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The Synthesis of Some Bridgehead Heterocyclic Monomethine Cyanine Dyes

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ABSTRACT

α-Chloroacteic acid and phenacyl bromide were used as reagents reacting with 8-hydroxyquinoline to form bridgehead heterocycles. Reaction of these heterocycles with equi-or bis-molar ratios of 2-(or 4-)methyl substituted heterocyclic quaternary salts afforded a series of monomethine and bismonomethine cyanine dyes. The electronic spectra of the monomethine cyanine dyes in various solvents are discussed. © 1998 Elsevier Science Ltd. All rights reserved

Keywords: reagents, quaternary reagent, phenacyl bromide, negative solvatochromism.

INTRODUCTION

Much work has been carried out on the synthesis of assembled heterocyclic systems to prepare and study the properties of different types of cyanine dyes [1–5]. Little attention has been focused on the use of bridgehead heterocycles in the synthesis of monomethine cyanine dyes. 8-Hydroxyquinoline derivatives and other heterocyclic moieties containing quinoline nuclei have prepared for their evaluation as chemotherapeutical agents and in treatment of various diseases [6, 7]. Monomethine cyanine dyes have also found various applications as photosensitizers in blue green light [8, 9] and as bacteriocidal agents [10, 11]. This present paper describes the synthesis of some bridgehead heterocycles and their application for monomethine dyes.

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RESULTS AND DISCUSSION

The reaction of α-chloroacetic acid with 8-hydroxyquinoline in benzene is a useful method to obtain the quaternary salt 8-hydroxyquinolinium chloride-1-acetic acid **1** [12]. The reaction proceeds via reaction of α-chloroacetic acid as quaternary reagent with the base of 8-hydroxyquinoline. Reaction of **1** with **2**-(and 4-)-methyl-substituted heterocyclic quaternary salts, (viz., α and γ- picoline and quinaldine ethiodides) in piperidine as basic catalyst gave the 8-hydroxyquinoline-1-acetic acid-4yl[2(4)]-monomethine cyanine dyes (**2a**–**2c**). Dehydration of **1** by fusion in the presence of basic catalysis afforded the corresponding bridgehead quinolinium[b,c]-1,4-oxazin-2-one chloride **3**, which was then condensed with equi-(bi)-molar ratios of **2**- and **4**-methyl-substituted heterocyclic quaternary salts to give the quinolino[b,c]-1,4-oxazine-2yl[2(4)]-mono-methine and 2,6 diyl[2(4)]-bis monomethine cyanine dyes (**4a**–**4c**) and (**5a**–**5c**) respectively. The reaction sequence is as shown in Scheme 1.

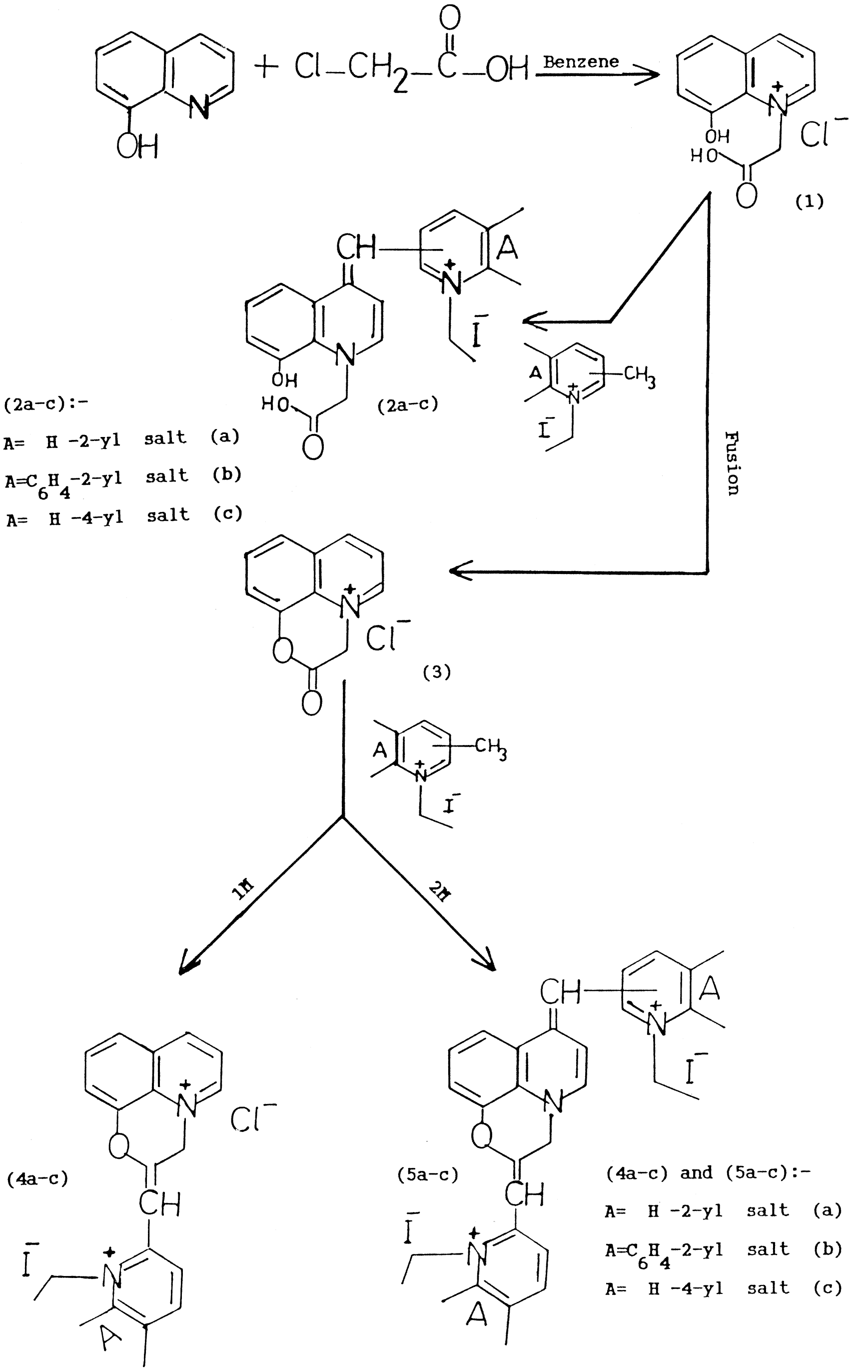
Characterisation data for the intermediates (**1** and **3**) and of the mono-methine cyanine dyes **2a**–**2c**, **4a**–**4c** and **5a**–**5c** are summarized in Table 1.

Reaction of phenacyl bromide and derivatives with 8-hydroxyquinoline in benzene [12] afforded the 8-hydroxyquinolinium-1-phenacyl bromide salts **6a**–**6c**. Interaction of **6a**–**6c** with 2-methyl quinolinium ethiodide in the presence of piperidine gave the 8-hydroxyquinolinium-1-phenacyl-4yl(2)-mono-methine cyanine dyes **7a**–**7c**. Dehydration of **6a**–**6c** by fusion in the presence of a basic catalyst gave the corresponding 2-arylquinolinium [b,c]-1,4-oxazine bromide salts **8a**–**8c**. Furthermore, reaction of compound **8c** with ammonium acetate in the presence of acetic acid and/or with hydrogen sulphide gas gave the 2(4-nitrophenyl)-quinolinium[b,c]-1,4-1H-quinoxaline bromide salt **8d** the 2(4-nitrophenyl)-quinolinium[b,c]-1,4-thiazine bromide salt **8e**. Interaction of compounds **8a**–**8e** with 2- and 4-methyl substituted heterocyclic quaternary salts in presence of a basic catalyst afforded the 2-arylquinolino[b,c]-1,4-(oxazine,-1H-quinoxaline and thiazine)-6yl[2(4)]-monomethine cyanine dyes **9a**–**9g**. The reaction sequence is as shown in Scheme 2.

Characterisation for the monomethine cyanine dyes **7a**–**7c**, **9a**–**9g** and of the intermediates **6a**–**6c** and **8a**–**8d** are summarized in Table 2.

Relation between structure and spectra of the monomethine cyanine dyes

The $\lambda_{\max}$ and $\varepsilon_{\max}$ for the monomethine cyanines (**2a**–**2c**, **4a**–**4c**, **5a**–**5c**, **7a**–**7c** and **9a**–**9c**) are shown in Tables 1 and 2. The absorption spectra of the 8-hydroxyquinoline-1-acetic acid-4yl[2(4)] monomethine cyanines (**2a**–**2c**), quinolino [**b**,**c**]-1,4-oxazine-2yl-[2(4)]-monomethine cyanines (**4a**–**4c**) and

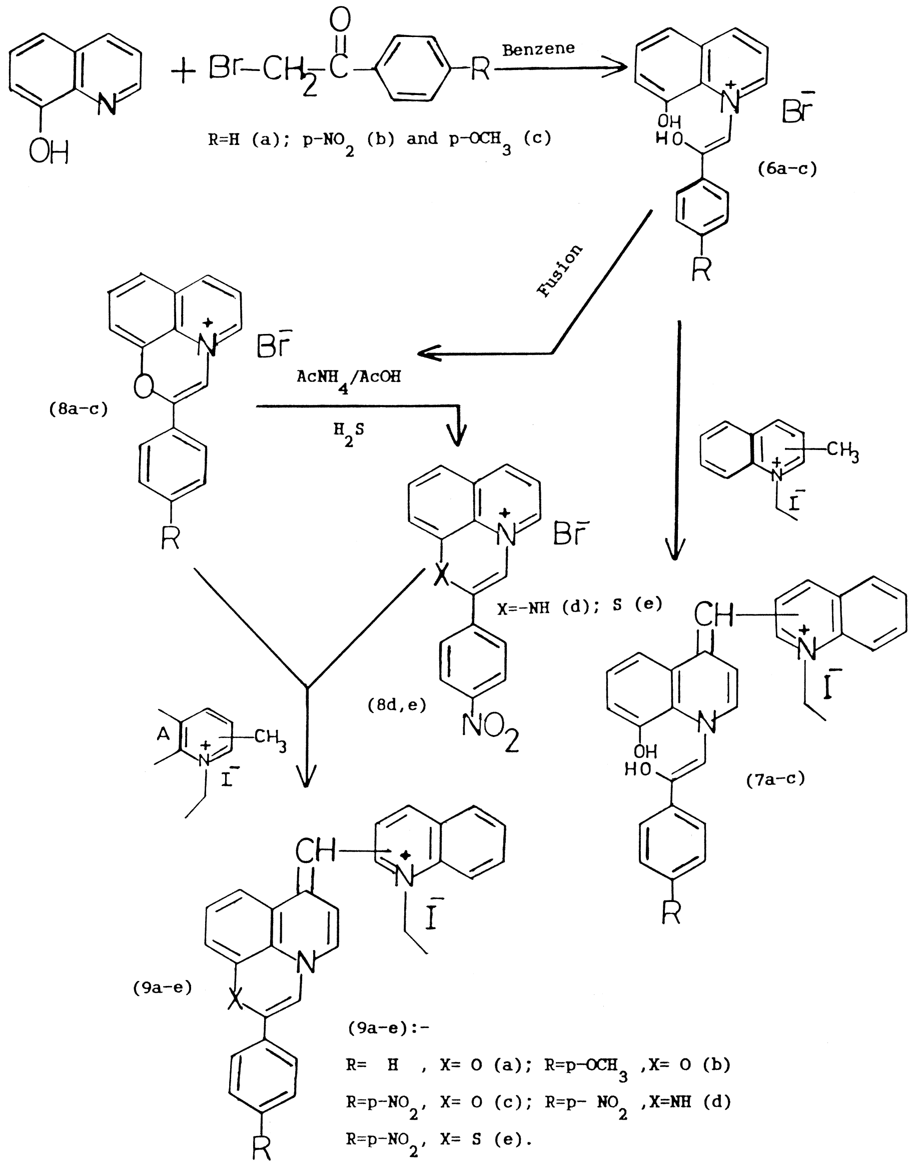

Benzene
(1)
Fusion
(2a-c)
(2a-c):-
A= H -2-yl salt (a)
A=C6H4-2-yl salt (b)
A= H -4-yl salt (c)
(3)
1M
2M
(4a-c)
(5a-c)
(4a-c) and (5a-c):-
A= H -2-yl salt (a)
A=C6H4-2-yl salt (b)
A= H -4-yl salt (c)

Scheme 1.

TABLE 1
Characterisation data for the monomethine cyanine dyes **2a**–**2c**, **4a**–**4c** and **5a**–**5c**

Compound no.	*Formula*	*Calc. %*					*Vis. spectra*	*IR(KBr)*	*^{1}H-NMR (CDCl$_3$)*
		Found %			*Yield*	*M.p.*	λ_{max} (log ε_{max})	λ_{max} /cm^{-1}	
		C	*H*	*N*	%	°C		*Assignment*	*δ Assignment*
2a	$C_{19}H_{19}N_2O_3I$ (450)	50.67 50.53	4.22 4.25	9.33 9.12	45	220-2	365 (4.24) 510 (3.90)	2960 (Ethiodide) 1690 (C=O) 3300 (-OH)	6.5–7.4 (m,9H, Ar- + het.-H) 6.2 (s, 1H, C=CH) 10.3 (s,1H,OH-acid) 4.5 (s,1H,OH-Ar) 2.2 (s,2H,CH_2-N)
2b	$C_{23}H_{21}N_2O_3I$ (500)	55.20 55.08	4.20 4.30	8.40 8.21	71	168-6	395 (3.95) 410 (3.91) 510 (3.95) 550 (4.09) 585 (4.25)	2960 (Ethiodide) 1695 (C=O) 300 (OH)	6.7–7.7 (m,11H,Ar- + het.-H) 6.5 (s,1H,C=CH) 10.3 (s,1H,OH-acid) 4.3 (s,1H,OH-Ar.) 2.2 (s,2H,CH_2-N)
2c	$C_{19}H_{19}N_2O_3I$ (450)	50.67 50.75	4.22 4.19	9.33 9.45	61	2353	365 (4.32) 400 (4.20) 480 (4.08) 513 (4.17) 540 (4.09)		
4a	$C_{19}H_{18}N_2OICl$	50.39	3.98	6.19	62	187-9	415 (4.46) 460 (4.34)	2960 (Ethiodide)	6.9–7.3 (m,12H,Ar- + het.-H) 5.9 (s,1H,-C=CH-N^+)

	(452.5)	50.23	4.06	6.21			510 (4.16)		5.9 (q,2H,CH$_2$-)
							560 (3.86)		1.8 (t,3H,CH$_3$-)
							595 (3.98)		
4b	$C_{23}H_{20}N_2OICl$	54.93	3.98	5.57	75	166-4	515 (4.13)		
							565 (4.18)		
	(502.5)	55.11	4.03	5.43			600 (4.11)		
							660 (3.86)		
4c	$C_{19}H_{18}N_2OICl$	50.39	3.98	6.19	64	198-6	420 (4.38)		
							500 (3.98)		
	(452.5)	50.46	3.92	6.22			510 (3.92)		
							560 (3.62)		
							600 (3.38)		
5a	$C_{27}H_{27}N_3OI_2$	48.87	4.07	6.34	66	222-4	460 (4.23)		
	(663)	48.95	3.98	6.44			510 (4.03)		
5b	$C_{35}H_{31}N_3OI_2$	55.05	4.06	5.51	85	210-2	500 (4.13)	2980 (Ethiodide)	6.2–7.3 (m,19H,Ar- + het.-H)
							525 (4.08)		5.8 (s,2H,two = CH)
	(763)	54.93	4.13	5.46			570 (4.35)	1130 (C-O-C)	4.1 (q,4H,two-CH$_2$-)
							620 (4.16)		
									1.8 (t,6H,two CH$_3$-N$^+$)
5c	$C_{27}H_{27}N_3OI_2$	48.87	4.07	6.34	68	194-6	410 (4.48)		
	(663)	48.65	4.15	6.45			460 (4.23)		
							520 (4.12)		



Scheme 2.

quinolino [**b**,**c**]-1,4-oxazine-2,6-diyl[2(4)]-monomethine cyanine (**5a**–**5c**) in 95% ethanol exhibit various bands within the wavelength range 365–660 nm. These bands are affected by the nature of the heterocyclic residue (A). For example, comparing A = pyridinium-2yl in compound **2a** with A = quinolinium-2-yl in compound **2b** red shifts of 30–40 nm occur, with the appearance

TABLE 2

Characterisation Data for the Intermediates and Monomethine Cyanine Dyes **6a**–**6c**, **7a**–**7c**, **8a**–**8e** and **9a**–**9e**

Compound no.	*Formula*	*Calc. %*					*Vis. spectra*	*IR(KBr)*	*^{1}H-NMR (CDCl$_3$)*
		Found %			*Yield*	*M.p.*	$\lambda_{max}(\log \varepsilon_{max})$	$\lambda_{max}/\text{cm}^{-1}$	
		C	*H*	*N*	%	°C		*Assignment*	*δ Assignment*
6a	$C_{17}H_{14}NO_3Br$	59.30	4.07	4.07	82	85-7		1710 (C=O)	6.5–7.3 (m,11H,Ar- + het.-H)
	(344)	58.97	3.96	4.12			3300 (-OH)	4.1 (s,2H,CH_2-N^+)	
									4.5 (s,1H,OH-)
6b	$C_{18}H_{16}NO_3Br$	55.75	4.28	3.74	89	71.3		1710 (C=O)	6.4–7.2 (m,10H,Ar- + het.-H)
		57.89	4.25	3.99				3300 (OH)	3.9 (s,2H,CH_2-N^+)
									4.5 (s,1H,OH-)
									2.8 (2,3H,OCH_3)
6c	$C_{17}H_{13}N_2O_4Br$	52.44	3.34	7.29	76	105-3			
	(389)	52.38	3.37	7.33					
7a	$C_{29}H_{25}N_2O_2I$	62.14	4.46	5.00	65	120-8	475 (3.68)	1700 (C=O)	6.5–7.4 (m,16H,Ar- + het.-H)
							500 (3.64)		5.9 (s,1H, =CH)
	(560)	62.23	4.53	4.91			550 (3.66)	3300 (OH)	4.5 (s,1H,OH)
							585 (3.81)	2980 (EtI)	3.9 (q,2H,CH_2-$^+$)
									2.1 (s,2H,CH_2-N)
									1.5 (t,3H,CH_3-)
7b	$C_{30}H_{27}N_2O_2I$	61.02	4.58	4.75	76	133.5	480 (3.89)		
							510 (3.86)		
	(590)	60.96	4.64	4.72			550 (4.00)		
							590 (4.19)		
7c	$C_{29}H_{26}N_3O_4I$	57.52	3.97	6.94	63	145-7	415 (3.44)		
							495 (3.64)		
	(605)	57.39	4.03	6.86			550 (3.71)		
							580 (3.89)		

(continued)

Table 2—*contd*

Compound no.	*Formula*	*Calc. %* *Found %* *C*	 *H*	 *N*	*Yield* %	*M.p.* °C	*Vis. spectra* $\lambda_{max}(\log \varepsilon_{max})$	*IR(KBr)* $\lambda_{max}/\mathrm{cm}^{-1}$ *Assignment*	*^{1}H-NMR (CDCl$_3$)* *δ Assignment*
8a	$C_{17}H_{12}NOBr$ (326)	62.58 62.63	3.68 4.59	4.30 4.33	68	65-7		1130 (C-O-C)	6.7–7.7 (m,12H,Ar- + het.-H)
8b	$C_{18}H_{14}NO_2Br$ (356)	60.67 60.49	3.93 4.03	3.93 3.90	76	54-2			
8c	$C_{17}H_{11}N_2O_3Br$ (371)	54.99 55.11	2.97 3.98	7.55 7.49	59	76-4			
8d	$C_{17}H_{12}N_2O_3Br$ (370)	55.14 55.21	3.24 3.26	11.35 11.25	64	118-6		3300 (NH)	6.4–7.5 (m,11H,Ar- + het.-H) 4.5 (s,1H,NH-)
8e	$C_{17}H_{11}N_2O_3SBr$ (387)	52.71 52.59	2.84 2.90	7.24 7.23	65	155-7			
9a	$C_{29}H_{23}N_2OI$ (542)	64.21 64.15	4.24 4.27	5.17 5.10	85	167.5	480 (3.57) 510 (3.61) 560 (3.80) 585 (4.02) 680 (3.08)	1130 (C-O-C)	6.5–7.4 (m,17H,Ar- + het.-H) 6.2 (s,1H, = CH) 3.9 (q,2H,CH_2-N^+) 1.7 (t,3H,CH_3-)

9b	$C_{30}H_{25}NO_2I$ (572)	62.94 63.10	4.37 4.40	4.90 5.07	88	135-3	485 (3.98) 510 (3.98) 565 (4.08) 595 (4.14) 690 (3.92)	1120 (C-O-C)	6.3–7.1 (m,16HAr. + -het.-H) 6.3 (s,1H,-CH) 3.9 (q,2H,CH_2-N) 2.2 (s,3H,OCH_3) 1.5 (t,3H,CH_3)
9c	$C_{29}H_{22}N_3O_3I$ (587)	59.29 59.11	3.75 3.79	7.16 7.12	74	210.2	460 (4.16) 505 (4.11) 550 (4.11) 582 (4.18) 670 (3.94) 685 (3.92)		
9d	$C_{29}H_{23}N_4O_2I$ (586)	59.39 59.32	3.93 3.90	9.56 9.61	70	120-2	470 (4.31) 540 (4.27) 585 (4.37) 680 (4.41) 690 (4.16)	3300(NH)	6.5–7.4 (m,16H,Ar- + het.-H) 6.3 (s,1H, = CH) 4.5 (s,1H,-NH) 3.9 (q,2H,CH_2-N^+) 1.4 (t,3H,CH_3-)
9e	$C_{29}H_{22}N_3O_2SI$ (603)	57.71 57.89	3.65 3.70	6.69 7.02	73	142-4	470 (3.78) 547 (4.00) 585 (4.20) 698 (3.20)		

of three new bands. This can be attributed to the more extensive π-delocalisation within the quinolinium 2-yl salt. Changing the linkage position of the pyridinium residue from the 2-yl to the 4-yl salt in compounds **2a**–**2c**, **4a**–**4c** and **5a**–**5c** resulted in bathochromic shifts, due to increase in the conjugation of the pyridine in the 4-yl linking (Table 1).

Comparison of the visible absorption spectra of the quinolino[b,c]-1,4-oxazine-2yl[2(4)] monomethine cyanine dye **4**–**b** with the quinolino[b,c]-1,4-oxazine-2yl[2(4)] bis monomethine cyanine dye **5b** showed that the former compound is the more bathochromic, due to the antagonistic effect in the bis monomethine cyanine **4**–**b**.

The electron spectra of the 8-hydroxyquinolino-1-phenacyl-4-yl(2)- monomethines **7a**–**7c** and of the 2-arylqeinolino[b,c]-1,4-(oxazine,-1,4-quinoxaline and thiazine)6yl(2)-monomethines **9a**–**9c** in ethanol reveal four and six absorption bands located in the wavelength range 375–698 nm. These bands are influenced by nature of the substituents R in compounds **7a**–**7c** and of the X-heteroatom in compounds **9a**–**9c**. For example, replacing $R = p\text{-}NO_2$ in compound **7c** by $R = p\text{-}OCH_3$ in compound **7b** results in red shifts of 15–60 nm, which can be attributed to an increase of delocalisation of electrons by the electron donor character of the $\text{-}OCH_3$ group. Similarly replacing $R = NO_2$ and X = O- in compound **9c** by $R = NO_2$ and X = -S- in compound **9e**, bathochromic shifts of 3–28 nm occur, which can be attributed to the more enhanced donor nature of the sulphur atom relative to oxygen.

Solvatochromic behaviour of some selected monomethine cyanines

The electronic spectra of some selected monomethine cyanine dyes, viz., **7b**, **8e** and **8f** were studied in different solvents [13], and the results are shown in Table 3. The difference between the values of λ_{max} are recorded in polar and nonpolar solvents and gives an indication of the relative solvotachromic behaviour. The experimental observation of negative solvatochromism, i.e., hypsochromic shift with increased solvent polarity (Table 3), is comparatively uncommon, and indicates that the lowest excited states of these monomethine cyanine dyes are less polar than the ground states [14, 15].

EXPERIMENTAL

Melting points are uncorrected. IR spectra were determined on a Unicam SP1200 spectrophotometer (KBr). Electronic spectra were recorded on a Shimadzu U.V/Vis-240 recording spectrophotometer and ^{1}H-NMR spectra on an EM-390 90 MHz NMR spectrometer.

TABLE 3
Visible absorption spectra of some selected monomethine cyanine dyes in organic solvents at 27°C

Compound no.	*DMF*	*EtOH* $\lambda_{\max}$ *nm*	*CHCl₃*	*1,4-Diox.* $\log \varepsilon_{\max}$ ($mol^{-1}\,cm^{-1}$)	*Benzene*	$\Delta\lambda$ (*DMF-Benzene*)
7a	470 (4.01)	475 (3.68)	480 (3.97)	486 (3.97)	492 (3.97)	22
	492 (3.92)	500 (3.64)	510 (3.95)	517 (3.92)	522 (3.95)	30
	538 (3.87)	550 (3.66)	562 (3.98)	570 (3.96)	576 (3.96)	38
	568 (4.12)	585 (3.81)	600 (4.13)	608 (4.13)	612 (4.12)	44
9b	473 (3.91)	485 (3.98)	491 (3.89)	495 (3.86)	498 (3.92)	25
	505 (3.90)	510 (3.98)	517 (3.92)	523 (3.85)	527 (3.89)	22
	553 (4.01)	565 (4.08)	573 (3.98)	578 (3.96)	584 (3.97)	31
	586 (4.07)	595 (4.14)	605 (4.06)	612 (4.04)	617 (4.05)	31
	580 (3.83)	590 (3.92)	692 (3.87)	695 (3.78)	698 (3.88)	18
9d	460 (4.30)	470 (4.31)	477 (4.31)	481 (4.32)	484 (4.32)	24
	532 (4.24)	540 (4.27)	545 (4.30)	552 (4.28)	559 (4.29)	27
	575 (4.36)	585 (4.37)	593 (4.40)	598 (4.38)	603 (4.40)	28
	688 (4.16)	680 (4.41)	685 (4.45)	688 (4.43)	690 (4.45)	22
	685 (4.07)	690 (4.16)	693 (4.19)	696 (4.21)	698 (4.22)	13

Synthesis of 8-hydroxyquinolinium chloride-1-acetic acid 1

A mixture of 8-hydroxyquinoline (0.01 mol) and α-chloroacetic acid (0.01 mol) was dissolved in benzene (40 ml). The reaction mixture was refluxed on a water bath for 30 min, after which excess of benzene evaporated. A yellow micro crystalline product was obtained, m.p-95°C, Yield 87%.

Analytical data for $C_{11}H_{10}NO_3CI$ (Mol. wt = 239.5)

Calc. %	C = 55.12	H = 4.18	N = 5.85
Found %	C = 55.32	H = 4.30	N = 6.19

IR(KBr): 1710 cm^{-1} ($\nu C{=}O$) and 2940 (νCH_2).

^1H NMR ($CDCl_3$): $\delta = 7.2$–8.1 (m, 6H, quinol.-H), 4.9 (s, 1H-OH-qinoline), 3.95 (s,2H, CH_2-N^+) and 10.0 (s,1H,OH-acid).

Synthesis of 8-hydroxyquinolinium-1-acetic acid 4yl[2(4)] monomethine cyanine dyes 2a–2c

A mixture of **1** (0.01 mol) and the appropriate 2-(or 4-)-methyl-substituted heterocyclic quaternary salt (0.01 mol) was dissolved in ethanol (30 ml) and piperidine (3–5 drops) was added. The reaction mixture was refluxed for 8–10 h, filtered hot, concentrated and cooled. The precipitated products, after dilution with water, were collected and recrystallised from ethanol. Characterisation data are given in Table 1.

Synthesis of quinolinium[b,c]-1,4-oxazin-2-one chloride 3

8-Hydroxyquinolinium chloride-1-acetic acid (2 gm) was heated on a sand bath without solvent in the presence of catalytic amount of piperidine for 30 min, and then cooled. The semi-solid product was dissolved in ethanol, refluxed for 30 min, filtered hot, concentrated and cooled. The resultant crude product was then crystallised from methanol. m.p = 55–7, Yield = 73%.

Analytical data for $C_{11}H_8NO_2CI$ (Mol. wt = 221.5)

Calc. %	C = 59.59	H = 3.61	N = 6.32
Found %	C = 59.23	H = 3.7	N = 6.51

IR(KBr): 1700 cm^{-1} (νC = O) and 1130 (νC-O-C).
^{1}H NMR ($CDCl_3$) : $\delta = 7.3–8.1$ (m, 6H, quinol.-H), and 3.9 (s,2H-CH_2-N^+).

Synthesis of quinolino[b,c]-1,4-oxazin-2yl[2(4)]monomethine 4a–4c and 2,6 diyl[2(4)]-bismonomethine 5a–5c

A mixture of **3** (0.01 mol) and the appropriate 2- or 4-substituted heterocyclic quaternary salt (0.01, 0.02 mol) was used. The reaction was essentially the method as that for **2a**–**2c**. Characterisation data are is listed in Table 1.

Synthesis of 8-hydroxyquinolinium-1-phencayl bromide 6a–6c

Essentially the same method as for **1** using phenacyl bromide and its derivatives, the products were purified by recrystallisation from methanol and relevant data are given in Table 2.

Synthesis of 8-hydroxyquinolinium-1-phencayl-4yl(2)-monomethine cyanine dyes 7a–7c

A mixture of **6a**–**6c** (0.01 mol) and quinaldine ethiodide (0.01 mol), the products were obtained essentially using the same method as for **2a**–**2c**. Characterisation data are listed in Table 2.

Synthesis of 2-arylquinolinium[b,c]-1,4-oxazine bromide salts 8a–8c

Essentially the same method as for **3**. Characterisation data are listed in Table 2.

Synthesis of 2-(4-nitro phenyl)quinolinium[b,c]-1,4-1H-quinoxaline bromide salt 8d

A mixture of **8c** (0.01 mol) and ammonium acetate (0.02 mol) was dissolved in acetic acid. The reaction mixture was refluxed for 3.5 h. Excess of acetic acid was distilled off, and the cooled residue neutralized with sodium bicarbonate. The product was recrystallised from ethanol (Table 2).

Synthesis of 2-(4-nitrophenyl)quinolinium[b,c]-1,4-thiazine bromide salt 8e

Compound **8c** (0.01 mol) was dissolved in ethanol (30 ml). Hydrogen sulphide gas was added through the solution for 20 min, and the liquor then concentrated and cooled. The product was obtained after dilution with water and was then recrystallised from ethanol (Table 2).

Synthesis of 2-arylquinolino[b,c]-1,4-(oxazine, 1H-quinoxaline and thiazine)-6yl[2(4)]-monomethine cyanine dyes 9a–9e

From a mixture of compounds **8a**–**8e** (0.01 mol) and the appropriate 2- or 4-methyl–substituted heterocyclic quaternary salts (0.01 mol), using the procedure described above for **2a**–**2c**. Characterisation data are listed in Table 2.

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