



Novel pyrazolo pyrazoly heterocyclic in the synthesis of positive solvatochromic cyanine dyes

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ABSTRACT

Novel cyanine dyes monomethine, bismonomethine and trimethine cyanine dyes were synthesized from 5-hydroxy-2-(5-hydroxy-3-methyl-1-phenyl-4,5-dihydro-1H-pyrazol-4-yl)-3-methyl-1-phenyl-4,5-dihydro-1H-pyrazol-2-ium as a nucleus. Structure confirmed by elemental analysis, IR, ¹H-NMR, mass and visible was determined. The electronic visible absorption spectra of all the newly synthesized cyanine dyes were investigated in 95% ethanol solution. Solvatochromism for the newly prepared cyanine dyes were performed in pure solvents having different polarities.

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Capsule Summary: Novel cyanine dyes have been synthesized and their visible and solvatochromism properties were investigated.

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INTRODUCTION

Cyanine dyes are cationic molecules in which two terminal nitrogen heterocyclic subunits are linked by a polymethine bridge which have been extensively used in wide range of applications, such as laser, bioanalysis and imaging of DNA and antitumor agent (Parvaathy, et al., 2015, Kazuhide, et al., 2016, Fadda and Rasha, 2013). Different methods and heterocyclic moieties were used for synthesis of various types of cyanine dyes that have extensively used as photosensitizers, optical recording, storage media, solar cell and semiconducting material (Abdel Aal et al., 2012, Fadda and Rasha 2015, Ansari et al., 2014, Owens et al., 2014, Giu, et al. 2016, Sandra et al., 2015).

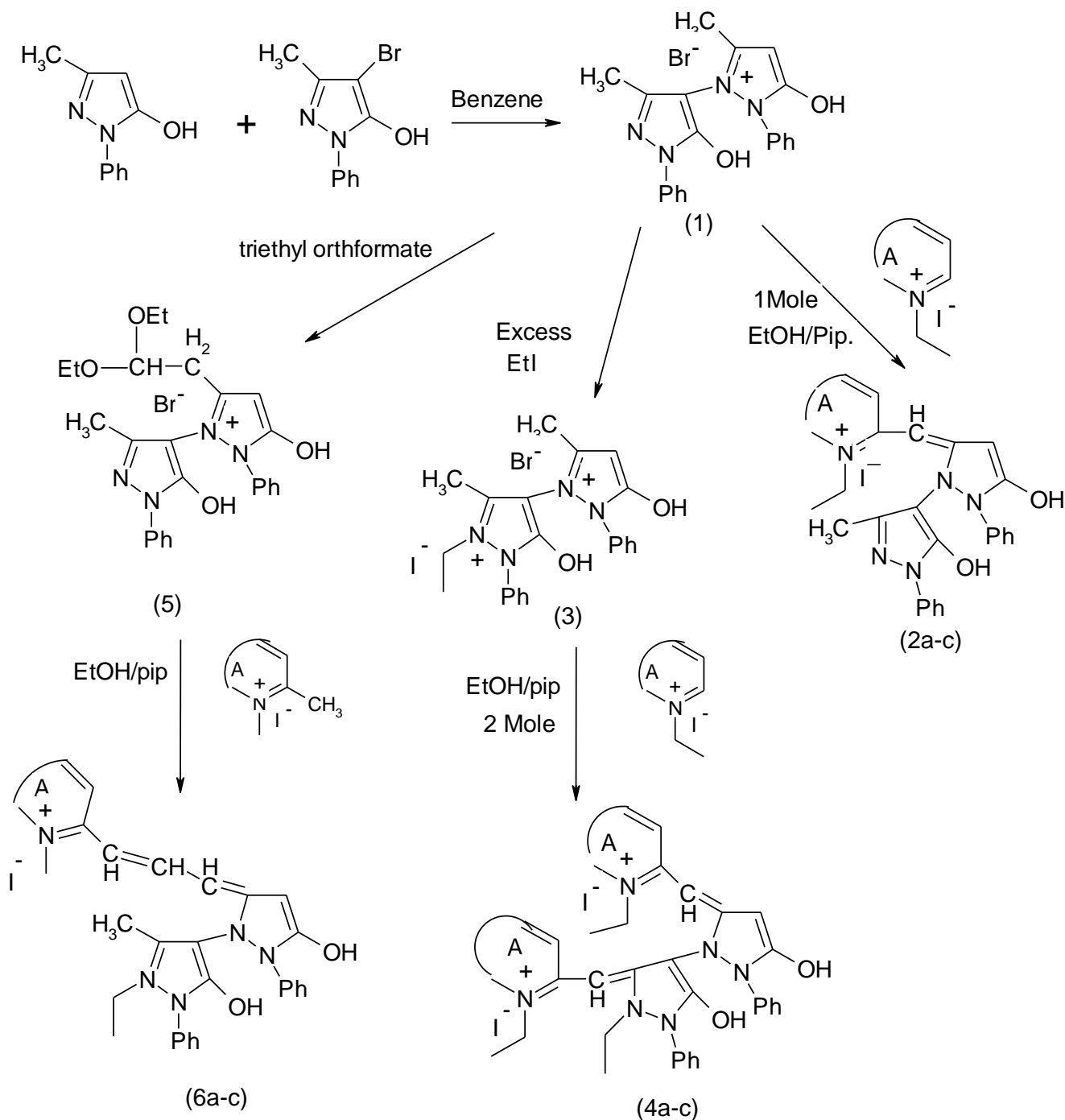
Herein novel monomethine, bismonomethine and trimethine cyanine dyes were synthesized, characterized, their visible and solvatochromic behavior have been studied which may be used as photosensitizer dyes.

MATERIAL AND METHODS

Chemical, reagents and instruments

Starting materials were synthesized according to (Mann and Saunders, 1960). All of the solvents are commercial products from Sigma Aldrich (USA) and were used without further purification.

Melting points are uncorrected. Elemental analyses were carried out at the micro analytical centre (Cairo-University). The IR spectra were determined with Perkin Elmer Infrared 137B spectrophotometer (Cairo University).



2a-c, 4a-c:

a: A= pyridin-2-ium ethiodide ,
 b: A= quinolin-2-ium ethiodide ,
 c: A= isoquinolin-2-ium ethiodide ,

6a-c:

a: A=1-ethylpyridin-2-ium methiodide
 b: A=1-ethylquinolin-2-ium methiodide
 c: A=1-ethylpyridin-2-ium methiodide

$^1\text{H-NMR}$ spectra were recorded with Burker AMX-300 spectrometer (Cairo University). Mass spectra were recorded on HpMs 6988 spectrometer (Cairo University). The electronic absorption spectra were recorded within the

wavelength range (350-700) on Shimadzu 1601A UV-visible spectrophotometer, Faculty of Science, Suez University.

Synthesis

Table 1: Characterization of compounds 1, 3 and 5

Comp. No.	m. p. °C	Yield %	Colour	Mol. Formula (M.wt)	Calcd. % (found)		
					C	H	N
1	95-99	57	White-yellow	C ₂₀ H ₁₉ N ₄ O ₂ Br (434.5)	55.23 (55.11)	4.37 (3.89)	12.88 (11.55)
3	178-183	65	Red	C ₂₅ H ₂₉₈ N ₄₅ O ₄ Br (528.5)	56.76 (55.8)	5.48 (4.7)	10.59 (10.2)
5	120-123	60	brown	C ₂₂ H ₂₄ N ₄ O ₂ BrI (581.5)	45.39 (45.11)	4.12 (3.9)	9.63 (10.4)

Table 2: Characterization of prepared dyes (2a-c), (4a-c) and (6a-c)

Comp. No.	m. p. °C	Yield %	Colour	Mol. Formula (M.wt)	Calcd. % (found)			Absorption Spectra in EtOH	
					C	H	N	λ_{max}	ϵ_{max}
2a	138-142°C	66	red	C ₂₇ H ₂₆ N ₅ O ₂ I (578)	56.05 (55.1)	4.5 (3.8)	12.00 (6.5)	486 515sh 560sh	972 1030 1120
2b	130-135°C	86	Reddish brown	C ₃₁ H ₂₈ N ₅ O ₂ I (628)	59.23 (57.1)	4.45 (3.9)	11.14 (10.4)	491 573sh	2455 2865
2c	165-168°C	37	brown	C ₃₁ H ₂₈ N ₅ O ₂ I (628)	59.23 (57.8)	4.45 (3.7)	11.14 (10.2)	512 553sh	1706 1843
4a	150-160°C	67	Faint brown	C ₃₄ H ₃₃ N ₆ O ₂ I ₂ (809)	50.43 (50.1)	4.07 (4.5)	11.58 (11.4)	510 599sh	1020 1018
4b	115-120°C	74	Reddish brown	C ₄₀ H ₃₇ N ₆ O ₂ I ₂ (885)	54.23 (52.1)	4.18 (3.9)	9.49 (8.4)	489 630sh	2445 3150
4c	110-115°C	70	brown	C ₄₀ H ₃₇ N ₆ O ₂ I ₂ (885)	54.23 (53.4)	4.18 (3.5)	9.49 (8.2)	465 566sh	1550 1886
6a	189-193°C	66	Reddish brown	C ₂₉ H ₂₈ N ₅ O ₂ I (604)	57.61 (55.1)	4.63 (4.5)	11.58 (11.4)	472 621sh	4720 6210
6b	169-176°C	86	violet	C ₃₃ H ₃₀ N ₅ O ₂ I (654)	60.55 (58.1)	4.58 (3.9)	10.70 (10.4)	504 606sh 642sh	1008 1212 1284
6c	156-164°C	37	brown	C ₂₉ H ₂₈ N ₅ O ₂ I (604)	57.61 (57.4)	4.63 (4.5)	11.58 (11.2)	492 634sh	492 634

Synthesis of 5-hydroxy-2-(5-hydroxy-3-methyl-1-phenyl-4,5-dihydro-1H-pyrazol-4-yl)-3-methyl-1-phenyl-4,5-dihydro-1H-pyrazol-2-ium (1)

A mixture of 4-bromo-3-methyl-1-phenyl-1H-pyrazol-5-ol (0.01mol) and 3-methyl-1-phenyl-1H-pyrazol-5-ol (0.01mol) in benzene (10mL). The reaction mixture was fused for 15 minutes. The red-mixture was poured into a clean 250 mL beaker to evaporate the excess solvent, filtered, dried and

crystallized from benzene. The results are registered in Table (1).

Synthesis of monomethinecyanine dyes 2-((5-hydroxy-2-(5-hydroxy-3-methyl-1-phenyl-1H-pyrazol-4-yl)-1-phenyl-1H-pyrazol-3(2H)-ylidene)methyl)-1-methylquinolinium pyridinium/isoquinolinium iodide (2a-c)

Table 3: Spectral data IR, ¹H-NMR and mass of compounds 2a, 4a and 6a

Comps.	IR Spectrum (KBr, Cm ⁻¹)	¹ H-NMR Spectrum (DMSO, δ) and Mass
2a	1218 (C-O) 1360 (C-N) 1598-1620 (C=C) 2952 (quaternary salt)	1.3 (s, 3H, CH ₃) 1.7 (t, 3H, CH ₃ of ethiodide) 2 (q, 2H, CH ₂ of ethiodide) 2.5 (s, 2H, 2-OH) 6.7-8 (m, 15H, Ar+Het. +=CH) M ⁺ = 578
4a	1118 (C-O) 1270 (C-N) 1600-1620 (C=C) 2932-2976 (quaternary salt)	1.6 (t, 6H, 2CH ₃ of ethiodide) 2.2 (q, 4H, 2CH ₂ of ethiodide) 2.4 (s, 2H, two OH) 6-8(m, 20H, Ar+Het+=2CH) M ⁺ =809
6a	1218 (C-O) 1360 (C-N) 1598-1620 (C=C) 2952 (quaternary salt)	1.3 (s, 3H, CH ₃) 1.65 (t, 3H, CH ₃ of ethiodide) 2 (q, 2H, CH ₂ of ethiodide) 2.5 (d, 1H =CH) 2.7 (d, 1H, CH=) 3 (t, 1H, CH) 6-7.7(m, 14H, Ar+Het.) M ⁺ =604

A mixture of equimolar amounts of compound 1 (0.001 mol) and 1-ethylpyridin-2-ium ethiodide (0.001 mol) were dissolved in ethanol (20 mL) and catalyzed by piperidine (0.5 mL). The reaction mixture was refluxed for 10 hours, filtered hot, concentrated, cooled and neutralized with acetic acid (0.3 mL). The precipitated compound was collected and recrystallized from methanol to afford 2a. Analogously, reaction of equimolar amounts of heterocyclic quaternary salts 1-ethylquinolin-2-ium ethiodide and 1-ethylisoquinolin-2-ium ethiodide and compound 2, respectively afforded 2b and 2c, Table (2).

Synthesis of 2'-ethyl-3,5'-dihydroxy-3',5'-dimethyl-1',2'-diphenyl-1'H,2H-1,4'-bipyrazole-1,2'-diium bromide iodide (3)

Compound 1 (2g) reacted with excess amount of ethyl iodide. The reaction mixture was refluxed gently for 2 hours. The precipitated product was collected, washed with ether and dried, Table (1).

Synthesis of bis-monomethine 2/4-((2-(2-ethyl-5-hydroxy-3-methyl-1-phenyl-1H-pyrazol-2-ium-4-yl)-5-hydroxy-1-phenyl-1H-pyrazol-3(2H)-ylidene)methyl)-1-methylquinolinium/pyridinium iodide cyanine dyes (4a-c)

Compound 3 (0.0003) reacted with bimolar amounts of 1-ethylpyridin-2-ium ethiodide (0.001 mol). The reaction mixture was dissolved in ethanol (20 mL), Piperidine (0.5 mL) was added as basic catalyst, refluxed for 11 hours, filtered hot, concentrated, cooled and neutralized by acetic acid. The solid product was collected and recrystallized from

ethanol to give compound 4a. Analogously, compound 3 was reacted with 1-ethylquinolin-2-ium ethiodide and 1-ethylisoquinolin-2-ium ethiodide to afford 4b and 4c, respectively, Table (2).

Synthesis of 5-(2,2-diethoxyethyl)-2'-ethyl-3,5'-dihydroxy-3'-methyl-1',2'-diphenyl-3,4,4',5'-tetrahydro-1'H,2H-1,4'-bipyrazole-1,2'-diium (5)

Compound 5 was prepared by reaction of compound 2 (0.001 mol) with triethylorthoformate (0.001 mol) in ethanol as solvent, purchased by piperidine as basic catalyst. The reaction mixture was refluxed for 7 hours, filtered hot, concentrated, cooled and neutralized by acetic acid. The solid product was collected and recrystallized from ethanol to give compound 5, Table (3).

Synthesis of 2/4-(3-(5-hydroxy-2-(5-hydroxy-3-methyl-1-phenyl-1H-pyrazol-4-yl)-1-phenyl-1H-pyrazol-3(2H)-ylidene)prop-1-enyl)-1-methyl quinolinium/ pyridinium trimethine cyanine dyes (6a-c)

A mixture of equimolar amounts of compound 5 (0.002mol) and 1-methyl pyridin-2-ium iodide (0.002mol) dissolved in ethanol and catalyzed by piperidine (0.5 mL). The reaction mixture was refluxed for 11 hours. The product was filtered hot, concentrated, cooled and neutralized by acetic acid (0.3 mL). The precipitated compound was recrystallized from ethanol to give 6a. Analogously, compound 5 reacted with 1-methylquinolin-2-ium methiodide and 1-methylpyridin-4-iummethiodide to afford 6b and 6c, respectively, Table (2).

Visible spectra studies

Table 4: Values of absorption (nm) and extinction coefficients ϵ_{\max} . ($10^3/\text{L mol}^{-1}\text{cm}^{-1}$) of compounds (2a-c), (4a-c) and (6a-c)

Comps.	H ₂ O		DMF		EtOH		CHCl ₃		acetonitrile		1,4-dioxane		CCl ₄	
	λ_{\max}	ϵ_{\max}	λ_{\max}	ϵ_{\max}	λ_{\max}	ϵ_{\max}	λ_{\max}	ϵ_{\max}	λ_{\max}	ϵ_{\max}	λ_{\max}	ϵ_{\max}	λ_{\max}	ϵ_{\max}
2a	476	952	495	990	486	972	489	978	491	982	488	976
	515sh	1030
	571sh	1142	560sh	1120	558sh	1116	557sh	1114	564sh	1128	550sh	1100
2b	443	2215	461	2305	491	2455	506	2530	490	2450	217.5	2587	487	2435
	523sh	2615	573sh	2865	576sh	2880	559sh	2790	590sh	2950	550sh	2750
2c	438	1460	513	1710	512	1706	509	1696	509	1696	496	1653	485sh	1616
	522sh	1740	582sh	1940	553sh	1843	564sh	1880	560sh	1866	581sh	1936
4a	509	1018	515	1030	510	1020	511	1022	511	1022	508	1016	505	1010
	590sh	1180	585sh	1170	599sh	1018	577sh	1154	575sh	1150	588sh	1176	575sh	1150
4b	477	2385	495	2475	489	2445	490	2450	487	2435	481	2405	464	2320
	617sh	3085	620sh	3100	630sh	3150	629sh	3145	628sh	3140	624sh	3120	575sh	2875
4c	459	1530	491	1636	465	1550	478	1593	473	1576	475	1583
	581sh	1936	591sh	1970	566sh	1886	579	1930	584sh	1946	573sh	1910	551sh	1836
6a	471	4710	484	4840	472	4720	471	4710	479	4790	471	4710	459	4590
	602sh	6020	616sh	6160	621sh	6210	578sh	5780	598sh	5970	568sh	5680	564sh	5640
6b	496	1653	512	1706	504	1008	512	1706	503	1676	504	1680	500	1666
	593sh	1976	593sh	1976	606sh	1212	606sh	2020	600sh	2000	602sh	2006	593sh	1976
	633sh	2110	658sh	2193	642sh	1284	642sh	2140	637sh	2123	642sh	2140	635sh	2116
6c	487	4870	502	5020	492	492	500	5000	494	4940	491	4910	492sh	4920
	624sh	6240	640sh	6400	634sh	634	643sh	6430	630sh	6300

The electronic visible absorption spectra of the newly synthesized cyanine dyes were examined in 95%ethanol solution. A stock solution of $1 \times 10^{-3} \text{M}$ of the dyes was prepared and used in suitable dilution to obtain the desired lower concentrations.

Solvatochromism

The electronic visible absorption spectra of the synthesized dyes were investigated in pure organic solvents of spectroscopic grade (Abdel Aal et al., 2012). Stock solution with 10^{-3}M was prepared and diluted to the desired lower concentrations.

RESULT AND DISCUSSION

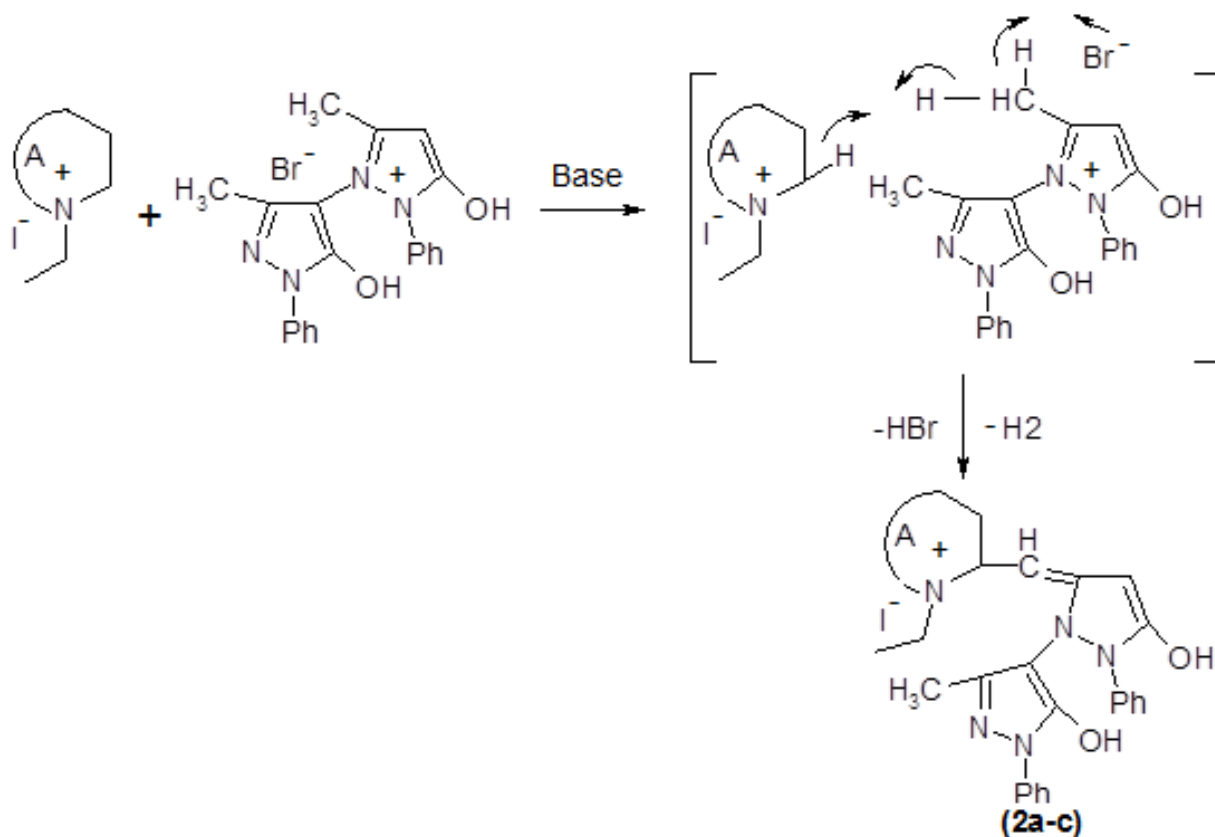
Synthesis

All the titled cyanine dyes (2a-c), (4a-c) and (6a-c) were started by preparation of compound 5-hydroxy-2-(5-hydroxy-3-methyl-1-phenyl-4,5-dihydro-1H-pyrazol-4-yl)-3-methyl-

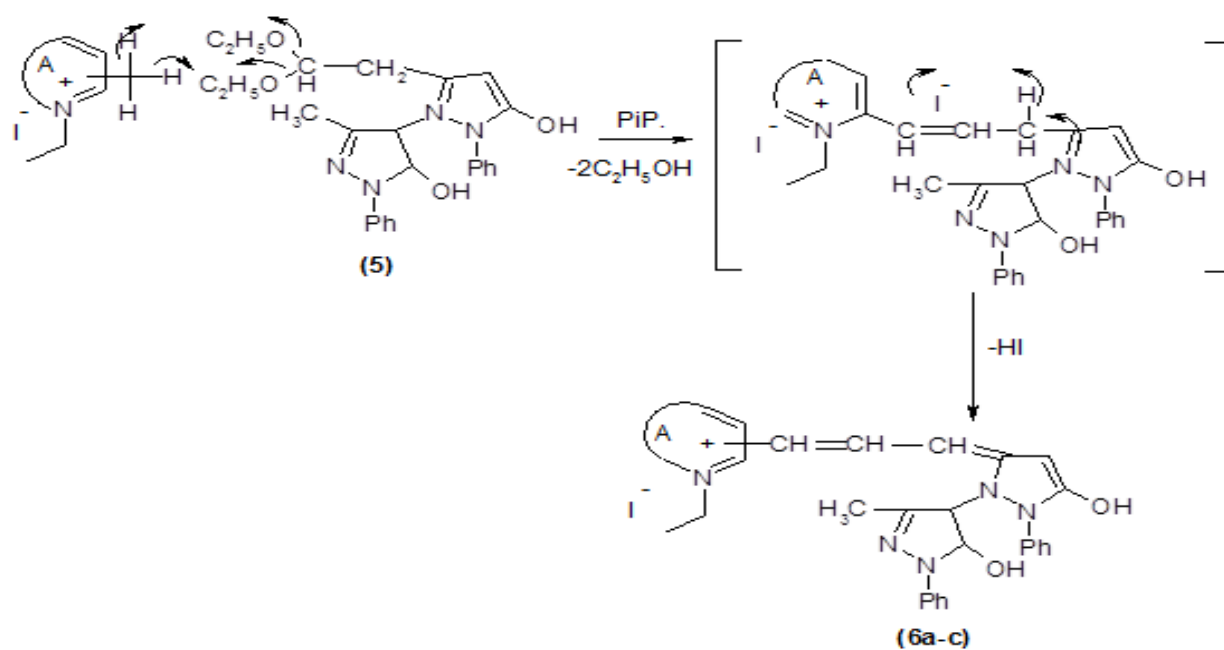
1-phenyl-4,5-dihydro-1H-pyrazol-2-ium (1) from reaction of 4-bromo-3-methyl-1-phenyl-1H-pyrazol-5-ol (O'Brein and Gates, 1966) and 3-methyl-1-phenyl-1H-pyrazol-5-ol (Mann and Saunders, 1960), Scheme (1).

The structure of compound 1 was established on analytical and spectral data. IR spectra showed characterization absorption bands at 3010 cm^{-1} (Aromatic C-H, str.), 1620 cm^{-1} (C=C ring, str.), 3200 cm^{-1} (-OH), 1340 cm^{-1} (C-N) and 730 cm^{-1} (=C-H bend, benzene ring). $^1\text{H-NMR}$ (DMSO, 300MHz) spectra (Wade, 1999) reveals signals at 2.2 (s, 6H, 2CH₃), 4.1 (s, 2H, two-OH), 6-8 (m, 13H, Ar-H+Hetero). Mass spectroscopy of compound 1: $M^+ = 434.5$, $M+1 = 435.5$.

Reaction of compound 1 with equimolar ratios of heterocyclic quaternary salts (pyridinium, quinolinium and isoquinolinium ethiodide) and piperidine as basic catalyst afforded the corresponding monomethine cyanine dyes (2a-c). The formation of monomethine cyanine dyes (2a-c) was suggested to proceed through oxidative elimination reaction followed by dehydrohalogenation of HBr to give (2a-c) according to Scheme 2.



Scheme 2: 2a-c structure (confirmed by analytical and spectral data)



Scheme 3: 6a-c structure (confirmed by analytical and spectral data)

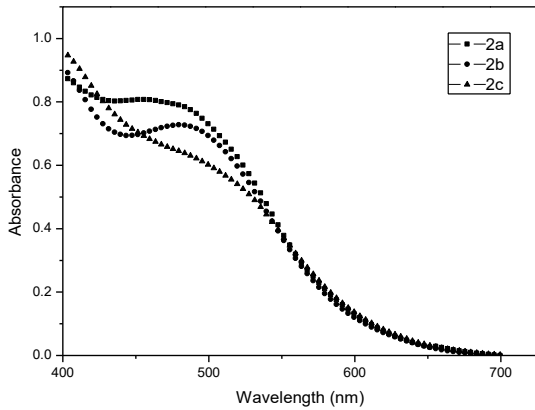


Fig. 1: Visible spectra of monomethine cyanine dyes (2a-c) in ethanol

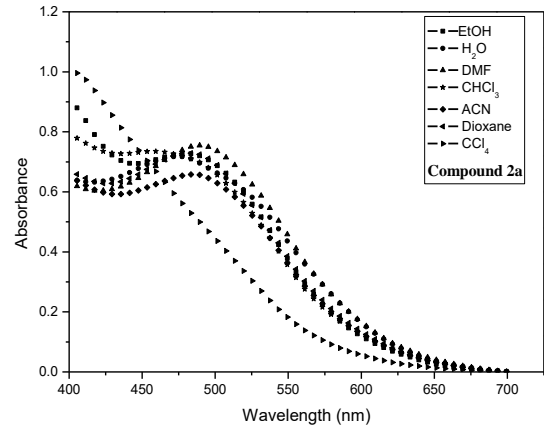


Fig. 4: Absorption spectra of monomethine cyanine dye 2a in different solvents

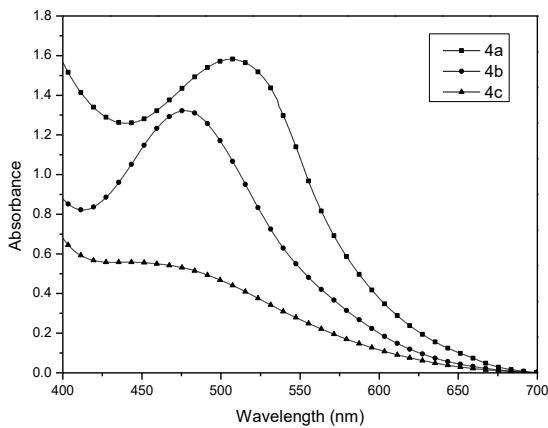


Fig. 2: Visible spectra of bis monomethine cyanine dyes (4a-c) in ethanol

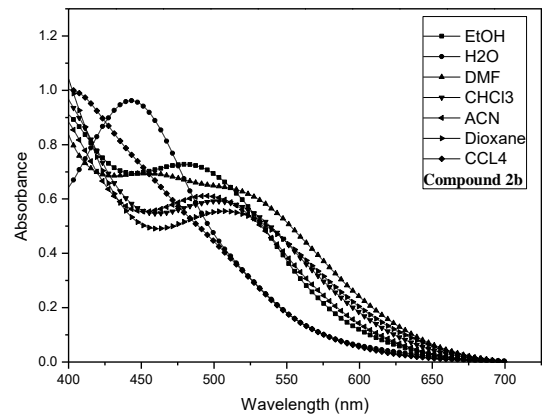


Fig. 5: Absorption spectra of monomethine cyanine dye 2b in different solvents.

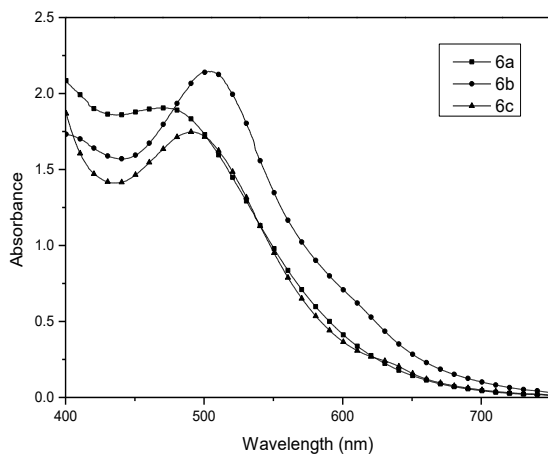


Fig. 3: Visible spectra of trimethine cyanine dyes (6a-c) in ethanol

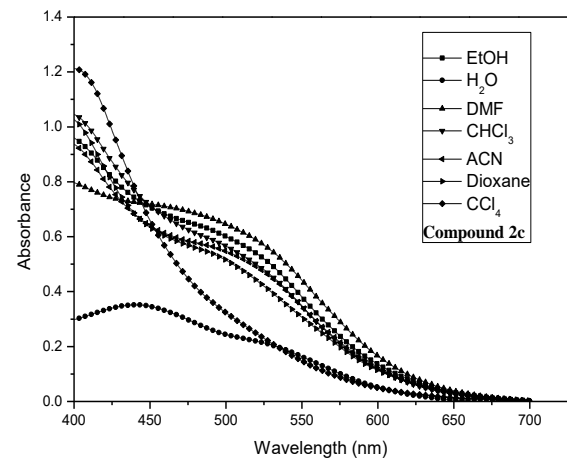


Fig. 6: Absorption spectra of monomethine cyanine dye 2c in different solvents.

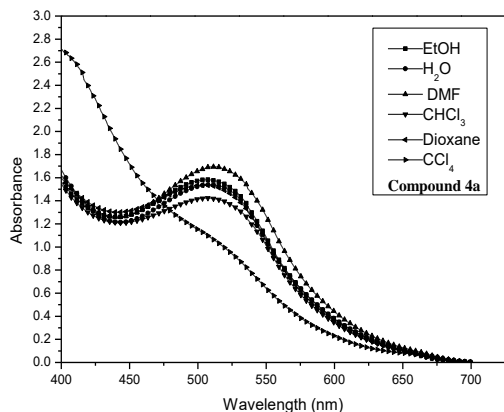


Fig. 7: Absorption spectra of bismonomethine cyanine dye 4a in different solvents.

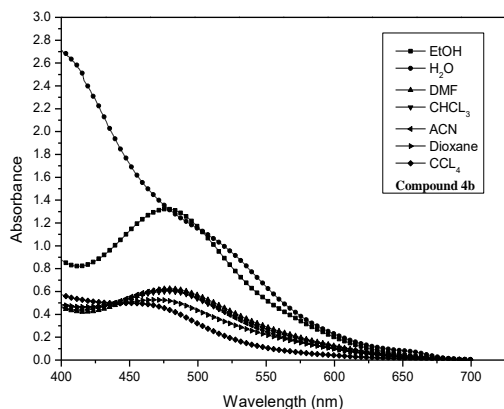


Fig. 8: Absorption spectra of bismonomethine cyanine dye 4b in different solvents

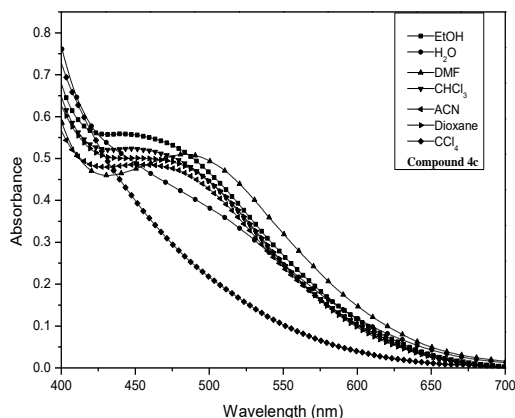


Fig. 9: Absorption spectra of bismonomethine cyanine dye 4c in different solvents

The structure of compounds (2a-c) was confirmed by analytical and spectral data, Table (3). Synthesis of bismonomethine cyanine dyes (4a-c) was performed by compound 3, which was prepared by reaction of compound 1 with excess amount of ethnocide. The structure of compound 3 was established on analytical and spectral data. IR spectra showed characterization absorption bands at $2958\text{--}2976\text{ cm}^{-1}$ ($\text{C}_2\text{H}_5\text{I}$), 3025 cm^{-1} (Aromatic C-H, str.), 1635 cm^{-1} (C=C ring, str.), 3200 cm^{-1} (-OH), 1340 cm^{-1} (C-N) and 727 cm^{-1} (=C-H bend, benzene ring). $^1\text{H-NMR}$ (DMSO, 300MHz) spectra (Wade, 1999) reveals signals at 1.7 (t, 3H, CH_3), 2.2 (s, 6H, 2CH_3), 4.4 (s, 2H, two-OH), 4.6 (q, 2H, N- CH_2) 6-8 (m, 13H, Ar-H+Hetero). Mass spectroscopy of compound 3: $M^+=443.5$.

Compound 3 reacted with bimolar ratios of heterocyclic quaternary salts in the presence of piperidine as basic catalyst afforded the corresponding bismonomethine cyanine dyes (4a-c). The reaction was proceeding through the same mechanism as mechanism of formation of monomethine cyanine dyes (2a-c). The structure of compounds (4a-c) was confirmed by analytical and spectral data, Table (3). Also, reaction of compound 1 with triethylorthoformate in presence of piperidine gave compound 5. The formation of compound 5 was suggested to proceed through elimination of two molecules of ethanol to give the corresponding intermediate compound 5, the structure of compound 5 was confirmed by elemental analysis, IR, $^1\text{H-NMR}$ and mass spectroscopy. Thus IR showed in addition to general absorption bands cited before in compound 1, the appearance of well define band $1089\text{--}1167$ (C-O-C). $^1\text{H-NMR}$ (DMSO, 300MHz) spectra (Wade, 1999) reveals signals at 1.5 (d, 2H, CH_2), 1.7 (t, 6H, 2CH_3 ethoxy group), 2.2 (q, 4H, 2CH_2), 2.5 (s, 3H, CH_3), 3, (t, 1H, CH), 4.4 (s, 2H, two-OH), 6-8 (m, 11H, Ar+Hetero). Mass spectroscopy of compound 5: $M^+=581.5$. Reaction of compound 5 with equimolar ratios of 2(4)-heterocyclic quaternary salts, reaction mixture was purchased by piperidine to afford the corresponding trimethine cyanine dyes (6a-c). The reaction suggested proceeding through elimination of two molecules of ethanol followed by dehydrohalogenation to give the corresponding cyanine dyes (6a-c), (Scheme 3).

Relation between structure and electronic absorption spectra of novel cyanine dyes

Electronic absorption spectra feature (λ_{max} and ϵ_{max} . Values) of newly synthesized cyanine dyes (2a-c), (4a-c) and (6a-c) in ethanol solution are shown in Table (3). The visible absorption of the novel synthesized cyanine dyes undergo bathochromic shift or hypsochromic shift depending on the nature of heterocyclic quaternary residue A and number of methane groups. Thus, substitution of A=pyridine-2-ium in compound 2a by A=quinolin-2-ium in compound 2b resulted in a bathochromic shift of 13 nm, which is due to increasing π -conjugation in quinolone-2-ium moiety. Similarly, increasing the number of methane groups in trimethine compound 6b with respect to monomethine compound 2b resulted in a bathochromic shift of 69 nm and appearance of shoulder at 642 nm, Figure (2).

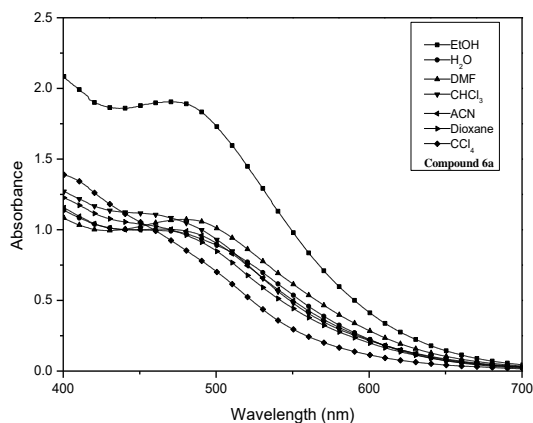


Fig. 10: Absorption spectra of trimethine cyanine dye 6a in different solvents.

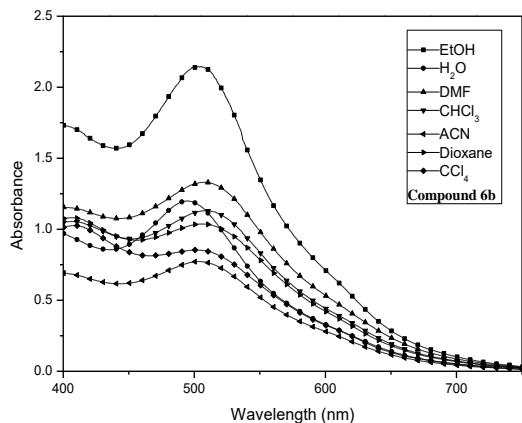


Fig. 11: Absorption spectra of trimethine cyanine dye 6b in different solvents.

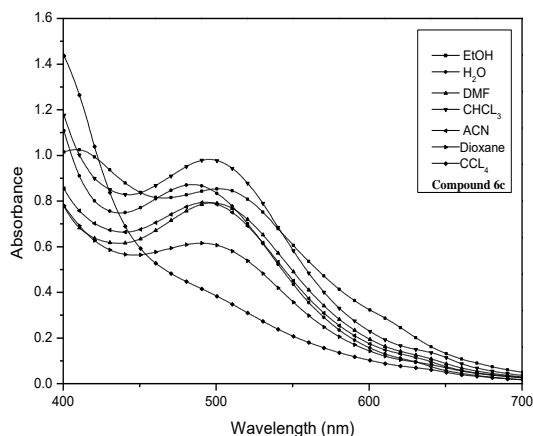


Fig. 12: Absorption spectra of trimethine cyanine dye 6c in different solvents.

This could be attributed to extensive π -conjugation in trimethine than monomethine. Also, increasing the heterocyclic residue in bismonomethine compound 4b with respect to monomethine cyanine 2b resulted in a bathochromic shift of 15 nm and appearing of a shoulder at 610 nm. A comparison of the visible absorption between compounds 2b, 4b and 6b gave a result that trimethine cyanine dyes reveals a bathochromic shift than both monomethine 2b and bismonomethine cyanine dyes 4b, Figure (3).

Solvatochromic behavior

The UV-visible spectra of newly synthesized cyanine dyes in different organic solvents were determined, Figures (4-12). All the data were measured at room temperature with concentration of approximately 10^{-4} mol/L. The λ_{\max} and ϵ_{\max} of the dyes in different solvents are presented in Table (4). It is clear that; table (4) shows λ_{\max} ranges from 476-590 nm for dyes (2a-c), 477-630 nm for dyes (4a-c) and from 492-640 nm for dyes (6a-c) in different solvents. At the same time the ϵ_{\max} values were in range from 952-2865 L mol⁻¹ cm⁻¹, 1018-3150 L mol⁻¹ cm⁻¹ and 4710-6430 L mol⁻¹ cm⁻¹ for dyes (2a-c), (4a-c) and (6a-c), respectively. The electronic absorption spectra of novel synthesized dyes showed positive solvatochromism with increasing solvent polarity this is attributed to the structure and type of the dye. Stabilization of ground state with respect to excited state is related to solvation by solvents of higher polarity. It is clear that the absorption bands of these dyes undergo bathochromic shift according to conjugation in the dye molecule.

CONCLUSIONS

Novel cyanine dyes were prepared from the nucleus 5-hydroxy-2-(5-hydroxy-3-methyl-1-phenyl-4,5-dihydro-1H-pyrazol-4-yl)-3-methyl-1-phenyl-4,5-dihydro-1H-pyrazol-2-ium. Physico-Chemical properties of the newly synthesized cyanine dyes were performed. Electronic absorption of the novel synthesized cyanine dyes (2a-c), (4a-c) and (6a-c) undergo bathochromic shift or hypsochromic shift depending on the nature of heterocyclic quaternary residue A and number of methine groups. Also, the spectral characterization of the investigated cyanine dyes in pure organic solvent with different polarities showed positive solvatochromism with increasing solvent polarity depending on increasing or decreasing the polarity and/or the dielectric constant of the solvent, beside type of hydrogen bond formed between the solute and the solvent used.

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