Orientation in the Synthesis and Absorption Spectra of 1*H*-Pyrazolo[4,3-*d*][1,3]oxazole Methine Cyanine Dyes

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3,5-Dimethyl-1-phenyl-1*H*-pyrazolo[4,3-*d*][1,3]oxazole was prepared and oriented as starting material in the synthesis of some mono-, di-, and trimethine cyanine dyes. The new cyanines were characterized by IR and ^{1}H NMR spectral data. The visible absorption spectra of the cyanine dyes are discussed.

Oxazole or its fused derivatives find extensive use in the industrial purposes and the interest in their chemistry has increased due to the application of such moieties in photosensitization or in valuable optical brighteners [1] and in analytics [2]. The recent discovery that cyanine dyes endowed with photosensitizers or optical brightening [3—5] agent has directed the attention to the synthesis of such dyes incorporating pyrazolo-oxazole ring system with the hope that a combination of the favourable properties of both fused heterocyclic and cyanine dyes may be achieved.

Methine cyanines holding mono-, di-, and trimethine types have found various applications as photographic sensitizers for colour and noncolour film [6] and textile dyes [7]. They are also useful as photosensitizers in the blue-green light [3—5] and as analytical reagents over a wide pH range [8]. Trimethine cyanines can be used as laser dyes and sensitizing panchromic layers of motion picture film [9] and in super and light photographic [3, 10] sensitizers for silver halide emulsions and also for producing offset printing plates [11].

The present paper deals with a novel synthesis of pyrazolo-oxazole cyanine dyes of mono-, di-, and trimethine types hoping that such dyes might be used as photosensitizers in blue-green light, as analytical agents, and as laser dyes.

EXPERIMENTAL

4-Bromo-3-methyl-1-phenyl-pyrazol-5-one (*Ia*) and 4-bromo-2-ethyl-3-methyl-5-oxo-1-phenylpyrazol-2-ium iodide (*Ib*) were prepared as described in Refs. [12, 13].

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 Unicam SP 1200 spectrophotometer (Philips). Absorption spectra were recorded on a UV VIS 240 recording spectrophotometer using 1 cm cells (SHIMADZU), and ^{1}H NMR (200 MHz) spectra on a Varian Gemini NMR spectrometer using TMS as an internal reference.

Characterization of the compounds is given in Table 1, spectral data in Table 2.

3,5-Dimethyl-1-phenyl-1*H*-pyrazolo[4,3-*d*]-[1,3]oxazole (*IIa*), its 2-Ethyl-2-ium Iodide *IIb*, and 5-Methyl-1-phenyl-1*H*-pyrazolo[4,3-*d*]-[1,3]oxazole-3-carbaldehyde (*IV*)

To ethanolic solution of equimolar amounts of either *Ia* (2.53 g), *Ib* (4.09 g) or *III* (2.67 g; 0.01 mol) acetamide (0.59 g; 0.01 mol) and pyridine (20 cm^3) were added. The reaction mixture was refluxed for 6—8 h, filtering while hot, concentrating and cooling gave coloured precipitates. These were filtered and crystallized from aqueous ethanol.

IIa: deep brown crystals, yield = 2.24 g (72 %), m.p. = 230—232 °C. For $C_{12}H_{11}N_3O$ (M_r = 213.24) w_i(calc.): 67.59 % C, 5.19 % H, 19.70 % N; w_i(found): 67.82 % C, 4.98 % H, 19.89 % N.

IIb: brown crystals, yield = 2.95 g (63 %), m.p. = 178—180 °C. For $C_{14}H_{16}IN_3O$ (M_r = 369.20) w_i(calc.): 45.54 % C, 4.36 % H, 11.38 % N; w_i(found): 45.52 % C, 4.40 % H, 11.42 % N.

IV: deep brown crystals, yield = 3.06 g (94 %), m.p. = 133—135 °C. For $C_{12}H_9N_3O_2$ (M_r = 227.22) w_i(calc.): 63.43 % C, 3.99 % H, 18.49 % N; w_i(found): 63.50 % C, 4.00 % H, 18.60 % N.

4-Bromo-5-oxo-1-phenyl-1*H*-pyrazole-3-carbaldehyde (*III*) and 3-Methyl-1-phenyl-1*H*-pyrazolo[4,3-*d*][1,3]oxazole-5-carbaldehyde (*V*)

A mixture of either *Ia* (2.53 g) or *IIa* (2.13 g; 0.01 mol) with SeO_2 (1.11 g; 0.01 mol) in dioxane (40 cm^3) was refluxed for 8—12 h. The mixture was filtered

while hot from selenium metal, cooled and refiltered. The filtrate was concentrated and the separated product was filtered off, washed, dried and crystallized from ethanol.

III: brown crystals, yield = 1.93 g (53 %), m.p. = 95—100 °C. For $C_{10}H_7BrN_2O_2$ (M_r = 267.08) w_i(calc.): 44.97 % C, 2.64 % H, 10.49 % N; w_i(found): 45.00 % C, 2.74 % H, 10.56 % N.

V: deep brown crystals, yield = 1.59 g (49 %), m.p. = 168—170 °C. For $C_{12}H_9N_3O_2$ (M_r = 227.22) w_i(calc.): 63.43 % C, 3.99 % H, 18.49 % N; w_i(found): 63.67 % C, 4.12 % H, 18.34 % N.

4-Ethyl-3,5-dimethyl-1-phenyl-1*H*-pyrazolo-[4,3-*d*][1,3]oxazol-4-ium Iodide (*VI*) and 2,4-Diethyl-2,4-diium Diiodide (*VII*)

An equimolar amount or two-molar excess (1.56 g or 3.12 g) of ethyl iodide was added to compound *IIa* (2.13 g; 0.01 mol). The reaction mixture was refluxed for 3—5 h on water bath, and the precipitate which formed was filtered, washed with diethyl ether, triturated with ethanol by refluxing, filtered hot, concentrated and cooled. The product which precipitated after dilution with water was collected and recrystallized from ethanol.

VI: deep brown crystals, yield = 2.69 g (73 %), m.p. = 203—205 °C. For $C_{14}H_{16}IN_3O$ (M_r = 369.20) w_i(calc.): 45.55 % C, 4.37 % H, 11.38 % N; w_i(found): 45.65 % C, 4.42 % H, 11.50 % N.

VII: deep brown crystals, yield = 4.25 g (81 %), m.p. = 186—188 °C. For $C_{16}H_{21}I_2N_3O$ (M_r = 525.17) w_i(calc.): 36.59 % C, 4.03 % H, 8.00 % N; w_i(found): 36.61 % C, 3.94 % H, 8.11 % N.

Unsymmetric Dimethine Cyanines Incorporating 1*H*-Pyrazolo[4,3-*d*][1,3]oxazole *VIIIa*—*VIIIc*, *IXa*—*IXc*

A mixture of *IV* or *V* (2.27 g; 0.01 mol) and the appropriate 2/4-methyl quaternary salt (1-ethyl-2/4-methylquinolinium/pyridinium iodide) (2.99 g or 2.49 g; 0.01 mol) was dissolved in ethanol (40 cm^3) and piperidine (3—5 drops) was added. The reaction mixture was refluxed for 10—12 h, filtered hot, concentrated and cooled. The precipitated products after dilution with water were collected and recrystallized from ethanol.

Unsymmetric 1*H*-Pyrazolo[4,3-*d*][1,3]oxazol-3[4(1)]-, -5(4)-, and -5[4(1)]-2-ium Iodide Monomethine Cyanines *Xa*—*Xc*, *XI*, and *XIIa*—*XIIc*

A mixture of *IIb*, *VI* (3.69 g) or *VII* (5.25 g; 0.01 mol) and appropriate methyl quaternary salt (*N*-ethylpyridinium/quinolinium/isoquinolinium iodide) (2.35 g or 2.85 g; 0.01 mol) was dissolved in ethanol (40 cm^3) and piperidine (3—5 drops) was added. The reaction mixture was refluxed for 10—12 h, filtered hot, concentrated and cooled. The products which precipitated on dilution with water were crystallized from ethanol.

Unsymmetric 1*H*-Pyrazolo[4,3-*d*][1,3]oxazol-3[2(4)]-, -5(2)-, and -5[2(4)]-2-ium Iodide Trimethine Cyanines *XVIa*—*XVIc*, *XVII*, and *XVIIIa*—*XVIIIc*

A mixture of *IIb*, *VI* (3.69 g) or *VII* (5.25 g; 0.01 mol) and equimolar ratios of triethyl orthoformate (1.48 g; 0.01 mol) in ethanol (25 cm^3) and piperidine (3—5 drops) was refluxed for 6—8 h. The reaction mixture was filtered hot, concentrated and cooled. The products were precipitated by adding of water and recrystallized from aqueous ethanol.

A mixture of *XIII* (4.71 g) or *XIV* (4.71 g) or *XV* (6.27 g; 0.01 mol) and the appropriate 1-ethyl-2(4)-methylquinolinium (2.99 g) or -pyridinium (2.49 g) iodide (0.01 mol) in ethanol (40 cm^3) and piperidine (3—5 drops) was refluxed for 8—10 h, filtered while hot, concentrated and cooled. The precipitated products after dilution with water were filtered off, washed several times with water, dried and crystallized from ethanol.

RESULTS AND DISCUSSION

Interaction of equimolar ratios of *Ia* or *Ib* and acetamide in pyridine resulted in formation of the desired key intermediates *IIa* and *IIb* (Scheme 1).

Selective SeO_2 oxidation [14] of a dioxane solution of *Ia* afforded the corresponding *III*, which upon the reaction with acetamide under pyridine catalysis gave *IV*. Meanwhile, the selective SeO_2 oxidation of *IIa* afforded *VI*.

For such oxidation process, it was suggested that the oxidation would have occurred at the methyl group attached to the oxazole ring rather than at that of pyrazole ring. This is due to a relatively higher acceptor nature of oxazole rings in comparison with pyrazole analogues [15].

The direct quaternization of *IIa* using ethyl iodide in equi(bi)molar ratios gave *VI* or *VII*. As it was suggested for oxidation using equimolar amounts of SeO_2, the quaternization of *IIa* using equimolar amounts of ethyl iodide would be more probable at oxazole nitrogen atom than at the pyrazole one. This is due to the same reason as cited before.

The structures of the prepared compounds were confirmed by elemental analysis (Table 1) and by the IR and ^{1}H NMR spectra (Table 2) according to the respective references [16, 17]. The starting materials *II*—*VII* are considered as key intermediates for the synthesis of mono-, di-, and trimethine cyanine in 3- or 5-linkage moieties. Thus, reaction of compound *IV* or

Table 1. Characterization Data of the Compounds Prepared

Compound	Formula M_r	w_i(calc.)/% / w_i(found)/%			Yield	M.p.	Colour	Absorption spectra in 95 % ethanol	
		C	H	N	%	°C		λ_{max} / nm	ε_{max} / $cm^2\ mol^{-1}$
VIIIa	$C_{20}H_{19}IN_4O$	52.42	4.18	12.22	26	172—175	Violet	345,	3600,
	458.30	52.51	4.20	12.30				410,	2400,
								545	400
VIIIb	$C_{24}H_{21}IN_4O$	56.70	4.16	11.02	35	187—190	Deep	455,	3000,
	508.36	56.75	4.20	11.18			violet	558,	1900,
								600,	1700,
								655	1400
VIIIc	$C_{20}H_{19}IN_4O$	52.42	4.18	12.22	24	182—185	Violet	350,	4600,
	458.30	52.55	4.20	12.35				420,	3000,
								550	700
IXa	$C_{20}H_{19}IN_4O$	52.42	4.15	12.22	39	147—150	Violet	500	114400
	458.30	52.43	4.17	12.20					
IXb	$C_{24}H_{21}IN_4O$	56.70	4.16	11.02	79	117—120	Deep	390,	282000,
	508.36	56.67	4.15	11.05			violet	505,	736000,
								587	322000
IXc	$C_{20}H_{19}IN_4O$	52.42	4.18	12.22	43	127—130	Violet	510	224000
	458.30	52.42	4.16	12.21					
Xa	$C_{21}H_{23}IN_4O$	53.18	4.89	11.81	45	182—185	Red	420,	1800,
	474.34	53.20	4.92	11.95				500	1400
Xb	$C_{25}H_{25}IN_4O$	57.40	4.90	10.80	42	185—188	Deep	420,	3300,
	524.40	57.31	4.83	10.76			red	462,	3800,
								515	3800
Xc	$C_{25}H_{25}IN_4O$	57.26	4.81	10.68	38	187—190	Red	420,	900,
	524.40	57.40	4.90	10.80				510	800
XI	$C_{25}H_{25}IN_4O$	57.26	4.81	10.68	68	192—195	Deep	420,	2400,
	524.40	57.45	4.85	10.89			red	485	2800
XIIa	$C_{22}H_{26}I_2N_4O$	42.88	4.25	9.09	54	162—165	Red	470	191200
	616.28	42.84	4.27	9.10					
XIIb	$C_{26}H_{28}I_2N_4O$	46.87	4.24	8.41	72	167—170	Deep	530	81600
	666.34	46.82	4.43	8.45			red		
XIIc	$C_{26}H_{28}I_2N_4O$	46.87	4.24	8.41	63	178—181	Red	480	103200
	666.34	46.81	4.24	8.44					
XIII	$C_{19}H_{26}IN_3O_3$	48.42	5.56	8.92	56	192—195	Deep	–	
	471.34	48.45	5.60	8.98			red		
XIV	$C_{19}H_{26}IN_3O_3$	48.42	5.56	8.92	50	182—185	Deep		
	471.34	48.50	5.61	9.00			red		
XV	$C_{21}H_{31}I_2N_3O_3$	40.21	4.98	6.70	83	176—179	Deep		
	627.30	40.25	4.95	6.68			red		
XVIa	$C_{23}H_{25}IN_4O$	55.21	5.04	11.20	44	182—185	Violet	420,	2100,
	500.38	55.22	5.06	11.24				505	1700
XVIb	$C_{27}H_{27}IN_4O$	58.92	4.94	10.18	70	212—215	Deep	420	3300
	550.44	58.97	4.93	10.20			violet	460,	3200,
								510,	3300,
								610,	1300,
								660	800
XVIc	$C_{23}H_{25}IN_4O$	55.21	5.04	11.20	45	184—187	Violet	420,	2900,
	500.38	55.25	5.08	11.27				510	2400
XVII	$C_{27}H_{27}IN_4O$	58.92	4.99	10.18	63	192—195	Deep	420	3800
	550.44	58.92	5.00	10.30			violet	460,	3900,
								510,	3300,
								610	1500
XVIIIa	$C_{25}H_{30}I_2N_4O$	45.75	4.60	8.54	61	212—215	Violet	485	160000
	656.35	45.51	4.33	8.60					
XVIIIb	$C_{29}H_{32}I_2N_4O$	49.30	4.57	7.93	78	199—202	Deep	490	104000
	706.41	49.54	4.61	8.15			violet	507,	124400,
								555	67920
XVIIIc	$C_{25}H_{30}I_2N_4O$	45.75	4.60	8.54	65	187—190	Violet	490	151200
	656.35	45.78	4.71	8.65					

Table 2. IR and ^{1}H NMR Spectral Data of the Prepared Compounds

Compound	IR spectrum, $\tilde{\nu}_{max}/cm^{-1}$	^{1}H NMR spectrum ($CDCl_3$), δ
IIa	690,715 (monosubst. benzene)	7—8.1 (m, 5H, H_{arom})
	1100,1130 (C—O—C cyclic)	1.2 (s, 3H, CH_3, C-5—Me)
	1560 (C=N)	0.95 (s, 3H, C-3—Me)
	1640 (C=C)	
IIb	690, 710 (monosubst. benzene)	7—8.1 (m, 5H, H_{arom})
	1080, 1130 (C-O-C cyclic)	3.8—4.5 (q, 2H, CH_2 of N-2—Et)
	1560 (C=N)	3.1—3.6 (t, 3H, CH_3 of N-2—Et)
	1640 (C=C)	1.2 (s, 3H, C-5—Me)
	2970 (quaternary salt)	1.0 (s, 3H, C-3—Me)
III	690, 715 (monosubst. benzene)	10.20 (s, 1H, CHO)
	730 (C—Br)	7—8.1 (m, 5H, H_{arom})
	1560 (C=N)	3.5 (s, 1H, CH—Br)
	1720 (CHO)	3.15 (s, 1H, enolic OH)
	1715 (C=O)	
	3210 (OH enolic)	
IV	690, 715 (monosubst. benzene)	10.20 (s, 1H, CHO)
	1100, 1130 (C—O—C cyclic)	7—8.1 (m, 5H, H_{arom})
	1560 (C=N)	1.2 (s, 3H, CH_3)
	1640 (C=C)	
	1710 (CHO)	
V	690, 715 (monosubst. benzene)	10.45 (s, 1H, CHO)
	1100, 1130 (C—O—C cyclic)	7—8.1 (m, 5H, H_{arom})
	1560 (C=N)	0.95 (s, 3H, CH_3)
	1640 (C=C)	
	1715 (CHO)	
VI	690, 715 (monosubst. benzene)	7.5—8.4 (m, 5H, H_{arom})
	1080, 1130 (C—O—C cyclic)	4.2—4.5 (q, 2H, CH_2 of N-4—Et)
	1560 (C=N)	3.2—3.6 (t, 3H, CH_3 of N-4—Et)
	1640 (C=C)	2.5 (s, 3H, C-5—Me)
	2970 (quaternary salt)	0.95 (s, 3H, C-3—Me)
VII	690, 715 (monosubst. benzene)	7.5—8.4 (m, 5H, H_{arom})
	1080, 1130 (C—O—C cyclic)	3.8—4.5 (4H, $2CH_2$ of N-2(4)—Et)
	1560 (C=N)	3.1—3.6 (6H, $2CH_3$ of N-2(4)—Et)
	1640 (C=C)	1.8 (s, 3H, C-5—Me)
	2970 (quaternary salt)	1.4 (s, 3H, C-3—Me)
VIIIb	690, 710 (monosubst. benzene)	7.3—8.1 (m, 13H, —CH=)
	1100, 1130 (C—O—C cyclic)	3.2—3.6 (q, 2H, CH_2 of N—Et)
	1300 (CH=CH)	2.5—3.0 (t, 3H, CH_3 of N—Et)
	1565 (C=N)	2.5 (s, 3H, CH_3)
	1640 (C=C)	
	2940 (quaternary salt)	
IXb	690, 710 (monosubst. benzene)	7.3—8.1 (m, 13H, —CH=)
	1080, 1130 (C—O—C cyclic)	3.4—3.8 (q, 2H, CH_2 of N—Et)
	1300 (CH=CH)	2.7—3.2 (t, 3H, CH_3 of N—Et)
	1565 (C=N)	2.3 (s, 3H, CH_3)
	1640 (C=C)	
Xb	690, 710 (monosubst. benzene)	7.4—8.3 (m, 13H, —CH=)
	1080, 1130 (C—O—C cyclic)	3.0—3.4 (q, 2H, CH_2 of N—Et, quinolinium)
	1570 (C=N)	2.0—2.5 (t, 3H, CH_3 of N—Et, quinolinium)
	1640 (C=C)	1.45 (q, 2H, CH_2 of N—Et, pyrazole)
	2970 (quaternary salt)	1.2 (s, 3H, CH_3)
	3100 (—CH=)	0.95 (t, 3H, CH_3 of N —Et, pyrazole)
XI	690, 710 (monosubst. benzene)	7.4—8.3 (m, 12H, —CH=)
	1080, 1130 (C—O—C cyclic)	3.2—3.7 (q, 2H, CH_2 of N—Et, quinolinium)
	1570 (C=N)	2.3—2.8 (t, 3H, CH_3 of N—Et, quinolinium)
	1640 (C=C)	1.65 (q, 2H, CH_2 of N—Et, oxazole)
	2970 (quaternary salt)	1.20 (t, 3H, CH_3 of N—Et, oxazole)
	3100 (—CH=)	0.95 (s, 3H, CH_3)
XIIb	690, 710 (monosubst. benzene)	7.4—8.3 (m, 12H, — CH=)
	1080, 1130 (C—O—C cyclic)	3.8—4.5 (q, 2H, CH_2 of N—Et, pyrazol-2-ium)*
	1570 (C=N)	3.4—3.8 (q, 2H, CH_2 of N—Et, quinolinium)*
	1640 (C=C)	3.1—3.6 (t, 3H, CH_3 of N—Et, pyrazol-2-ium)*
	2870 (quaternary salt, pyrazole-2-ium)	2.4—2.9 (t, 3H, CH_3 of N—Et, quinoli ium)*
	2970 (quaternary salt, quinolinium iodide)	1.65 (q, 2H, CH_2 of N—Et, oxazole)
	3100 (—CH=)	1.4 (s, 3H, CH_3)
		1.2 (t, 3H, CH_3 of N—Et, oxazole)

Table 2 (Continued)

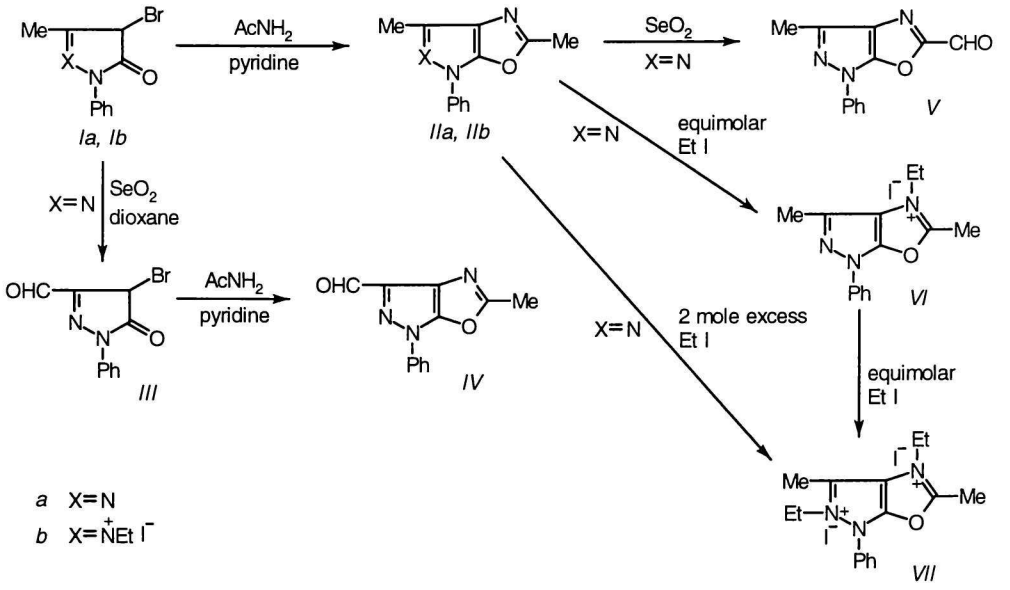
Compound	IR spectrum, $\tilde{\nu}_{max}/cm^{-1}$	^1H NMR spectrum ($CDCl_3$), δ
XIII	690, 710 (monosubst. benzene)	7.3—8.1 (m, 5H, H_{arom})
	1100 (C—O—C acetal)	3.8—4.5 (q, 2H, CH_2 of N-2—Et)
	1050, 1130 (C—O—C cyclic)	3.1—3.6 (t, 3H, CH_3 of N-2—Et)
	1570 (C=N)	3.3 (d, 2H, CH_2 of diethoxyethyl)
	1615 (C=C)	3.2 (t, 1H, O—CH—O)
	2965 (quaternary salt)	3.1 (q, 4H, $2CH_2$ of ethoxy)
		2.7 (t, 6H, $2CH_3$ of ethoxy)
		1.3 (s, 3H, CH_3)
XIV	690, 710 (monosubst. benzene)	7.3—8.1 (m, 5H, H_{arom})
	1080, 1130 (C—O—C cyclic)	3.9—4.6 (q, 2H, CH_2 of N-4—Et)
	1150 (C—O—C acetal)	3.2—3.7 (t, 3H, CH_3 of N-4—Et)
	1570 (C=N)	3.4 (d, 2H, CH_2 of diethoxyethyl)
	1615 (C=C)	3.3 (t, 1H, O—CH—O)
	2965 (quaternary salt)	3.2 (q, 4H, $2CH_2$ of ethoxy)
		2.8 (t, 6H, $2CH_3$ of ethoxy)
		0.96 (s, 3H, CH_3)
XV	690, 710 (monosubst. benzene)	7.3—8.1 (m, 5H, H_{arom})
	1090, 1130 (C—O—C cyclic)	4.1—4.8 (q, 2H, CH_2 of N-4—Et)
	1200 (C—O—C cyclic ether)	4—4.7 (q, 2H, CH_2 of N-2—Et)
	1570 (C=N)	3.4—3.9 (t, 3H, CH_3 of N-2—Et)
	1615 (C=C)	3.3—3.8 (t, 3H, CH_3 of N-2—Et)
	2870 (quaternary salt at N-2)	3.5 (d, 2H, CH_2 of diethoxyethyl)
	2965 (quaternary salt at N-4)	3.4 (t, 1H, O—CH—O)
		3.3 (q, 4H, $2CH_2$ of ethoxy)
		3.1 (t, 6H, $2CH_3$ of ethoxy)
		0.98 (s, 3H, CH_3)
XVIb	690, 710 (monosubst. benzene)	7.4—8.4 (m, 14H, —CH=)
	1080, 1130 (C—O—C cyclic)	2.9 (q, 2H, CH_2 of N—Et, quinolinium)
	1565 (C=N)	2.8 (q, 2H, CH_2 of N—Et pyrazol)
	1620 (conjugated CH=CH)	2.6 (t, 3H, CH_3 of N—Et, quinolinium)
	1640 (C=C)	2.4 (t, 3H, CH_3 of N—Et, pyrazole)
	2975 (quaternary salt)	1.3 (s, 3H, CH_3)
XVII	690, 710 (monosubst. benzene)	7.4—8.4 (m, 14H, —CH=)
	1100, 1130 (C—O—C cyclic)	3.1 (q, 2H, CH_2 of N—Et, quinolinium)
	1565 (C=N)	3.0 (q, 2H, CH_2 of N—Et, oxazole)
	1630 (conjugated CH=CH)	2.8 (t, 3H, CH_3 of N—Et, quinolinium)
	1640 (C=C)	2.6 (t, 3H, CH_3 of N—Et, oxazole)
	2975 (quaternary salt)	0.96 (s, 3H, CH_3)
XVIIIb	690, 710 (monosubst. benzene)	7.4—8.4 (m, 14H, —CH=)
	1100, 1130 (C—O—C cyclic)	3.2 (q, 2H, CH_2 of N—Et, quinolinium)
	1565 (C=N)	3.1 (q, 2H, CH_2 of N—Et, oxazole)
	1630 (conjugated CH=CH)	3.0 (q, 2H, CH_2 of N—Et, pyrazol-2-ium)
	1640 (C=C)	2.9 (t, 3H, CH_3 of N—Et, quinolinium)
	2980 (quaternary salt)	2.7 (t, 3H, CH_3 of N—Et, oxazole)
		2.6 (t, 3H, CH_3 of N—Et, pyrazol-2-ium)
		0.98 (s, 3H, CH_3)

*The δ values of triplets or quartets in these cases are afected by the adjacent electronwithdrawing character of the quaternary nitrogen.

V with equimolar amounts of methylquaternary salts yielded the corresponding *VIIIa—VIIIc* and *IXa—IXc* (Scheme 2).

The dimethine cyanines were coloured compounds ranging from orange to intense violet, and were fairly (partially) soluble in polar (nonpolar) organic solvents exhibiting a green fluorescence. They gave a reversible colour change violet $\rightleftharpoons$ colourless in basic and acidic medium, respectively.

The electronic absorption spectra of the unsymmetric dimethine cyanines *VIIIa—VIIIc* and *IXa—IXc* in 95 % ethanol showed absorption bands, their positions and molar extinction coefficients were influenced by the nature of the heterocyclic residue (A), linkage position of both heterocyclic quaternary moieties of the biheterocyclic ring. Thus, the electron absorption spectra of both dimethine cyanines *VIIIa, IXa* incorporating pyridinium-2-yl moiety showed absorption bands hypsochromically shifted if compared with those incorporating quinolinium-2-yl one in compounds *VIIIb, IXb,* with increasing the wavelength number of absorption bands for the latter dyes. This is due to that a more extensive π-delocalization leads to an easier charge transfer from pyrazole (oxazole)



Scheme 1

hetero atoms towards quinolinium moiety. On the other hand, changing the linkage position from ium-2-yl moieties in *VIIIa* and *IXa* into ium-4-yl ones in *VIIIc* and *IXc* resulted in a bathochromic shift of 5, 10 nm in absorption bands, respectively. This is due to the extended conjugation present in the latter dyes *VIIIc* and *IXc*. Meanwhile, changing the linkage of dimethine cyanine dye molecule from 5[2(4)] in *IXa—IXc* into 3[2(4)] positions in *VIIIa—VIIIc* resulted in bathochromic shift in absorption bands and increased their wavelength numbers. This is due to the existence of two unsymmetrical hetero atoms (N, O) in oxazole ring acting as stronger electron acceptors than those of pyrazole ring and better electron donors towards the heterocyclic quaternary moiety.

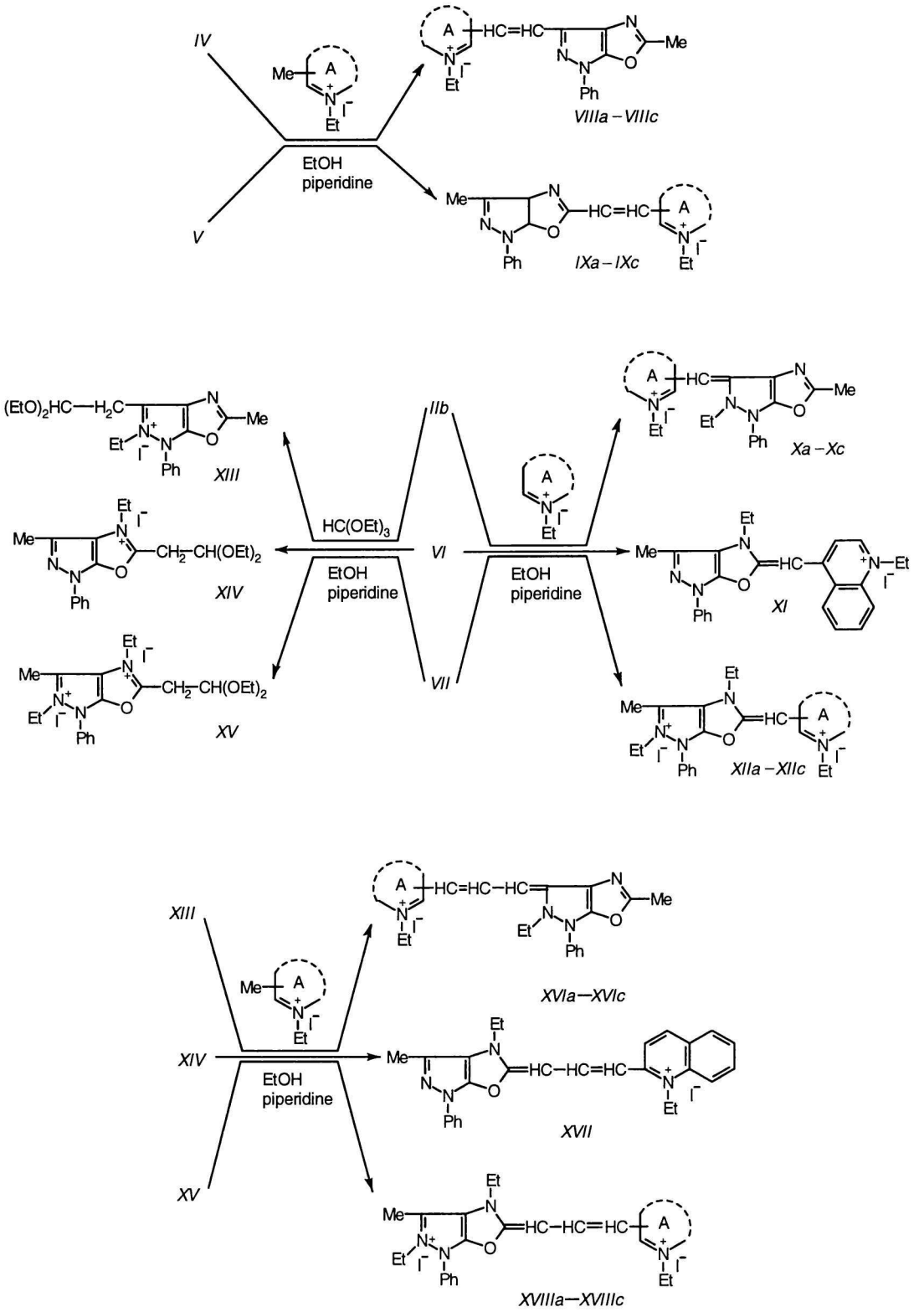
Interaction of equimolar ratios of *IIb, VI,* or *VII* and 1-ethylpyridinium (quinolinium) or 2-ethylisoquinolinium iodide under piperidine catalysis afforded the corresponding unsymmetric pyrazole 3[4(1)] or oxazole 5[4(1)] monomethine cyanines *Xa—Xc, XI* or *XIIa—XIIc,* respectively. For the unsymmetric 5[4(1)] monomethine cyanine dyes *XIIa—XIIc,* it was suggested that the reaction was proceeding towards the active methyl group of oxazol-4-ium moiety due to a relatively better acceptor nature of its atoms than that of pyrazol-2-ium moiety of the biheterocyclic system of 1*H*-pyrazolo[4,3-*d*][1,3]oxazole-2,4-diium diiodide *VII.*

The monomethine cyanine dyes were highly coloured compounds ranging from reddish-violet to intense violet and they were soluble in polar solvents, in which they exhibited a green fluorescence. They underwent a reversible colour change violet ⇌ yellow in basic and acidic media.

Absorption bands in the electronic spectra of *Xa—Xc, XI, XIIa—XIIc* in 95 % ethanol were dependent on the nature of the heterocyclic quaternary moieties and the biheterocyclic rings. For example, monomethine cyanines containing quinolinium or isoquinolinium moieties *Xb, Xc, XIIb,* and *XIIc* were bathochromically shifted with respect to the pyridinium analogues *Xa* and *XIIa.* Changing the linkage position from 2-ium-1-yl moiety in *Xc* and *XIIc* into 1-ium-4-yl moiety in *Xb* and *XIIb* resulted in a bathochromic shift of absorption bands. This is due to the extended conjugation present in the latter dyes. On the other hand, as observed in the electronic absorption spectra of dimethine cyanines *VIIIa—VIIIc* and *IXa—IXc,* it was obvious that changing the linkage of monomethine cyanine molecule from 5[4(1)] into 3[4(1)] positions resulted in absorption bands bathochromically shifted or increasing of their wavelength number. Additionally, it was obvious that the extra quaternized 2-ium moiety in monomethine dye *XIIb* in comparison with *XI* causes a decrease in the wavelength number of absorption bands. This is due to the antagonistic charge transfer towards either quinolinium-4-yl moiety or pyrazolo[4,3-*d*][1,3]oxazolium-5-yl moiety (Scheme 3*a*).

Interaction of compounds *IIb, VI, VII* and equimolar amounts of triethyl orthoformate in the presence of piperidine afforded respective compounds *XIII—XV.* These compounds are considered as key intermediates for the synthesis of unsymmetric trimethine cyanines *XVIa—XVIc, XVII,* and *XVIIIa—XVIIIc* through their condensation with equimolar amounts of 2(4)-methylquaternary salt under piperidine catalysis.

The trimethine cyanine dyes were reddish-violet to



Scheme 2

VIIIa—VIIIc, IXa—IXc, XVIa—XVIc, XVIIIa—XVIIIc:

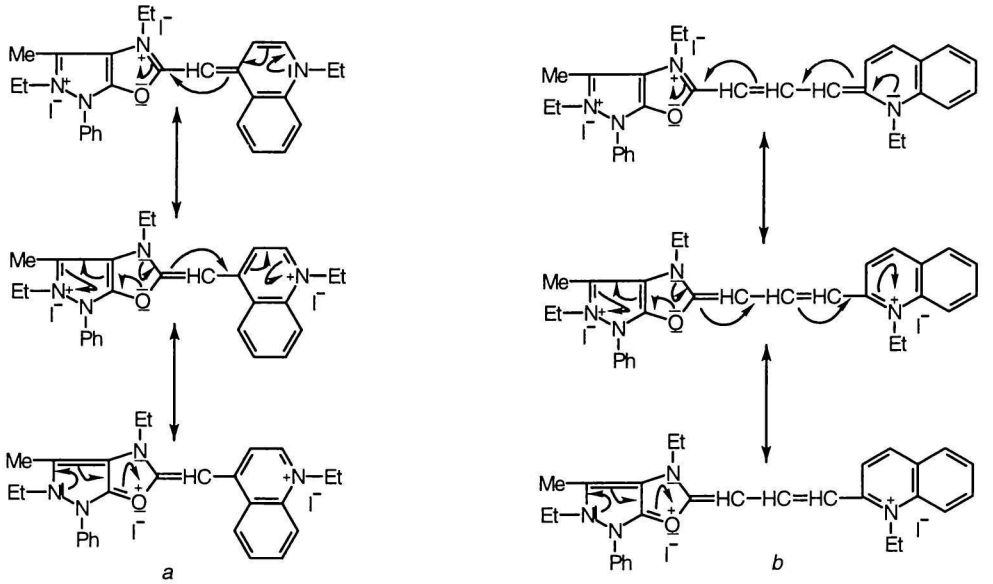
A

a 1-ethylpyridinium-2-yl iodide
b 1-ethylquinoli ium-2-yl iodide
c 1-ethylpyridinium-4-yl iodide

Xa—Xc, XIIa—XIIc:

A

a 1-ethylpyridinium-4-yl iodide
b 1-ethylquinolinium-4-yl iodide
c 1-ethylisoquinolinium-1-yl iodide



Scheme 3

intense violet in colour and were soluble in polar solvents in which they exhibited a green fluorescence. A reversible colour change violet ⇌ yellow occurred in basic and acidic media.

Similarly as observed in the electronic absorption of di- and monomethine cyanine dyes, it was obvious that the absorption bands of unsymmetrical trimethine cyanine dyes *XVIa—XVIc, XVII,* and *XVIIIa—XVIIIc* in 95 % ethanol underwent bathochromic or hypsochromic shifts depending upon the nature of the heterocyclic quaternary residue (A), their linkage position (1-ium-2-yl or -4-yl moiety), cyanine molecule linkage 3[2(4)] or 5[2(4)] of their moieties, and nature of the heterocyclic system. Thus, the electronic absorption spectra of both trimethine cyanine dyes *XVIa* and *XVIIIa,* incorporating pyridinium-2-yl moiety showed absorption bands at λ_{max} = 420 nm, 505 nm (ε_{max} = 2100 mol^{-1} cm^2, 1700 mol^{-1} cm^2) for *XVIa* and λ_{max} = 485 nm (ε_{max} = 160000 mol^{-1} cm^2) for *XVIIIa.* Substituting pyridinium-2-yl moiety in compounds *XVIa, XVIIIa* by quinolinium-2-yl one in compounds *XVIb, XVIIIb* resulted in a bathochromic shift of absorption bands and increasing of their wavelength numbers. This is due to the more extensive π-delocalization which leads to an easier charge transfer from pyrazole (oxazole) hetero atoms towards quinolinium-2-yl moiety. On the other hand, changing the linkage position from 1-ium-2-yl moiety (*XVIa, XVIIIa*) into 1-ium-4-yl one (*XVIc, XVIIIc*) resulted in a 5 nm bathochromic shift of the absorption band. This is due to the extended conjugation present in the latter dyes.

As it was observed in the electronic absorption spectra of either mono- or dimethine cyanine dyes, changing the linkage position of trimethine cyanine dye molecule from 5[2(4)] in *XVII* and *XVIIIa—XVIIIc* into 3[2(4)] positions in *XVIa—XVIc* resulted in absorption bands bathochromically shifted with an increase in their wavelength numbers. This is due to the same reasons as cited before. Additionally, it was obvious that the extra quaternization to 2-ium iodide in trimethine dye *XVIIIb* in comparison with *XVII* caused hypsochromic shift in absorption bands with a decrease of their wavelength number. This is also due to the antagonistic charge transfer from oxazole hetero atoms towards either quinolinium-2-yl moiety or pyrazolo[4,3-*d*][1,3]oxazolium-5-yl moiety (Scheme 3*b*).

Comparison of the absorption spectra of the unsymmetric pyrazolo-3[2(4)]-trimethine cyanines *XVIa—XVIc* with those of unsymmetric 3[2(4)]-dimethine cyanines *VIIIa—VIIIc* or comparison of the absorption spectra of unsymmetric oxazole-5[2(4)]-trimethine cyanine dye *XVII* and either dimethine dye *IXb* or monomethine dye *XI,* showed that the trimethines were relatively red-shifted to the di- and monomethine types. This is due to the increase in number of methine groups between the *N*-ethyl group and the positively charged nitrogen-heterocyclic quaternary salts, enhancing the charge transfer.

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