

# Some New Fused Heterocyclic Cyanine Dyes with Ring Junction Heteroatom

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Received 1 March 1996

New asymmetrical pyrazolio[4',5':4,5]imidazo[3,2-*a*]/pyrrolo[1,2-*a*]pyridinium/quinolinium bromide iodide 1[4(1)]-monomethine cyanines, 1[2(4)]-trimethine cyanines and/or 1-styryl cyanines were synthesized to study their spectral behaviour, solvatochromism, mixed solvents, and acid-base properties.

These dyes are characterized by elemental analysis, IR, <sup>1</sup>H NMR, and electronic absorption spectra.

The application of cyanine dyes is expanded progressively to a new area and new members of special interest are added. The physical properties of selected cyanines have been studied using modern technique [1, 2] to get more information about their application to a specific purpose and their behaviour depended on the nature of heterocycles, the solvent used, and the presence of other additives [3–7].

Within these respects, new asymmetrical monomethine (*Va–Vi*), trimethine (*VIIa–VIIIh*), and styryl (*VIIIa–VIIIg*) cyanine dyes incorporating pyrazolio[4',5':4,5]imidazo[3,2-*a*]/pyrrolo[1,2-*a*]pyridinium/quinolinium moieties were prepared to study their spectral behaviour, as well as solvatochromic and acid-base behaviours of some selected dyes to make suitable selection for their application as photosensitizers.

## EXPERIMENTAL

All melting points are uncorrected. Elemental analysis was carried out at the microanalytical centre (Cairo University) and the data are given in Tables 1 and 2.

The IR spectra were determined with Perkin–Elmer 127B spectrophotometer (Assiut University) (Table 3).

The visible spectra, solvatochromism, and pH-sensitive studies were recorded within the wavelength 300–700 nm on a Shimadzu UV VIS 240 spectrophotometer using 1 cm cells (Faculty of Science, Aswan) (Table 4).

The <sup>1</sup>H NMR spectra were recorded with EM-390 90 MHz spectrometer (Cairo University) (Table 3).

Synthesis of 4-bromo-3-methylpyrazol-5-one *Ia* or its 1-phenyl derivative *Ib* was performed in a way similar to that described in Ref. [8].

At the investigation of solvatochromism and acid-

base properties, the organic solvents used were of spectroscopic grade or purified according to the recommended method [9]. An accurate volume of the stock solution ( $c = 10^{-3}$  mol dm<sup>-3</sup>) 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 1.30–12.0 was prepared as recommended by Britton [10]. An accurate volume of the stock solutions ( $c = 10^{-3}$  mol dm<sup>-3</sup>) was added to 0.5 cm<sup>3</sup> of buffer solution in 5 cm<sup>3</sup> measuring flask, then it was completed to the mark with redistilled water. The pH of buffer solution was checked before spectral measurements.

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

### 1-Methylpyrazolo[4',5':4,5]imidazo[3,2-*a*]/pyrrolo[1,2-*a*]pyridinium/quinolinium Bromides (*IIIa–IIIId*)

Equimolar ratios of *Ia* or *Ib* (0.01 mol) and 2-aminopyridine,  $\alpha$ -picoline, and quinaldine *IIa–IIc* (0.01 mol) were dissolved in 1-butanol (20 cm<sup>3</sup>) and the reaction mixture was refluxed for 5 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.

### 2-Ethyl-1-methylpyrazolio[4',5':4,5]imidazo[3,2-*a*]/pyrrolo[1,2-*a*]pyridinium/quinolinium Bromides Iodides (*IVa–IVd*)

A pure sample of compounds *IIIa–IIIId* 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.

**2-Ethylpyrazolio[4',5':4,5]imidazo[3,2-*a*]/pyrrolo[1,2-*a*]pyridinium/quinolinium Bromide Iodide 1[4(1)]-Monomethine Cyanine Dyes (Va—Vi)**

The quaternary salts *IVa*—*IVd* (0.01 mol) were refluxed with *N*-methylpyridinium, -quinolinium, and -isoquinolinium iodide (0.01 mol) in the presence of absolute ethanol (30 cm<sup>3</sup>) and few drops of piperidine. The monomethine cyanines *Va*—*Vi* were collected, washed with ether and then crystallized from aqueous ethanol.

**2-Ethylpyrazolio[4',5':4,5]imidazo[3,2-*a*]/pyrrolo[1,2-*a*]pyridinium/quinolinium Bromide Iodide 1[2(4)]-Trimethine Cyanine Dyes (*VIIa*—*VIIh*)**

A mixture of quaternary salts *IVa*—*IVc* (0.01 mol) and equimolar ratios of triethyl orthoformate (0.01 mol) was refluxed in ethanol (30 cm<sup>3</sup>) 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 compounds *VIa*—*VIc*.

To a mixture of the latter intermediate compounds *VIa*—*VIc* (0.01 mol) and *N*-ethyl- $\alpha$ -picolinium, -quinaldinium, resp. - $\gamma$ -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 *VIIa*—*VIIh* were separated out on dilution with ice water and crystallized from absolute ethanol.

**2-Ethyl-1-styrylpyrazolio[4',5':4,5]imidazo[3,2-*a*]/pyrrolo[1,2-*a*]pyridinium/quinolinium Bromide Iodide Cyanine Dyes (*VIIIa*—*VIIIg*)**

A mixture of quaternary salts *IVa*—*IVc* (0.01 mol) and aromatic aldehydes (benzaldehyde, *p*-methoxybenzaldehyde, and *p*-nitrobenzaldehyde) (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 to give the corresponding styryl cyanine dyes *VIIIa*—*VIIIg*.

**RESULTS AND DISCUSSION**

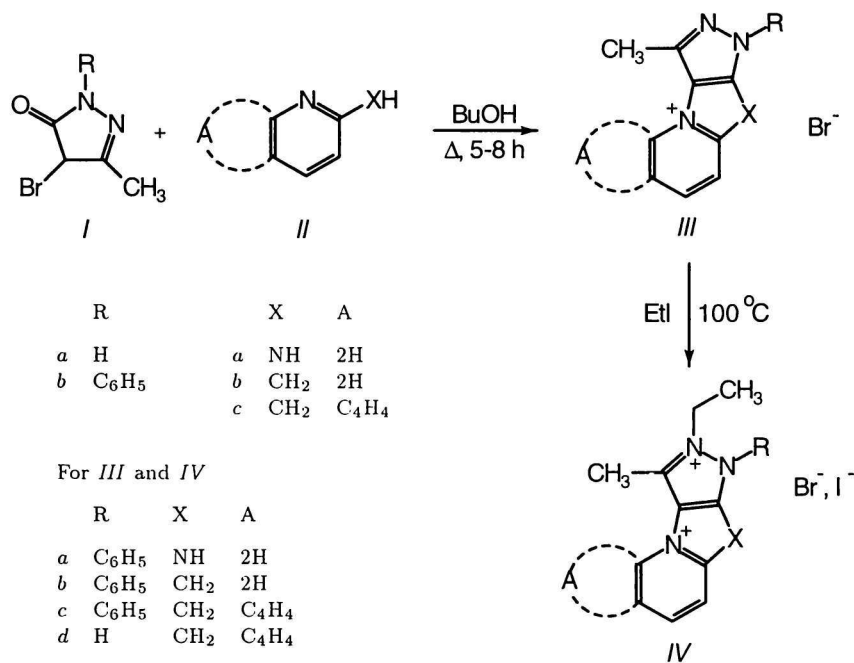
Interaction of 4-bromo-3-methylpyrazol-5-one *Ia* or its 1-phenyl derivative *Ib* [8] with 2-aminopyridine,  $\alpha$ -picoline or quinaldine *IIa*—*IIc* in 1-butanol solution afforded the corresponding new bridgehead nitrogen-fused heterocyclic bromide salts, namely 1-methylpyrazolo[4',5':4,5]imidazo[3,2-*a*]/pyrrolo[1,2-*a*]pyridinium/quinolinium bromides *IIIa*—*IIId* (characterization of compounds is given in Tables 1 and 2). Direct quaternization of compounds *IIIa*—*IIId* using

**Table 1.** Characterization Data for Starting and Intermediate Compounds *IIIa*—*IIId*, *IVa*—*IVd*, and *VIa*—*VIc*

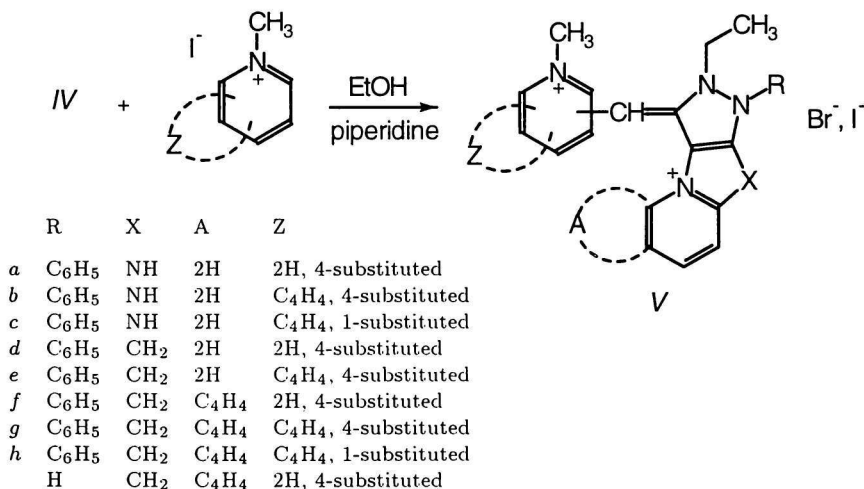
Compound	Formula <i>M<sub>r</sub></i>	$w_i(\text{calc.})/\%$ $w_i(\text{found})/\%$			Yield %	M.p. °C	Colour
		C	H	N			
<i>IIIa</i>	C <sub>15</sub> H <sub>13</sub> N <sub>4</sub> Br	54.71	3.95	17.02	68	165—168	Red
	329.21	54.05	3.88	17.21			
<i>IIIb</i>	C <sub>16</sub> H <sub>14</sub> N <sub>3</sub> Br	58.54	4.27	12.81	65	173—175	Brownish red
	328.23	58.45	4.33	12.68			
<i>IIIc</i>	C <sub>20</sub> H <sub>16</sub> N <sub>3</sub> Br	63.49	4.23	11.11	74	198—200	Red
	378.29	63.15	4.45	10.97			
<i>IIId</i>	C <sub>14</sub> H <sub>12</sub> N <sub>3</sub> Br	55.63	3.97	13.91	61	215—218	Brown
	302.19	55.44	3.78	13.80			
<i>IVa</i>	C <sub>17</sub> H <sub>18</sub> N <sub>4</sub> BrI	42.06	3.71	11.55	69	187—189	Reddish brown
	485.18	41.86	3.77	11.65			
<i>IVb</i>	C <sub>18</sub> H <sub>19</sub> N <sub>3</sub> BrI	44.63	3.93	8.68	67	213—215	Brown
	484.19	44.36	3.75	8.91			
<i>IVc</i>	C <sub>22</sub> H <sub>21</sub> N <sub>3</sub> BrI	49.44	3.93	7.87	78	226—228	Deep brown
	534.25	49.15	4.16	8.01			
<i>IVd</i>	C <sub>16</sub> H <sub>17</sub> N <sub>3</sub> BrI	41.92	3.71	9.17	63	239—241	Pale yellow
	458.15	41.63	3.57	9.25			
<i>VIa</i>	C <sub>22</sub> H <sub>28</sub> N <sub>4</sub> O <sub>2</sub> BrI	44.98	4.77	9.54	81	149—153	Brown
	587.29	44.71	4.52	9.33			
<i>VIb</i>	C <sub>23</sub> H <sub>29</sub> N <sub>3</sub> O <sub>2</sub> BrI	47.10	4.95	7.17	76	167—169	Red
	586.31	46.89	5.18	7.36			
<i>VIc</i>	C <sub>27</sub> H <sub>31</sub> N <sub>3</sub> O <sub>2</sub> BrI	50.94	4.87	6.60	85	187—190	Yellow
	636.37	51.21	4.63	6.72			

Table 2. Characterization Data for Asymmetrical Monomethine, Trimethine, and Styryl Cyanine Dyes *Va—Vi*, *VIIa—VIIIh*, and *VIIIa—VIIIg*

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				$\lambda_{\text{max}}$ nm	$\epsilon_{\text{max}}$ $\text{cm}^2 \text{mol}^{-1}$
		<i>Va</i>	$\text{C}_{23}\text{H}_{23}\text{N}_5\text{BrI}$ 576.29	47.92 47.76	3.99 3.90	12.15 12.01	59	140—142	Brownish violet
<i>Vb</i>	$\text{C}_{27}\text{H}_{25}\text{N}_5\text{BrI}$ 626.35	51.76 51.61	3.99 3.73	11.18 11.28	68	169—170	Violet	510	1080
<i>Vc</i>	$\text{C}_{27}\text{H}_{25}\text{N}_5\text{BrI}$ 626.35	51.76 51.82	3.99 3.77	11.18 10.92	54	175—178	Reddish violet	345 500 sh	4500 1000
<i>Vd</i>	$\text{C}_{24}\text{H}_{24}\text{N}_4\text{BrI}$ 575.30	50.09 49.88	4.17 4.25	9.74 9.46	63	189—191	Reddish violet	500	1533
<i>Ve</i>	$\text{C}_{28}\text{H}_{26}\text{N}_4\text{BrI}$ 625.36	53.76 53.69	4.16 3.96	8.96 9.01	71	162—165	Violet	465 490 515	5100 5000 4600
<i>Vf</i>	$\text{C}_{28}\text{H}_{26}\text{N}_4\text{BrI}$ 625.36	53.76 53.93	4.16 4.22	8.96 8.81	73	174—177	Violet	365 500	6240 1520
<i>Vg</i>	$\text{C}_{32}\text{H}_{28}\text{N}_4\text{BrI}$ 675.42	56.89 56.71	4.15 4.33	8.30 8.18	77	185—188	Intense violet	370 440 520	6200 3800 3600
<i>Vh</i>	$\text{C}_{32}\text{H}_{28}\text{N}_4\text{BrI}$ 675.42	56.89 56.94	4.15 3.95	8.30 8.05	64	193—196	Violet	505	2800
<i>Vi</i>	$\text{C}_{22}\text{H}_{22}\text{N}_4\text{BrI}$ 549.27	48.09 47.81	4.01 3.95	10.20 10.01	60	192—195	Brownish violet	455	2790
<i>VIIa</i>	$\text{C}_{26}\text{H}_{27}\text{N}_5\text{BrI}$ 616.36	50.65 50.55	4.38 4.51	11.36 11.12	66	150—152	Violet	370 500 sh	17200 4200
<i>VIIb</i>	$\text{C}_{30}\text{H}_{29}\text{N}_5\text{BrI}$ 666.42	54.05 53.85	4.35 4.53	10.51 10.45		165—167	Deep violet	370 460 510	10933 4800 3787
<i>VIIc</i>	$\text{C}_{26}\text{H}_{27}\text{N}_5\text{BrI}$ 616.36	50.65 50.79	4.38 4.44	11.36 11.26	68	164—167	Brownish violet	350 370 490	8300 7440 2420
<i>VIIId</i>	$\text{C}_{27}\text{H}_{28}\text{N}_4\text{BrI}$ 615.37	52.68 52.51	4.55 4.69	9.11 8.93	65	185—188	Violet	360 400 525	12480 10800 8780
<i>VIIe</i>	$\text{C}_{31}\text{H}_{30}\text{N}_4\text{BrI}$ 665.43	55.94 56.15	4.51 4.39	8.42 8.65	74	168—170	Violet	460 530	1800 1334
<i>VIIIf</i>	$\text{C}_{31}\text{H}_{30}\text{N}_4\text{BrI}$ 665.43	55.94 55.86	4.51 4.63	8.42 8.51	69	175—178	Reddish violet	355 430 530	3134 2267 2680
<i>VIIg</i>	$\text{C}_{35}\text{H}_{32}\text{N}_4\text{BrI}$ 715.49	58.74 58.66	4.48 4.13	7.83 7.52	89	195—198	Intense violet	515 610 670	2934 1467 1054
<i>VIIIh</i>	$\text{C}_{31}\text{H}_{30}\text{N}_4\text{BrI}$ 665.43	55.94 55.73	4.51 4.19	8.42 8.26	73	133—135	Violet	350 460 530	3067 2294 2307
<i>VIIIa</i>	$\text{C}_{24}\text{H}_{22}\text{N}_4\text{BrI}$ 573.29	50.26 50.31	3.84 3.76	9.77 9.51	63	190—193	Brownish red	355 520	11600 3520
<i>VIIIb</i>	$\text{C}_{25}\text{H}_{24}\text{N}_4\text{OBrI}$ 603.31	49.75 49.56	3.98 4.15	9.29 9.51	66	110—113	Brown	360 525	6800 1520
<i>VIIIc</i>	$\text{C}_{24}\text{H}_{21}\text{N}_5\text{O}_2\text{BrI}$ 618.27	46.60 46.46	3.40 3.75	11.33 11.18	54	150—152	Intense brown	360	4934
<i>VIIIId</i>	$\text{C}_{26}\text{H}_{25}\text{N}_3\text{OBrI}$ 602.32	51.83 52.05	4.15 3.97	6.98 7.12	59	185—187	Yellow	365 500	4400 1800
<i>VIIIe</i>	$\text{C}_{25}\text{H}_{22}\text{N}_4\text{O}_2\text{BrI}$ 617.28	48.62 48.56	3.57 3.71	9.08 8.93	53	160—162	Brownish red	460 520	2400 1800
<i>VIIIIf</i>	$\text{C}_{29}\text{H}_{25}\text{N}_3\text{BrI}$ 622.36	55.95 56.13	4.02 3.89	6.75 6.55	56	165—167	Yellow	370 520	6440 1640
<i>VIIIg</i>	$\text{C}_{30}\text{H}_{27}\text{N}_3\text{OBrI}$ 652.38	55.22 55.46	4.14 4.04	6.44 6.37	61	158—160	Brownish violet	350 370 430 520	8100 7600 4820 2600



Scheme 1



Scheme 2

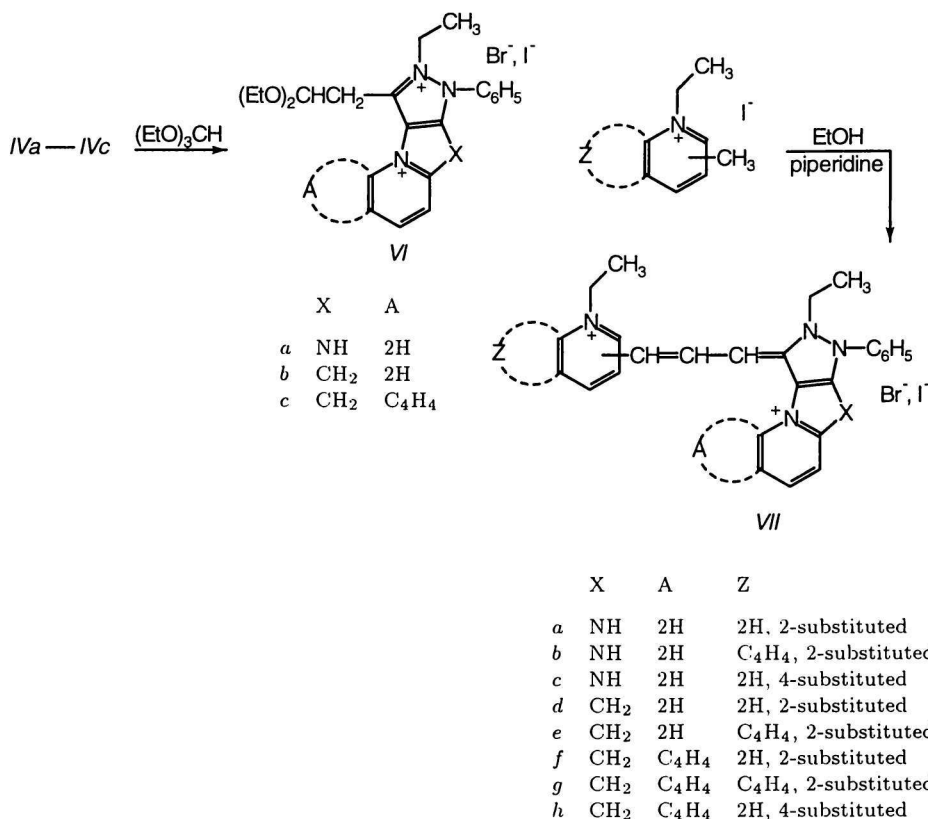
excess amount of ethyl iodide under controlled conditions gave 2-ethyl-1-methylpyrazolio[4',5':4,5]imidazo[3,2-*a*]/pyrrolo[1,2-*a*]pyridinium/quinolinium bromides iodides *IVa*—*IVd* (Scheme 1).

Asymmetrical 2-ethylpyrazolio[4',5':4,5]imidazo[3,2-*a*]/pyrrolo[1,2-*a*]pyridinium/quinolinium bromide iodide 1[4(1)]-monomethine cyanine dyes *Va*—*Vi* were synthesized through interaction of equimolar ratios of the quaternary salts *IVa*—*IVd* and *N*-methylpyridinium, -quinolinium, resp. -isoquinolinium iodide under piperidine catalysis (Scheme 2).

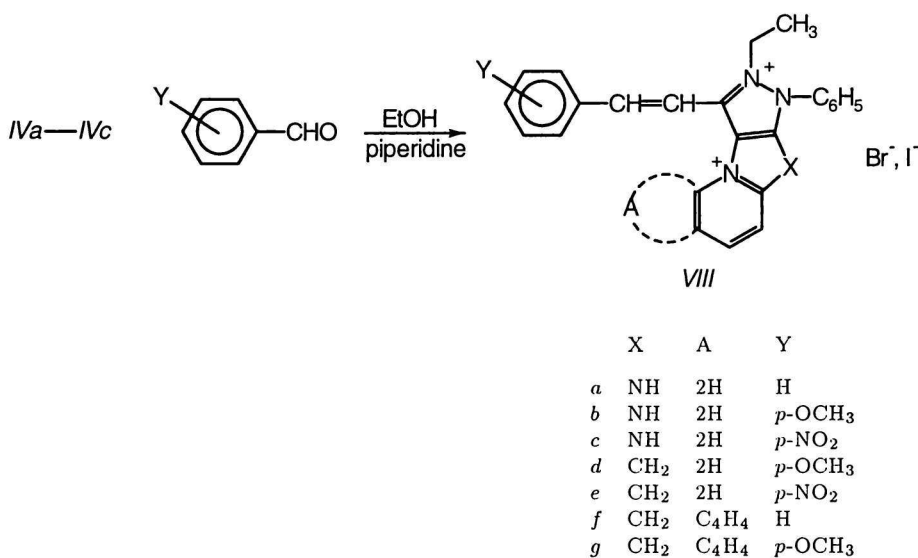
The asymmetrical monomethine cyanine dyes *Va*—

*Vi* are fairly soluble in polar organic solvents and in concentrated H<sub>2</sub>SO<sub>4</sub> liberating iodine vapour on heating. Their solutions in polar organic solvents exhibited intense green fluorescence depending upon the solvents used. Their ethanolic solutions give violet colour in alkaline medium which discharges on acidification and restore their permanent colour on basification.

The condensation reaction of equimolar ratios of the quaternary salts *IVa*—*IVc* with triethyl orthoformate under piperidine catalysis and ethanol as solvent afforded the corresponding intermediate compounds *VIa*—*VIc*. The latter compounds are



Scheme 3



Scheme 4

considered as key intermediates for the synthesis of asymmetrical 2-ethylpyrazolio[4',5':4,5]imidazo[3,2-*a*]/pyrrolo[1,2-*a*]pyridinium/quinolinium bromide iodide 1[2(4)]-trimethine cyanine dyes *VIIa*—*VIIh* when interacted with *N*-ethyl- $\alpha$ -picolinium, -quinaldinium, resp. - $\gamma$ -picolinium iodide in the presence of piperidine

as basic catalyst (Scheme 3).

The asymmetrical trimethine cyanine dyes *VIIa*—*VIIh* are highly coloured in polar organic solvent solutions, exhibiting intense green fluorescence. They are soluble in concentrated H<sub>2</sub>SO<sub>4</sub> releasing iodine vapour on warming. Their ethanolic solutions gave permanent

**Table 3.** IR and  $^1\text{H}$  NMR Spectral Data of Some Selected Starting Compounds and their Monomethine, Trimethine, and Styryl Cyanine Derivatives

Compound	IR spectrum, $\bar{\nu}(\text{KBr})/\text{cm}^{-1}$	$^1\text{H}$ NMR spectrum ( $\text{CDCl}_3$ ), $\delta^a$
<i>IIIa</i>	3200—3500 (NH group)	6.6—8.0 (m, 9H, $\text{H}_{\text{arom}}$ (het.), —H)
	2900—3000 (CH of $\text{CH}_3$ )	4.2 (s, 1H, NH group) exchangeable with $\text{D}_2\text{O}$
	1690—1700 ( $\text{C}=\text{C}$ )	1.3 (s, 3H, $\text{CH}_3$ group)
	1595—1620 ( $\text{C}=\text{N}$ )	
	700—760 (monosubstituted aromatic ring)	
<i>IIIc</i>	2900—2980 (CH of $\text{CH}_3$ )	7.2—8.6 (m, 13H, $\text{H}_{\text{arom}}$ (het.), —H)
	1660—1680 ( $\text{C}=\text{C}$ )	1.3 (s, 3H, $\text{CH}_3$ group)
	1595—1620 ( $\text{C}=\text{N}$ )	
	680—760 (mono- and disubstituted aromatic ring)	
<i>IVa</i>	2850—2980 (ethyl pyrazolium iodide)	7.0—8.0 (m, 9H, $\text{H}_{\text{arom}}$ (het.), —H)
	3200—3500 (NH group)	4.2 (s, 1H, NH group) exchangeable with $\text{D}_2\text{O}$
	1690—1700 ( $\text{C}=\text{C}$ )	1.3 (s, 3H, $\text{CH}_3$ group)
	1595—1620 ( $\text{C}=\text{N}$ )	0.8—0.95 (t, 3H, $\text{CH}_3\text{CH}_2\text{N}^+$ )
	700—760 (monosubstituted aromatic ring)	1.8—2.5 (q, 2H, $\text{CH}_3\text{CH}_2\text{N}^+$ )
<i>IVc</i>	2900—3060 (ethyl pyrazolium iodide)	7.2—8.6 (m, 13H, $\text{H}_{\text{arom}}$ (het.), —H)
	1660—1680 ( $\text{C}=\text{C}$ )	1.3 (s, 3H, $\text{CH}_3$ group)
	1595—1620 ( $\text{C}=\text{N}$ )	0.8—0.95 (t, 3H, $\text{CH}_3\text{CH}_2\text{N}^+$ )
	680—760 (mono- and disubstituted aromatic ring)	1.5—2.0 (q, 2H, $\text{CH}_3\text{CH}_2\text{N}^+$ )
<i>Vg</i>	2900—3060 (methyl quinolinium iodide)	7.2—8.7 (m, 20H, $\text{H}_{\text{arom}}$ (het.), —H, =CH)
	1620—1650 ( $\text{C}=\text{CH}$ )	3.6 (s, 3H, $\text{CH}_3$ joined to immonium centre)
	1660—1680 ( $\text{C}=\text{C}$ )	1.25 (t, 3H, $\text{CH}_3\text{CH}_2\text{N}$ )
	1595—1620 ( $\text{C}=\text{N}$ )	2.2 (q, 2H, $\text{CH}_3\text{CH}_2\text{N}$ )
	680—760 (mono- and disubstituted aromatic ring)	
<i>VIb</i>	2950—3080 (ethyl pyrazolium iodide)	7.1—8.0 (m, 11H, $\text{H}_{\text{arom}}$ (het.), —H)
	2900—2950 (CH of $\text{CH}_3$ )	3.8 (t, 1H, —CH<)
	1680—1690 ( $\text{C}=\text{C}$ )	1.0 (d, 2H, — $\text{CH}_2$ —)
	1590—1610 ( $\text{C}=\text{N}$ )	1.35 (t, 6H, $2\text{CH}_3\text{CH}_2\text{O}$ )
	1090—1250 ( $\text{C}-\text{O}-\text{C}_{\text{aliph}}$ )	0.8—0.95 (t, 3H, $\text{CH}_3\text{CH}_2\text{N}^+$ )
	680—750 (monosubstituted aromatic ring)	1.95—2.41 (m, 6H, $2\text{CH}_3\text{CH}_2\text{O}$ , $\text{CH}_3\text{CH}_2\text{N}^+$ )
<i>VIIg</i>	2950—3080 (ethyl quinolinium iodide)	7.0—8.2 (m, 22H, $\text{H}_{\text{arom}}$ (het.), —H, $\text{CH}=\text{CH}-\text{CH}=\text{CH}$ )
	2900—2950 (CH of $\text{CH}_3$ )	3.70 (q, 2H, $\text{CH}_3\text{CH}_2\text{N}^+$ )
	1680—1690 ( $\text{C}=\text{C}$ )	1.60 (t, 3H, $\text{CH}_3\text{CH}_2\text{N}^+$ )
	1590—1610 ( $\text{C}=\text{N}$ )	0.8—0.95 (t, 3H, $\text{CH}_3\text{CH}_2\text{N}$ )
	1680—1710 ( $\text{CH}=\text{CH}$ )	2.25 (q, 2H, $\text{CH}_3\text{CH}_2\text{N}$ )
	680—750 (monosubstituted aromatic ring)	
<i>VIIIa</i>	2850—3040 (ethyl pyrazolium iodide)	7.0—8.15 (m, 16H, $\text{H}_{\text{arom}}$ (het.), —H, $\text{CH}=\text{CH}$ )
	3200—3650 (NH group)	4.2 (s, 1H, NH group) exchangeable with $\text{D}_2\text{O}$
	1680—1700 ( $\text{CH}=\text{CH}$ )	2.25 (q, 2H, $\text{CH}_3\text{CH}_2\text{N}^+$ )
	1560—1610 ( $\text{C}=\text{N}$ )	1.10 (t, 3H, $\text{CH}_3\text{CH}_2\text{N}^+$ )
	670—760 (monosubstituted aromatic ring)	

a) s - singlet, d - doublet, t - triplet, m - multiplet.

colour in basic medium which faded on acidification with changes in colour.

Interaction of equimolar ratios of quaternary salts *IVa*—*IVc* and equimolar ratios of aromatic aldehydes (benzaldehyde, *p*-methoxybenzaldehyde, and *p*-nitrobenzaldehyde) under piperidine catalysis afforded the corresponding asymmetrical 2-ethyl-1-styrylpyrazolio[4',5':4,5]imidazo[3,2-*a*]/pyrrolo[1,2-*a*]pyridinium/quinolinium bromide iodide cyanine dyes *VIIIa*—*VIIIg* (Scheme 4).

The asymmetrical styryl cyanine dyes *VIIIa*—*VIIIg* are fairly soluble in polar organic solvents and in concentrated  $\text{H}_2\text{SO}_4$  liberating iodine vapour on heating. Their ethanolic solutions gave a brown colour in alkaline medium, discharged on acidification.

The structures of compounds *III*—*VIII* were es-

tablished by elemental analysis (Tables 1 and 2), and IR [11] and  $^1\text{H}$  NMR [12] spectral data (Table 3). Thus, IR spectra ( $\bar{\nu}(\text{KBr})/\text{cm}^{-1}$ ) for *IIIa*, *IIIc* and *IVa*, *IVc* disclose general absorption bands at  $\bar{\nu} = 1660$ — $1700$  ( $\nu(\text{C}=\text{C})$ ),  $1595$ — $1620$  ( $\nu(\text{C}=\text{N})$ ),  $2850$ — $3000$  ( $\nu(\text{CH})$  of  $\text{CH}_3$  for *IIIa*, *IIIc* and ethyl pyrazolium iodide for *IVa*, *IVc*),  $670$ — $680$  ( $\nu$  mono- and disubstituted aromatic ring), and  $3200$ — $3500$  ( $\nu(\text{NH})$  for *IIIa* and *IVa*). In addition to the absorption bands cited in compounds *IVa*, *IVc*, the IR spectrum for *VIb* reveals characteristic absorption band at  $\bar{\nu} = 1090$ — $1250$  ( $\nu(\text{C}-\text{O}-\text{C})_{\text{aliph}}$ ).

$^1\text{H}$  NMR spectra ( $\text{CDCl}_3$ ),  $\delta$  for compounds *IIIa*, *IVa* reveal general signals at chemical shifts  $6.6$ — $8.0$  (m, 9H,  $\text{H}_{\text{arom}}$  (het.), —H),  $4.2$  (s, 1H, NH group exchangeable with  $\text{D}_2\text{O}$ ),  $1.3$  (s, 3H,  $\text{CH}_3$ ), and char-

acteristic signals at 0.8—0.95 (t, 3H,  $\text{CH}_3\text{CH}_2\text{N}^+$ ) and 1.8—2.5 (q, 2H,  $\text{CH}_3\text{CH}_2\text{N}^+$ ) for *IVa*. Meanwhile,  $^1\text{H}$  NMR spectrum for compounds *IIIc*, *IVc* reveals signals at 7.2—8.6 (m, 13H,  $\text{H}_{\text{arom}}$  (het.), —H), 1.3 (s, 3H,  $\text{CH}_3$ ), and characteristic signals at 0.8—0.95 (t, 3H,  $\text{CH}_3\text{CH}_2\text{N}^+$ ), 1.5—2.0 (q, 2H,  $\text{CH}_3\text{CH}_2\text{N}^+$ ).

$^1\text{H}$  NMR spectra for compound *VIb* reveal signals at 7.1—8.0 (m, 11H,  $\text{H}_{\text{arom}}$  (het.), —H), 3.8 (t, 1H,  $>\text{CH}-$ ), 1.0 (d, 2H,  $>\text{CH}_2$ ), 1.35 (t, 6H,  $2\text{CH}_3\text{CH}_2\text{O}$ ), 0.8—0.95 (t, 3H,  $\text{CH}_3\text{CH}_2\text{N}^+$ ), 1.95—2.41 (m, 6H,  $2\text{CH}_3\text{CH}_2\text{O}$ ,  $\text{CH}_3\text{CH}_2\text{N}^+$ ).

IR spectrum ( $\bar{\nu}(\text{KBr})/\text{cm}^{-1}$ ) for mono/trimethine and styryl cyanines *Vg*, *VIIg*, and *VIIIa* exhibits in addition to general absorption bands at  $\bar{\nu} = 1620$ — $1710$  ( $\nu(\text{C}=\text{CH})$  or conjugated diene),  $1660$ — $1690$  ( $\nu(\text{C}=\text{C})$ ),  $1560$ — $1620$  ( $\nu(\text{C}=\text{N})$ ),  $680$ — $760$  ( $\nu$  mono- and disubstituted aromatic ring), characteristic bands at  $\bar{\nu} = 2850$ — $3060$  ( $\nu$  methyl/ethyl quinolinium/pyrazolinium iodide), and at  $\bar{\nu} = 3200$ — $3650$  ( $\nu(\text{NH})$  group for *VIIIa*).

$^1\text{H}$  NMR spectrum ( $\text{CDCl}_3$ ),  $\delta$  for mono/trimethine and styryl cyanines *Vg*, *VIIg*, and *VIIIa* reveals the following signals: 7.2—8.7 (m, 20H,  $\text{H}_{\text{arom}}$  (het.), —H,  $=\text{CH}$ ), 3.6 (s, 3H,  $\text{CH}_3\text{I}$ ), 1.25 (t, 3H,  $\text{CH}_3\text{CH}_2\text{N}$ ), and 2.2 (q, 2H,  $\text{CH}_3\text{CH}_2\text{N}$ ) for monomethine cyanine *Vg*; 7.0—8.2 (m, 22H,  $\text{H}_{\text{arom}}$  (het.), —H,  $\text{CH}=\text{CH}-\text{CH}=\text{CH}$ ), 3.70 (q, 2H,  $\text{CH}_3\text{CH}_2\text{N}^+$ ), 1.60 (t, 3H,  $\text{CH}_3\text{CH}_2\text{N}^+$ ), 0.8—0.95 (t, 3H,  $\text{CH}_3\text{CH}_2\text{N}$ ), and 2.25 (q, 2H,  $\text{CH}_3\text{CH}_2\text{N}$ ) for trimethine cyanine *VIIg*, and 7.0—8.15 (m, 16H,  $\text{H}_{\text{arom}}$  (het.), —H,  $\text{CH}=\text{CH}$ ), 4.2 (s, 1H, NH group exchangeable with  $\text{D}_2\text{O}$ ), 2.25 (q, 2H,  $\text{CH}_3\text{CH}_2\text{N}^+$ ), and 1.10 (t, 3H,  $\text{CH}_3\text{CH}_2\text{N}^+$ ) for styryl cyanine *VIIIa*.

Absorption spectra of methine cyanines, *e.g.* mono- and trimethine types (*Va*—*Vi*, *VIIa*—*VIIh*) and related dyes, *e.g.* styryl cyanine (*VIIIa*—*VIIIg*) in ethanol are taken as a criterion for their synthesizing effect for silver halide emulsion. The effectiveness of compounds as photosensitizers increases when they are present in the ionic form which has higher planarity.

In view of spectral visible determination of the cited newly synthesized mono/trimethine and styryl cyanines in 95 % ethanol, the absorption spectra of such dyes are therefore considered to be more potentially sensitive as photosensitizers depending upon the nature of quaternary heterocyclic residue (Z), their linkage position, type of condensed pyrazolo ring or aryl substituents and cyanine dye molecule. Thus, mono- and trimethine cyanine dyes incorporating quinolinium-4(2)-yl salt (*Vb*, *Ve*, *Vg* and *VIIb*, *VIIe*, *VIIg*) are quite potentially sensitive as photosensitizers compared with those containing pyridinium analogues (*Va*, *Vd*, *Vf* and *VIIa*, *VIIId*, *VIIIf*) as they have high absorption values.

Changing the linkage position of heterocyclic quaternary residue (Z) from 4-yl salt to 1-yl salt in both

*Vb* and *Vg* (*Vc* and *Vh*) resulted in less potential sensitivity. This can be explained in terms of the higher planarity and greater stability of dyes involving 4-substituted quinolinium which favours intramolecular charge transfer more than pyridinium and 1-substituted quinolinium analogues.

On the other hand, the dye 2-ethylpyrazolio[4',5':4,5]pyrrolo[1,2-*a*]quinolinium bromide iodide 1[4(1)]-monomethine cyanine *Vf* involving  $\text{R} = \text{C}_6\text{H}_5$  is more potentially sensitive as photosensitizer than the dye *Vi* involving  $\text{R} = \text{H}$  because of its high absorption value. This is due to the mesomeric effect of phenyl group which causes higher planarity and greater stability in dye *Vf*.

Additionally, the mono/trimethine cyanine dyes involving pyrrolo[1,2-*a*]pyridinium/quinolinium-4(2)-yl salts (*Vd*, *Ve* and *VIIId*, *VIIe*) are more potentially sensitive as photosensitizers than those involving imidazo[3,2-*a*] analogues (*Va*, *Vb* and *VIIa*, *VIIb*) as they have high absorption values. This could be attributed to the interaction of the lone pair electrons of imidazo heteroatom ( $\text{X} = \text{NH}$ ) with pyridinium/quinolinium bromide salts which decreases slightly the electron density on imidazo heteroatom and consequently decreases to some extent the mobility of the  $\pi$ -electrons attached to the conjugated pathway.

The effectiveness of the asymmetrical trimethine cyanine dyes as photosensitizers increases more when they are substituted with quinolinium bromide salts (*VIIIf* and *VIIg*) than in case of the substitution with pyridinium bromide salt analogues (*VIIId* and *VIIe*) as their absorption values shift is of 5—30 nm with the increasing number of absorption bands.

On comparison of asymmetrical trimethine cyanine dyes (*VIIa*—*VIIh*) with monomethine analogues (*Va*—*Vi*) in view of spectral visible determination, it was concluded that trimethine types are more potentially sensitive as photosensitizers as they have high absorption values shift of 20 nm. This is due to the increasing number of methine groups, which causes an increase in the electron mobility of cyanine pathway and higher planarity or greater stability.

The effectiveness of styryl cyanine dyes (*VIIIa*—*VIIIg*) as photosensitizers increases more when they are substituted with electron-donating groups in aryl moiety (*VIIIb* and *VIIIg*) than in case of unsubstituted (*VIIIa* and *VIIIf*) or substituted with electron-withdrawing groups (*VIIIc*) as they have high absorption values. This is due to the partial mixing of the lone pair orbitals of oxygen ( $\text{OCH}_3$  group) with the  $\pi$ -system for the heterocyclic ring leading to a modified set of energy levels and consequently the mobility of the  $\pi$ -electrons attached to conjugated pathway increases to some extent.

The colours and electronic absorption spectra changes of some selected mono/trimethine cyanine dyes *Ve*, *Vg*, and *Vi* (*VIIe* and *VIIg*) in some organic

**Table 4.** Electronic Absorption Spectra Characteristic of the Selected Monomethine (*Ve*, *Vg*, and *Vi*) and Trimethine (*VIIe* and *VIIg*) Cyanines in Pure Solvents

Compound	$\lambda_{\max}/\text{nm}$ ( $\epsilon_{\max}/(\text{mol}^{-1} \text{cm}^2)$ )											
	Water		DMF		Ethanol		CHCl <sub>3</sub>		Dioxane		CCl <sub>4</sub>	
<i>Ve</i>			460	(4800)	465	(5100)	350	(4560)	355	(2240)		
					490	(5000)	410	(3840)				
<i>Vg</i>	500	(1150)	535	(4390)	515	(4600)	530	(1600)	510	(1100)		
			370	(15200)	370	(6200)	370	(18000)			370	(14800)
	440	(2000)	445	(9040)	440	(3800)					390	(13960)
<i>Vi</i>	510	(1960)	540	(8680)	520	(3600)	530	(6000)	510	(5200)	510	(2800)
	365	(5800)	365	(7800)			365	(7680)	370	(9400)	370	(6200)
	455	(4400)	440	(3200)	455	(2790)	450	(3440)				
<i>VIIe</i>			460	(3100)								
	440	(2400)	410	(4000)			430	(3920)			365	(5760)
			465	(3160)	460	(1800)	465	(3200)			380	(5400)
<i>VIIg</i>	520	(1400)	530	(1598)	530	(1333)	520	(1998)	510	(1200)		
	490	(3700)					400	(5600)	410	(5200)	405	(5778)
			530	(5360)	515	(2934)	520	(5200)	510	(3400)	515	(5040)
		620	(3000)	610	(1467)	615	(3280)					
		670	(2380)	670	(1054)	670	(2600)					

solvents were examined in the visible region in order to shed some light on their solvatochromic behaviour. Thus, the electronic absorption spectra of selected dyes in pure organic solvents of different electric relative permittivity  $\epsilon_r$ , viz. water (78.54), DMF (36.70), EtOH (24.3), CHCl<sub>3</sub> (4.806), CCl<sub>4</sub> (2.238), and dioxane (2.209) [13], respectively, gave different values of  $\lambda_{\max}$  and  $\epsilon_{\max}$  of the absorption bands due to different electronic transitions within the solute molecule in those solvents (Table 4).

It is clear that the spectra of dyes *Ve*, *Vg*, and *VIIg* in ethanol medium are characterized by three essential bands in the visible region (above 350 nm), while the spectra of dyes *Vi* and *VIIe* consist of one or two essential absorption bands in the visible region. The shorter bands can be assigned to  $\pi^* \leftarrow \pi$  transitions within the benzenoid and heterocyclic rings. These bands are little influenced by changing the polarity of the medium. The other bands at longer wavelengths can be attributed to  $\pi^* \leftarrow n$  transitions and to intramolecular charge-transfer (CT) interaction [14].

Careful examination of the results reported in Table 4 reveals that the bands corresponding to  $\pi^* \leftarrow n$  or CT transitions show a bathochromic shift on changing the organic solvent from ethanol to DMF and CHCl<sub>3</sub>, 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 CHCl<sub>3</sub>.

The small blue shift observed on changing the organic solvent from ethanol to dioxane and CCl<sub>4</sub> can be explained as a result of the lower solvent polarity of dioxane and CCl<sub>4</sub>. It is worth mentioning that the slight blue shift observed in the  $\lambda_{\max}$  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 nitrogen atom and consequently decreases to some extent the mobility of the  $\pi$ -electrons attached to the conjugated pathway.

The electronic spectra in mixed solvents were recorded in order to evaluate the possibility of the formation of a hydrogen-bonded solvated complex between the solute molecules and DMF. The visible spectra of dye *Ve* in DMF containing progressively increasing quantities of CCl<sub>4</sub>, revealed a decrease in the absorbance of the CT band with increasing proportion of CCl<sub>4</sub>.

Evidence for hydrogen bond formation between the solute molecules and DMF can be obtained from 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 a consideration of the behaviour in the mixed solvent [15, 16] using the relationship (2) (Fig. 1)

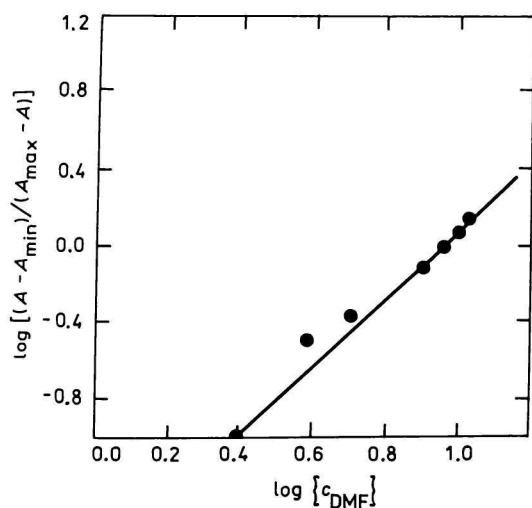
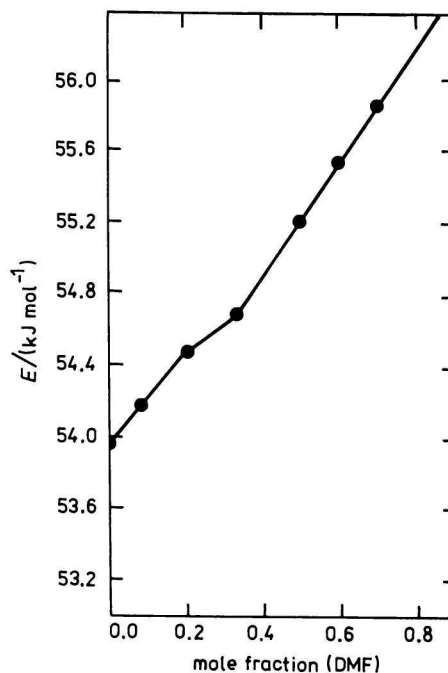
$$\log K_f = \log[(A - A_{\min})/(A_{\max} - A)] - n \log\{c_{\text{DMF}}\} \quad (2)$$

Excitation energy of dye *Ve* in pure CCl<sub>4</sub> is 53.96 kJ mol<sup>-1</sup>, while in pure DMF it is 55.86 kJ mol<sup>-1</sup>. In the system CCl<sub>4</sub>-DMF orientation energy is 0.25 kJ mol<sup>-1</sup>, H-bond energy is 0.21 kJ mol<sup>-1</sup>,  $n = 1$ ,  $K_f = 9.12$ , and  $\Delta G$  is 1.199 kJ mol<sup>-1</sup>. The values of



Table 5. The Variation of Absorbance in  $\lambda_{\max}$  Typical for Cyanine Dyes in Different Universal Buffer Solutions

Compound	pH															$pK_a$
	1.30	1.48	2.55	3.13	3.55	4.33	4.60	5.53	5.60	7.00	8.46	9.07	9.69	10.98	12.00	
<i>Ve</i> $\lambda_{500}$	0.52		0.44		0.42	0.56		0.56		0.60		0.70	–	0.55		3.8, 7.4
<i>Vg</i> $\lambda_{520}$	0.32		0.41		0.40	0.36		0.60		0.62		0.50	–	0.40		4.8
<i>Vi</i> $\lambda_{500}$	0.32		0.30		0.34	0.36		0.40		0.41		0.38	–	0.34		4.4
<i>VIIe</i> $\lambda_{520}$		0.30		0.40			0.48		0.44	0.44	0.32		0.32		0.28	7.4
<i>VIIIf</i> $\lambda_{530}$		0.19		0.30			0.42		0.44	0.38	0.36		0.32		0.30	8.0
<i>VIIg</i> $\lambda_{500}$		0.25		0.41			0.40		0.41	0.52	0.56		0.46		0.47	4.2, 9.2

Fig. 1.  $\log[(A - A_{\min})/(A_{\max} - A)]$  vs.  $\log\{c_{\text{DMF}}\}$  for dye *Ve* in  $\text{DMF}-\text{CCl}_4$  mixture at  $27^\circ\text{C}$ .Fig. 2. CT band excitation energy ( $E$ ) vs. DMF mole fraction for dye *Ve* in the  $\text{DMF}-\text{CCl}_4$  mixture at  $27^\circ\text{C}$ .

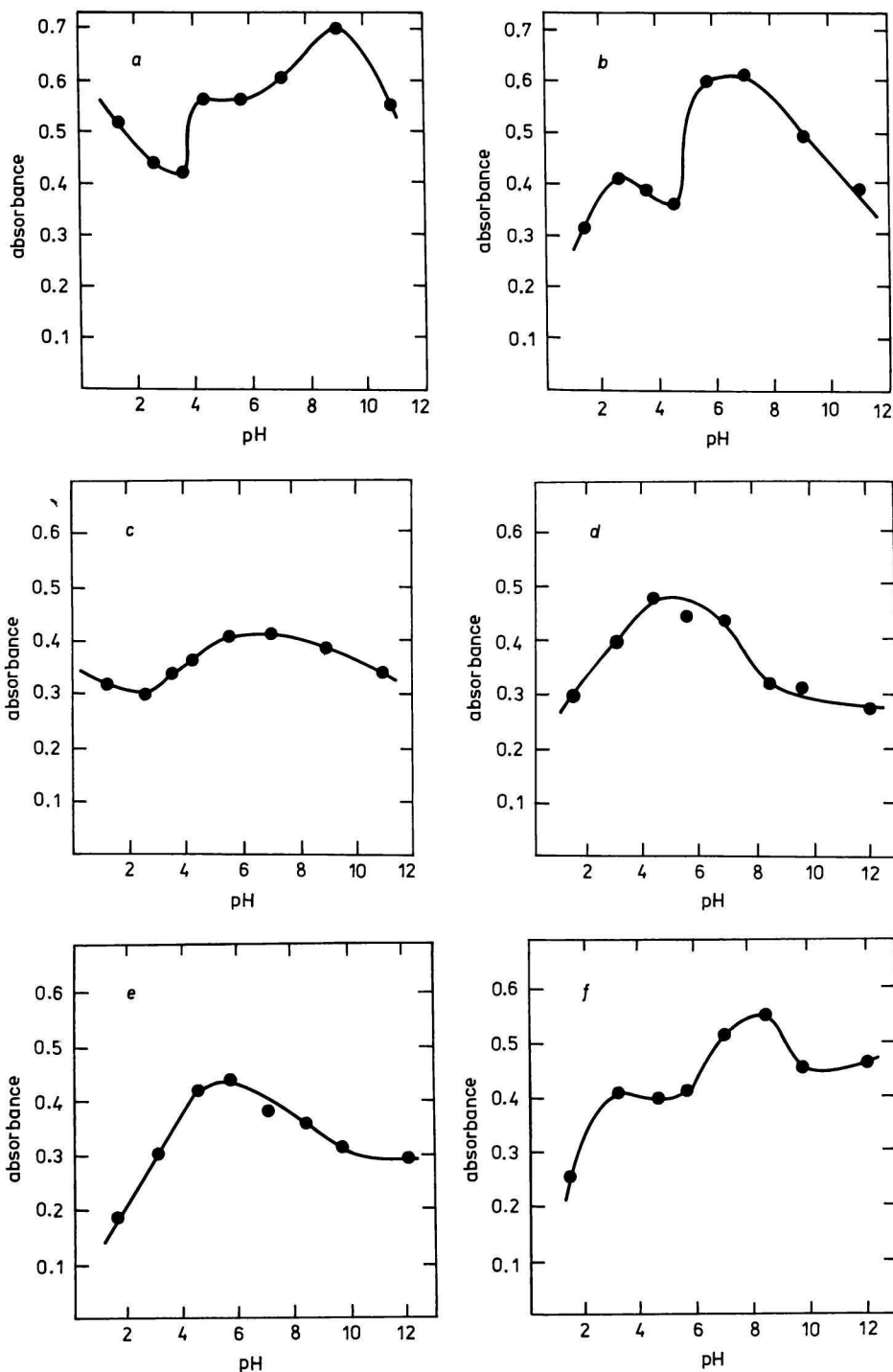
$K_f$ ,  $\Delta G$ , and  $n$  (the number of DMF molecules which are complexed with the solute molecule) indicate that a 1:1 complex is formed.

On drawing the excitation energy ( $E$ ) of the CT band in the mixed solvent vs. the DMF mole fractions (cf. Fig. 2), a broken line with three segments is obtained [17]. 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 above.

The ethanolic solutions of newly synthesized monomethine cyanine dyes *Va*–*Vi* and trimethine cyanine dyes *VIIa*–*VIIh* 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 find suitable pH medium when applied as photosensitizers. The ef-

fectiveness of the compounds as photosensitizers increases when they are present in the ionic form which has a higher planarity [14].

The electronic absorption spectra of selected monomethine cyanine dyes (*Ve*, *Vg*, and *Vi*) and trimethine cyanine dyes (*VIIe*, *VIIIf*, and *VIIg*) in aqueous universal buffer of varying pH (1.30–12.00) show regular changes with increasing pH of the medium, which results 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 disappears at  $\text{pH} < 3.55$ . This behaviour can be interpreted on the principle that the fused pyrazolo-nitrogen atom becomes protonated in solution of low pH values and therefore the CT in-



**Fig. 3.** Dependence of the absorbance on pH for *Ve* ( $c = 2.5 \times 10^{-6}$  mol dm $^{-3}$ ) at  $\lambda_{\max} = 500$  nm.  $pK_a = 3.8$  and  $7.4$  (a), for *Vg* ( $c = 5 \times 10^{-5}$  mol dm $^{-3}$ ) at  $\lambda_{\max} = 520$  nm.  $pK_a = 4.8$  (b), for *Vi* ( $c = 2.5 \times 10^{-6}$  mol dm $^{-3}$ ) at  $\lambda_{\max} = 500$  nm.  $pK_a = 4.4$  (c), for *VIIe* ( $c = 2.5 \times 10^{-6}$  mol dm $^{-3}$ ) at  $\lambda_{\max} = 520$  nm.  $pK_a = 7.4$  (d), for *VIIg* ( $c = 2.5 \times 10^{-7}$  mol dm $^{-3}$ ) at  $\lambda_{\max} = 530$  nm.  $pK_a = 8$  (e), for *VIIg* ( $c = 3 \times 10^{-6}$  mol dm $^{-3}$ ) at  $\lambda_{\max} = 500$  nm.  $pK_a = 4.2$  and  $9.2$  (f).

teraction 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 pH of the medium increases (pH > 7.00), the protonated dyes become de-

protonated and 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 (*Ve*, *Vg*, *Vi*, *VIIe*, *VIIIf*, and *VIIg*) have been determined in order to ensure the optimal pH in the application as photosensitizers. Such determination was performed on plotting the variation of absorbance with pH using the spectrophotometric half-height limiting absorbance and *Collete* methods [18].

The results of the  $pK_a$  values of the trimethine dyes *VIIg* (4.2, 9.2), *VIIIf* (8.00), and *VIIe* (7.4) are higher than those of monomethine dyes *Ve* (3.8, 7.4), *Vg* (4.8), and *Vi* (4.4), respectively (Table 5, Fig. 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 monomethine cyanine dye analogues.

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