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Studies on some new bridgehead nitrogen heterocyclic cyanine dyes

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Abstract. New asymmetrical mono-(tri)-methine and azomethine cyanine dyes of pyrazolo[5,4-*b*] quinolino [*a*, *b*]-1,4-pyra-(oxa)-zinium bromide salts were prepared. The new synthesized cyanines were identified by elemental and spectral analyses. The visible absorption spectra of some selected dyes were investigated in single and mixed solvents, and also in aqueous buffer solutions. The spectral shifts were studied in relation to molecular structure and in terms of medium effects. Molecular complex formation with DMF was verified through mixed-solvent studies.

Keywords. Cyanine dyes; synthesis; solvatochromism; mixed solvents; acid–base behaviour.

1. Introduction

As an extension to our earlier work on the synthesis and studies of cyanine dyes [1–3], some new bridgehead nitrogen heterocyclic cyanine dye moieties have been synthesized in view of the applicability of such compounds in the production of photothermographic imaging materials [4], electrophotographic lithographic printing material for semiconductor laser exposure [5], as indicators and *p*H sensors [6], and as anti-tumor agents [7].

With these ideas, pyrazolo[5,4-*b*]quinolino[*a*, *b*]-1,4-pyra-(oxa)-zinium bromide salts (**3a–c**) were used as key intermediates for dye synthesis.

2. Results and discussion

2.1 *Synthesis*

Interaction of 4-bromo-3-methyl-1-(hydro/phenyl)-pyrazol-5-one (**1a,1b**) [8] and 8-amino-/hydroxy-quinoline (**2a,b**), in the presence of *n*-butanol as solvent, afforded under dehydration and selective quaternization processes, new bridgehead nitrogen heterocycles (key intermediate compounds), namely 3-methyl-1-(hydro/phenyl)-pyrazolo-[5,4-*b*] quinolin[*a*, *b*]-1,4-pyra-(oxa) zinium bromide salts (**3a–c**). The polarizability of the N–H (OH) bonds of 8-amino-(hydroxy)quinoline showed the higher nucleophilic character of the nitrogen (oxygen) atoms and proceeded by stronger and faster nucleophilic attack on the electron-deficient five-carbon atom (that of N-substituted phenyl pyrazolone being easier than those of the N-unsubstituted analogues). The resulting OH group abstracts a proton from the protonated secondary amine or oxygenated ether groups leading to loss of

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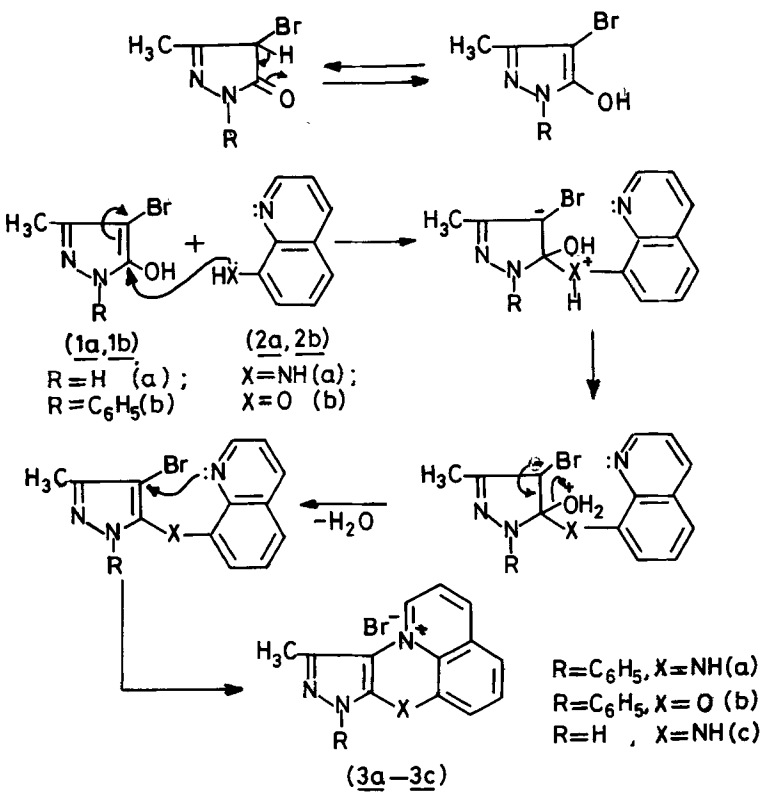
a water molecule followed by transfer of the negative charge and formation of a double bond. Polarization of the C–Br bond was increased and the carbon atom was attacked by the lone pair of the quinolino-nitrogen atom leading to the formation of bridgehead heterocyclic quaternary bromide salts (scheme 1). Thus, pyrazinium bromide salt is practically prepared by a relatively short reaction as compared to that needed for oxazinium bromide formation.

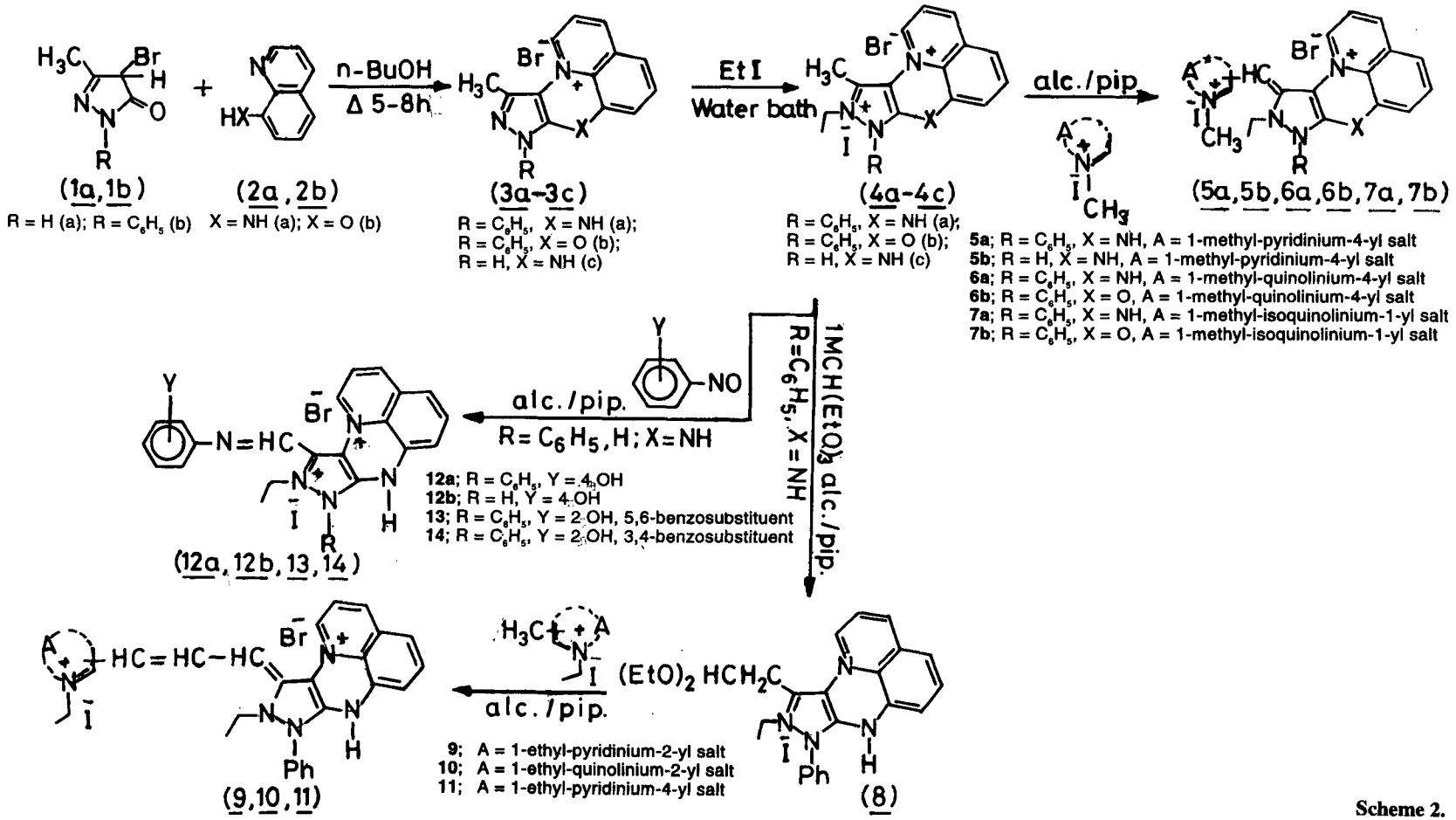
Extra quaternization of the former intermediates using excess ethyl iodide under controlled conditions gave 3-methyl-1-(hydro/phenyl)-pyrazolium-[5,4-*b*]-quinolino[*a*, *b*]-1,4-pyra-(oxa)-zinium-2(4)-ethiodide (bromide) salts (**4a–c**). Further reaction of the latter compounds with pyridinium-quinolinium-, and isoquinolinium-methiodide involving active hydrogen atom in 4-ium or 1-ium moieties under piperidine catalysis gave the corresponding asymmetrical 2-ethyl-1-(hydro/phenyl) pyrazolo-[5,4-*b*]-quinolino[*a*, *b*]-1,4-pyra-(oxa)-zinium bromide-3[4(1)]-mono-methine cyanine dyes **5a,b**; **6a,b**; **7a,b** (scheme 2).

Meanwhile the condensation reaction of (**4a**) with triethylorthoformate under piperidine catalysis gives the intermediate compound (**8**). Further reaction of the latter intermediate compound (**8**) with N-ethyl (α-picolinium-, quinaldinium-, and γ-picolinium) iodide in the presence of piperdine afforded the corresponding asymmetrical trimethine cyanine dyes **9**, **10**, **11** (scheme 2).

Interaction of equimolar ratios of (**4a,c**) and nitroso phenols (p-nitroso-phenol, $\alpha(\beta)$nitroso-$\beta(\alpha)$-naphthol) under basic catalyses achieved the corresponding



Scheme 1.


n-BuOH
Δ 5-8h
EtI
Water bath
alc./pip
alc./pip.
1MCH(EtO)3 alc./pip.
R=C6H5, X=NH
R = C6H5, H; X=NH
(1a,1b)
R = H (a); R = C6H5 (b)
(2a,2b)
X = NH (a); X = O (b)
(3a-3c)
R = C6H5, X = NH (a);
R = C6H5, X = O (b);
R = H, X = NH (c)
(4a-4c)
R = C6H5, X = NH (a);
R = C6H5, X = O (b);
R = H, X = NH (c)
(5a,5b,6a,6b,7a,7b)
5a; R = C6H5, X = NH, A = 1-methyl-pyridinium-4-yl salt
5b; R = H, X = NH, A = 1-methyl-pyridinium-4-yl salt
6a; R = C6H5, X = NH, A = 1-methyl-quinolinium-4-yl salt
6b; R = C6H5, X = O, A = 1-methyl-quinolinium-4-yl salt
7a; R = C6H5, X = NH, A = 1-methyl-isoquinolinium-1-yl salt
7b; R = C6H5, X = O, A = 1-methyl-isoquinolinium-1-yl salt
(12a,12b,13,14)
12a; R = C6H5, Y = 4-OH
12b; R = H, Y = 4-OH
13; R = C6H5, Y = 2-OH, 5,6-benzosubstituent
14; R = C6H5, Y = 2-OH, 3,4-benzosubstituent
(9,10,11)
9; A = 1-ethyl-pyridinium-2-yl salt
10; A = 1-ethyl-quinolinium-2-yl salt
11; A = 1-ethyl-pyridinium-4-yl salt
(8)

Scheme 2.

asymmetrical 1-(hydro-phenyl)-pyrazolium-[5,4-*b*]-quinolino [*a*, *b*]-1,4-pyrazinium-2(4)-ethiodide(bromide)-3-azomethine cyanine dyes **12a,b**; **13**; **14** (scheme 2).

Structures of the newly synthesized compounds **3a–c**, **4a–c**, **5a,b**; **6a,b**; **7a,b**; **8**, **9**, **10**, **11**; **12a,b**; **13** and **14** were established by elemental analysis (tables 1 and 2), IR [9] and ^{1}H NMR [10] spectral data (table 3).

2.2 *Relation between molecular structure and spectral behaviour of the synthesized cyanine dyes*

The electronic absorption spectra of asymmetrical mono-(tri)-methine cyanine dyes **5a,b**; **6a,b**; **7a,b**; (**9**; **10**; **11**) in 95% ethanol showed absorption bands which underwent a strong bathochromic shift on increasing the conjugation of the quaternary heterocylic residue. Thus, the absorption spectra of dyes **5a** (**9** and **11**) incorporating a pyridinium salt moiety showed absorption bands that were hypsochromically shifted compared to their analogue dyes, **6a** (**10**) containing the quinolinium moiety (table 2). This can be attributed to the more extensive π-delocalization within the respective quaternary heterocyclic system.

Changing the linkage position of the heterocyclic quaternary residue from 4-ium to 1-ium iodide in monomethine [compounds **6a** (**6b**) and **7a** (**7b**)] and/or from 4-ium to 2-ium in trimethine cyanines (compounds **9** and **11**) showed that the 1-ium or 2-ium linkage results in a hypsochromic shift in the absorption bands (table 2). This is due to the decreased extended conjugation in 1-ium or 2-ium linkage resulting in decrease of the π-delocalization of electrons through the cyanine molecule pathway.

Table 1. Characterization data for starting and intermediate compounds (**3a–c**; **6a–c** and **8**).

Compound*	m.p. (°C)	Yield (%)	Mol. formula (mol. wt)	Colour	Analysis (%): Calcd. (found) C	H	N
3a	164–167	72	$C_{19}H_{15}BrN_4$ 379·26	Brownish red	60·17 (59·90)	3·99 (4·13)	14·78 (14·53)
3b	142–145	67	$C_{19}H_{14}BrN_3O$ 380·24	Red	60·02 (59·85)	3·71 (3·78)	11·05 (10·95)
3c	182–185	63	$C_{13}H_{11}BrN_4$ 303·16	Yellow	51·51 (51·63)	3·66 (3·60)	18·48 (18·25)
4a	182–185	76	$C_{21}H_{20}BrIN_4$ 535·22	Red	47·13 (46·86)	3·77 (3·83)	10·47 (12·75)
4b	190–193	73	$C_{21}H_{19}BrIN_3O$ 536·21	Brownish red	47·04 (46·77)	3·57 (3·31)	7·84 (7·70)
4c	207–210	64	$C_{15}H_{16}BrIN_4$ 459·13	Brown	39·24 (39·01)	3·51 (3·33)	12·20 (11·99)
8	164–167	92	$C_{26}H_{30}BrIN_4O_2$ 637·36	Reddish violet	49·00 (49·15)	4·74 (4·65)	8·79 (8·51)

*Compounds (**3a–c**) were treated in saturated KI giving iodine vapour in conc. H_2SO_4; **4a–c**, **8** dissolved in conc. H_2SO_4 liberating iodine vapour on heating

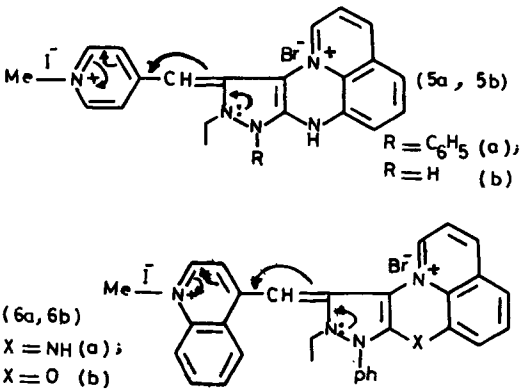
Table 2. Characterization data for asymmetrical mono-, tri-, and azo-methine cyanine dyes (**5a,b**; **6a,b**; **7a,b**; **9**; **10**; **11**; **12a,b**; **13** and **14**).

Compound	m.p. (°C)	Yield (%)	Mol. formula (mol. wt)	Colour	Analysis (%): Calcd. (found) C	H	N	Absorption spectra in 95% ethanol λ_{max} (nm)	ε_{max} (mol^{-1} cm^2)
5a	172–175	65	$C_{27}H_{25}BrIN_5$ 626·34	Reddish violet	51·78 (51·61)	4·02 (4·05)	11·18 (11·35)	400	3200
5b	217–220	64	$C_{21}H_{21}BrIN_5$ 550·24	Reddish violet	45·86 (46·01)	3·85 (3·77)	12·73 (12·88)	450	1218
6a	180–183	75	$C_{31}H_{27}BrIN_5$ 676·40	Violet	55·05 (54·82)	4·02 (4·24)	10·35 (10·30)	520	1600
6b	154–157	71	$C_{31}H_{26}BrIN_5O$ 677·38	Violet	54·97 (55·21)	3·87 (3·39)	8·27 (8·41)	415 515	2106 1173
7a	190–193	67	$C_{31}H_{27}BrIN_5$ 676·40	Brownish violet	55·05 (54·91)	4·02 (4·10)	10·35 (10·50)	500	2584
7b	165–168	67	$C_{31}H_{26}BrIN_4O$ 677·38	Brownish violet	54·97 (54·81)	3·87 (3·70)	8·27 (8·39)	460	1800
9	174–177	59	$C_{30}H_{29}BrIN_5$ 666·40	Brownish violet	54·07 (53·81)	4·38 (4·62)	10·51 (10·46)	500	4600
10	202–205	73	$C_{34}H_{31}BrIN_5$ 716·46	Deep violet	56·99 (57·13)	4·36 (4·25)	9·77 (9·91)	465 510 555	2520 2532 2200
11	188–191	62	$C_{30}H_{29}BrIN_5$ 666·40	Reddish violet	54·07 (53·89)	4·38 (4·22)	10·51 (10·77)	510	1360
12a	135–138	58	$C_{27}H_{23}BrIN_5O$ 640·32	Brown	50·65 (50·73)	3·62 (3·65)	10·94 (11·27)	522	2120
12b	142–140	55	$C_{21}H_{19}BrIN_5O$ 564·22	Brown	44·70 (44·71)	3·39 (3·52)	12·41 (12·46)	470	1800
13	167–170	65	$C_{31}H_{25}BrIN_5O$ 690·38	Brownish violet	53·93 (54·25)	3·65 (3·52)	10·14 (9·91)	530	2720
14	207–210	63	$C_{31}H_{25}BrIN_5O$ 690·38	Red	53·93 (53·87)	3·65 (3·88)	10·14 (10·43)	525	2800

Monomethine dyes incorporating either 1-hydro pyrazolo-(**5b**) or 1,4-pyrazine moieties (**6a** and **7a**) are bathochromically-shifted compared to those incorporating 1-phenyl pyrazolo (**5a**) or 1,4-oxazine analogues (**6b** and **7b**) (table 2). This is due to the antagonistic effect of the N-phenyl pyrazole and/or the greater electron-withdrawing ability of the oxazine nuclei.

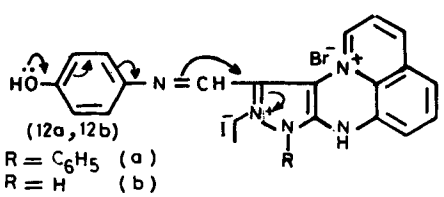
On the other hand, comparison of the spectrum of either asymmetrical mono(tri)-methine cyanine dyes **5a** (**11**) involving pyridinium 4-ium iodide moiety, shows that the absorption band of trimethine dye (**11**) is further bathochromically-shifted by 110 nm than those of the monomethine dye **5a** (table 2). This is due to increasing the number of methine groups which causes an increase in the electron mobility of the cyanine pathway.

The electronic spectra of asymmetrical azomethine cyanine dyes (**12a,b**; **13**; **14**) in 95% ethanol disclose absorption bands which undergo bathochromic or hypsochromic



shifts depending upon the nature of the pyrazolo substituent (R), and the type of phenol involved. Thus, azomethine cyanine dyes incorporating quinolino [*a*, *b*]-1,4-pyrazinium bromide salt and involving naphth-B-OH (**13**) possess absorption band more bathochromically shifted than those involving naphth-*α*-OH analogues (**14**). This is due to greater planarity in the former dye.

On the other hand, it was obvious that the absorption bands of azomethine dye (**12a**) which involved 1-phenyl pyrazolium[5,4-*b*]quinolino[*a*, *b*]-1,4-pyrazinium-2(4)-ethiodide (bromide) salt (R = C_6H_5) are more bathochromically-shifted by 52 nm compared to those of the 1-hydro pyrazolium analogues (**12b**). This is considered as a reverse observation if compared to the electronic absorption spectra of the previous monomethine dyes (**5a,b**). This reversibility is due to the fact that the azomethine cyanine dye moves its electrons from the phenol residue, as a source, to the positively charged N-pyrazolium as a sink, causing intensification of pyrazolium nitrogen fraction deficiency and consequently increases the electrons moving through azomethine cyanine pathway (table 2).



2.3 *Solvatochromic behaviour of asymmetrical mono-, tri-, and azo-methine cyanine dyes (**6b**, **10** and **14**) in pure solvents*

The colours and electronic absorption spectra of some selected dyes **6b**, **10** and **14** in pure organic solvents of different electric relative permittivity, viz. water (78.54), dimethylformamide (DMF) (36.70), ethanol (24.3), chloroform (4.806), carbon tetrachloride (2.238), and dioxane (2.209)[11] respectively, reveal their solvatochromic behaviour due to the different electronic transitions within the solute molecules in the solvents (table 4).

Table 3. IR and ^{1}H NMR spectral data of some selected starting materials, mono-, tri-, and azo-methine cyanine dye derivatives.

Comp.	IR spectrum, ν_{max}^{KBr} (cm^{-1})	^{1}H NMR ($CDCl_3$) spectrum, δ (ppm)
3a	3200–3500 (NH group) 2900–3000 (CH str. of CH_3) 1690–1700 (C=C) 1595–1620 (C=N) 700–760 (Ar. monosubstituted)	7·2–8·9 (*m*, 11H, H_{arom}, H_{hetero}) 4·1 (*s*, 1H, NH group) exchangeable with D_2O 1·25 (*s*, 3H, CH_3 group)
3b	2900–2980 (CH str. of CH_3) 1660–1680 (C=C) 1595–1620 (C=N) 1100–1125 (C–O–C cyclic) 700–760 (Ar. monosubstituted)	7·2–8·8 (*m*, 11H, H_{arom}, H_{hetero}) 1·2 (*s*, 3H, CH_3 group)
4a	2850–2980 (ethiodide) 3200–3500 (NH group) 1690–1700 (C=C) 1595–1620 (C=N)	7·1–8·8 (*m*, 11H, H_{arom}, H_{hetero}) 4·25 (*s*, 1H, NH group) exchangeable with D_2O 1·3 (*s*, 3H, CH_3 group) 0·8–0·95 (*t*, 3H, CH_3*CH_2N^+) 2·0–2·3 (*q*, 2H, CH_3CH_2*N^+)
4b	2900–3060 (ethiodide) 1660–1680 (C=C) 1595–1620 (C=N) 1100–1120 (C–O–C cyclic)	7·2–8·8 (*m*, 11H, H_{arom}, H_{hetero}) 1·2 (*s*, 3H, CH_3 group) 0·8–0·95 (*t*, 3H, CH_3*CH_2N^+) 1·9–2·3 (*q*, 2H, CH_3CH_2*N^+)
6a	2980–3080 (methiodide) 3210–3530 (NH group) 1620–1650 (C=CH) 1660–1680 (C=C)	6·7–8·7 (*m*, 18H, H_{arom}, H_{hetero}, =CH) 2·6 (*s*, 3H, CH_3 joined to immonium centre) 1·4 (*t*, 3H, CH_3*CH_2N^+) 2·2 (*q*, 2H, CH_3CH_2*N^+) 3·3 (*s*, 1H, NH group) exchangeable with D_2O
8	2950–3080 (ethiodide) 3200–3550 (NH group) 2900–2950 (CH str.) 1680–1690 (C=C) 1090–1250 (C–O–C aliph.)	7·2–8·8 (*m*, 11H, H_{arom}, H_{hetero}) 3·65 (*t*, 1H, –CH<) 1·5 (*d*, 2H, $-CH_2-$) 1·35 (*t*, 6H, $2CH_3$*CH_2O) 2·0–2·4 (*m*, 6H, $2CH_3$*$CH_2O_2CH_3$*CH_2N^+)
9	2950–3080 (ethiodide) 3200–3550 (NH group) 2900–2950 (CH str.) 1680–1690 (C=C) 1680–1710 (CH=CH)	6·8–8·8 (*m*, 20H, H_{arom}, H_{hetero}, CH=CH–CH=) 3·00 (*q*, 2H, CH_3CH_2*N^+) 2·20 (*t*, 3H, CH_3*CH_2N^+) 1·2–1·4 (*t*, 3H, CH_3*CH_2N) 2·5 (*q*, 2H, CH_3CH_2*N) 4·2 (*s*, 1H, NH group) exchangeable with D_2O
12a	2850–3040 (ethiodide) 3100–3650 (NH group) 1680–1700 (C=C) 1560–1610 (C=N)	7·2–8·9 (*m*, 16H, H_{arom}, H_{hetero}, N=CH) 4·2 (*s*, 1H, NH group) exchangeable with D_2O 2·25 (*q*, 2H, CH_3CH_2*N^+) 1·10 (*t*, 3H, CH_3*CH_2N) 5·8 (*s*, 1H, phenolic OH) exchangeable with D_2O

Thus, careful examination of the results reported in table 4 shows that the longer bands corresponding to n–π^* transitions and to intramolecular charge transfer (CT) interactions [12] show a bathochromic shift on changing the organic solvent from ethanol to DMF and $CHCl_3$, which can be attributed to the increase in solvent polarity of DMF, and

to the solute–solvent interaction through intermolecular hydrogen bond formation in the case of $CHCl_3$.

The small blue shift observed on changing the organic solvent from ethanol to dioxane and CCl_4 can be explained as being a result of the lower solvent polarity of dioxane and CCl_4. It is worth mentioning that the slight blue shift observed in the λ_{max} in water medium, relative to ethanol, can be mainly ascribed to the interaction of water molecule with the lone electron pair of the fused pyrazolo-nitrogen atom through H-bonding. This decreases slightly the electron density on the nitrogen atom and consequently decreases to some extent the mobility of the π-electrons attached to the conjugated pathway (table 4).

2.4 *Spectral behaviour of dye (14) in mixed solvents*

In order to evaluate the possibility of the formation of a hydrogen-bonded solvated complex between the solute molecules and DMF, the electronic spectra of dye **14** in $CHCl_3$, CCl_4 and dioxane containing progressively increasing quantities of DMF (mixed solvents) were taken and showed an increase in the absorbance of the CT band with increasing proportion of DMF.

Evidence for hydrogen bond formation between the solute molecules and DMF can be obtained from data on the free energy change of formation (ΔG) of the molecular complex, calculated using the relationship,

$$\Delta G = -RT \ln K_f. \tag{1}$$

The stability constant (K_f) of the complex can be determined from a consideration of the behaviour in the mixed solvent[13,14] using the relationship (figure 1)

$$\log K_f = \log [(A - A_{min})/(A_{max} - A)] - n \log C_{DMF}. \tag{2}$$

The values of K_f and ΔG of the hydrogen-bonded molecular complex liable to be formed in solution between the molecules of dye **14** and DMF are given in table 5.

Table 4. Electronic absorption spectra [(λ_{max} nm (ε_{max} mol^{-1} cm^2) of mono-, tri, and azo-methine cyanine dyes (**6b, 10, 14**) in pure solvents.

	Water		DMF		Ethanol		$CHCl_3$		CCl_4		Dioxane	
Comp.	λ	ε	λ	ε	λ	ε	λ	ε	λ	ε	λ	ε
6b	–	–	385	(2840)	–	–	385	(3998)	–	–	–	–
	–	–	450	(2040)	415	(2106)	435	(2980)	410	(2300)	–	–
	–	–	–	–	–	–	455	(2600)	490	(1400)	–	–
	460	(1200)	520	(1400)	515	(1173)	520	(1800)	–	–	510	(1000)
10	420	(3600)	420	(3900)	–	–	415	(3800)	425	(4300)	425	(3700)
	470	(3200)	–	–	465	(2520)	–	–	–	–	–	–
	520	(2960)	510	(3840	510	(2532)	510	(3799)	–	–	–	–
	–	–	540	(3720)	555	(2200)	535	(3740)	530	(3520)	530	(3080)
	–	–	665	(1880)	–	–	665	(1880)	–	–	–	–
14	425	(4240)	–	–	–	–	410	(5100)	405	(5400)	400	(5980)
	510	(3640)	540	(4200)	525	(2800)	530	(4400)	–	–	–	–

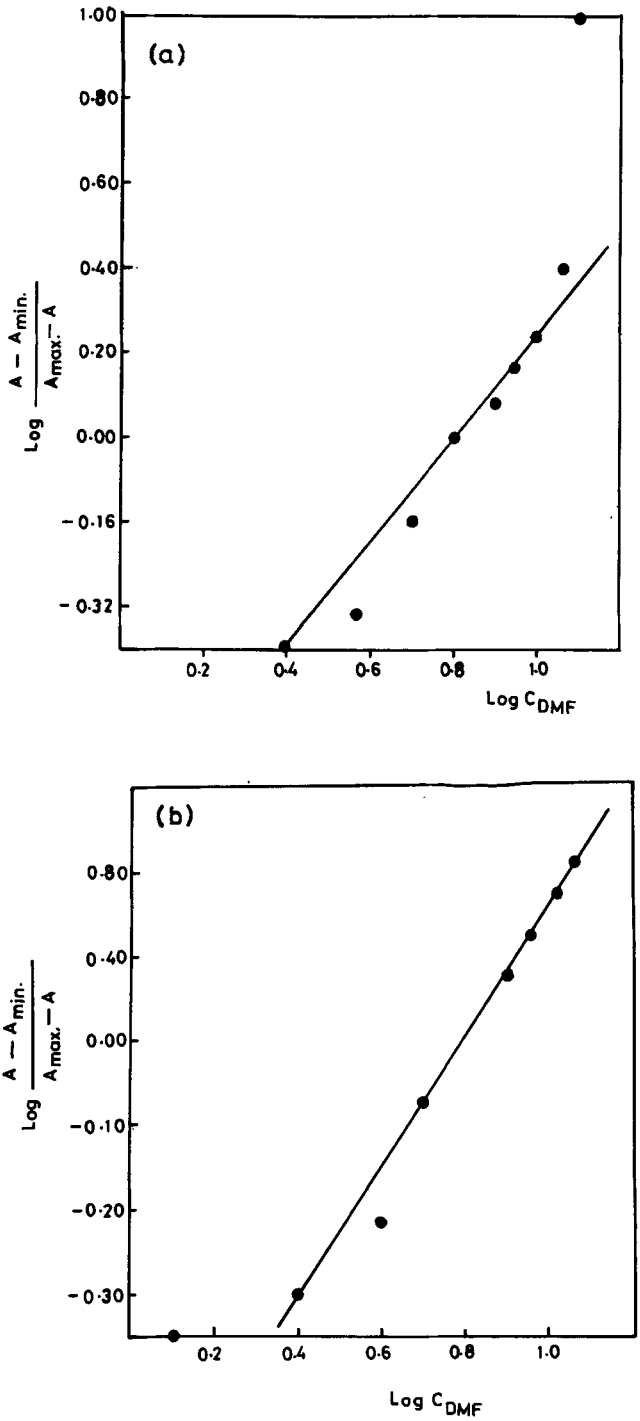


Figure 1. (a) and (b). (Continued, for caption, see next page.)

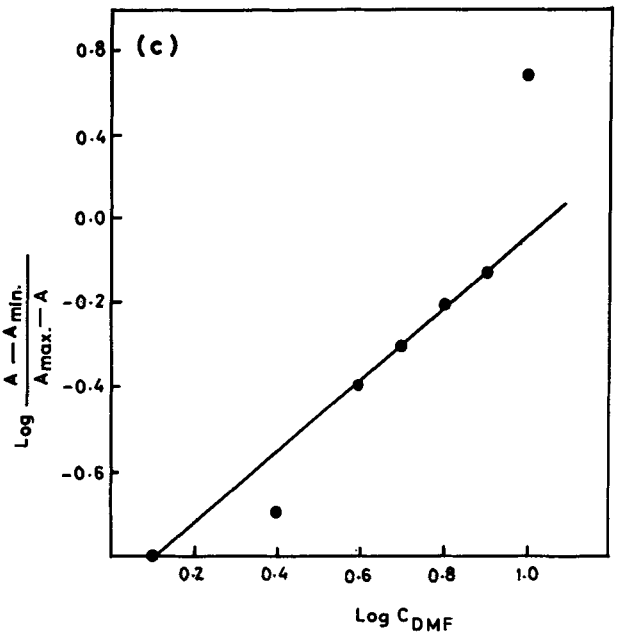


Figure 1. Log$[(A-A_{min})/(A_{max}-A)]$ versus log C_{DMF} for dye **14** in DMF–$CHCl_3$ (**a**), DMF–CCl_4 (**b**), and DMF–dioxane (**c**) mixtures at 27°C.

Table 5. Commutative data obtained for dye **14** in mixed solvents.

System	Excitation energy (kJ mole^{-1})		Orientation energy (kJ mole^{-1})	H-bond energy (kJ mole^{-1})	N	K_f	ΔG (kJ mole^{-1})
	Pure solvent	Pure DMF					
DMF–$CHCl_3$	52·77 ($CHCl_3$)	54·48	1·22	0·3	1	6·31	0·998
DMF–CCl_4	52·48 (CCl_4)	54·48	1·52	0·09	1	5·25	0·899
DMF–dioxane	52·48 (diox.)	54·79	0·73	0·3	1	5·01	0·873

The values of K_f, ΔG, and n (the number of DMF molecules which are complexed with the solute molecule) indicate that a 1:1 complex is formed.

On drawing the excitation energy (E) of the CT band in the mixed solvent versus the DMF mole fractions (figure 2), a broken line with three segments is obtained[15]. The first segment indicates the orientation of the solvent molecules around the solute molecule. The second segment represents the molecular complex formation, while the third one represents the steady state of the energy attained after the complete formation of the molecular complex. The values of orientation and H-bond energies are given in table 5.

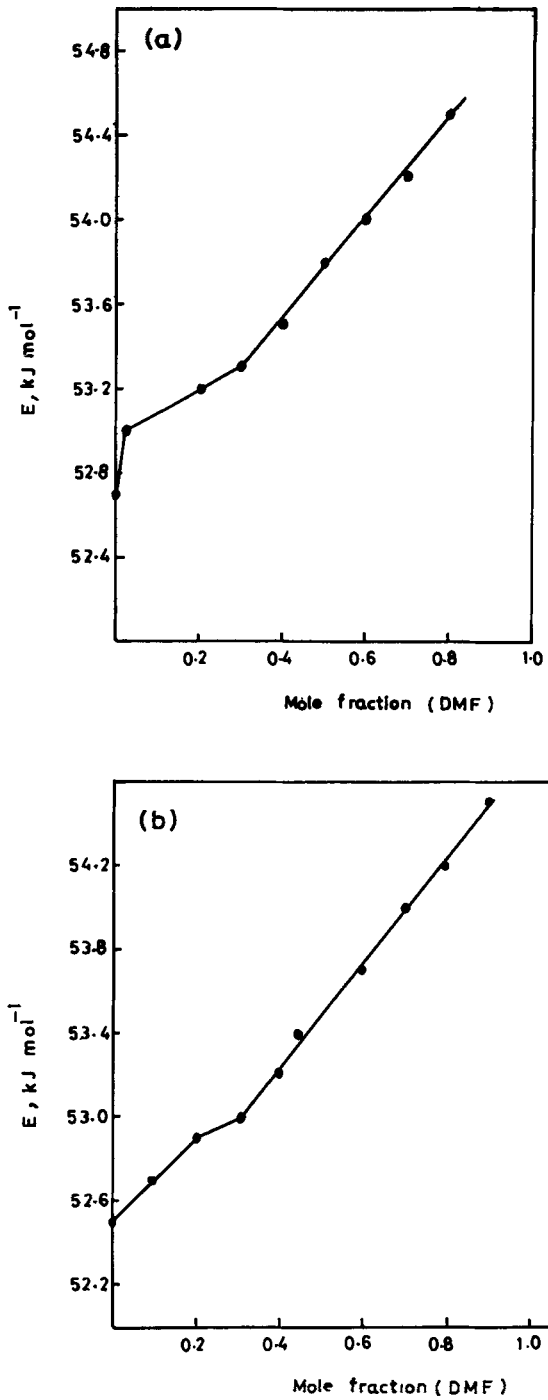


Figure 2. (a) and (b). (Continued, for caption see next page.)

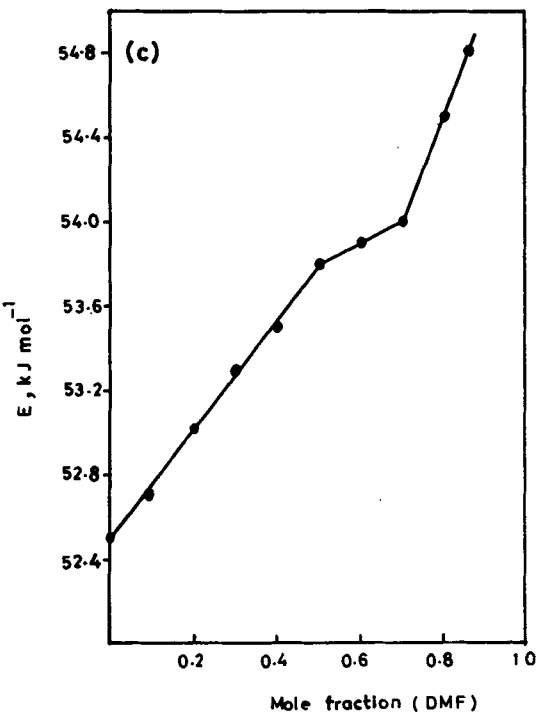


Figure 2. CT band excitation energy (E) versus DMF mole fraction for dye **14** in DMF–$CHCl_3$ (**a**), DMF–CCl_4 (**b**) and DMF–dioxane (**c**) mixtures at 27°C.

2.5 *Acid–base properties of some selected tri- and azo-methine cyanine dyes (10 and 13) in aqueous universal buffer solution*

The ethanolic solutions of newly synthesized monomethine cyanine dyes **5a,b**; **6a,b**; **7a,b** and trimethine cyanine dyes **9**, **10**, **11** and azomethine cyanine dyes **12a,b**; **13**, **14** show a permanent colour in basic medium which discharges on acidification. This prompted us to study their spectral behaviour in different aqueous buffer solutions in order to permit suitable *p*H medium when applied as photosensitizers. The effectiveness of the compounds as photosensitizers increases when they are present in the ionic form which have a higher planarity [12].

The electronic absorption spectra of selected trimethine cyanine dye (**11**) and azomethine cyanine dye (**13**) in aqueous universal buffer of varying *p*H (1·48–12·00) show regular changes with increasing *p*H of the medium which results in an increase in absorbance of the CT bands. As the *p*H of the medium decreases, the extinction of these bands becomes lower and undergoes a hypsochromic shift or disappearance at $pH < 4{\cdot}60$. This behaviour can be interpreted on the principle that the fused pyrazolo-nitrogen atom and/or azomethine nitrogen atom becomes protonated in solution of low *p*H values and therefore the CT interaction within the protonated form is expected to be difficult i.e. the protonated form does not absorb energy in the visible region. On the other hand, as the *p*H of the medium increases ($pH > 7{\cdot}00$), the protonated dyes become deprotonated and

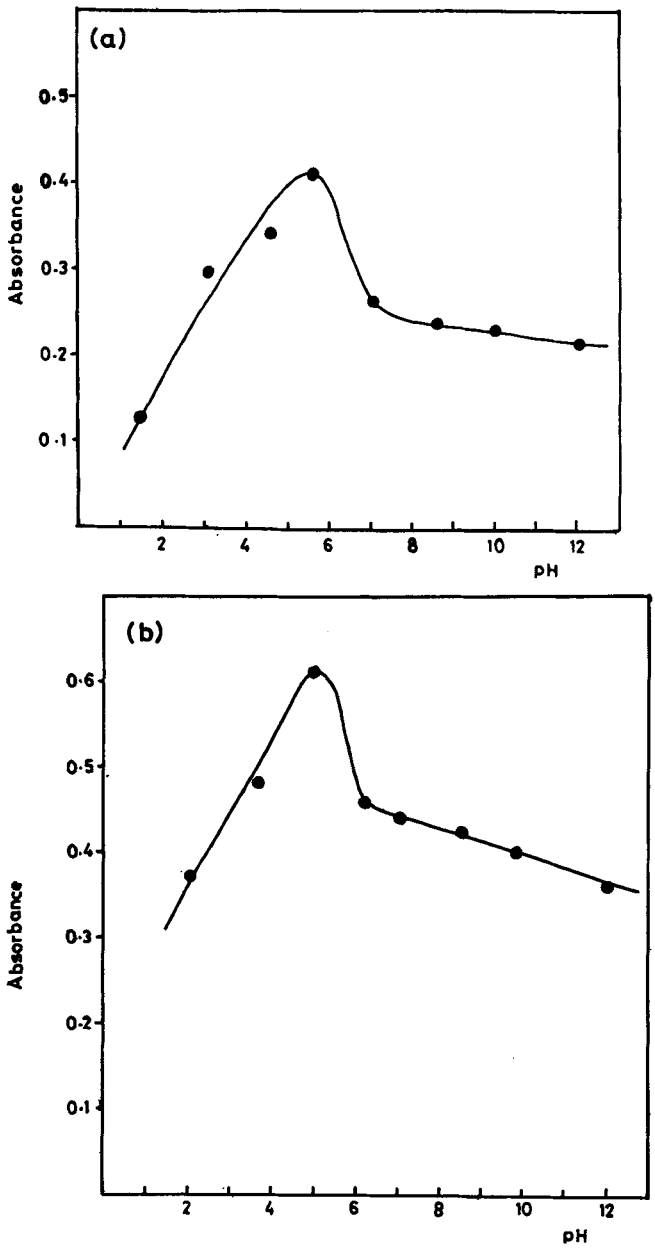


Figure 3. S-curves of $2{\cdot}5 \times 10^{-6}$ mol^{-1} cm^2 for **11** at λ_{max} 530 nm $pK_a = 6{\cdot}4$ (**a**) and $2{\cdot}5 \times 10^{-5}$ mol^{-1} cm^2 for **13** at λ_{max} 530 nm. $pK_a = 5{\cdot}6$ (**b**).

therefore their mesomeric interaction with the rest of the molecule is intensified. Consequently, the CT interaction within the free base is facilitated, i.e. the free base absorbs energy in the visible region (bathochromic shifts).

The acid dissociation or protonation constants of cyanine dyes under study (**10** and **13**) have been determined in order to ensure the optimal *p*H in the application as

photosensitizers. Such determination was measured on plotting the variation of absorbance with *p*H using both the spectrophotometric half-height limiting absorbance and Colleter methods [16].

The results of the pK_a values of the trimethine dye **10** (6·4); is higher than those of azomethine dye **13** (5·6); (table 6, figure 3). This behaviour refers to the higher planarity and greater stability of asymmetrical trimethine cyanine dyes which favour the intramolecular charge transfer. Such dyes might be suggested to be more sensitive as photosensitizers than the asymmetrical azomethine cyanine dye analogues.

3. Experimental

3.1 *General*

All melting points are uncorrected. Elemental analysis was carried out at the microanalytical centre by an automatic analyzer (Heraeus). IR spectra (KBr pellets) were determined on a 1278 spectrophotometer (Perkin–Elmer). Absorption spectra, solvatochromism and *p*H-sensitive studies were recorded on a UV-VIS 240 recording spectrophotometer using 1 cm cells (Shimadzu), and ^{1}H NMR (200 MHz) spectra on a varian Geminy NMR spectrometer using TMS as internal reference.

As the investigation of solvatochromism and acid–base properties, the organic solvents used were of spectroscopic grade or purified according to the recommended method [17]. An accurate volume of the stock solution (10^{-3} M) of the dyes was diluted to the appropriate volume in order to obtain the required concentrations.

A series of buffer solutions with *p*H values ranging from 1·48–12·0 was prepared as recommended by Britton [18]. An accurate volume of the stock solutions (10^{-3} M) was added to 0·5 ml buffer solution in a 5 ml measuring flask and then completed to the mark with redistilled water. The *p*H of buffer solution was checked before spectral measurements.

The spectra, either in pure solvents or in aqueous universal buffer solutions, were then recorded.

3.2 *Synthesis of 4-bromo-3-methyl-1-(hydro/phenyl)-pyrazole-5-one (**1a,b**)*

Compounds **1a** and **1b** were performed in a way similar to that described earlier [7].

Table 6. The variation of absorbance in λ_{max} typical for cyanine dyes (**11** and **13**) in different universal buffer solutions.

	*p*H												
A	1·48	2·00	3·13	3·71	4·60	5·00	5·60	6·12	7·00	8·45	9·80	9·96	12·0	pK_a
11 λ_{530}	0·13	–	0·30	–	0·34	–	0·41	–	0·26	0·24	–	0·23	0·21	6·4
13 λ_{530}	–	0·37	–	0·48	–	0·61	–	0·46	0·44	0·42	0·40	–	0·36	5·6

3.3 *Synthesis of 3-methyl-1-(hydro/phenyl)-pyrazolo-[5,4-b]quinolino-[a,b]-1,4-pyra(oxa)-zinium bromide salts (**3a–c**)*

Equimolar ratios of **1a** or **1b** (0·01 M) and 8-amino-/hydroxy-quinoline **2a** and **2b** (0·01 M) were dissolved in *n*-butanol (20 cm^3) and the reaction mixture was refluxed for 5–8 h. The reaction mixture was concentrated to its half, allowed to cool overnight and then diethyl ether was added. The precipitate which formed was filtered, washed with ether and then crystallized from absolute ethanol (table 1).

3.4 *Synthesis of 3-methyl-1-(hydro/phenyl)-pyrazolium[5,4-b]-quinolino-[a,b]-1,4-pyra(oxa)-zinium-2(4)-ethiodide(bromide) salts (**4a–c**)*

A pure sample of compounds (**3a–c**) was suspended in excess ethyl iodide and heated on a water bath for 3–5 h. The precipitate which formed was washed with ether and recrystallised from absolute ethanol (table 1).

3.5 *Synthesis of asymmetrical 2-ethyl-1-(hydro/phenyl)-pyrazolo[4,5-b]-quinolino[a,b]-1,4-pyra(oxa)-zinium bromide-3[4(1)]-monomethine cyanine dyes (**5a,5b; 6a,b; 7a,b**)*

Equimolar amounts of (**4a–c**) and appropriate 1- or 4-quaternary salts (0·01 M) were dissolved in ethanol (30 cm^3), and piperidine (3–5 drops) was added. The reaction mixture was refluxed for 4–6 h, filtered hot, concentrated, cooled and acidified with acetic acid. The precipitated products after dilution with water were collected and crystallized from aqueous ethanol (table 2).

3.6 *Synthesis of asymmetrical 2-ethyl-1-(hydro/phenyl)-pyrazolo-[5,4-b]-quinolino-[a,b]-1,4-pyrazinium bromide-3[2(4)]-trimethine cyanine dyes (**9, 10, 11**)*

A: A mixture of quaternary salt **4a** (0·01 M) and equimolar ratios of triethylorthoformate (0·01 M) was refluxed in ethanol (30 cm^3) containing piperidine (3–6 drops) for 8 h. The reaction mixture was filtered hot, allowed to cool and the precipitated products were collected and recrystallized from ethanol to give the intermediate compound **8** (table 1).

B: To a mixture of the latter intermediate compound **7** (0·01 M) and *N*-ethyl(α-picolinium-, quinaldinium-, and -γ-picolinium) iodide (0·01 mol) in absolute ethanol (40 cm^3) few drops of piperidine were added. The reaction mixture was refluxed for 8–10 h, filtered hot and then cooled. The products **9**, **10**, **11** were separated out on dilution with ice-water and crystallized from absolute ethanol (table 2).

3.7 *Synthesis of asymmetrical-1-(hydro/phenyl)-pyrazolium-[5,4-b]quinolino-[a,b]-1,4-pyrazinium-2(4)-ethiodide(bromide)-3-azomethine cyanine dyes (**12a,b; 13, 14**)*

A mixture of quaternary salts **4a** and **4c** (0·01 M) and nitroso phenols (*p*-nitroso phenols, $\alpha(\beta)$-nitroso-$\beta(\alpha)$-naphthols (0·01 M) were dissolved in ethanol (50 cm^3) and piperidine (3–5 drops) was added. The reaction mixture was refluxed for 10–12 h, filtered hot, concentrated, cooled and acidified with acetic acid. The products were collected after dilution and crystallization from absolute ethanol, to give the corresponding azomethine cyanine dyes **12a,b**; **13**; **14** (table 2).

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