

# Some New Nitrogen Bridgehead Heterocyclic Cyanine Dyes

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New monomethine, trimethine, and azomethine cyanine dyes of pyrazolo[4',5':5,6](pyrazinio/1,4-oxazinio)[2,3,4-*i,j*]quinolin-11-ium bromides were prepared. These 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 are discussed in relation to molecular structure and in terms of medium effects. Molecular complex formation with DMF was verified through mixed-solvent studies.

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

Within these respects, pyrazolo[4',5':5,6](pyrazinio/1,4-oxazinio)[2,3,4-*i,j*]quinolin-11-ium bromides *IIIa–IIIc* were used as key intermediates for the dye synthesis.

Interaction of 4-bromo-3-methyl-1-*R*-pyrazol-5-one (*Ia/Ib*) [8] and 8-amino/hydroxyquinoline (*IIa/IIb*) in the presence of butan-1-ol as solvent afforded under dehydration and selective quaternization processes the new nitrogen bridgehead heterocycles (key intermediate compounds), namely 8-*R*-10-methylpyrazolo[4',5':5,6](pyrazinio/1,4-oxazinio)[2,3,4-*i,j*]quinolin-11-ium bromides *IIIa–IIIc* (Scheme 1, Table 1). The polarizability of N–H/O–H bonds of 8-amino/hydroxyquinoline expressed a higher nucleophilic character of nitrogen/oxygen atoms and the nucleophilic attack proceeded stronger and faster on the electron-deficient C-5 atom (in case of *N*-phenyl-substituted pyrazolone it was easier than in case of unsubstituted derivatives). The resulted OH group abstracts a proton from protonated secondary amine or oxygenated ethereal groups leading to the loss of water molecule followed by transfer of negative charge forming the double bond. The electron deficiency of the C–Br bond was increased and attacked by the lone pair of the quinoline-nitrogen atom leading to the formation of bridgehead heterocyclic quaternary salts. Thus, pyrazinium bromide is separated practically after a relatively short-time reflux when compared with that for oxazinium bromide formation.

Extra quaternization of the former intermediates using an excess amount of ethyl iodide under controlled conditions gave 9-ethyl-8-*R*-10-methylpyrazolo[4',5':5,6](pyrazinio/1,4-oxazinio)[2,3,4-*i,j*]quinolin-11(9)-ium bromides iodides (*IVa–IVc*). Further reaction of the latter compounds with *N*-methylpyridinium, -quinolinium, resp. -isoquinolinium iodide involving active hydrogen atom in the position 11 or 8 under piperidine catalysis gave the corresponding unsymmetrical bromides iodides of 9-ethyl-8-*R*-pyrazolo[4',5':5,6](pyrazinio/1,4-oxazinio)[2,3,4-*i,j*]quinolin-11-ium-10[4(1)]-monomethine cyanine dyes *Va, Vb, VIa, VIb, VIIa, VIIb* (Scheme 2, Table 2).

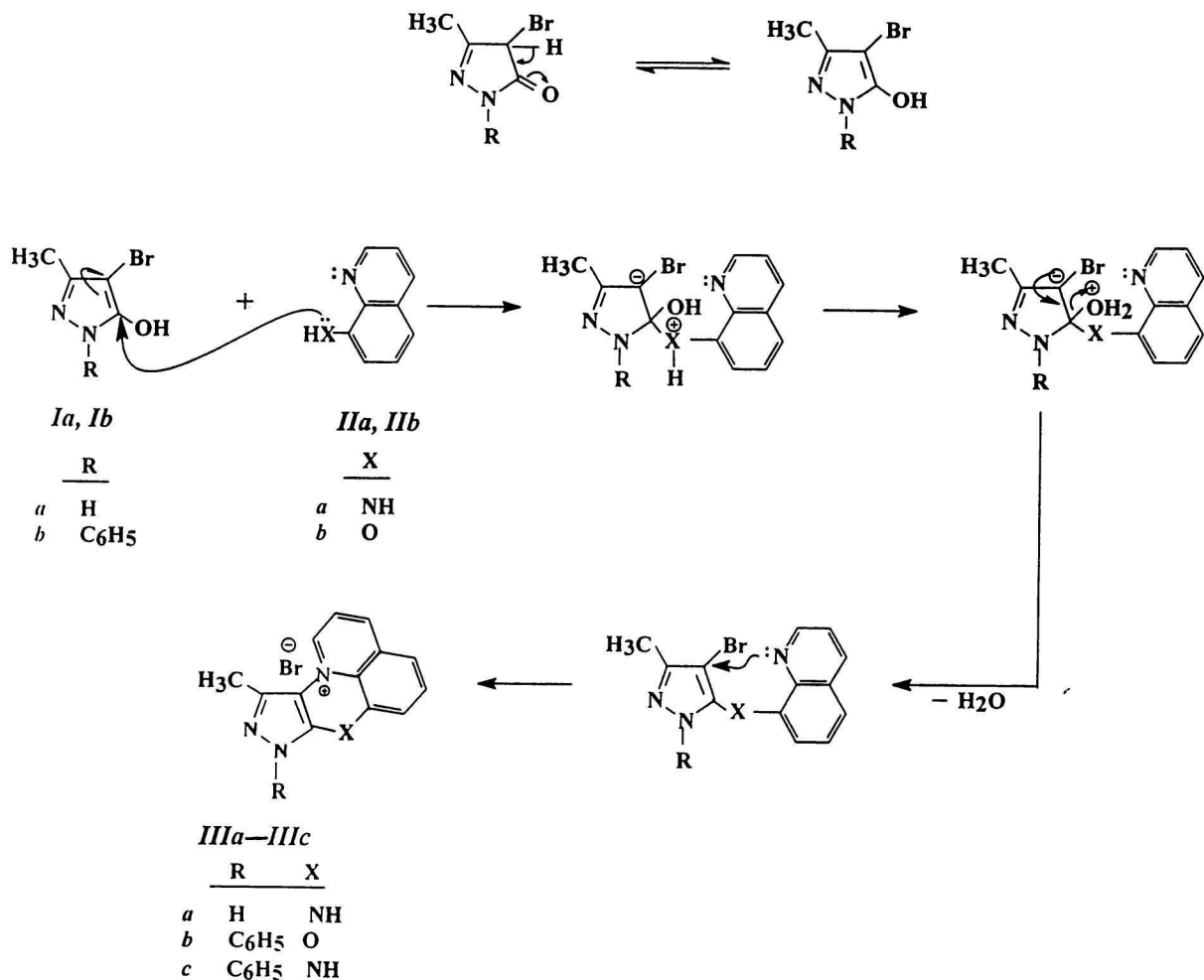
Meanwhile the condensation reaction of *IVc* with triethyl orthoformate under piperidine catalysis gave the intermediate compound *VIII*. Further reaction of compound *VIII* with *N*-ethyl- $\alpha$ -picolinium, -quinolidinium, and - $\gamma$ -picolinium iodide in the presence of piperidine afforded the corresponding unsymmetrical trimethine cyanine dyes *IX, X, XI*.

Interaction of equimolar ratios of *IVa* or *IVc* and nitrosophenols (4-nitrosophenol, 1(2)-nitroso-2(1)-naphthol) under basic catalysis afforded the corresponding unsymmetrical bromides iodides of 9-ethyl-8-*R*-pyrazolo[4',5':5,6](1,4-pyrazinio)[2,3,4-*i,j*]quinolin-11(9)-ium-10-azomethine cyanine dyes *XIIa, XIIb, XIII, XIV*.

The structure of the newly synthesized compounds *IIIa–IIIc, IVa–IVc, Va, Vb, VIa, VIb, VIIa, VIIb, VIII, IX, X, XI, XIIa, XIIb, XIII, and XIV* was established by elemental analysis and IR [9] and <sup>1</sup>H NMR [10] spectral data (Table 3).

## Relation between Molecular Structure and Spectral Behaviour of the Synthesized Cyanine Dyes

The electronic absorption spectra of unsymmetri-



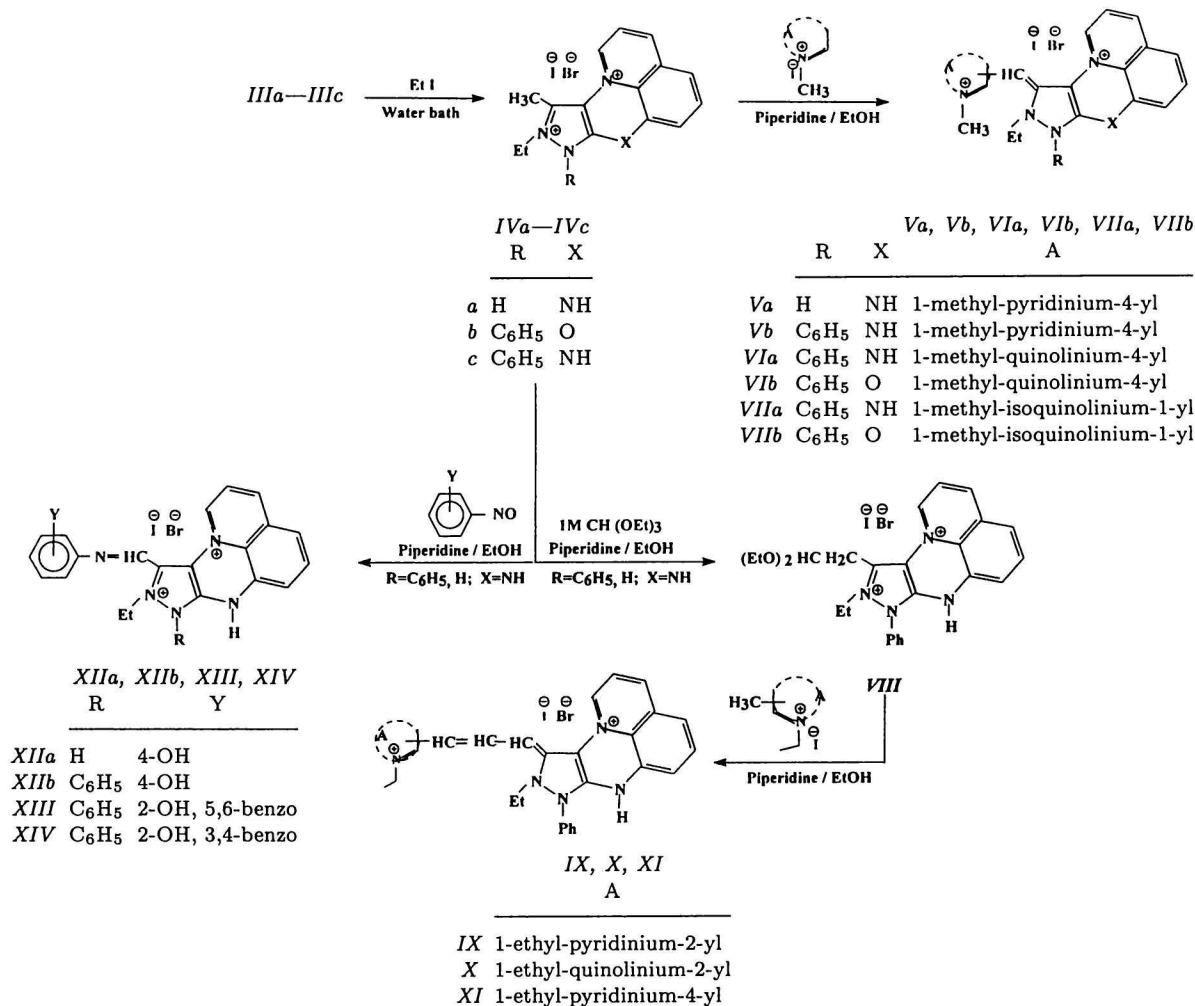
Scheme 1

Table 1. Characterization Data for New Starting and Intermediate Compounds

Compound	Formula <i>M<sub>r</sub></i>	<i>w<sub>i</sub></i> (calc.)/% <i>w<sub>i</sub></i> (found)/%			Yield %	M.p. °C	Colour
		C	H	N			
<i>IIIa</i>	C <sub>13</sub> H <sub>11</sub> BrN <sub>4</sub> 303.16	51.51	3.66	18.48	63	182—185	Yellow red
		51.63	3.60	18.25			
<i>IIIb</i>	C <sub>19</sub> H <sub>14</sub> BrN <sub>3</sub> O 380.24	60.02	3.71	11.05	67	142—145	Red
		59.85	3.78	10.95			
<i>IIIc</i>	C <sub>19</sub> H <sub>15</sub> BrN <sub>4</sub> 379.26	60.17	3.99	14.78	72	164—167	Brownish red
		59.90	4.13	14.53			
<i>IVa</i>	C <sub>15</sub> H <sub>16</sub> BrIN <sub>4</sub> 459.13	39.24	3.51	12.20	64	207—210	Brown
		39.01	3.33	11.99			
<i>IVb</i>	C <sub>21</sub> H <sub>19</sub> BrIN <sub>3</sub> O 536.21	47.04	3.57	7.84	73	190—193	Brownish red
		46.77	3.31	7.70			
<i>IVc</i>	C <sub>21</sub> H <sub>20</sub> BrIN <sub>4</sub> 535.22	47.13	3.77	10.47	76	182—185	Red
		46.86	3.83	10.75			
<i>VIII</i>	C <sub>26</sub> H <sub>30</sub> BrIN <sub>4</sub> O <sub>2</sub> 637.36	49.00	4.74	8.79	92	164—167	Reddish violet
		49.15	4.65	8.51			

Compounds *IIIa—IIIc* treated in saturated KI gave iodine vapour in concentrated H<sub>2</sub>SO<sub>4</sub>.

Compounds *IVa—IVc* and *VIII* were soluble in concentrated H<sub>2</sub>SO<sub>4</sub> liberating iodine vapour on heating.

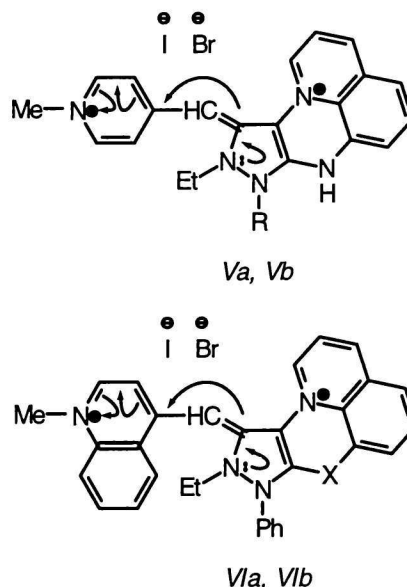


Scheme 2

cal mono/trimethine cyanine dyes *Va*, *Vb*, *VIa*, *VIb*, *VIIa*, *VIIb*, *IX*, *X*, *XI* in 95 % ethanol showed absorption bands with a strong bathochromic shift on increasing the conjugation of the quaternary heterocyclic residue. Thus, the absorption spectra of dyes *Vb*, *IX*, and *XI* incorporating pyridinium salt moiety showed an absorption band hypsochromically shifted if compared with dyes *VIa* and *X* containing the quinolinium moiety. This can be attributed to a more extensive  $\pi$ -delocalization within the respective quaternary heterocyclic system.

Changing the linkage position of heterocyclic quaternary residue from 4 to 2 in monomethine (compounds *VIa* (*VIb*) and *VIIa* (*VIIb*)) and/or from 4 to 2 in trimethine cyanines (compounds *IX* and *XI*) showed that the linkage in the position 2 results in a hypsochromic shift in the absorption bands. This is due to lower extended conjugation in the linkage in the position 2 resulting in a decrease of the  $\pi$ -delocalization of electron through cyanine molecule pathway.

Monomethine dyes incorporating either pyrazolo (*Va*) or pyrazine moieties (*VIa* and *VIIa*) are batho-



chromically shifted in comparison with those incorporating 8-phenylpyrazole (*Vb*) or oxazine derivatives

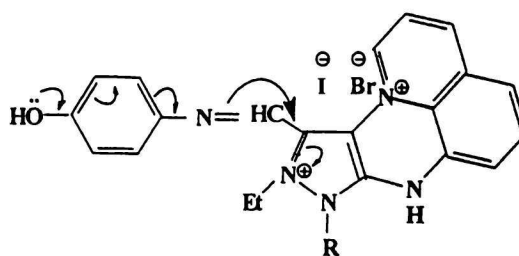
**Table 2.** Characterization Data for Unsymmetrical Mono-, Tri-, and Azomethine Cyanine Dyes

Compound	Formula $M_r$	$w_i(\text{calc.})/\%$ $w_i(\text{found})/\%$			Yield %	M.p. °C	Colour	Absorption spectra in 95% ethanol	
		C	H	N				$\lambda_{\text{max}}$	$\epsilon_{\text{max}}$
								nm	$\text{cm}^2 \text{mol}^{-1}$
<i>Va</i>	C <sub>21</sub> H <sub>21</sub> BrIN <sub>5</sub> 550.24	45.86	3.85	12.73	64	217—220	Reddish violet	450	1218
		46.01	3.77	12.88					
<i>Vb</i>	C <sub>27</sub> H <sub>25</sub> BrIN <sub>5</sub> 626.34	51.78	4.02	11.18	65	172—175	Reddish violet	400	3200
		51.61	4.05	11.35					
<i>VIa</i>	C <sub>31</sub> H <sub>27</sub> BrIN <sub>5</sub> 676.40	55.05	4.02	10.35	75	180—183	Violet	520	1600
		54.82	4.24	10.30					
<i>VIb</i>	C <sub>31</sub> H <sub>26</sub> BrIN <sub>5</sub> O 677.38	54.97	3.87	8.27	71	154—157	Violet	415, 515	2106, 1173
		55.21	3.39	8.41					
<i>VIIa</i>	C <sub>31</sub> H <sub>27</sub> BrIN <sub>5</sub> 676.40	55.05	4.02	10.35	67	190—193	Brownish violet	500	2584
		54.91	4.10	10.50					
<i>VIIb</i>	C <sub>31</sub> H <sub>26</sub> BrIN <sub>4</sub> O 677.38	54.97	3.87	8.27	67	165—168	Brownish violet	460	1800
		54.81	3.70	8.39					
<i>IX</i>	C <sub>30</sub> H <sub>29</sub> BrIN <sub>5</sub> 666.40	54.07	4.38	10.51	59	174—177	Brownish violet	500	4600
		53.81	4.62	10.46					
<i>X</i>	C <sub>34</sub> H <sub>31</sub> BrIN <sub>5</sub> 716.46	56.99	4.36	9.77	73	202—205	Deep violet	465, 510, 555	2520, 2532, 2200
		57.13	4.25	9.91					
<i>XI</i>	C <sub>30</sub> H <sub>29</sub> BrIN <sub>5</sub> 666.40	54.07	4.38	10.51	62	188—191	Reddish violet	510	1360
		53.89	4.22	10.77					
<i>XIIa</i>	C <sub>21</sub> H <sub>19</sub> BrIN <sub>5</sub> O 564.22	44.70	3.39	12.41	55	140—142	Brown	470	1800
		44.71	3.52	12.46					
<i>XIIb</i>	C <sub>27</sub> H <sub>23</sub> BrIN <sub>5</sub> O 640.32	50.65	3.62	10.94	58	135—138	Brown	522	2120
		50.73	3.65	11.27					
<i>XIII</i>	C <sub>31</sub> H <sub>25</sub> BrIN <sub>5</sub> O 690.38	53.93	3.65	10.14	65	167—170	Brownish violet	530	2720
		54.25	3.52	9.91					
<i>XIV</i>	C <sub>31</sub> H <sub>25</sub> BrIN <sub>5</sub> O 690.38	53.93	3.65	10.14	63	207—210	Red	525	2800
		53.87	3.88	10.43					

(*VIb* and *VIIb*). This is due to the antagonistic effect of *N*-phenylpyrazole and/or a greater electron-withdrawing ability of the oxazine rings.

On the other hand, comparison of the spectra of unsymmetrical mono- and trimethine cyanine dyes (e.g. *Vb* and *XI*) involving pyridin-4-ium iodide moiety shows that the absorption band of trimethine dye *XI* is more bathochromically shifted by 110 nm than that of monomethine dye *Vb*. This is due to increasing the number of methine groups, which causes an increase in the electron mobility of cyanine pathway.

The electronic spectra of unsymmetrical azomethine cyanine dyes *XIIa*, *XIIb*, *XIII*, and *XIV* in 95% ethanol disclose that their absorption bands undergo bathochromic or hypsochromic shifts depending upon the nature of the pyrazolo substituent R, and the type of phenol involved. Thus, the azomethine cyanine dye *XIII* incorporating quinoliniopyrazinium salt and involving 2-naphthol moiety possesses an absorption band more bathochromically shifted than that of derivative *XIV* involving 1-naphthol. This is due to a better planarity of the former dye.

*XIIa*, *XIIb*

On the other hand, it was obvious that the absorption band of bromide iodide of azomethine dye *XIIb* which involved 9-ethyl-8-phenylpyrazolio[4',5':5,6](1,4-pyrazinio)[2,3,4-*i,j*]quinolin-11(9)-ium moiety is more bathochromically shifted by 52 nm than that of unsubstituted pyrazolium derivative *XIIa*. This is considered as a reverse observation if compared with the electronic absorption spectra of the previous monomethine dyes *Va* and *Vb*. This reversibility is due to the fact that azomethine cyanine dye moves its electrons

**Table 3.** IR and  $^1\text{H}$  NMR Spectral Data of Some Selected Starting Materials, Mono- Tri-, and Azomethine Cyanine Dyes Derivatives

Compound	IR spectrum, $\tilde{\nu}_{\text{max}}$ (KBr)/ $\text{cm}^{-1}$	$^1\text{H}$ NMR spectrum ( $\text{CDCl}_3$ ), $\delta$
<i>IIIb</i>	2900—2980 (CH str. of $\text{CH}_3$ ) 1660—1680 (C=C) 1595—1620 (C=N) 1100—1125 (C—O—C cyclic) 700—760 (ar. monosubstituted)	7.2—8.8 (m, 11H, $\text{H}_{\text{arom}}$ , $\text{H}_{\text{hetero}}$ ) 1.2 (s, 3H, $\text{CH}_3$ group)
<i>IIIc</i>	3200—3500 (NH group) 2900—3000 (CH str. of $\text{CH}_3$ ) 1690—1700 (C=C) 1595—1620 (C=N) 700—760 (ar. monosubstituted)	7.2—8.9 (m, 11H, $\text{H}_{\text{arom}}$ , $\text{H}_{\text{hetero}}$ ) 4.1 (s, 1H, NH group) exchangeable with $\text{D}_2\text{O}$ 1.25 (s, 3H, $\text{CH}_3$ group)
<i>IVb</i>	2900—3060 (ethiodide) 1660—1680 (C=C) 1595—1620 (C=N) 1100—1120 (C—O—C cyclic)	7.2—8.8 (m, 11H, $\text{H}_{\text{arom}}$ , $\text{H}_{\text{hetero}}$ ) 1.2 (s, 3H, $\text{CH}_3$ group) 0.8—0.95 (t, 3H, $\text{CH}_3\text{CH}_2\text{N}^+$ ) 1.9—2.3 (q, 2H, $\text{CH}_3\text{CH}_2\text{N}^+$ )
<i>IVc</i>	2850—2980 (ethiodide) 3200—3500 (NH group) 1690—1700 (C=C) 1595—1620 (C=N)	7.1—8.8 (m, 11H, $\text{H}_{\text{arom}}$ , $\text{H}_{\text{hetero}}$ ) 4.25 (s, 1H, NH group) exchangeable with $\text{D}_2\text{O}$ 1.3 (s, 3H, $\text{CH}_3$ group) 0.8—0.95 (t, 3H, $\text{CH}_3\text{CH}_2\text{N}^+$ ) 2.0—2.3 (q, 2H, $\text{CH}_3\text{CH}_2\text{N}^+$ )
<i>VIa</i>	2980—3080 (methiodide) 1620—1650 (C—CH) 1660—1680 (C=C)	6.7—8.7 (m, 18H, $\text{H}_{\text{arom}}$ , $\text{H}_{\text{hetero}}$ , =CH) 1.4 (t, 3H, $\text{CH}_3\text{CH}_2\text{N}^+$ ) 2.2 (q, 2H, $\text{CH}_3\text{CH}_2\text{N}^+$ )
<i>VIII</i>	2950—3080 (ethiodide) 3200—3550 (NH group) 2900—2950 (CH str.) 1680—1690 (C=C)	7.2—8.8 (m, 11H, $\text{H}_{\text{arom}}$ , $\text{H}_{\text{hetero}}$ ) 3.65 (t, 1H, —CH<) 1.5 (d, 2H, — $\text{CH}_2$ —) 1.35 (t, 6H, $2\text{CH}_3\text{CH}_2\text{O}$ )
<i>X</i>	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, $\text{H}_{\text{arom}}$ , $\text{H}_{\text{hetero}}$ , CH=CH—CH=) 3.00 (q, 2H, $\text{CH}_3\text{CH}_2\text{N}^+$ ) 2.20 (t, 3H, $\text{CH}_3\text{CH}_2\text{N}^+$ ) 1.2—1.4 (t, 3H, $\text{CH}_3\text{CH}_2\text{N}^+$ ) 2.5 (q, 2H, $\text{CH}_3\text{CH}_2\text{N}^+$ ) 4.2 (s, 1H, NH group) exchangeable with $\text{D}_2\text{O}$
<i>XIIIb</i>	2850—3040 (ethiodide) 3100—3650 (NH group) 1680—1700 (C=C) 1560—1610 (C=N)	7.2—8.9 (m, 16H, $\text{H}_{\text{arom}}$ , $\text{H}_{\text{hetero}}$ , N=CH) 4.2 (s, 1H, NH group) exchangeable with $\text{D}_2\text{O}$ 2.25 (q, 2H, $\text{CH}_3\text{CH}_2\text{N}^+$ ) 1.10 (t, 3H, $\text{CH}_3\text{CH}_2\text{N}^+$ ) 5.8 (s, 1H, phenolic OH) exchangeable with $\text{D}_2\text{O}$

from the phenol residue as a source to the positively charged *N*-pyrazolium moiety as a sink causing a decrease of the electron density at the pyrazolium nitrogen and consequently an increase of the electron motion through azomethine cyanine pathway.

### Solvatochromic Behaviour of Unsymmetrical Mono- (*VIb*), Tri- (*X*), and Azomethine (*XIV*) Cyanine Dyes in Pure Solvents

The colours and electronic absorption spectra of some selected dyes *VIb*, *X*, and *XIV* 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 differ-

ent electronic transitions within the solute molecule in those solvents (Table 4).

Thus, careful examination of the results reported in Table 4 reveals that the longer wave bands corresponding to  $n \rightarrow \pi^*$  transitions and to intramolecular charge transfer (CT) interaction [12] show a bathochromic shift on changing the organic solvent from ethanol to DMF and  $\text{CHCl}_3$ , which can be attributed to the increase in solvent polarity of DMF, and to the solute—solvent interaction through intermolecular hydrogen bond formation in case of  $\text{CHCl}_3$ .

The small hypsochromic shift observed on changing the organic solvent from ethanol to dioxane and  $\text{CCl}_4$  can be explained as a result of the lower solvent polarity of dioxane and  $\text{CCl}_4$ . It is worth mentioning that the slight hypsochromic shift in aqueous medium relative to ethanol can be mainly ascribed to

**Table 4.** Electronic Absorption Spectra ( $\lambda_{\max}/\text{nm}$  ( $\epsilon_{\max}/(\text{mol}^{-1} \text{cm}^2)$ )) Characteristic of Selected Mono-, Tri-, and Azomethine Cyanine Dyes in Pure Solvents

Compound	Water		DMF		EtOH		CHCl <sub>3</sub>		CCl <sub>4</sub>		Dioxane	
	$\lambda_{\max}$	( $\epsilon_{\max}$ )	$\lambda_{\max}$	( $\epsilon_{\max}$ )	$\lambda_{\max}$	( $\epsilon_{\max}$ )	$\lambda_{\max}$	( $\epsilon_{\max}$ )	$\lambda_{\max}$	( $\epsilon_{\max}$ )	$\lambda_{\max}$	( $\epsilon_{\max}$ )
	nm		nm		nm		nm		nm		nm	
<i>VIb</i>	–	–	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)
<i>X</i>	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	(1800)	–	–	665	(1880)	–	–	–	–
<i>XIV</i>	425	(4240)	–	–	–	–	410	(5100)	405	(5400)	400	(5980)
	510	(3640)	540	(4200)	525	(2800)	530	(4400)	–	–	–	–

**Table 5.** Commutative Data Obtained for Dye *XIV* in Mixed Solvents

System	Excitation energy		Orientation energy	H-bond energy	<i>N</i>	<i>K<sub>f</sub></i>	$\Delta G$
	kJ mol <sup>-1</sup>		kJ mol <sup>-1</sup>	kJ mol <sup>-1</sup>			kJ mol <sup>-1</sup>
	Pure solvent	Pure DMF					
DMF—CHCl <sub>3</sub>	52.77 (CHCl <sub>3</sub> )	54.48	1.22	0.3	1	6.31	0.998
DMF—CCl <sub>4</sub>	52.48 (CCl <sub>4</sub> )	54.48	1.52	0.09	1	5.25	0.899
DMF—dioxane	52.48 (Dioxane)	54.79	0.73	0.3	1	5.01	0.873

the interaction of water molecule with the lone electron pair of the fused pyrazolo-nitrogen atom through H-bonding. This slightly decreases the electron density on the nitrogen atom and consequently decreases to some extent the mobility of  $\pi$ -electrons attached to the conjugated pathway.

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 *XIV* in CHCl<sub>3</sub>, CCl<sub>4</sub>, and dioxane containing progressively increasing quantities of DMF (mixed solvents) 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 the data on the free energy change of formation  $\Delta G$  of the molecular complex, calculated using the following relationship

$$\Delta G = -RT \ln K_f \quad (1)$$

The stability constant ( $K_f$ ) of the complex can be determined from the consideration of its behaviour in

the mixed solvent [13, 14] using the relationship (2) (Fig. 1).

$$\log K_f = \log[(A - A_{\min})/(A_{\max} - A)] - N \log x(\text{DMF}) \quad (2)$$

The values of  $K_f$  and  $\Delta G$  of the hydrogen-bonded molecular complex liable to be formed in solution between the molecules of dye *XIV* and DMF are given in Table 5. The values of  $K_f$ ,  $\Delta G$ , 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 *vs.* the DMF mole fractions (Fig. 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.

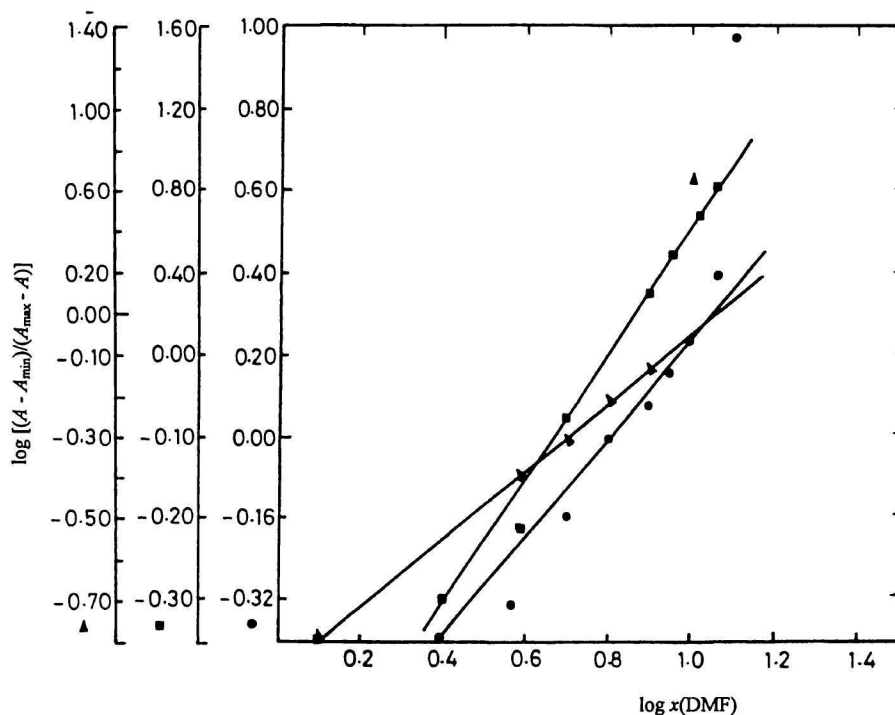


Fig. 1. The  $\log [(A - A_{\min})/(A_{\max} - A)]$  vs.  $\log x(\text{DMF})$  for dye XIV in DMF— $\text{CHCl}_3$  (●), DMF— $\text{CCl}_4$  (■), and DMF—dioxane (▲) mixtures at 27°C.

### Acid-Base Properties of Selected Tri- and Azomethine Cyanine Dyes X and XIII in Aqueous Universal Buffer Solution

The ethanolic solutions of newly synthesized monomethine cyanine dyes Va, Vb, VIa, VIb, VIIa, VIIb and trimethine cyanine dyes IX, X, XI and azomethine cyanine dyes XIIa, XIIb, XIII, and XIV show a permanent colour in basic medium which discharges on acidification. This promoted us to study their spectral behaviour in different aqueous buffer solutions in order to permit suitable pH medium when applied as photosensitizers. The effectiveness of the compounds as photosensitizers increases when they are present in the ionic form which has a better planarity [12].

The electronic absorption spectra of the selected trimethine cyanine dye XI and azomethine cyanine dye XIII in aqueous universal buffer of varying pH (1.48—12.00) show regular changes with increasing pH of the medium, resulting in an increase in absorbance of the CT bands. As the pH of the medium decreases, the extinction of these bands becomes lower and undergoes a hypsochromic shift or disappearance at  $\text{pH} < 4.6$ . 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 pH 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

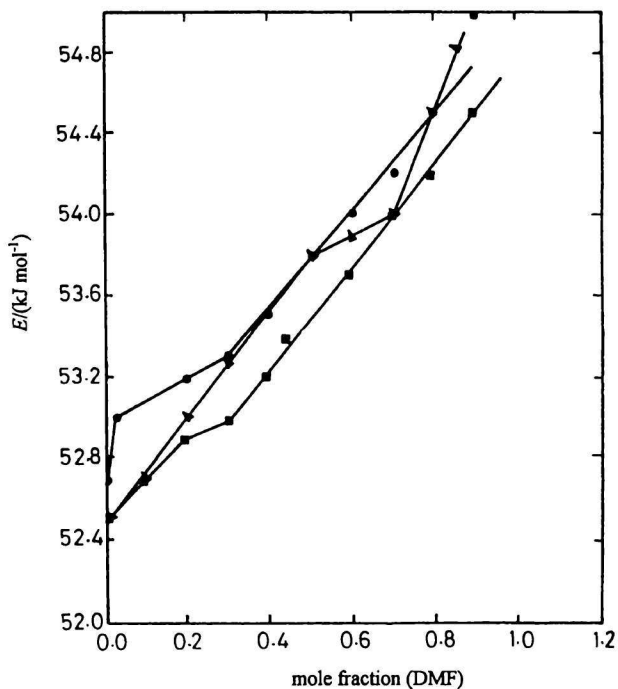
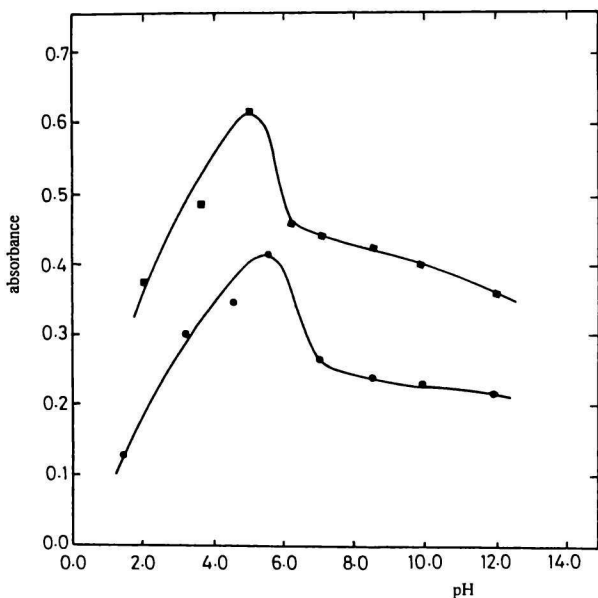


Fig. 2. CT band excitation energy ( $E$ ) vs. DMF mole fraction for dye XIV in DMF— $\text{CHCl}_3$  (●), DMF— $\text{CCl}_4$  (■), and DMF—dioxane (▲) mixtures at 27°C.

hand, as the pH of the medium increases ( $\text{pH} > 7.0$ ), the protonated dye becomes deprotonated and there-

**Table 6.** The Variation of Absorbance at  $\lambda_{\max} = 530$  nm Typical for Cyanine Dyes *XI* and *XIII* in Different Universal Buffer Solutions

Dyes	pH														$pK_a$
	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		
<i>XI</i>	0.13	–	0.30	–	0.34	–	0.41	–	0.26	0.24	–	0.23	0.21	6.4	
<i>XIII</i>	–	0.37	–	0.48	–	0.61	–	0.46	0.44	0.42	0.40	–	0.36	5.6	

**Fig. 3.** S-Curves of  $E = 2.5 \times 10^{-6} \text{ mol}^{-1} \text{ cm}^2$  for *XI* at  $\lambda_{\max} = 530$  nm,  $pK_a = 6.4$  (●), and  $E = 2.5 \times 10^{-5} \text{ mol}^{-1} \text{ cm}^2$  for *XIII* at  $\lambda_{\max} = 530$  nm,  $pK_a = 5.6$  (■).

fore, its 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 *X* and *XIII* have been determined in order to ensure the optimal pH in the application as photosensitizers. The variation of absorbance with pH has been found using the spectrophotometric half-height limiting absorbance and the *Collete* methods [16].

The  $pK_a$  value of the trimethine dye *XI* (6.4) is higher than that of the azomethine dye *XIII* (5.6) (Table 6, Fig. 3). This behaviour refers to a better planarity and greater stability of unsymmetrical trimethine cyanine dyes which favour the intramolecular charge transfer. Such dyes might be suggested to be more sensitive as photosensitizers than the unsymmetrical azomethine cyanine dye analogues.

## EXPERIMENTAL

Compounds *Ia* and *Ib* were prepared in a way similar to that described in Ref. [8].

All melting points are uncorrected. Elemental analysis was carried out in the microanalytical centre by an automatic analyzer (Heraeus). IR spectra (KBr pellets) were determined on a 1278 spectrophotometer (Perkin–Elmer). Absorption spectra, solvatochromism, and pH-sensitivity were recorded on a UV VIS 240 spectrophotometer using 1 cm cells (Shimadzu), and  $^1\text{H}$  NMR (200 MHz) spectra ( $\text{CDCl}_3$ ) on a Varian Gemini NMR spectrometer using TMS as internal reference.

For 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 ( $10^{-3} \text{ mol dm}^{-3}$ ) of the dyes was diluted to the appropriate volume in order to obtain the required concentrations.

A series of buffer solutions with pH values ranging from 1.48 to 12.0 were prepared as recommended by Britton [18]. The pH of buffer solution was checked before spectral measurements.

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

### 8-R-10-Methylpyrazolo[4',5':5,6](pyrazinio/1,4-oxazinio)[2,3,4-*i,j*]quinolin-11-ium Bromides *IIIa–IIIc*

Equimolar ratios of *Ia* resp. *Ib* (0.01 mol) and 8-amino- (*IIa*) resp. hydroxyquinoline (*IIb*) (0.01 mol) were dissolved in butan-1-ol ( $20 \text{ cm}^3$ ) and the reaction mixture was refluxed for 5–8 h. The reaction mixture was concentrated to its half, allowed to cool over night and then diethyl ether was added. The precipitate which formed was filtered, washed with ether and then crystallized from absolute ethanol.

### 9-Ethyl-8-R-10-methylpyrazolo[4',5':5,6](pyrazinio/1,4-oxazinio)[2,3,4-*i,j*]quinolin-11(9)-ium Bromides Iodides *IVa–IVc*

A pure sample of compounds *IIIa–IIIc* 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 recrystallized from absolute ethanol.

**Bromides Iodides of 9-Ethyl-8-R-pyrazolo-[4',5':5,6](pyrazinio/1,4-oxazinio)[2,3,4-i,j]-quinolin-11-ium-10[4(1)]-monomethine Cyanine Dyes Va, Vb, VIa, VIb, VIIa, VIIb**

Equimolar amounts of IVa–IVc and appropriate 1- or 4-quaternary salts (0.01 mol) were dissolved in ethanol (30 cm<sup>3</sup>) 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.

**Bromides Iodides of 9-Ethyl-8-R-pyrazolo-[4',5':5,6](1,4-pyrazinio)[2,3,4-i,j]quinolin-11-ium-10[2(4)]-trimethine Cyanine Dyes IX–XI**

A mixture of quaternary salt IVc (0.01 mol) and equimolar ratios of triethylorthoformate (0.01 mol) was refluxed (8 h) in ethanol (30 cm<sup>3</sup>) containing piperidine (3–6 drops). The reaction mixture was filtered hot, allowed to cool and the precipitated products were collected and recrystallized from ethanol to give the intermediate compound VIII. To a mixture of VIII (0.01 mol) and *N*-ethyl- $\alpha$ -picolinium, -quinaldinium, and - $\gamma$ -picolinium iodide (0.01 mol) in absolute ethanol (40 cm<sup>3</sup>) few drops of piperidine were added. The reaction mixture was refluxed for 8–10 h, filtered hot and cooled. The products were separated out on dilution with ice water and crystallized from absolute ethanol.

**Bromides Iodides of 9-Ethyl-8-R-pyrazolo-[4',5':5,6](1,4-pyrazinio)[2,3,4-i,j]quinolin-11(9)-ium-10-azomethine Cyanine Dyes XIIa, XIIb, XIII, XIV**

A mixture of quaternary salts IVa resp. IVc (0.01 mol) and nitrosophenols (4-nitrosophenols, 1(2)-nitroso-2(1)-naphthols) (0.01 mol) was dissolved in ethanol (50 cm<sup>3</sup>) 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.

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