of 5-acetyl-6-amino-3-methyl-1-phenyl-benzo[4,5-b]pyrazolo-4,7-dione (**5**)*

This compound was prepared as described in reference [12] to give a deep brownish red compound, m.p. 220–222 °C, yield = 70%.

Analytical data for $C_{16}H_{13}N_3O_3$ (mol. wt. 295): Calcd %: C = 65.09, H = 4.41, N = 14.24; Found %: C = 65.05, H = 4.39, N = 14.21.

*2.5. Synthesis of 3,5-dimethyl-8-metalo-1-phenyl-benzo[4,5-b;4′,5′-b′]pyrazolo-oxazino-4,9-dione ylide chloride compounds (**6a–c**)*

Mixture of compound **5** (2.95 g, 0.01 mol) and metal divalent (Cu^{++}, Co^{++}, Ni^{++}) (0.01 mol) was dissolved in ethanol in the presence of little plats of sodium hydroxide. The precipitated solid was collected by filtration, washed with ethanol and dried. Characterization data are listed in Table 1.

*2.6. Synthesis of 3-methyl-8-metalo-1-phenyl-benzo[4,5-b;4′,5′-b′]pyrazolo-oxazino-4,9-dione-5[4(1)] monomethine cyanine dyes (**7a–e**)*

Mixture of compounds (**6a–c**) (0.01 mol) and *N*-methyl heterocyclic quaternary salts (pyridinium, quinolinium and isoquinolinium) iodide (0.01 mol) was dissolved in ethanol (20 ml), and a few drops of piperidine were added. The reaction mixture was refluxed for 12 h, filtered hot, cooled and acidified with acetic acid. The precipitated products, after dilution with water were collected and crystallized from ethanol to give the corresponding compounds **7a–e**. Characterization data are listed in Table 1.

*2.7. Synthesis of 6-amino-3,5-dimethyl-1-phenyl-benzo[4,5-b]pyrazolo-4,7-dione-meso-substituted-5[2(4)]-dimethine cyanine dyes (**8a–c**)*

Mixture of compound **5** (0.295 g, 0.001 mol) and 2(4)-methyl heterocyclic quaternary salts (α-picoline, quinaldine and γ-picoline) methyl iodide (0.001 mol) was dissolved in ethanol (20 ml) and a few drops of piperidine were added. The reaction mixture was refluxed for 6–8 h, filtered hot and cooled. The precipitated solid so obtained was acidified with a few drops of acetic acid, diluted with water, collected and crystallized from ethanol to give the corresponding compounds **8a–c**. Characterization data are listed in Table 1.

*2.8. Synthesis of symmetrical (unsymmetrical) 3,5-dimethyl-1-phenyl-benzo[4,5-b] pyrazolo 4,7-dione-meso-substituted-5,4[2(4)]-pentamethine cyanine dyes (**9a–d**)*

Mixture of compound **5** (0.295 g, 0.001 mol) and 2(4)-methyl heterocyclic quaternary salts (α-picoline, quinaldine and γ-picoline) methyl iodide (0.002 mol) was fused in the presence of piperidine (3–5 drops) for 5 min, cooled, dissolved in ethanol, refluxed for 3 h, filtered hot, concentrated and cooled. The precipitated solid so obtained was acidified with a few drops of acetic acid, diluted with water, collected and crystallized from ethanol to give the corresponding compounds **9a–d**. Characterization data are listed in Table 1.

*2.9. Synthesis of 3-methyl-1-phenyl-benzo[4,5-b] pyrazolo-4,7-dione-2-ium salt (**10**)*

Mixture of compound **4** (2.38 g, 0.01 mol) and methyl iodide (1.42 g, 0.01 mol) was dissolved in ethanol (20 ml). The reaction mixture was refluxed for 2 h on water bath, filtered hot and cooled. The precipitated solid, after dilution with water, was collected and crystallized from ethanol to give a deep brown powder. m.p. 140–142 °C, yield = 80%.

Analytical data for $C_{15}H_{13}N_2O_2I$ (mol. wt. 380): Calcd %: C = 47.37, H = 3.42, N = 7.37; Found %: C = 47.35, H = 3.40, N = 7.36.

*2.10. Synthesis of 1-phenyl-benzo[4,5-b] pyrazolo-4,7-dione-3[4(1)]-monomethine cyanine dyes (**11a–c**)*

Mixture of compound **5** (0.295 g, 0.001 mol) and *N*-methyl heterocyclic quaternary salts (pyridinium, quinolinium and isoquinolinium) iodide (0.001 mol) was dissolved in ethanol (20 ml), and a few drops of piperidine were added. The reaction mixture was refluxed for 12 h, filtered hot, cooled and acidified with acetic acid. The precipitated solid, after dilution with water was collected and crystallized from ethanol to give the corresponding compounds **11a–c**. Characterization data are listed in Table 1.

*2.11. Synthesis of 3-[diethoxyethane]-1-phenyl-benzo[4,5-b]pyrazolo-2-ium salt (**12**)*

Mixture of compound **10** (3.80 g, 0.01 mol) and ethylorthoformate (1.33 g, 0.01 mol) was dissolved in ethanol (20 ml) and a few drops of piperidine were added. The reaction mixture was refluxed for 5 h, filtered hot, cooled, and acidified with acetic acid. The precipitated products, after dilution with water, were collected and crystallized from ethanol to give a red powder. m.p. 140–142 °C, yield = 60%.

Analytical data for $C_{20}H_{23}N_2O_4I$ (mol. wt. 482): Calcd %: C = 49.79, H = 4.77, N = 5.81; Found %: C = 49.78, H = 4.76, N = 5.80.

*2.12. Synthesis of 1-phenyl-benzo[4,5-b] pyrazolo-4,7-dione-3[2(4)]-trimethine cyanine dyes (**13a–c**)*

Mixture of compound **12** (0.48 g, 0.001 mol) and 2(4)-methyl heterocyclic quaternary salts

Table 1
Characterization data of the newly synthesized cyanine dyes

Compd. no.	Mol. formula (mol. wt.)	Calcd. %, Found %			Yield %	m.p., °C	IR ($\nu^{KBr}{}_{max}$), cm^{-1}	^{1}H-NMR ($CDCl_3$)	M$^+$
		C	H	N				δ, ppm, Assignment	
6a	$C_{16}H_{12}N_3O_3CuCl$ (393)	48.85 48.73	3.05 3.29	10.69 10.7	70	250–252	1497 (C=N), 1590 (C=C), 1681 (C=O quinone), 510 (M–O), 2923 (heterocyclic metal chelate)	1.14 (s, 3H, CH_3 pyrazol), 3.10 (s, 3H, CH_3, heterocyclic metal chelate), 7.27–7.92 (m, 6H, Ar-H + Het-H + NH)	393
6b	$C_{16}H_{12}N_3O_3NiCl$ (388)	49.46 49.41	4.07 4.12	10.85 10.89	80	250–253	1492 (C=N), 1585 (C=C), 1681 (C=O quinone), 515 (M–O), 2923 (heterocyclic metal chelate)	1.14 (s, 3H, CH_3 pyrazol), 3.10 (s, 3H, CH_3 heterocyclic metal chelate), 7.27–7.92 (m, 6H, Ar-H + Het-H+ NH)	
6c	$C_{16}H_{12}N_3O_3CoCl$ (388)	49.42 49.3	3.09 3.15	10.82 10.86	75	250–252			389
7a	$C_{22}H_{17}N_4O_3CoI$ (571)	46.23 46.20	2.98 2.95	9.81 9.79	62	140–143	1496 (C=N), 1594 (C=C), 1688 (C=O quinone), 512 (M–O), 2920 (CH_3N^+I)	1.15 (s, 3H, $CH_{3,}$ pyrazol), 3.85 (s, 3H, CH_3N^+), 7.25–7.90 (m, 11H, Ar-H + Het-H + =CH + NH)	572
7b	$C_{26}H_{19}N_4\ O_3CoI$ (621)	50.24 50.21	3.06 3.02	9.02 9.04	55	134–136	1490 (C=N), 1593 (C=C), 1688 (C=O quinone), 523 (M–O), 2920 (CH_3N^+I)	1.15 (s, 3H, CH_3, pyrazol), 3.95 (s, 3H, CH_3N^+), 7.25–7.90 (m, 13H, Ar-H + Het-H+ =CH + NH)	
7c	$C_{26}H_{19}N_4\ O_3CoI$ (621)	50.24 50.22	3.06 3.03	9.02 9.00	42	132–133	1494 (C=N), 1598 (C=C), 1687 (C=O quinone), 530 (M–O), 2920 (CH_3N^+I)	1.15 (s, 3H, CH_3, pyrazol), 3.95 (s, 3H, CH_3N^+), 7.25–7.90 (m, 13H, Ar-H + Het-H + =CH + NH)	
7d	$C_{26}H_{19}N_4\ O_3CuI$ (625)	49.88 49.86	3.04 3.01	8.95 8.93	40	140–141			627
7e	$C_{26}H_{19}N_4\ O_3CoI$ (620.69)	50.27 50.11	3.06 3.23	9.02 9.13	55	157–159	1494 (C=N), 1598 (C=C), 1687 (C=O quinone), 530 (M–O), 2920 (CH_3N^+I)	1.15 (s, 3H, CH_3, pyrazol), 3.95 (s, 3H, CH_3N^+), 7.25–7.90 (m, 13H, Ar-H + Het-H + =CH + NH)	622
8a	$C_{23}H_{21}N_4\ O_2I$ (512)	53.91 53.89	4.10 4.07	10.94 10.90	51	130–132	1495 (C=N), 1588 (C=C), 1688 (C=O quinone), 2920 (CH_3N^+I)	1.16 (s, 3H, CH_3, pyrazol), 3.95 (s, 3H, CH_3N^+), 1.90 (s, 3H, CH_3–), 6.55–8.00 (m, 10H, Ar-H + Het-H + CH=), 8.75 (s, 2H, NH_2)	512
8b	$C_{27}H_{23}N_4\ O_2I$ (562)	57.62 57.59	4.09 4.12	9.96 9.92	73	160–163	1493 (C=N),1586 (C=C), 1688 (C=O), 2927 (CH_3N^+I)	1.16 (s, 3H, CH_3, pyrazol), 3.95 (s, 3H, CH_3N^+), 1.90 (s, 3H, CH_3–), 6.55–8.00 (m, 12H, Ar-H + Het-H + CH=), 8.75 (s, 2H, NH_2)	

8c	$C_{23}H_{21}N_4O_2I$ (512)	53.91 53.57	4.10 4.08	10.94 10.88	56	133–135			513
9a	$C_{30}H_{27}N_4O_2I$ (602)	59.80 59.77	4.49 4.46	9.30 9.28	44	132–133	1499 (C=N), 1598 (C=C), 1681 (C=O quinone), 2929 (CH_3N^+I)	1.15 (s, 3H, CH_3, pyrazol), 3.90 (s, 3H, CH_3N^+), 2.00 (s, 3H, CH_3N), 1.80 (s, 3H, CH_3–C=CH), 7.20–8.00 (m, 15H, Ar-H + Het-H + =CH)	602
9b	$C_{38}H_{31}N_4O_2I$ (702)	64.96 64.90	4.42 4.38	7.98 7.94	84	160–163	1492 (C=N), 1590 (C=C), 1687 (C=O quinone), 2920 (CH_3N^+I)	1.15 (s, 3H, CH_3, pyrazol), 3.90 (s, 3H, CH_3N^+), 2.00 (s, 3H, CH_3N), 1.80 (s, 3H, CH_3–C=CH), 7.20–8.00 (m, 19H, Ar-H + Het-H + =CH)	
9c	$C_{30}H_{27}N_4O_2I$ (602)	59.80 59.75	4.49 4.47	9.30 9.27	49	138–140			603
9d	$C_{30}H_{27}N_4O_2I$ (602)	59.80 59.77	4.49 4.45	9.30 9.26	40	135–137	1499 (C=N), 1598 (C=C), 1681 (C=O quinone), 2929 (CH_3N^+I)	1.15 (s, 3H, CH_3, pyrazol), 3.90 (s, 3H, CH_3N^+), 2.00 (s, 3H, CH_3N), 1.80 (s, 3H, CH_3–C=CH), 7.20–8.00 (m, 15H, Ar-H + Het-H + =CH)	
11a	$C_{19}H_{18}N_3O_2I$ (447)	51.01 51.03	4.03 3.06	9.40 9.36	50	250–252	1490 (C=N), 1586 (C=C), 1681 (C=O quinone), 2922(CH_3N^+I)	2.10 (s, 3H, CH_3N), 3.95 (s, 3H, CH_3N^+), 6.70–7.95 (m, 12H, Ar-H + Het-H + =CH)	
11b	$C_{23}H_{20}N_3O_2I$ (497)	55.53 55.50	4.02 4.08	8.45 8.44	75	160–161	1491 (C=N), 587 (C=C), 1683 (C=O quinone), 2926 (CH_3N^+I)	2.10 (s, 3H, CH_3N), 3.95 (s, 3H, CH_3 N^+), 6.65–7.95 (m, 14H, Ar-H + Het-H + =CH)	498
11c	$C_{23}H_{20}N_3O_2I$ (497)	55.53 55.55	4.02 4.06	8.45 8.48	49	250–252			497
13a	$C_{22}H_{20}N_3O_2I$ (485)	54.43 54.42	4.12 4.14	8.66 8.64	44	134–136	1495 (C=N), 1584 (conjugated cyclic C=C), 1689 (C=O quinone), 2922 (CH_3N^+I)	2.15 (s, 3H, CH_3N), 3.90 (s, 3H, CH_3N^+), 6.70–7.95 (m, 14H, Ar-H + Het-H + =CH)	486
13b	$C_{26}H_{22}N_3O_2I$ (535)	58.32 58.30	4.11 4.13	7.85 7.80	59	140–142	1493 (C=N), 1585 (conjugated cyclic C=C), 1689 (C=O quinone), 2921 (CH_3N^+I)	2.15 (s, 3H, CH_3N), 3.90 (s, 3H, CH_3N^+), 6.70–7.95 (m, 16H, Ar-H + Het-H + =CH)	
13c	$C_{22}H_{20}N_3O_3I$ (485)	54.43 54.40	4.12 4.16	8.66 8.62	42	132–134			485

(α-picoline, quinaldine and γ-picoline) iodide (0.001 mol) was dissolved in ethanol (20 ml) and a few drops of piperidine were added. The reaction mixture was refluxed for 10 h, filtered hot, cooled, and acidified with acetic acid. The precipitated products, after dilution with water, were collected and crystallized from ethanol to give the corresponding compound **13a–c**. Characterization data are listed in Table 1.

3. Results and discussion

3.1. Synthesis

4-acetyl-3-methyl-1-phenylpyrazol-5-one (**1**), [12] was oxidized with an equimolar amount of selenium dioxide in 1,4-dioxane to form 3-methyl-(5-oxo-1-phenyl-4,5-dihydro-1H-pyrazol-4-yl)-oxo-acetaldehyde (**2**). Condensation of compound **2** with equimolar amount of acetaldehyde in acetic acid gave 3-methyl-1-phenylpyrazol-5-one-4-(oxo-but-2-ene aldehyde) (**3**), that at 130 °C and in the presence of catalytic quantity of piperidine, underwent ring closing of compound **3** involving a dehydration process to give 3-methyl-1-phenyl-benzo[4,5-b]pyrazolo-4,7-dione (**4**) (Scheme 1).

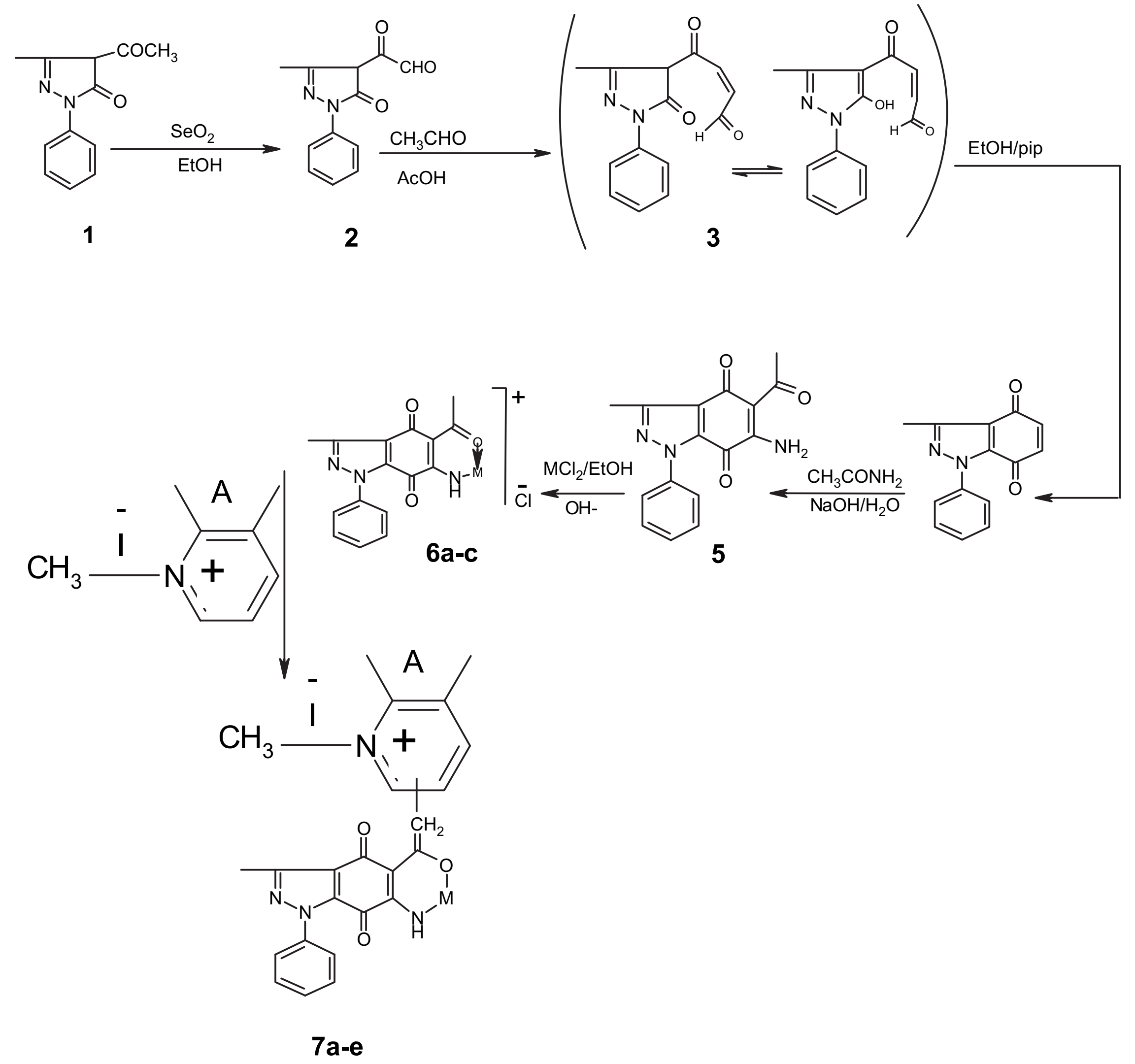
Structures of compounds **2–4** were established on analytical and spectral data. IR spectra [13] showed general absorption bands at 1497 cm^{-1} (ν C=N), 1594 cm^{-1} (ν C=C) and specific band 1711 cm^{-1} (ν CHO) for compound **2**, 1690 cm^{-1} (ν CH=CH–CHO) for compound **3** and 1670 cm^{-1} (ν quinone ring) for compound **4**. ^{1}H-NMR ($CDCl_3$ 250 MHz) [14] of compounds **2–4** showed signals at 9.50 ppm (s, 1H, CHO), 1.11 ppm (s, 3H, CH_3), 6.75–7.95 ppm (m, 6H, Ar-H + Het-H, pyrazole ring) for compound **2**, 1.13 ppm (s, 3H, CH_3 pyrazol), 6.76–7.85 ppm (m, 8H, Ar-H + Het-H of pyrazole ring) and 9.50 ppm (s, 1H, CHO) for compound **3** and no signal of CHO group for compound **4**. Mass spectroscopy (m/z) of the latter compounds are $m/z = 231$, 256 and 239 for compounds (**2**), (**3**) and (**4**), respectively.

The reaction of 3-methyl-1-phenyl-benzo[4,5-b] pyrazolo-4,7-dione (**4**) with acetamide in the presence of sodium hydroxide resulted in 5-acetyl-6-amino-3-methyl-1-phenyl-benzo[4,5-b]pyrazolo-4,7-dione compound (**5**), whose reaction in ethanol with an equivalent amount of metal divalent chlorides ($CuCl_2$, $NiCl_2$, $CoCl_2$) and in sodium hydroxide as catalyst afforded the desired 3,5-dimethyl-8-metalo-1-phenyl-benzo[4,5-b;4′,5′-b′] pyrazolo-oxazino-4,9-dione ylide chloride compounds (**6a–c**). Structure of compound (**5**) was established based on analytical and spectral data. IR spectra [13] of **5** reveal absorption bands 1498 cm^{-1} (C=N), 1690 cm^{-1} (conjugated cyclic or acyclic C=O), and 3400 cm^{-1} (spreading NH_2). ^{1}H-NMR ($CDCl_3$, 250 MHz) 1.35 ppm (s, 3H, CH_3), 1.14 ppm (s, 3H, CH_3 of pyrazol), 7.2–8.50 ppm (m, 7H, Ar-H + NH_2). The EI-mass spectrum of compound **5** did not exhibit a molecular ion peak $[M]^+$, however auxiliary peak was found at $m/z = 279$ $[M - NH_2]^+$.

Reaction of equimolar ratios of compounds **6a–c** with *N*-methylpyridinium, *N*-methylquinolinium and *N*-methylisoquinolinium iodide in the presence of piperidine as basic catalyst and ethanol as solvent afforded the desired 3-methyl-8-metalo-1-phenyl-benzo[4,5-b;4′,5′-b′]pyrazolo-oxazino-4, 9-dione-5[4(1)] monomethine cyanine dyes (**7a–e**). The reaction was suggested to proceed through oxidative elimination followed by rearrangement with dehydrohalogenated HCl to give compounds (**7a–e**) [15] (Scheme 1). The structure of compounds (**6a–c**) and (**7a–e**) was confirmed by analytical and spectral data, reported in Table 1.

The desired 6-amino-3,5-dimethyl-1-phenyl-benzo[4,5-b; 4′,5′-b′]pyrazolo-4,7-dione-5[4(1)]-meso-substituted-5[2(4)]-dimethine cyanine dyes **8a–c** and meso-substituted-5,6[2(4)]-pentamethine cyanine dyes compounds **9a–d**, were obtained under thermal condition by reaction of equi (bi) molar ratios of compound **5** with 2(4)-methyl quaternary salts of α-picoline, quinaldine and γ-picoline methiodide in ethanol as solvent solution, respectively (Scheme 2). The structure of compounds (**8b**) and (**9b**) was confirmed by analytical data and spectral data (Table 1).

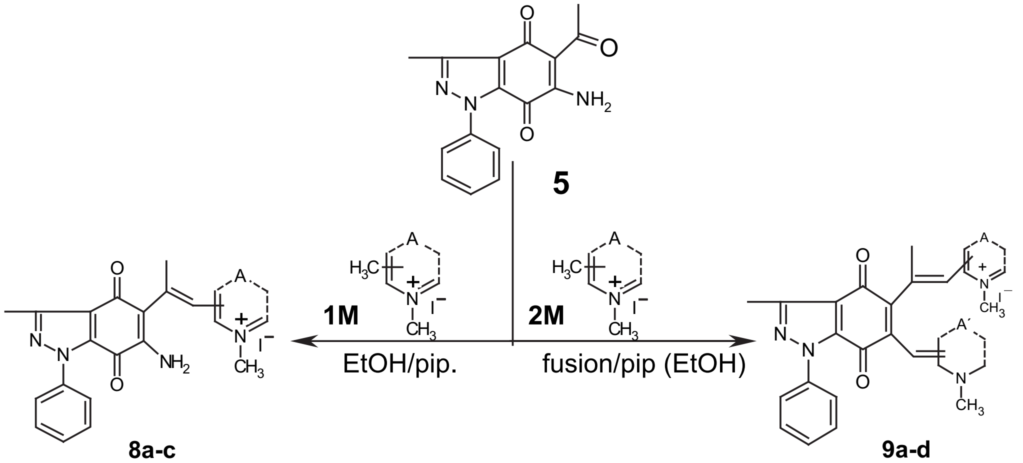
Quaternization of compound **4** by reaction with equimolar amounts of methyl iodide gave the corresponding 3-methyl-1-phenyl-benzo[4,5-b]



Scheme 1. (**6a–c**): M = Cu^{++} (a), M = Co^{++} (b), M = Ni^{++} (c). (**7a–e**): A = *N*-methylpyridin-4-ium, M = Co^{++} (a), A = *N*-methylquinolin-4-ium, M = Co^{++} (b), A = *N*-methylisoquinolin-1-ium, M = Co^{++} (c), A = *N*-methylquinolin-4-ium, M = Cu^{++} (d), A = *N*-methylquinolin-4-ium, M = Ni^{++} (e).

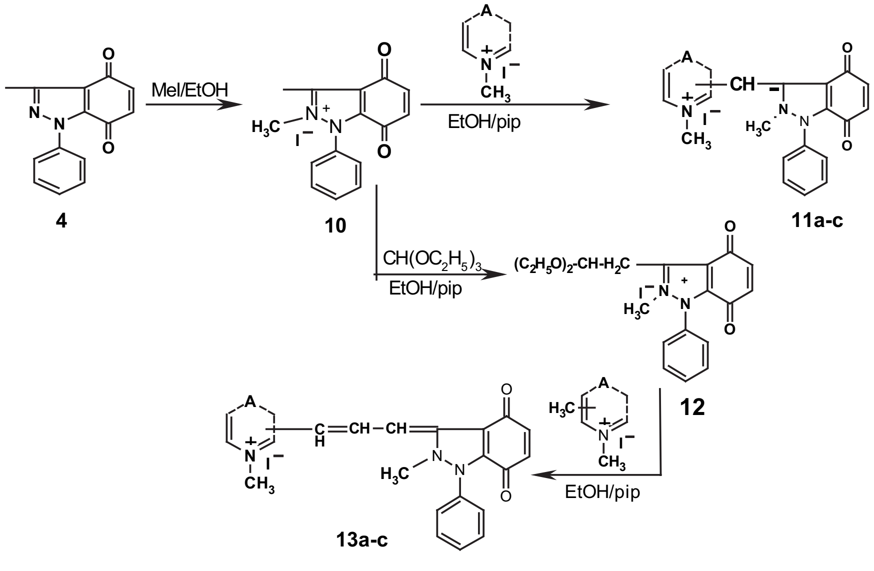
pyrazolo-4,7-dione-2-ium salt compound (**10**) (Scheme 3). IR spectra [13] of **10** reveal absorption bands 1497 cm^{-1} (C=N), 1718 cm^{-1} (C=O) and 2923 cm^{-1} (CH_3I). ^{1}H-NMR ($CDCl_3$, 250 MHz) 1.13 ppm (s, 3H, CH_3), 3.95 ppm (s, 3H, CH_3N) and 7.19–7.80 ppm (m, 7H Ar-H) and mass spectra $(m/z) = 381$.

Reaction of equimolar ratios of salt **10** with *N*-methylpyridinium, *N*-methylquinolimium and *N*-methylisoquinolinium iodide in the presence of piperidine as basic catalyst and ethanol as solvent formed the desired 1-phenyl-benzo[4,5-b] pyrazolo-4,7-dione 3[4(1)]-monomethine cyanine dyes **11a–c**. The reaction was suggested to proceed through oxidative elimination followed by rearrangement with dehydrohalogenated HI to give compounds (**11a–c**) [15] (Scheme 3) while reacting of equimolar amounts of salt **10** with ethylorthoformate in the same conditions afforded the intermediate salt **12**. IR spectra [13] of **12**



Scheme 2. (**8a–c**): A = 1-methylpyridin-2-ium (a), A = 1-methylquinolin-2-ium (b), A = 1-methylpyridin-4-ium (c). (**9a–c**): A = A′ = 1-methylpyridin-2-ium (a), A = A′ = 1-methylquinolin-2-ium (b), A = A′ = 1-methylpyridin-4-ium (c), A = 1-methylpyridin-4-ium, A′ = 1-methylpyridin-2-ium (d).

reveal absorption bands of 1594 cm^{-1} (conjugated cyclic C=C), 1491 cm^{-1} (cyclic C=C), 1718 cm^{-1} (C=O), 2923 cm^{-1} (heterocyclic quaternary salt) and 1070–1253 cm^{-1} (OEt). ^{1}H-NMR ($CDCl_3$, 250 MHz) 1.21 ppm (d, 2H, CH_2, pyrazole), 1.51 ppm (t, 6H, $2CH_3$–), 1.90 ppm (q, 4H, $2CH_2$–), 3.11 ppm (t, 1H, CH) and 7.10–7.95 ppm (m, 8H, Ar-H + Het-H) and mass spectra $(m/z) = 482$. Further reaction of intermediate **12** with 2(4)-methyl heterocyclic quaternary salts of α- or γ-picolines and quinaldine methiodide gave the corresponding 1-phenylbenzo[4,5-b]pyrazolo-4,7-dione-3[2(4)]-trimethine cyanine dyes compounds **13a–c** (Scheme 3). The structures of



Scheme 3. (**11a–c**): A = *N*-methylpyridin-4-ium (a), A = *N*-methyl quinolin-4-ium, (b), A = *N*-methyl isoquinolin-1-ium (c). (**13a–c**): A = 1-methylpyridin-2-ium (a), A = 1-methylquinolin-2-ium (b), A = 1-methylpyridin-4-ium (c).

compounds (**11a–c**), (**12**) and (**13a–c**) were confirmed by analytical data (Table 1).

3.2. *Electronic absorption spectra of the newly synthesized cyanine dyes*

The electronic absorption spectral features (λ_{max} and ϵ_{max} values) of the newly synthesized cyanine dyes **7a–e, 8a–c**, **9a–d, 11a–c**, and **13a–c** in ethanol (alochromic behaviour) solution are shown in Table 2, and Figs. 1–5. The visible absorption maxima of the newly synthesized cyanine dyes in ethanol undergo bathochromic or hypsochromic shift depending on the nature of heterocyclic quaternary residue A, their linkage position and metal divalent moieties M. Thus, substitution of A = *N*-methylpyridin-4-ium in compound **7a** by A = *N*-methylquinolin-4-ium in compound **7b** resulted in a bathochromic shift of 35 nm for the increasing of π-conjugation in quinolin-4-ium moiety. Analogously, changing the linkage position of quinoline residue from quinolin-1-ium in compound **7c** to quinolin-4-ium in compound **7b** resulted in a bathochromic shift of 25 nm. This could be attributed to the more

Table 2
The visible absorption spectra of newly synthesized cyanine dyes in 95% EtOH

λ_{max} (nm)/log ε_{max} (mol^{-1} cm^{-1})				
Monomethine cyanine dyes **7a–e**				
7a	**7b**	**7c**	**7d**	**7e**
475 (3.36)	495 (3.26)	485 (3.29)	465 (3.34)	510 (3.28)
Meso-substituted dimethine cyanine dyes **8a–c**				
8a	**8b**	**8c**		
–	510 (4.13)			
–	–	500 (3.91)		
	545 (4.16)			
535 (3.46)	665 (3.40)	620 (3.09)		
–				
Meso-substituted pentamethine cyanine dyes **9a–c**				
9a	**9b**	**9c**	**9d**	
–	440 (4.28)	–	–	
515 (3.43)	525 (3.39)	530 (3.45)	530 (3.44)	
–	555 (3.43)	580 (3.09)	–	
–	695 (2.56)	–	–	
Monomethine cyanine dyes **11a–c**				
11a	**11b**	**11c**		
425 (3.29)	480 (3.13)	455 (3.35)		
Trimethine cyanine cyanine dyes **13a–c**				
13a	**13b**	**13c**		
500 (3.43)	500 (3.43)	–		
525 (3.34)	530 (3.45)	520 (3.44)		
–	670 (2.64)	610 (2.85)		

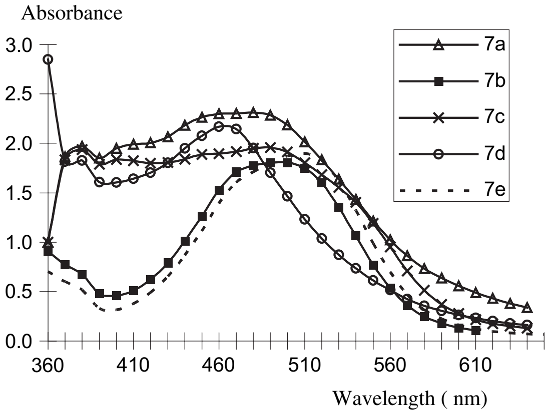


Fig. 1. Absorption spectra of monomethine cyanine dyes (**7a–e**) in ethanol solution in 360–630 nm wavelength range.

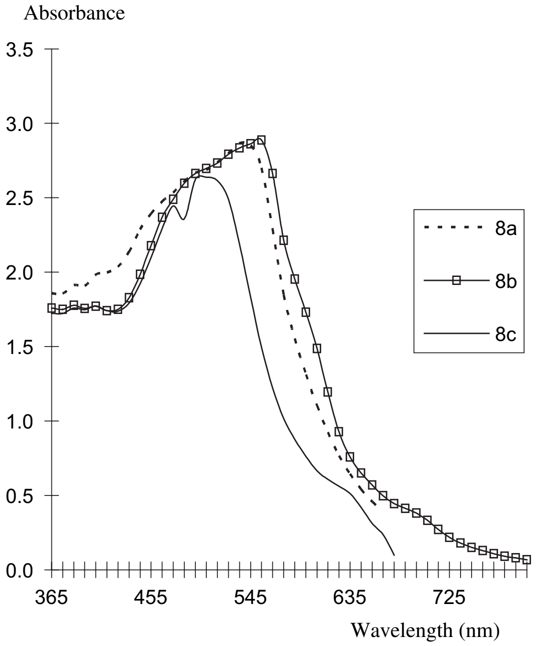


Fig. 2. Absorption spectra of dimethine cyanine dyes (**8a–c**) in ethanol solution in 365–765 nm wavelength range.

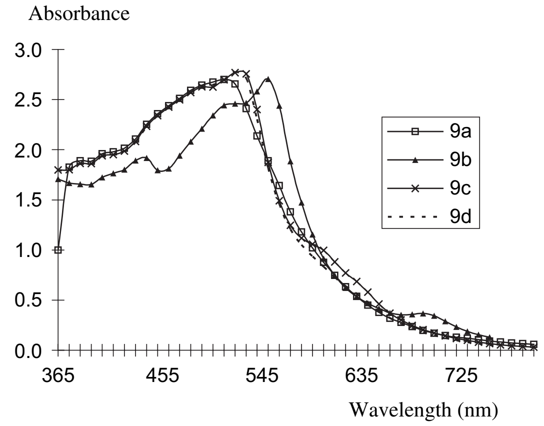


Fig. 3. Absorption spectra of pentamethine cyanine dyes (**9a–d**) in ethanol solution in 365–765 nm wavelength range.

extensive π-conjugation within quinolin-4-ium rather than quinolin-1-ium moieties.

Additionally, the visible absorption maxima are influenced by metal divalent moieties M. Thus, substitution of $M = Co^{++}$ in compound **7b** with $M = Ni^{++}$ in compound **7e** and $M = Cu^{++}$ in compound **7d** caused a bathochromic shift of 30 nm and 45 nm, respectively. This is due to the vacant orbital, which increases gradually from copper to cobalt leading to the more extensive π-conjugation in compounds **7b** and **7e** (Fig. 1).

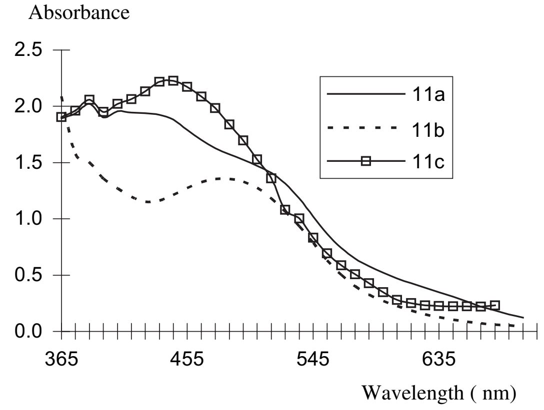


Fig. 4. Absorption spectra of monomethine cyanine dyes (**11a–c**) in ethanol solution in 365–665 nm wavelength range.

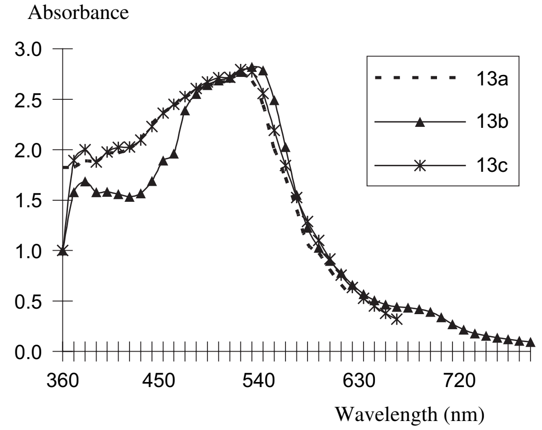


Fig. 5. Absorption spectra of trimethine cyanine dyes (**13a–c**) in ethanol solution in 365–765 nm wavelength range.

The visible absorption maxima of 6-amino-3,5-dimethyl-1-phenyl-benzo[4,5-b;4′,5′-b′] pyrazolo-4,7-dione-5[4(1)]-meso-substituted-5[2(4)]-dimethine cyanine dyes compounds (**8a–c**) are influenced by heterocyclic quaternary salts residue, A. Thus, the substitution of A = 1-methylpyridin-2-ium in compound **8a** by A = 1-methylquinolin-2-ium in compound **8b** causes a bathochromic shift of 10 nm with the appearance of an absorption and a shoulder at 510 nm and 660 nm, respectively. This could be attributed to the more extensive π-conjugation in compound **8b**. Analogously, changing the linkage position of pyridine residue from pyridin-2-ium in compound **8a** to pyridin-4-ium in compound **8c** a new shoulder at 620 nm appeared for the increasing, more extensive π-conjugation in pyridin-4-ium than pyridin-2-ium moieties (Fig. 2).

Quaternary residues A, A′ and their linkage position influence in the visible absorption maxima of meso-substituted-5,6[2(4)]-pentamethine cyanine dyes **9a–d**. Thus, the substitution of A = *N*-methylpyridine, A′ = 1-methylpyridin-2-ium in compound **9a** by A = *N*-methylquinoline, A′ = 1-methylquinolin-2-ium in compound **9b** causes a bathochromic shift of 10 nm with the appearance of new absorption bands at 440, 555 and 695 nm, respectively. This could be attributed to the more extensive π-conjugation in quinolin-2-ium moiety. Changing the linkage position of the pyridine residue from pyridin-2-ium in compound **9a** to pyridin-4-ium in compound **9c** a bathochromic shift of 15 nm resulted with the appearance of a new absorption band with $\lambda_{max} = 580$ nm. This is due to the more extensive π-conjugation in pyridin-4-ium than pyridin-2-ium moieties (Fig. 3).

The visible absorption maxima of 1-phenylbenzo[4,5-b]pyrazolo-4,7-dione 3[4(1)]-monomethine cyanine dyes **11a–c** are influenced by the nature of the quaternary residue A and their linkage position. Thus, substitution of A = *N*-methylpyridin-4-ium in compound (**11a**) by A = *N*-methylquinolin-4-ium in compound **11b** resulted in a bathochromic shift of the shorter and longer wavelength 350–700 nm of 70 and 25 nm, respectively for the more extensive π-conjugation in quinolin-4-ium moiety. Also, changing the linkage position of quinoline residue from *N*-methylisoquinolin-1-ium in compound **11c** to *N*-methylquinolin-4-ium in compound **11b** causes a bathochromic shift of 45 nm. This is due to the more extensive π-conjugation in quinolin-4-ium moiety (Fig. 4).

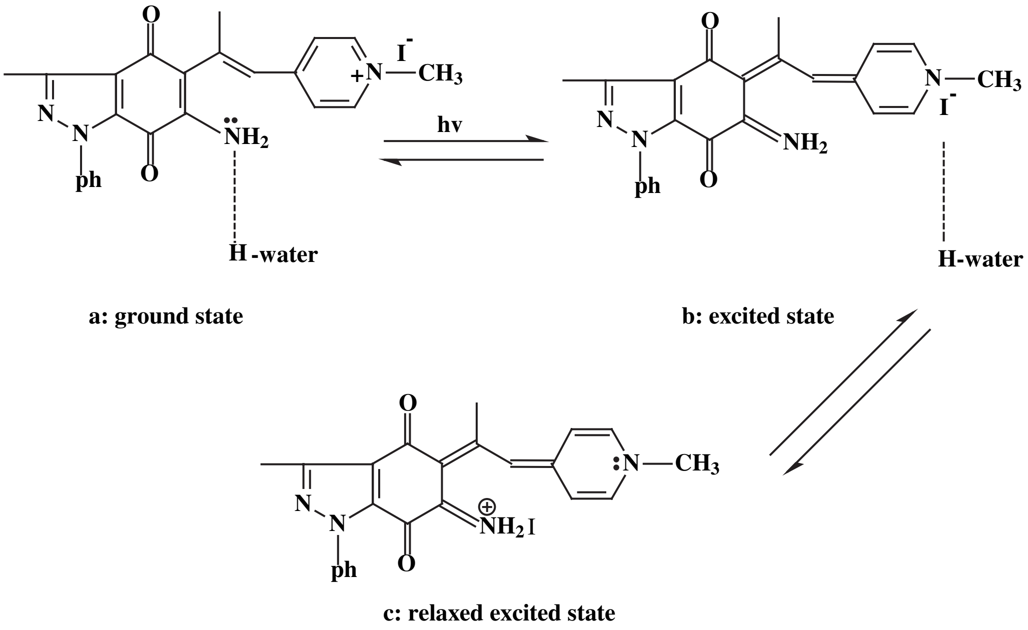
The visible absorption maxima of 1-phenylbenzo[4,5-b]pyrazolo-4,7-dione-3[2(4)]-trimethine cyanine dyes **13a–c** are influenced by the nature of the quaternary residue A and their linkage position. Thus, substitution of A = 1-methylpyridin-2-ium in compound **13a** by A = 1-methylquinolin-2-ium in compound **13b** resulted in a bathochromic shift of the longer wavelength at 530 nm of 5 nm with the appearance of longer shoulder of absorption band at 670 nm. This is due to the increasing π-conjugation. Also, changing the linkage position from pyridin-2-ium in compound **13a** to pyridin-4-ium in compound **13c** resulted in the appearance of a new shoulder in the absorption band at 610 nm. This is due to the more extensive π-conjugation in pyridin-4-ium rather than pyridin -2-ium moieties (Fig. 5).

3.3. Aquachromic behaviour of a selected series of cyanine dyes in water at 27 °C

The electronic absorption spectra of some selected cyanine dyes **8b**, **8c**, **11b** and **13b** in 350–700 nm wavelength range, have been studied in water as aquachromic behaviour. These dyes show hypsochromic shift with water with respect to ethanol. The visible spectra of dyes **8b**, **8c**, **11b** and **13b** in water are at $\lambda_{max} = 495$, 475, 455 and 495 nm, respectively. Meanwhile, these dyes in ethanol reveal absorption bands at $\lambda_{max} = 510$, 545, 665 nm for dye (**8b**), $\lambda_{max} = 500$, 620 nm for dye (**8c**), $\lambda_{max} = 480$ nm for dye (**11b**) and $\lambda_{max} = 500$, 530, 670 nm for dye (**13b**). The hypsochromic shift of these dyes is caused by strong hydrogen-bonding of water which stabilized structure **a** (Scheme 4) and thereby the electron-donating ability of the nitrogen. In addition the intramolecular charge transfer (ICT) interaction with the pyridinium moiety decreases. In the excited state, hydrogen-bonding takes place between water and iodide ions and stabilizes structure **b** and prevents its conversion to the structure **c** (Scheme 4). The energy gap between the excited state and the relaxed excited state is small and increases with a decrease in the polarity of the solvents.

3.4. Acid–base properties of a selected series of cyanine dyes

Aqueous solutions of here reported cyanine dyes gave permanent colours in neutral and basic media but worked decoloration was observed in acid conditions. This prompted us to study the behaviour of such dyes in different aqueous universal buffer solutions (pH range: 1.98–11.98) in order to ensure the optimal pH in the application of these dyes as photosensitizers. The effectiveness of the compounds as photosensitizers increases when they are present in ionic form, which has higher planarity [16–19]. The electronic absorption spectra of cyanine dyes **8b**, **8c**, **9a**, and **13b**, were taken as examples of relative series, in universal buffer solutions. Thus, in acid medium dyes **8b**, **8c**, and **9a**, and **13b** undergo a hypsochromic colour change due to the protonation of the amino group nitrogen atom (in dyes **8b** and **8c**) or of the heterocyclic nitrogen atom (in dyes **9a** and **13b**). In such cases, the intramolecular charge transfer (CT) between the amino group



Scheme 4. Mesomeric structure of dye (**8a**) in water as aquachromic behaviour.

(or heterocyclic) donor nitrogen and heterocyclic acceptor nitrogen atoms does not occur, and long wavelength CT band disappears. A new short wavelength band is observed, which could be assigned to a localized π–π^* transition (Figs. 6–9).

The spectrophotometric determination of pk_a values of these dyes can be performed through the variation of the absorbance with solution pH according to Colleter method [20–23]. The pk_a values of dyes, taken as examples **8b**, p$k_a = 4$, **8c**, p$k_a = 4$, **9a**, p$k_a = 10.02$ and **13b**, p$k_a = 3.63$

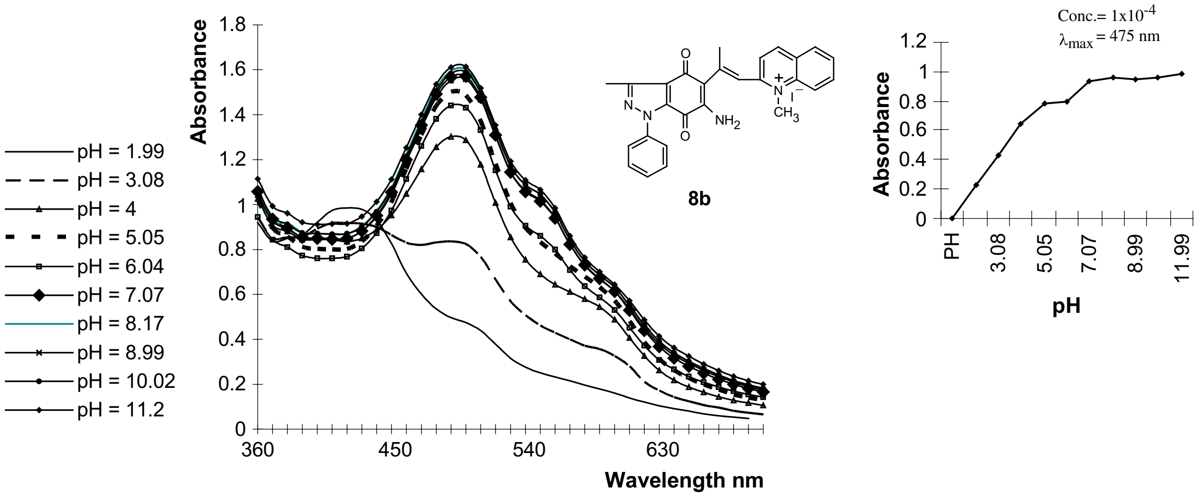


Fig. 6. Absorption spectra of compound (**8b**) in universal buffer solutions and pk_a curve.

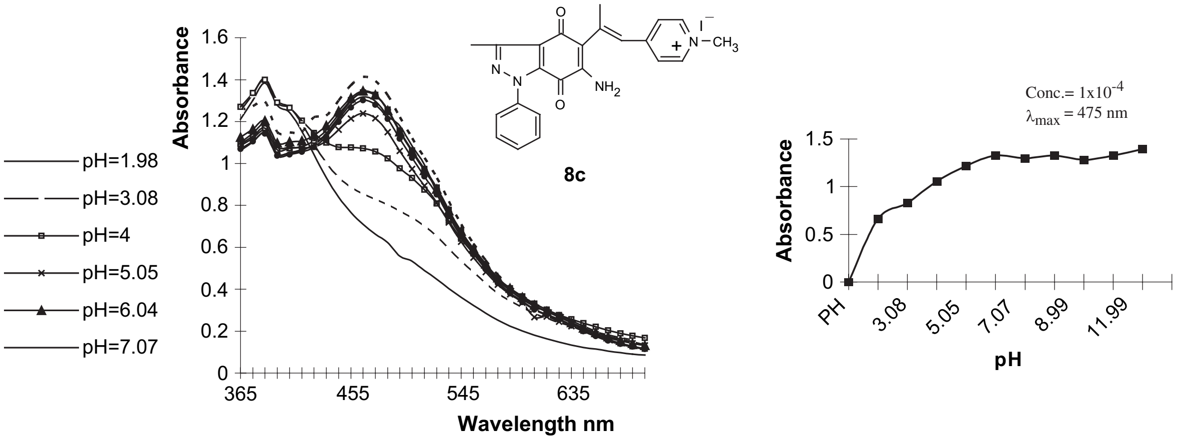


Fig. 7. Absorption spectra of compound (**8c**) in universal buffer solutions and pk_a curve.

depend upon the nature of heterocyclic quaternary salts.

4. Conclusion

An efficient six-step synthesis of the precursors of new cyanine dyes is presented. The absorption spectra of the newly synthesized cyanine dyes were investigated in ethanol as alochromic behaviour. The results indicated that the absorption spectra of these dyes undergo batho (hypso) chromic shift depending on the type of both heterocyclic quaternary residue A and metal complex. The absorption spectra of some selected dyes in water as aquachromic behaviour showed hypsochromic shift to the formation of hydrogen-bonding with water. The acid–base

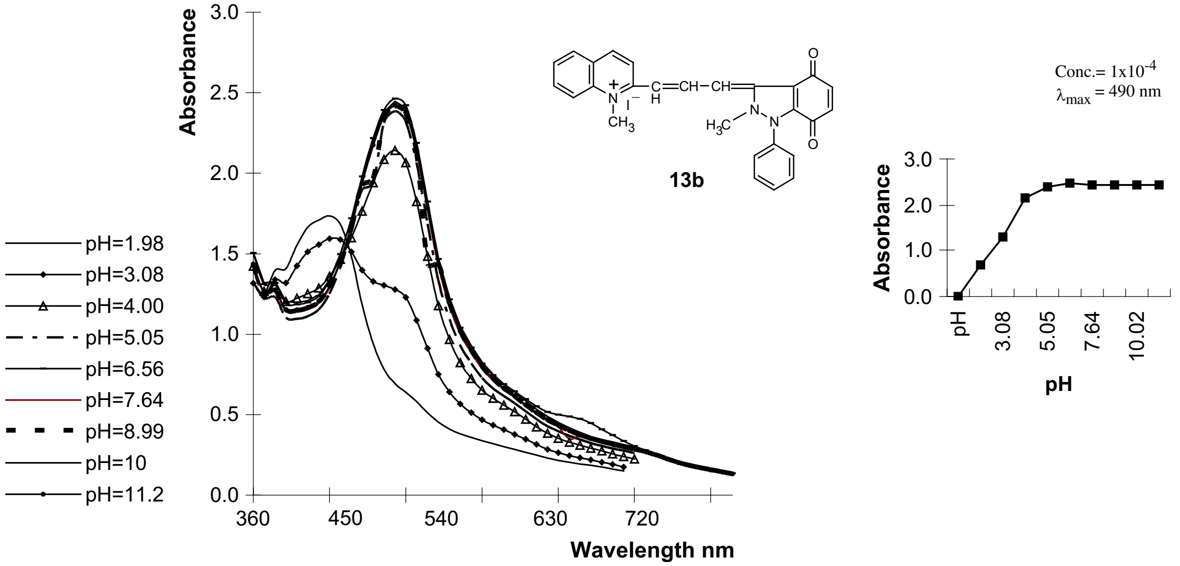


Fig. 8. Absorption spectra of compound (**9a**) in universal buffer solutions and pk_a curve.

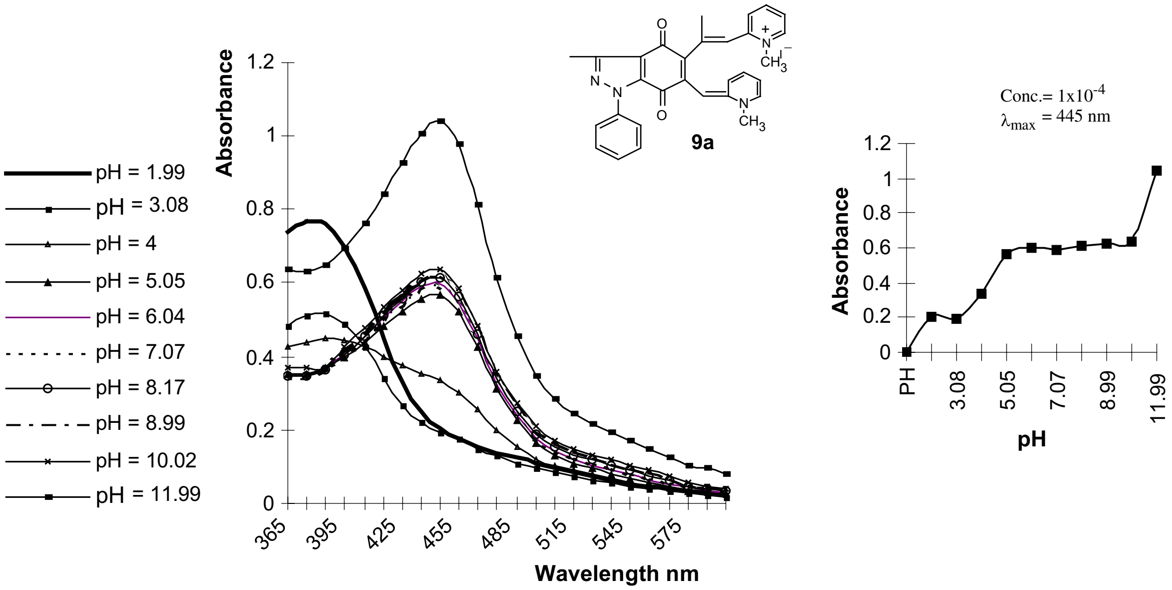


Fig. 9. Absorption spectra of compound (**13b**) in universal buffer solutions and pk_a curve.

properties of some selected dyes indicated that these dyes are useful for photosensitizers in both acid and base medium.

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