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Thiazoline and thiazoloxazole in synthesis of novel meso-substituted mono-, tri-, and hepta-methine cyanine dyes

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Abstract

2-Cyanomethylene (2-ethoxy carbonylmethylene)-4,5-dihydrothiazolin-4-one **1a,b** and 2-cyanomethylene (2-ethoxy carbonylmethylene)-4,5-dihydrothiazolo [3,2-a]oxazole **3a**,**b** were synthesized as starting material. Reaction of both compounds **2a**,**b** and **3a**,**b** with N-methylheterocyclic quaternary salts afforded meso-substituted monomethine cyanine dyes **4a**–**d** and **9a**–**d**, respectively. Reaction of compounds **1a**,**b** and **8a**,**b** with ethyl orthoformate gave the intermediate compounds **5a**,**b** and **10a**,**b**, followed by the reaction with 1,2-dimethyl quinolinium iodide resulted in meso-substituted trimethine cyanine dyes **6a**,**b** and **11a**,**b**, respectively. Also, reaction of both **2a**,**b** and **3a**,**b** with 2-chlorocyclohexane-1,3-dicarboxaldehyde followed by the reaction with 1,2-dimethyl quinolinium iodide afforded the asymmetrical heptamethine dyes **8a**,**b** and **13a**,**b**. The new compounds were characterized by elemental analysis, visible absorption, ^{1}H NMR, IR Spectroscopy and Ms spectral data. Relation between the constitution and the UV/Vis spectroscopic properties of these dyes has been studied.

Keywords: Heptamethine; Electronic absorption spectra; Solvatochromism; Molar transition energy

1. Introduction

Intense research activity has been devoted to the synthesis of polymethine cyanine dyes, due to their relative stability, high molar extinction coefficient, high fluorescent intensity etc. They have found a wide application in various fields, such as near-infrared laser dyes [1] and fluorescent labeling agents for proteins [2]. Polymethine cyanine dyes also belong to a well-known class of organic compounds which have used in photography and information storage [3,4], in laser technology [5] and as photopolymerization initiators [6]. Monomethine cyanine dyes have also found various applications as photosensitizers in blue green light [7,8] and as bacteriocidal agents [9,10].

The object of this investigation is to report the synthesis, electronic absorption spectra in ethanolic solution and solvatochromic behavior of new meso-substituted mono-, tri-, and heptamethine cyanine dyes to be used as photosensitizers. Solvatochromic behaviour of some selected cyanine dyes in different organic solvents was investigated in order to make a suitable selection for their application as photosensitizers.

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2. Results and discussion

2.1. Synthesis

Reaction of equimolar amounts of 2-canyomethylene (2-ethoxy carbonyl methylene)-4,5-dihydrothiazolin-4-one **1a**,**b** [11] with iodopropane and/or phenacyl bromide in a non polar solvent [12] afforded the corresponding compound 2-canyomethylene (2-ethoxy carbonylmethylene)-4,5-dihydro-4-oxo-thiazolium iodide **2a**,**b** and 2-canyomethylene (2-ethoxy carbonylmethylene)-7-(H)-5-phenylthiazolo[3,2-a]oxazole bromide **3a**,**b**, respectively. The reaction was thought to proceed through the quaternization reaction of iodopropane with compound **1a**,**b** to give quaternary heterocyclic **2a**,**b**. The other starting material **3a**,**b** was formed through the quaternization of phenacyl bromide followed by ring closure to give the N-bridgehead heterocyclic thiazolo[3,2-a]oxazole derivatives **3a**,**b**. The structures of compounds **2a**,**b** and **3a**,**b** were established based on analytical and spectral data. Thus, IR of compound **2a** showed an absorption band at $\nu = 2980–2870$ cm^{-1} for quaternary salt and presence of carbonyl group at $\nu = 1720$ cm^{-1} . ^{1}H NMR showed signals at δ 5.5 (s, 2H, CH_2-thiazole), 3.9 (t, 2H, CH_2-N^+), 2.3 (s, 2H, CH_2-CN), 1.3 (m, 2H, CH2) and 0.9(t,3H,CH_3) for compound **2a**.

Interaction of compounds **2a**,**b** and **3a**,**b** with equimolar amounts of 1-methylpyridinium, quinolinium, and/or isoquinolinium iodide in basic catalyst afforded the desired 2-canyomethylene (2-ethoxy carbonylmethylene)-4,5-dihydro-4-oxo-thiazolium-2[4(1)]-monomethine dyes **4a–d** and 2-canyomethylene (2-ethoxy carbonyl methylene)-7-(H)-5-phenylthiazolo[3,2-a]oxazole-2[4(1)]-monomethine dyes **9a**,**b**, respectively. ^{1}H NMR of compound **9a** showed signals at δ 6.9–7.8 (m, 13H, Ar-H + heter-H + -CH=), 3.9 (s, 3H, CH_3-N^+–), Table 1. Reaction of equimolar amounts of ethyl orthoformate in the presence of piperidine achieved the corresponding intermediate compounds **5a**,**b** and **10a**,**b**, respectively. Further reaction of compounds **5a**,**b** and **10a**,**b** with 2-methylquinolinium methyl iodide in piperidine as a basic catalyst gave the corresponding 2-cyanomethylene(2-ethoxycarbonylmethylene)-4,5-dihydrothiazolo-2(2)-trimethine cyanine **6a**,**b** and 2-cyanomethylene(2-ethoxycarbonylmethylene)-7(H)-5 - phenylthiazolo[3,2 - a]oxazole - 2(2) - trimethine cyanine dyes **11a**,**b**. ^{1}H NMR for compound **6a** showed signals at δ 6.9–7.9 (m,8H,Ar-H + heter-H + –CH=CH), 5.4 (s, 2H, CH_2-thiazol.), 3.9 (s, 3H, CH_3–N^+–), 1.9 (t, 2H, CH_2–), 1.3 (m, 2H, CH_2–) and 0.9 (t,3H,CH_3-), Table 1.

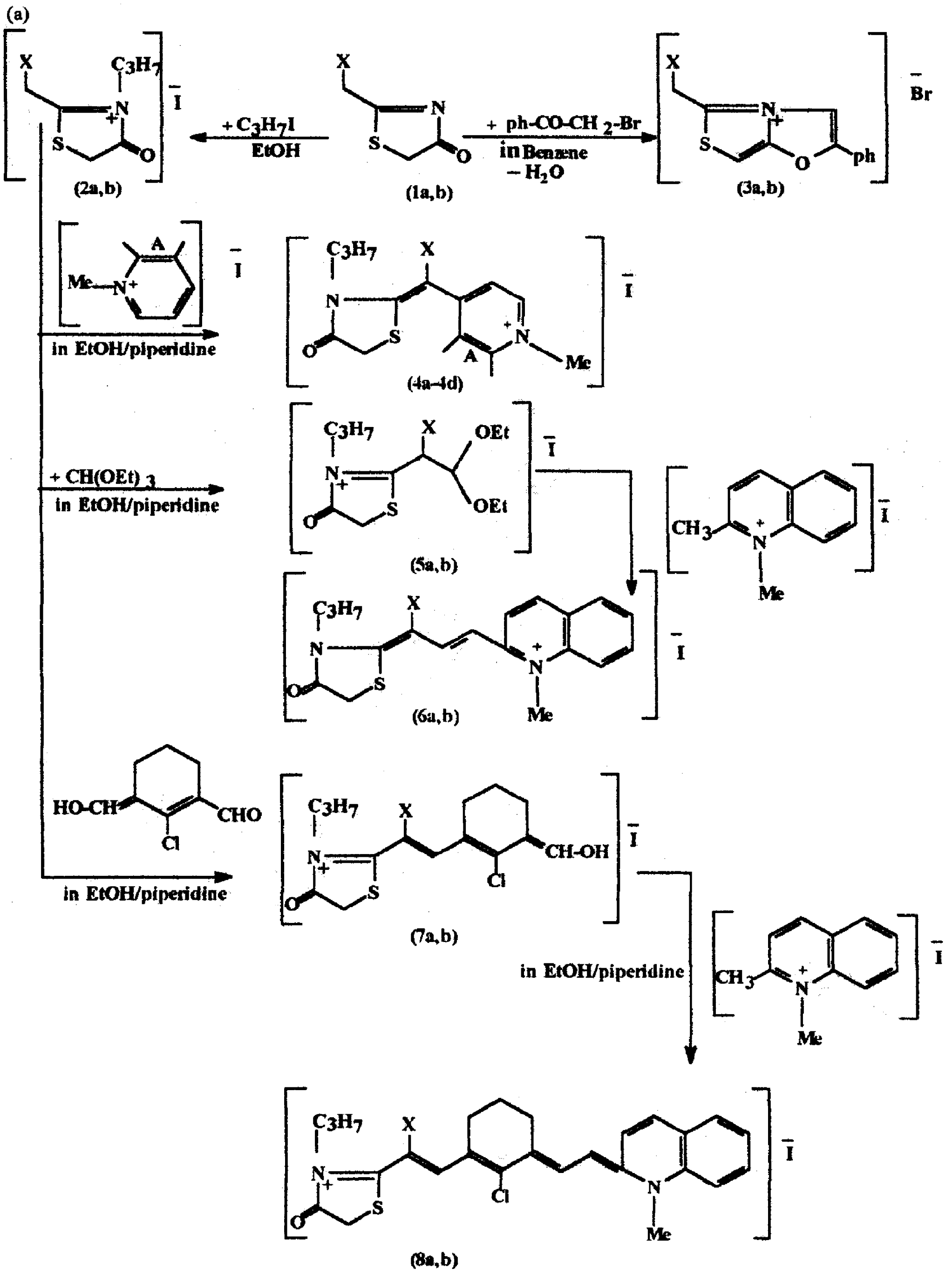
On the other hand, reaction of compounds **2a**,**b** and **3a**,**b** with equimolar amounts of 2-chloro-cyclohexan-1,3-dicarboxaldehyde [13] in piperidine as a basic catalyst gave the intermediate compounds **7a**,**b** and **12a**,**b**, respectively. Further, reaction of the intermediate compounds **7a**,**b** and **12a**,**b** with equimolar amounts of 1,2-dimethyl quinolinum iodide in piperidine as basic catalyst afforded the desired heptamethine cyanine dyes **8a**,**b** and **13a**,**b**, respectively.

The structure of compounds **4a–d**; **9a**,**b**; **5a**,**b**; **10a**,**b**; **6a**,**b**; **11a**,**b**; **7a**,**b**; **12a**,**b**; **8a**,**b** and **13a**,**b** were confirmed by elemental analysis Table 1, IR and H-NMR spectral data are shown in Table 2.

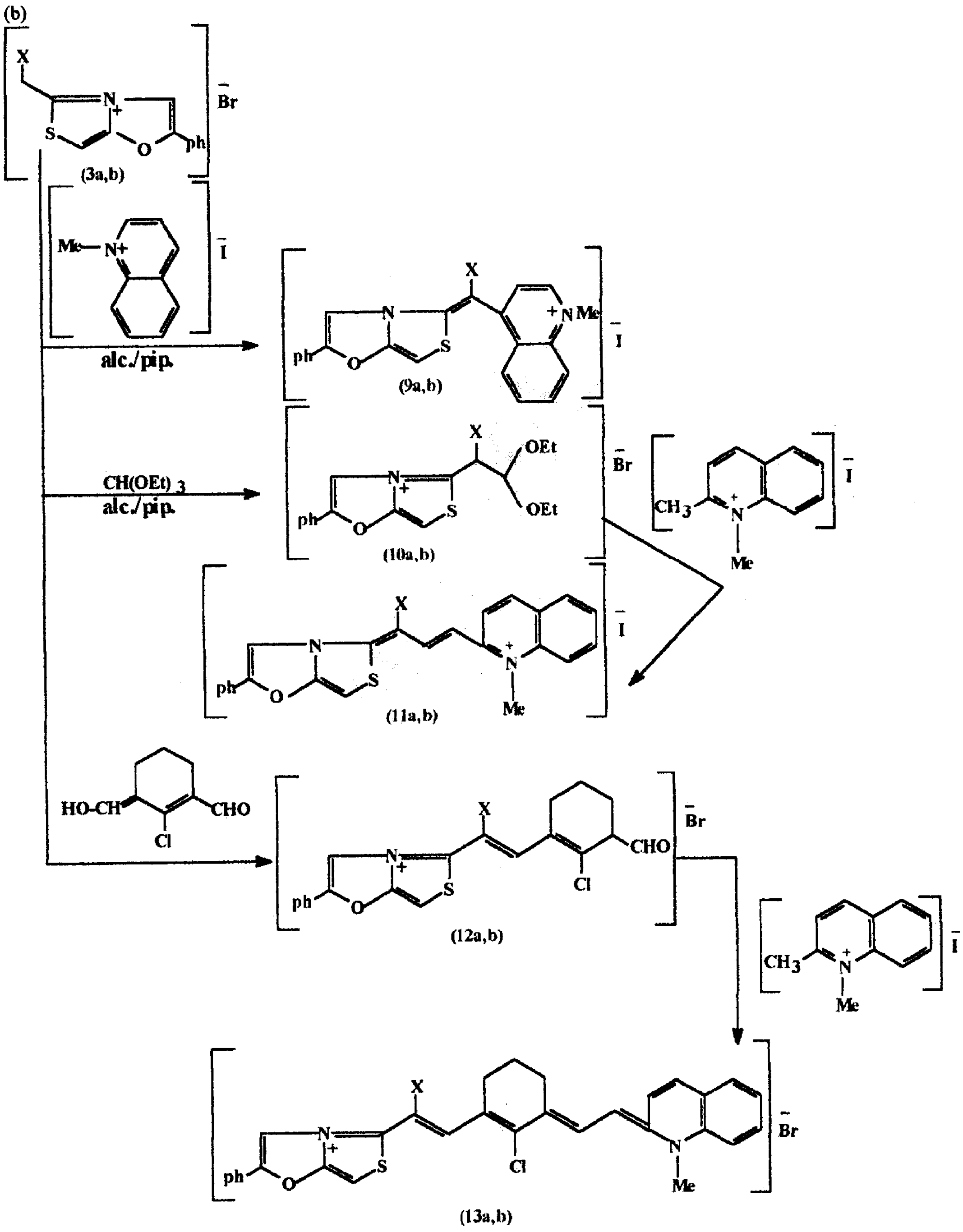
Ethanolic solution of the new synthesized meso-substituted mono-, tri-, and heptamethine cyanine dyes possess reddish violet to intense violet colour. They are fairly soluble in polar solvents and in conc. H_2SO_4 liberating iodine vapour on gentle warming.

3. Relation between molecular structure and the visible absorption maxima of the novel synthesized mono-, tri-, and heptamethine cyanine dyes

The long-wavelength visible absorption maxima λ_{max} and ϵ_{max} of meso-substituted monomethine (**4a–d**; **9a**,**b**), trimethine (**6a**,**b**; **11a**,**b**) and heptamethine cyanine (**8a**,**b**; **13a**,**b**), respectively are shown in Table 2. The visible absorption spectra of the synthesized cyanines in ethanol exhibit various absorption bands within the wavelength range $\lambda = 350–700$ nm. These absorption bands of the new synthesized cyanine dyes depend primarily on the terminal group [14], the length of the conjugated system, and the meso-substituents groups. Thus, substituting A = 1-methylpyridin-4-ium in compound **4b** by A = 1-methylquinolin-4-ium in compound **4c** causes a bathochromic shift of Δ


(a)
X
C3H7
N
S
O
I
+C3H7I
EtOH
(2a,b)
(1a,b)
+ ph-CO-CH 2-Br
in Benzene
− H2O
ph
Br
(3a,b)
A
Me
in EtOH/piperidine
(4a-4d)
+ CH(OEt) 3
OEt
(5a,b)
CH3
(6a,b)
HO-CH
CHO
Cl
CH-OH
(7a,b)
(8a,b)

Scheme 1a.


(b)
X
N+
S
O
ph
Br
(3a,b)
Me–N+
I
alc./pip.
+N Me
(9a,b)
CH(OEt) 3
alc./pip.
OEt
OEt
(10a,b)
CH3
N+
Me
(11a,b)
HO-CH
CHO
Cl
(12a,b)
(13a,b)

Scheme 1b.

Table 1
Characterization data of the synthesized cyanine dyes

Compd. no.	Mol. formula (Mol.wt)	Calcd % Found %			M.p. (°C)	Yield (%)	IR$(\nu_{\max}^{KBr})$ cm^{-1}	^{1}H NMR(CDCl$_3$) δ Assignment	M
		C	H	N					
2a	$C_8H_{11}N_2OSI$ (310)	30.97 31.12	3.55 3.37	9.03 8.93	140-2	67	2980-2940 (ν-N–C_3H_7I), 2250 (ν CN), 1720 (ν C=O)	5.5(s,2H,CH_2-thiazole), 3.9 (t,2H,CH_2-N^+), 2.3(s,2H,CH_2-CN), 1.3(m,2H,CH_2), 0.9(t,3H,CH_3).	311
2b	$C_{10}H_{16}NO3SI$ (357)	33.61 33.77	4.48 4.57	3.92 4.11	135-7	71	2970-2940 (ν-N–C_3H_7I) 2255 (ν CN), 1730 (ν C=O)	5.3(s,2H,CH_2-thiazole), 4.1 (t,2H,CH_2-N^+),2.35(s,2H,CH_2-CN), 2.1(q,2H,CH_2), 1.4(t,3H,CH_3) 1.1(m,2H,CH_2), 0.9(t,3H,CH_3).	
3a	$C_{13}H_9N_2OSBr$ (321)	48.60 48.49	2.80 3.01	8.72 8.63	62-4	65	2250 (ν CN), 1030 (νC–OC)	6.7-7.8(m,7H,Ar-H,het-H), 2.1 (s,2H,CH_2-CN).	323
3b	$C_{15}H_{14}NO_3SBr$ (368)	48.91 49.13	3.80 3.67	3.80 3.91	95-7	68	2960-2920, (ν C_2H_5), 1050 (ν C–O–C)	6.8-7.9(m,7H,Ar-H),1.9(q,2H,CH_2), 1.1(t,3H,CH_3).	367
4a	$C_{18}H_{18}N_3OSI$ (451)	47.89 47.77	3.99 4.13	9.30 8.89	125-7	69	2980-2840 (ν $C_3H_7I_7$, CH_3I) 1730 (ν C=O)	7.1-8.2(m,6H,Ar-H),5.5(s,2H,CH_2-thiazole),3.9(s,3H,CH_3-N^+) 1.9 (t,2H,CH_2),1.1(m,2H,CH2), 0.9 (t,3H,CH3).	
4b	$C_{16}H_{21}N_2O_3SI$ (448)	42.86 43.01	4.69 7.79	6.25 6.15	135-7	58	2980-2925 (ν C_3H_7I, CH_3I) 1725 (ν C=O)		449
4c	$C_{20}H_{23}N_2O_3SI$ (498)	48.19 47.97	4.62 4.71	4.68 4.55	85-7	79	2995-2940 (ν $C_3H_7I_7$, CH_3I) 1730 (ν C=O)	6.9-7.8(m,6H,Ar-H + het-H), 2.3(q,2H,CH_2-),1.5(t,3HCH_3), 1.3(t,2H,CH_2),1.1(m,2H,CH_2), 0.9(t3H,CH_3),5.5(S,2H,CH_2 thiazole),3.9(s,3H,CH_3-N^+)	500
4d	$C_{16}H_{21}N_2O_3SI$ (448)	42.86 43.01	4.69 7.79	6.25 6.15	71-3	65	2980-2940(ν C_3H_7I,CH_3I) 1735(ν C=O)		
9a	$C_{21}H_{16}N_3OSI$ (485)	51.96 52.11	3.30 3.17	8.66 8.49	105-7	79	2980-2930(ν CH_3I) 2250 (ν CN)	6.6-7-9(m,13H,Ar-H + het-H), 3.9(s,3H, CH_3-N^+)	484

(continued on next page)

Table 1 (*continued*)

Compd. no.	Mol. formula (Mol.wt)	Calcd % Found %			M.p. (°C)	Yield (%)	IR(ν_{max}^{KBr}) cm^{-1}	^{1}H NMR(CDCl$_3$) δ Assignment	M
9b	$C_{23}H_{21}N_2O_3SI$ (532)	56.39 56.51	3.95 3.87	5.26 5.35	70-62	77	2985-2940 (ν CH_3I) 1030 (ν C–O–C)	6.9-7.8(m13H,Ar-H + het-H), 3.9(s,3H,CH_3), 2.1(q.2HCH_2), 1.1(t,3H,CH_3).	533
5a	$C_{13}H_{21}N_2O_3SI$ (412)	37.86 38.03	5.10 5.15	6.80 6.69	115-7	83	2960-22920(ν CH3I) 2255(ν CN)	5.3(s,2H,CH_2-thiaz.),3.9(t,2H,CH_2), 1.8 (d,1H,CH), 1.4(m,2H,CH_2), 1.3(d,1H,CH_2), 1.6(q,4H,2CH_2), 1.1(t,6H,2CH_3), 0.9 (t,3H,CH_3).	
5b	$G_5H_{26}NO_5SI$ (459)	39.22 39.35	5.67 5.53	3.05 3.37	130	85	2985-2940 (ν CH3I)		460
10a	$C_{18}H_{19}N_2O_3SBr$ (423)	51.06 50.91	4.49 4.63	6.62 6.87	120-2	81	2250 (ν CN)	6.7 7.9(m,7H,Ar-H + het.H), 1.5(q,4H,2CH_2), 1.1(t,6H,2CH_3) 1.7(d,1H,CH), 1.3(d,1H,CH).	
10b	$C_{20}H_{24}NO_5SBr$ (470)	51.06 51.23	5.11 4.95	2.99 3.14	80-2	83	1030(νC–OC), 3220(ν C_2H_5)		469
6a	$C_{20}H_{20}N_3OSI$ (477)	50.32 50.13	4.19 4.33	8.81 8.95	190-2	82	2250(ν CN) 2980–240 (ν C_3H_7I,CH_3I)	6.9-7.8(m,8H,Ar-H + het-H),5.4 (s,2H,CH_2–), 3.9(s,3H,CH_3N^+) 1.9(t,2H,CH_2-), 1.3(m,2H,CH_2) 5.9 (t,3H.CH_3).	478
6b	$C_{22}H_{25}N_2O_3SI$ (524)	50.38 50.53	4.77 4.60	5.34 5.49	130-2	87	2990-2940 (ν CH_3I) 1730 (ν C=O)		426
11a	$C_{25}H_{18}N_3OSI$ (535)	56.08 56.13	3.55 3.69	7.85 7.67	105	85	2250(ν CN) 2980–2940 (ν CH_3I)	6.7-7.9(m, 15H,Ar-H + het-H + CH=CH), 3.9(s,3H,CH_3N^+)	
11b	$C_{27}H_{23}N_2O_3SI$ (582)	55.67 55-39	3.95 4.17	4.81 4.97	175	89	2975–2940 (ν CH_3I) 1130(ν–O–C)		481
7a	$C_{16}H_{18}N_2O_2SCLI$ (464.5)	41.34 53-57	3.88 4-53	6.03 7.07	95	63	2990–2930(ν CH_3I), 1735(ν C=O) 3400(ν OH)	5.3(s,2H,CH_2,-thiazol.), 3.9 (s,2H,CH_2N^+), 6.5(s,2H,2CH=), 1.9(d,2H,CH_2), 1.7(d,2H,CH_2), 1.3(m,2H,CH_2), 1.2(m,2H,CH_2), 0.9(t,3H,CH_3), 9.5(s,1H,OH)	

(*continued on next page*)

Table 1 (*continued*)

Compd. no.	Mol. formula (Mol.wt)	Calcd % Found %			M.p. (°C)	Yield (%)	IR(ν_{max}^{KBr}) cm^{-1}	^{1}H NMR(CDCl$_3$) δ Assignment	M
7b	$C_{18}H_{23}NO_4SclI$	42.23	4.50	2.74	110	65	2980–2940(ν $C_3H_7ICH_3I$), 1730(ν C=O) 3450(ν OH)		513
	(511.5)	42.35	4.63	2.81					
8a	$C_{27}H_{28}N_3OSClI$	53.59	4.63	6.95	120	73	2250(ν CN) 2980-2940 (ν C_3H_7I), 1640(ν C=O)		603
	(604.5)	53.67	4.53	7.11					
8b	$C_{29}H_{33}N_2O_3SclI$	53.42	5.07	4.30	135	77	2980-2940(ν C_3H_7I,CH_3I) 1650(ν C=O) 1735(ν C=O)	6.5–8.2(m,10H,Ar-H + het-H + CH=CH ~), 5.2(s,2H,CH_2thiaz.), 1.3(s,3H,CH_3), 3.9(t,2H,CH_2N^+), 1.2(m,2H,CH_2), 1.1(t,3H,CH_3), 2.9(t,2H,CH_2), 1.4(q,3H,CH_3), 2.6(t,4H,2CH_2), 1.6(m,2H,CH_2)	
	(651.5)	53.27	5.09	4.41					
12a	$C_{20}H_{17}N_2O_2SBrCl$	51.67	3.66	6.03	115	63	3450(ν OH) 2260(ν CN)	10.5(s,1H,OH), 6.7-8.1(m,10H, Ar-H + het-H + CH=CH), 2.8(t,4H,CH_2), 1.7(m,2H,CH_2)	466
	(464.5)	51.89	3.61	6.19					
12b	$C_{22}H_{22}NO_4SBrCl$	51.61	4.30	2.73	85-7	66	2987-2940(ν C_2H_5), 1730(ν C=O)		510
	(511.5)	51.37	4.47	2.99					
13a	$C_{32}H_{26}N_3OSBrCl$	62.39	4.22	6.82	190	87	2975-2930(ν CH_3), 2250(ν CN)	6.5–8.2(m,17H,Ar-H + het-H + CH=CH),2.6(t,4H,CH_2), 1.7(m,2H CH_2),1.2(s,3H,CH_3)	
	(615.5)	62.37	4.15	6.77					
13b	$C_{34}H_{31}N_2O_3SBrCl$	61.59	4.68	4.2	80-2	85	2985-2935(ν C_2H_5), 1735(ν C=O)		664
	(662.5)	61.53	4.1	4.39					

Table 2
The visible absorption maxima of meso-substituted mono-, tri-, and heptamethine cyanine dyes in 95% EtOH

4a	4b	4c	4d	9a	9b
Meso-Substituted monomethine cyanine dyes					
λ_{max} (nm)/log ϵ_{max} mol^{-1} cm^{-1}					
434(3.18)	440(4.00)	–	–	–	–
492(3.22)	465(2.72)	497(3.21)	471(3.08)	543(4.00)	525(3.78)
Meso-substituted trimethine cyanine dyes					
6a	6b	11a	11b		
410(4.52)	419(4.95)	–	–		
520(4.70)	512(4.92)	–	–		
595(4.61)	–	595.5(4.78)	580(4.62)		
662(4.12)	–	697(4.03)	683(3.86)		
Heptamethine cyanine dyes					
7b	13a	13b			
412(4.58)	–	–			
515(4.64)	557(4.62)	555(4.58)			
–	593(4.72)	584(4.75)			
654(4.03)	700(3.98)	692(3.78)			

λ_{max} = 32 nm with appears new absorption band at 524 nm. Meanwhile, substituting A = 1-methyl isoquinolin-1-ium in compound **4d** by A = 1-methylquinolin-4-ium in compound 4c resulted in bathochromic shift Δ λ_{max} = 26 nm accompanied by a new absorption band at λ_{max} = 524 nm. This may be due to increasing conjugation of quinolin-4-ium moiety than both pyridin-4-ium and iso-quinolin-1-ium.

Also, the meso-subsistent groups influence in the visible absorption maxima of meso-substituted trimethine cyanine dyes. Thus, substituting X = CN in compound **11a** by X = CO_2Et in compound **11b** resulted in a hypsochromic shift by Δ λ_{max} = 14–14.5 nm. This is attributed to that the position of such ionization energy of the electron donor and on the electron affinity of the electron acceptor [15]. The main cause is that the introduction of a cyano group increases the delocalizing range of π-electrons in the chromophore of the dye and decreases the excitation energy of the dyes [16]. On the other hand, the length of the conjugated system influences the position of the absorption bands. Thus, comparison of the absorption band of trimethine dye in compound **11b** and heptamethine in compound **13b** resulted in a bathochromic shift Δ λ_{max} = 4–9 nm with appearance of new absorption band at λ_{max} = 555 nm. This is may be attributed to the more extensive π-delocalization within the long length conjugated system [17].

4. Negative solvatochromism and determination of the transition molar energies $E_T(X)$ of some selected cyanine dyes

The positions of the longest-wavelength absorption band in the UV/visible solution spectra of some selected newly synthesized cyanine dyes depend on the polarity of solvent (solvatochromism). The unusually long negative solvatochromism of some pyridinium N-phenolate betaine dyes have been used to introduce UV/Visible spectroscopically derived empirical parameters of solvent polarity, the so-called $E_T(30)$-values [18], which are known for numerous solvents and many binary solvent mixtures [18,19]. The visible absorption spectra of some selected newly synthesized cyanine dyes show also a pronounced negative solvatochromism, as measured in 13 solvents of different polarity. Thus, by changing the solvent from non-polar chloroform to polar water, the long-wavelength UV/visible absorption band of **4a**, **4c**, **5b**, **7b**, **13a**, and **13b** undergoes a hypsochromic shift of about Δ λ_{max} = 106 nm, which corresponds

Table 3
Empirical parameters of solvent polarity, $E_T(30)$, Vis-absorption maxima, λ_{ma} and molar transition energies, $E_T(X)$, of the cyanine dyes X = 3a, 3c, 5b, 9b, 13a, and 13b, measured in thirteen solvents of different polarity at 25 °C

Solvents	$E_T(30)$ Kcal. mol[a]	λ_{max} nm (3a)[b]	$E_T(3a)$ Kcal.mol	λ_{max} nm (3c)	$E_T(3c)$ Kcal.mol	λ_{max} nm (5b)	$E_T(5b)$ Kcal.mol	λ_{max} nm (9b)	$E_T(9b)$ Kcal.mol	λ_{max} nm (13a)	$E_T(13a)$ Kcal.mol	λ_{max} nm (13b)	$E_T(13b)$ Kcal.mol
Water	63.1	470	60.77	500	57.18	485	58.95	466	61.35	567	50.43	551	51.89
Ethane-1,2-diol	56.3	481	59.38	510	56.06	493	58.00	481	59.44	579	49.38	559	51.06
Methanol	55.4	487	58.71	515	55.52	502	56.95	503	56.84	581	49.21	569	50.25
Ethanol	51.9	492.	58.11	524	54.56	512	55.80	515	55.52	593	48.21	584	48.96
1-Propano1	50.7	498	57.41	532	53.74	521	54.88	523	54.67	605	47.26	593	48.21
1-Butanol	50.2	504	56.61	541	52.49	533	53.64	534	53.54	613	46.61	601	47.57
2-Propanol	48.4	512	55.84	550	51.98	539	53.05	543	52.65	619	46.19	613	46.64
Acetonitrile	45.6	521	54.88	559	51.15	547	52.27	549	52.08	627	45.60	621	46.04
DMSO	45.1	535	53.39	567	50.43	555	51.52	557	51.33	635	45.03	629	45.46
Acetone	42.2	547	52.27	573	49.90	561	50.96	565	50.60	647	44.19	635	45.03
Dichloroethane	41.3	557	51.19	579	49.40	569	50.25	573	49.90	659	43.39	643	44.47
Dichloromethane	40.7	563	50.78	583	49.04	575	49.72	579	49.38	667	42.87	651	43.92
Chloroform	39.1	570	50.16	591	48.38	589	48.54	587	48.71	679	42.11	659	43.39
$\Delta\lambda$ $_{\text{resp.}}$ ΔE_T[c,d]	24.0	−100	10.67	−91	8.80	−104	10.41	−121	12.64	−112	8.32	−108	8.50

[a] $E_T(30)$ values were taken from ref. [18].
[b] $E_T[\text{kcal.mol}^{-1}] = {}_{28591}/\lambda_{max}[\text{nm}]$ [19].
[c] $\Delta\lambda = \lambda_{max}$ (H_2O) _ λ_{ma} $(CHCl_3)$.
[d] $\Delta E_T = E_T$ (H_2O) _ E_T $(CHCl_3)$.

to an increase of their molar transition energies E_T of about 9.88 k cal/mol (Table 3). With increasing solvent polarity the electron dipolar ground state of these cyanine dyes is increasingly stabilized by solvation, relative to the less dipolar excited state-with the observed hypsochromic band shifts as consequence.

5. Experimental

Melting points (m.p.) were recorded on a Galenkanp melting point apparatus and are uncorrected. Elemental analyses were carried out at the micro analytical 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 Spectrophotometer.

The organic solvents were of spectroscopic grades and the new dyes were purified using TLC chromatographic procedure. The visible spectra of the synthesized dyes were recorded on a Shimadzu UV/visible 160-A spectrophotometer. The stock solution was about 1X 10^{-3}, the lower molarities were obtained by accurate dilution.

2-Cyanomethylene (2-ethoxy carbonylmethylene)-4,5-dihydrothiazolin-4-one 1a,b was prepared in accordance to reference [11].

5.1. Synthesis of 2-cyanomethylene (2-ethoxy carbonylmethylene)-4,5-dihydro-4-oxo-N-propylthiazolium iodide ***2a,b***

A pure sample of **1a,b** (0.01 mol) was suspended in excess iodopropane and heated on a water-bath for 5 h. The precipitates formed were washed with ethanol. The results are given in Table 1.

5.2. Synthesis of 2-cyanomethylene (2-ethoxy carbonylmethylene)-7H-4-phenyl thiazolo[3,2-a]oxazolo bromide ***3a,b***

A mixture of compound **1a,b** (0.01 mol) and phenacyl bromide (0.01 mol) was dissolved in benzene (30 ml). The reaction mixture was refluxed on a water-bath for 30 min, after which the excess of benzene evaporated. The synthesized product was refluxed under thermal condition in the presence of piperidine (3–5 drops) for 10 min, followed by triturating with ethanol to give compound **3a,b**. Characterized data are listed in Table 1.

5.3. Synthesis of 2-cyanomethylene (2-ethoxy carbonylmethylene)-4,5-dihydrothiazolone-2[4(1)]-mono-methine ***4a-d*** *and thiazolo[3,2-a]oxazolo-2[4(1)]-monomethine cyanine dyes* ***9a,b***

Mixtures of compounds **2a,b** and/or **3a,b** (0.01 mol) and 1-methyl pyrimidinium, quinolinium, or isoquinolinium iodide were dissolved in ethanol (30 ml) and piperidine was added (2 ml). The reaction mixture was refluxed for 10 h, filtered hot and cooled. The precipitated products, after dilution with water, were collected and recrystallized from methanol. Characterization data are listed in Table 1.

5.4. Synthesis of 2-cyanomethylene (2-ethoxy carbonylmethylene)-4,5-dihydrothiazole and thiazolo[3,2-a]oxazolo-2(2)-trimethine cyanine dyes ***6a,b*** *and* ***11a,b***

Mixtures of compounds **2a,b** and/or **3a,b** (0.01 mol) and ethyl orthoformate (0.01 mol) were dissolved ethanol (20 ml), and piperidine (2 ml) was added. The reaction mixture was refluxed for 5 h, filtered hot and cooled. The precipitated product was crystallized from ethanol to give the intermediate compounds **5a,b** and **10a,b**. Characterization date are listed in Table 1.

Mixtures of **5a,b** and **10a,b** (0.01 mol) and 1,2-di methyl quinolinium iodide (0.01 mol) were used. The reaction was essentially the same as that for **4a–d** and **9a,b**. Characterization data are listed in Table 1.

5.5. Synthesis of 2-cyanomethylene (2-ethoxy carbonylmethylene)-4,5-dihydrothiazolo and thiazolo[3,2-a]oxazolo-2(2)-heptamethine cyanine dyes ***8a,b*** *and* ***13a,b***

Mixtures of **2a,b** and/or **3a,b** (0.01 mol) and 2-chlorocyclohexane-1,3-dicarboxaldehyde (0.01 mol) were dissolved in ethanol (30 ml) and piperidine

(3 ml) was added. The reaction was essentially the same as that for **5a**,**b** and **10a**,**b**. characterization data of intermediate compound **7a**,**b** and **12a**,**b** are listed in Table 1.

Mixtures of **7a**,**b** and **12a**,**b** (0.01 mol) and 1,2-dimethyl quinoline iodide (0.01 mol) were dissolved in ethanol (30 ml) and piperidine (1–3 ml) was added. The products were obtained essentially using the same method as for **4a–d** and **9a**,**b**. Characterization data of **8a**,**b** and **13a**,**b** are listed in Table 1.

Uncited schemes

Schemes 1a and 1b are not cited in the text.

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