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Synthesis and Electronic Spectra of Some Mono-, Di- and Tri-cationic Di- and Tetra-methine Cyanine Dyes

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ABSTRACT

*5-Aryl-3-methyl-1-phenylpyrazolo[3,4-*d*]oxazoles were prepared as starting materials in the synthesis of some cationic di- and tetra-methine cyanine dyes. The new cyanines were characterized by IR and* ^1H*-NMR spectra data. The visible absorption spectra of the cyanines are discussed and the acid–base properties of selected compounds are investigated.*

1 INTRODUCTION

The sensitiser use of cyanine dyes is well established. They can be used as photosensitisers in blue–green light,[1–3] and are also considered as being suitable for light[4] and super-photographic sensitisers for silver halide emulsion.[5] Other applications are as sensitiser dyes for flash-exposure silver-halide photographic emulsions,[6] as sensitising panchromic layers of motion pictures[7] and as photothermographic sensitisers.[8] They can also be used for producing offset printing plates.[9]

In this present paper, 5-aryl-3-methyl-1-phenyl-pyrazolo[3,4-*d*]oxazoles were selected as the starting materials for the synthesis of some new mono-, di- and tri-cationic di- and (tetra-) methine cyanine dyes which might be of value in the photosensitisation processes and to study their pH sensitivity for acid–base properties.

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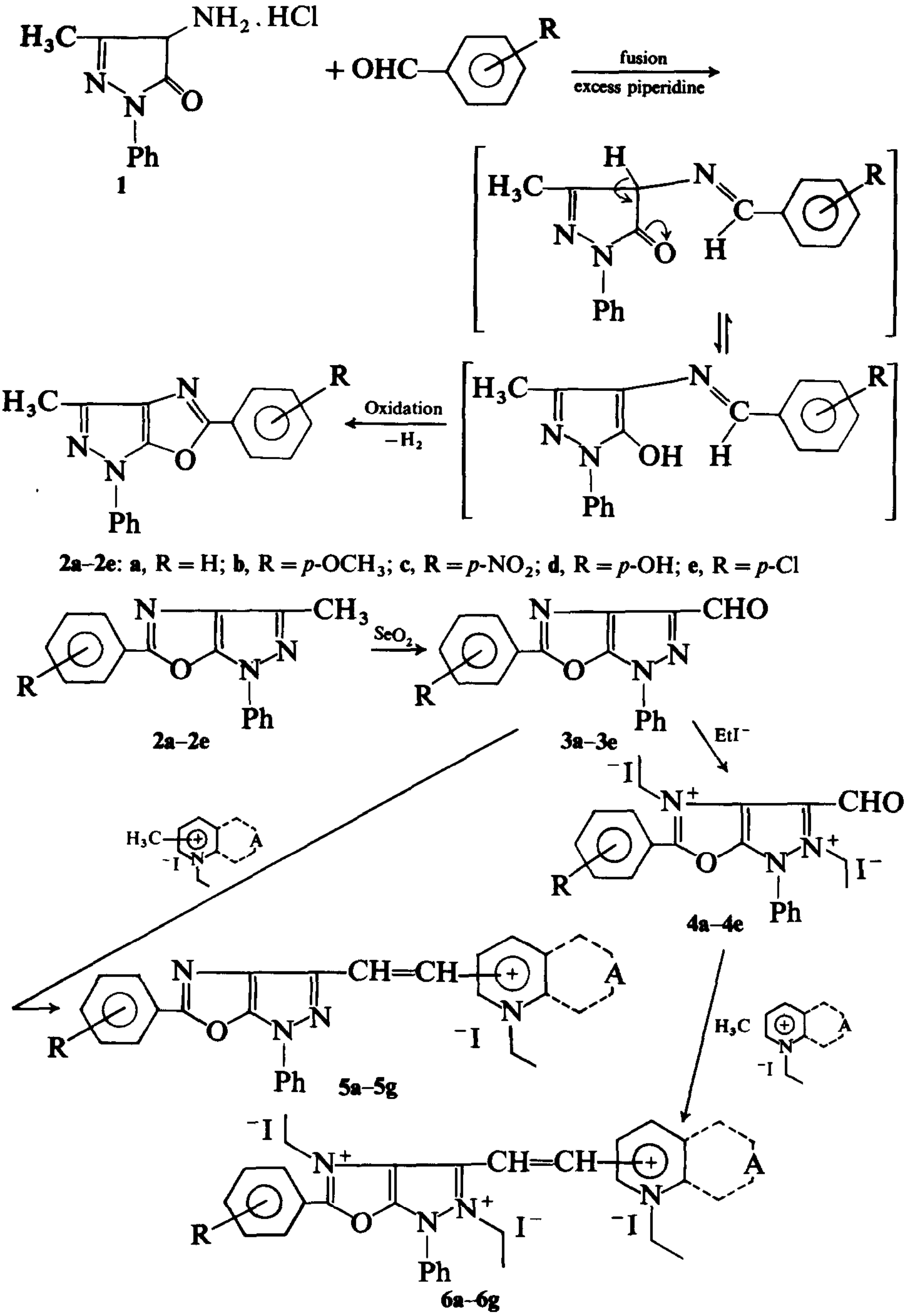
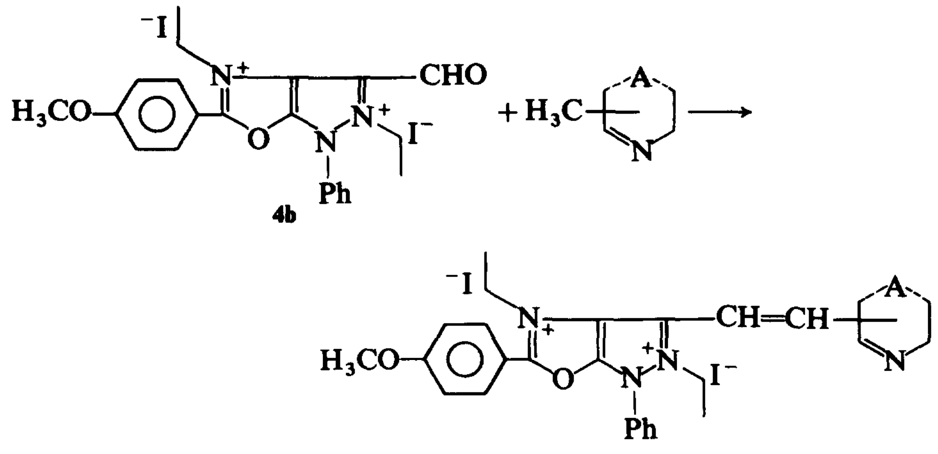


2a–2e: **a**, R = H; **b**, R = p-OCH$_3$; **c**, R = p-NO$_2$; **d**, R = p-OH; **e**, R = p-Cl

3, 4: **a**, R = H; **b**, R = p-OCH$_3$; **c**, R = p-NO$_2$; **d**, R = p-OH; **e**, R = p-CL

5a–5g, 6a–6g: **a**, R = H, A = H-2-yl salt; **b**, R = H, A = C$_4$H$_4$-2-yl salt;
c, R = H, A = H-4-yl salt; **d**, R = p-OCH$_3$, A = C$_4$H$_4$-2-yl salt;
e, R = p-NO$_2$, A = C$_4$H$_4$-2-yl salt; **f**, R = p-OH, A = C$_4$H$_4$-2-yl salt;
g, R = p-Cl, A = C$_4$H$_4$-2-yl salt

Scheme 1



4b

7a–7c

7: **a**, A = pyridine-2; **b**, A = quinoline-2; **c**, A = pyridine-4

Scheme 1 (*continued*)

2 RESULTS AND DISCUSSION

Synthesis of 5-aryl-3-methyl-1-phenylpyrazolo[3,4-*d*]oxazole (**2a**–**2e**) was achieved by interaction of 4-amino-3-methyl-1-phenylpyrazol-5-one hydrochloride (**1**)[10] with different aromatic aldehydes in the presence of suitable solvents and of piperidine as a basic catalyst.[11] The same reaction could be conducted by fusion[12] of the reactants, but the yields of pyrazolo[3,4-*d*]oxazoles were lower.

The reaction involves the condensation of 4-amino-3-methyl-1-phenylpyrazol-5-one hydrochloride (**1**) with aromatic aldehydes to give an intermediate Schiff's base. This intermediate then undergoes oxidation and simultaneous cyclodehydrogenation between the two hydrogen atoms of the methineimine and the enolate hydroxyl groups[13] with the formation of 5-aryl-3-methyl-1-phenylpyrazolo[3,4-*d*]oxazoles (**2a**–**2e**) (Scheme 1).

The structures of compounds **2a**–**2e** were confirmed by elemental analysis (Table 1) and IR spectra which showed characteristic absorption bands at 1180 and 1210 cm^{-1} (ν cyclic C—O—C of oxazole ring) and 1575–1590 cm^{-1} (ν C=N). The ^{1}H-NMR spectra of the compounds in $CDCl_3$ showed a multiplet at δ 6·7–7·4 ppm (m, 10H, 2Ar—H) and a singlet at 1·3 ppm (s, 3H, CH_3).

Selective oxidation of **2a**–**2e** using SeO_2 in ethanol[14] afforded the corresponding 5-aryl-1-phenyl-pyrazolo[3,4-*d*]oxazole 3-carboxaldehydes (**3a**–**3e**) in satisfactory yield. The IR spectra of these compounds showed similar absorption bands to **2a**–**2e** and also a well-defined band at 1665 cm^{-1}, confirming the aldehyde group. The ^{1}H-NMR spectra of **3a**

TABLE 1

Characterisation Data for 5-Aryl-1-phenylpyrazolo[3,4-*d*]oxazole-3-methyl Derivatives, 3-Carboxaldehydes and their 2,4-yl Salts (**2a–2e**, **3a–3e**, **4a–4e**)

Compd	*M.p. (°C)*	*Yield (%)*	*Mol. formula (mol. wt)*	*Analysis (%): Calcd/(Found)*		
				C	*H*	*N*
2a	174–176	70	$C_{17}H_{13}N_3O$	74·2	4·7	15·3
			(303)	(73·95)	(5·0)	(15·1)
2b	175–177	75	$C_{18}H_{15}N_3O_2$	70·8	4·9	13·8
			(333)	(71·2)	(5·05)	(14·0)
2c	173–175	63	$C_{17}H_{12}N_4O_3$	63·75	3·75	13·1
			(348)	(63·25)	(3·9)	(13·4)
2d	169–171	68	$C_{17}H_{13}N_3O_2$	70·1	4·5	14·4
			(319)	(70·55)	(4·8)	(14·7)
2e	177–179	60	$C_{17}H_{12}N_3OCl$	66·9	3·9	13·6
			(337·5)	(66·3)	(4·2)	(14·0)
3a	132–133	70	$C_{17}H_{11}N_3O_2$	70·6	13·8	14·5
			(289)	(71·0)	(14·0)	(14·9)
3b	139–140	80	$C_{18}H_{13}N_3O_3$	67·7	4·1	13·2
			(319)	(67·95)	(4·55)	(14·3)
3c	128–130	73	$C_{17}H_{10}N_4O_4$	61·1	2·9	16·2
			(334)	(61·6)	(3·2)	(15·9)
3d	145–147	68	$C_{17}H_{11}N_3O_3$	66·9	3·6	13·8
			(305)	(67·0)	(4·1)	(14·1)
3e	170	85	$C_{17}H_{10}N_3O_2Cl$	63·1	3·1	13·0
			(323·5)	(63·6)	(3·9)	(13·15)
4a	143–145	54	$C_{21}H_{21}N_3O_2I_2$	41·9	3·5	7·0
			(601)	(41·6)	(3·6)	(7·2)
4b	151–153	67	$C_{22}H_{23}N_3O_3I_2$	41·8	3·65	6·7
			(631)	(42·0)	(3·9)	(6·75)
4c	120–122	53	$C_{21}H_{21}N_4O_4I_2$	39·1	3·3	8·7
			(645)	(39·4)	(2·5)	(8·2)
4d	135–137	70	$C_{21}H_{21}N_3O_3I_2$	40·8	3·4	6·8
			(617)	(40·75)	(3·65)	(7·0)
4e	160–162	57	$C_{21}H_{21}N_3O_2I_2Cl$	39·65	3·3	6·6
			(635·5)	(40·0)	(3·65)	(6·8)

(as a representative example) in $CDCl_3$ showed a multiplet at δ 6·6–7·5 (m, 10H, 2Ar—H) and a singlet at 9·9 ppm (s, 1H, CHO).

Quaternisation of compounds **3a**–**3e** with ethyl iodide gave the corresponding 5-aryl-1-phenylpyrazolo[3,4-*d*]oxazole-3-carboxaldehyde-2,4-yl salts (**4a**–**4e**). The IR spectra of these showed well-defined absorptions at 2990–2940 cm^{-1} (ν ethiodide of the biheterocyclic nuclei), at 1180 and 1210 cm^{-1} (ν cyclic C—O—C of oxazole ring), at 1580 cm^{-1} (ν C═N), at 1620–1600 cm^{-1} (ν C═C) and at 1665 cm^{-1} (ν CHO).

The ^{1}H-NMR spectra of **4a** in $CDCl_3$ showed, in addition to the signals for **3a**, signals at 2·5 ppm (q, 4H, $2CH_2N$), 1·6 ppm (t, 6H, $2CH_3$), 10·5 ppm (s, 1H, CHO) and at 6·7–7·4 ppm (m, 10H, 2Ar—H).

The reaction of compounds **3a**–**3e** and **4a**–**4e** and 2-(and 4-)methyl quaternary salts such as 2-(or 4-)methylpyridinium (or quinolinium) 2-(or 4-yl salts in equimolar amounts and in the presence of piperidine as basic catalyst gave the corresponding asymmetrical pyrazolo[3,4-*d*]oxazole-3[2-(or 4-)]mono (or tri-)cationic dimethine cyanines **5a**–**5g** and **6a**–**6e** respectively (Scheme 1).

The structures of the compounds thus synthesised were confirmed by elemental analysis, IR and ^{1}H-NMR spectra data (Tables 1, 2 and 4). The dyes were coloured compounds (orange to intense violet) and were fairly soluble in polar and nonpolar organic solvents, exhibiting a green fluorescence. They were soluble in concentrated sulphuric acid, liberating iodine vapour on heating. Their ethanolic solutions gave reddish violet to intense violet colours in alkaline medium discharged on acidification, in a reversible colour change; the compounds thus have potential application as acid–base indicators in protometric titrations.

The visible absorption spectra of compounds **5a**–**5g** and **6a**–**6g** in 95% ethanol showed a single broad band, the position and molar extinction coefficient of which were influenced by the nature of the heterocyclic quaternary residue A, by the aryl substituent R and by the nature of the hetero atom of the pyrazolo[3,4-*d*]oxazole moieties. Thus, mono- (and tri-) cationic unsubstituted aryl oxazole dimethine cyanines (R = H) (**5b, 6b**) incorporating a quinolinium-2-yl salt showed a large bathochromic shift of 95 nm and increased intensity compared with the pyridinium 2-(and 4-)yl analogues **5a** and **6a** (Table 2). Introduction of an electron-donating group, e.g. where $R = p\text{-}OCH_3$ gave a bathochromic shift of 30 nm, but the presence of an electron-accepting group, e.g. where $R = p\text{-}NO_2$ caused a slight red shift (Table 2).

Comparison of the spectra of **6b** with its dimethine cyanine analogue **5b** (A = 1-ethylquinolinium-4-yl salt) indicates that the additional quaternisation in **6b** gives a red shift of 8 nm. This is due to internal charge transfer within the biheterocyclic system (Table 2).

The reaction of a selected compound, viz. **4b**, with equimolar amounts of 2-methylpyridine (or 2-methylquinoline) in presence of piperidine for a prolonged time gave the corresponding di-cationic pyrazolium[3,4-*d*]-oxazolium-3-[2- (or 4-)]dimethine bases **7a**–**7c** in low yield (Scheme 1). This is attributed to the decrease in the polarisation of the aldehyde group in **4b**.

The structures of compounds **7a**–**7c** were confirmed by elemental analysis, IR and ^{1}H-NMR spectra data (Tables 3 and 4). These compounds were brown to reddish violet and were soluble in polar organic solvents with a

TABLE 2

Characterisation Data for Asymmetrical Mono- and Tri-cationic Pyrazolo[3,4-*d*]oxazole 3[2- (and 4-)]-Dimethine Cyanine Dyes (**5a–5g**, **6a–6g**)

Compd	*M.p.* (°*C*)	*Yield* (%)	*Mol. formula* (*mol. wt*)	*Analysis* (%): *Calcd*/(*Found*)			*Absorption spectra in 95% ethanol*	
				C	*H*	*N*	λ_{max} (*nm*)	ε_{max} ($M^{-1}cm^{-1}$)
5a	110–112	45	$C_{25}H_{21}N_4OI$	57·7	4·0	10·8	470	840
			(520)	(57·9)	(3·95)	(10·9)		
5b	210–212	67	$C_{29}H_{23}N_4OI$	61·05	4·1	9·8	480	16 800
			(570)	(62·0)	(4·5)	(9·8)	565	5 440
5c	137–139	46	$C_{25}H_{21}N_4OI$	57·7	4·0	10·8	520	736
			(520)	(57·6)	(4·15)	(10·9)		
5d	185–187	62	$C_{30}H_{25}N_4O_2I$	60·0	4·2	9·3	440	7 060
			(600)	(59·5)	(4·15)	(9·5)	510	7 460
							535	7 180
							595	6 620
5e	140–142	65	$C_{29}H_{22}N_5O_3I$	56·6	3·6	11·4	510	6 800
			(615)	(56·8)	(4·0)	(11·0)		
5f	168–170	69	$C_{29}H_{23}N_4O_2I$	59·4	3·9	9·6	515	6 120
			(586)	(60·0)	(4·1)	(9·7)	550	6 360
							585	7 280
5g	175–177	55	$C_{29}H_{22}N_4OICl$	57·6	3·6	9·3	446	4 580
			(604·5)	(57·2)	(4·0)	(9·5)	510	4 940
							545	6 060
6a	144–146	39	$C_{29}H_{31}N_4OI_3$	41·8	3·7	6·7	602	1 372
			(832)	(42·8)	(4·0)	(6·95)		
6b	160–162	65	$C_{33}H_{33}N_4OI_3$	44·9	3·7	6·35	505	6 320
			(882)	(45·15)	(4·1)	(6·9)	575	5 192
6c	128–130	43	$C_{29}H_{31}N_4OI_3$	41·8	3·7	6·7	480	1 040
			(832)	(42·15)	(4·0)	(6·95)	612	324
6d	188–190	57	$C_{34}H_{35}N_4O_2I_3$	44·5	3·8	6·1	525	8 200
			(913)	(45·1)	(4·1)	(6·8)	560	10 880
							587	10 600
6e	138–140	51	$C_{33}H_{32}N_5O_3I_3$	42·7	3·45	7·55	520	13 080
			(927)	(43·2)	(4·1)	(8·1)	565	13 040
							665	380
6f	178–180	53	$C_{33}H_{33}N_4O_2I_3$	44·1	3·7	6·2	505	94 800
			(898)	(45·0)	(4·1)	(7·0)		
6g	150–152	49	$C_{33}H_{32}N_4OClI_3$	43·2	3·5	6·1	505	7 080
			(916·5)	(44·0)	(4·1)	(6·95)	585	5 880

slight green fluorescence. Their ethanolic solutions gave yellow/orange colours in basic solution, discharged on acidification. The absorption bands in the electronic spectra of **7a–7c** in 95% ethanol also showed bathochromic or hypsochromic shift depending on the nature of the heterocyclic residue A (Table 3).

Interaction of equimolar ratios of **3a** or **3b** and acetophenone derivatives in ethanol under basic conditions yielded the corresponding 5-aryl-

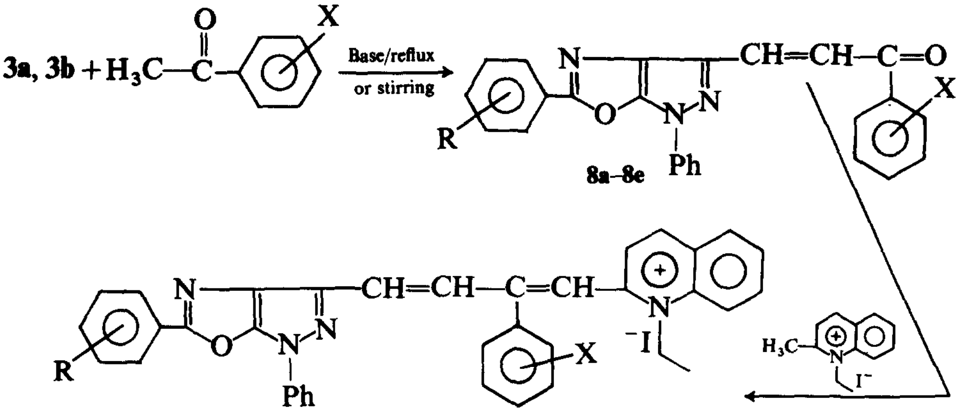
TABLE 3

Characterisation Data for 5-Aryl-1-phenyl Di-cationic Pyrazolo[3,4-*d*]oxazole 3[2- (and 4-)] Dimethines (**7a**–**7c**), 3-Cinnamoyl Derivatives and their 3-[*β*-Substituted] 3- and 2-Tetramethine Cyanines (**8a**–**8e**, **9a**–**9e**)

Compd	*M.p. (°C)*	*Yield (%)*	*Mol. formula (mol. wt)*	*Analysis (%): Calcd/(Found)*			*Absorption spectra in 95% ethanol*	
				C	*H*	*N*	λ_{max} (*nm*)	ε_{max} (M^{-1} cm^{-1})
7a	140–142	35	$C_{28}H_{28}N_4O_2I_2$ (706)	47·6 (48·0)	4·0 (4·15)	7·9 (8·1)	530	1 040
7b	188–190	45	$C_{32}H_{30}N_4OI_2$ (756)	50·8 (51·1)	4·0 (4·1)	7·4 (7·7)	535	924
7c	154–156	43	$C_{28}H_{28}N_4O_2I_2$ (706)	47·6 (47·9)	3·8 (4·25)	7·9 (7·6)	526	1 440
8a	128–130	39	$C_{25}H_{17}N_3O_2$ (407)	73·7 (72·3)	4·2 (4·6)	10·3 (9·5)	— —	— —
8b	133–135	41	$C_{26}H_{19}N_3O_3$ (437)	71·4 (70·9)	4·35 (4·85)	9·6 (10·1)	—	—
8c	145–147	28	$C_{25}H_{16}N_4O_4$ (448)	67·0 (67·5)	3·6 (4·1)	12·5 (11·9)	—	—
8d	139–140	45	$C_{26}H_{19}N_3O_3$ (437)	71·4 (70·8)	4·35 (4·55)	9·6 (10·2)	—	—
8e	148–150	49	$C_{27}H_{21}N_3O_4$ (467)	69·4 (70·0)	4·5 (3·95)	9·0 (10·7)	—	—
9a	148–152	65	$C_{27}H_{29}H_4OI$ (672)	66·1 (65·5)	4·3 (3·9)	8·3 (8·4)	450 485 535	1 620 7 200 4 120
9b	142–144	68	$C_{38}H_{31}N_4O_2I$ (702)	65·0 (65·3)	4·4 (4·9)	8·0 (8·4)	450 487 585	1 020 7 020 4 020
9c	168–170	36	$C_{37}H_{28}N_5O_3I$ (717)	61·9 (60·5)	3·9 (4·15)	9·8 (10·0)	445 486	8 400 6 640
9d	160–162	42	$C_{38}H_{31}N_4O_2I$ (702)	65·0 (65·1)	4·4 (4·8)	8·0 (8·3)	475 510 605	600 17 080 9 120
9e	152–154	63	$C_{39}H_{33}N_4O_3I$ (732)	65·0 (65·3)	4·4 (4·9)	8·0 (8·4)	478 515 570	3 200 11 592 6 800

1-phenylpyrazolo[3,4-*d*]oxazole-3-cinnamoyl derivatives **8a**–**8e** in satisfactory yield. The carbonyl group in these compounds showed high reactivity with 2-methyl-1-ethylquinolinium-2-yl salt in the presence of 2% sodium hydroxide, giving the corresponding 3-[*β*-substituted aryl]3-(and 2-) tetramethine cyanine dyes **9a**–**9e** (Scheme 2).

The structures of compounds **8** and **9** was established by elemental analysis, IR and ^{1}H-NMR spectral data (Tables 3 and 4). These derivatives were strongly coloured (reddish violet to intense violet) and they were fairly soluble in polar organic solvents, giving intense violet hues with a green



9a–9e

8, 9: a, R = H, X = H; **b**, R = H, X = *p*-OCH_3; **c**, R = H, X = *p*-NO_2;
d, R = *p*-OCH_3, X = H; **e**, R = *p*-OCH_3, X = *p*-OCH_3

Scheme 2

TABLE 4

IR and ^{1}H-NMR Spectra Data of Some Selected Pyrazolo[3,4-*d*]oxazole 3[2- (and 4-)] Dimethine and Tetramethine Cyanine Derivatives

Compd	*IR spectrum,* ν_{max}^{KBr} *(cm^{-1})*	^{1}*H-NMR* (*CDCl$_3$*) *spectrum δ* (*ppm*)[a]
5a	1 620–1 600 (ν C=C)	6·7–7·4 [m, 14H, Ar(het.)—H]
	2 980–2 945 (ν ethiodide)	1·6–1·8 (d, 2H, CH=CH)
	1 580 (ν C=N)	1·2–1·4 (m, 5H, ethiodide)
	1 180, 1 210 (ν oxazole C—O—C)	
6b	840–830 (ν CH=CH)	6·9–7·8 [m, 16H, Ar(het.)—H]
	1 615–1 600 (ν C=C)	3·4–3·8 (d, 2H, CH=CH)
	2 980–2 940 (ν ethiodide)	1·3–0·7 (m, 10H, ethiodide)
	1 180, 1 210 (ν oxazole C—O—C)	
7a	1 610–1 600 (ν C=C)	6·8–7·2 [m, 13H, Ar(het.)—H]
	1 720–1 700 (ν C=N)	1·1–1·6 (m, 12H, CH=CH and ethiodide)
	2 980–2 940 (ν ethiodide)	
	1 180, 1 210 (ν oxazole C—O—C)	2·3 (s, 3H, OCH_3)
8b	840–820 (ν CH=CH)	7·3–7·9 (m, 9H, Ar—H)
	1 680–1 600 (ν C=O)	3·7–3·9 (d, 2H, CH=CH)
	1 580 (ν C=N)	2·3 (s, 3H, OCH_3)
	1 180, 1210 (ν oxazole C—O—C)	
9b	840–820 (ν CH=CH)	6·9–7·8 [m, 20H, Ar(het.)—H]
	1 600 (ν CH=CH—C=CH)	2·8–3·9 (m, 6H, CH_3O— and 3H, CH=CH—C=CH)
	2 980–2 940 (ν ethiodide)	
	1 180–1 210 (ν oxazole C—O—C)	1·2–1·7 (m, 5H, ethiodide)

[a] Abbreviations: s, singlet; d, doublet; m, multiplet.

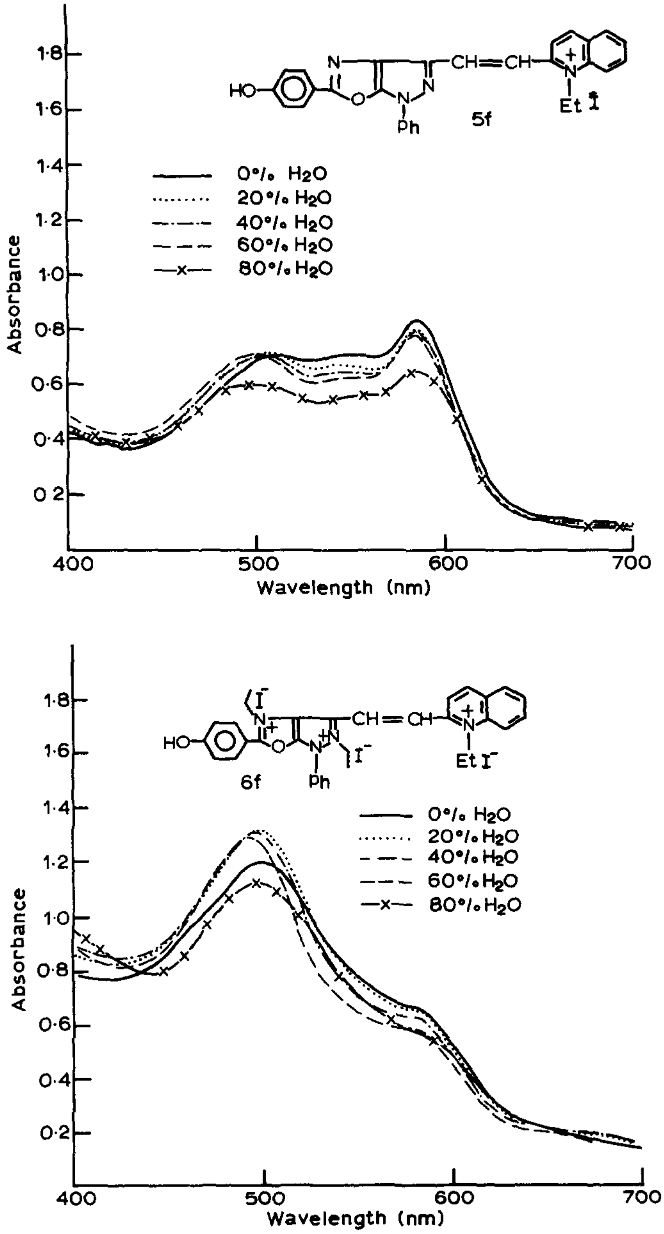


Fig. 1. The absorption spectra of two selected cyanines (**5f** and **6f**) recorded in ethanol/water mixtures.

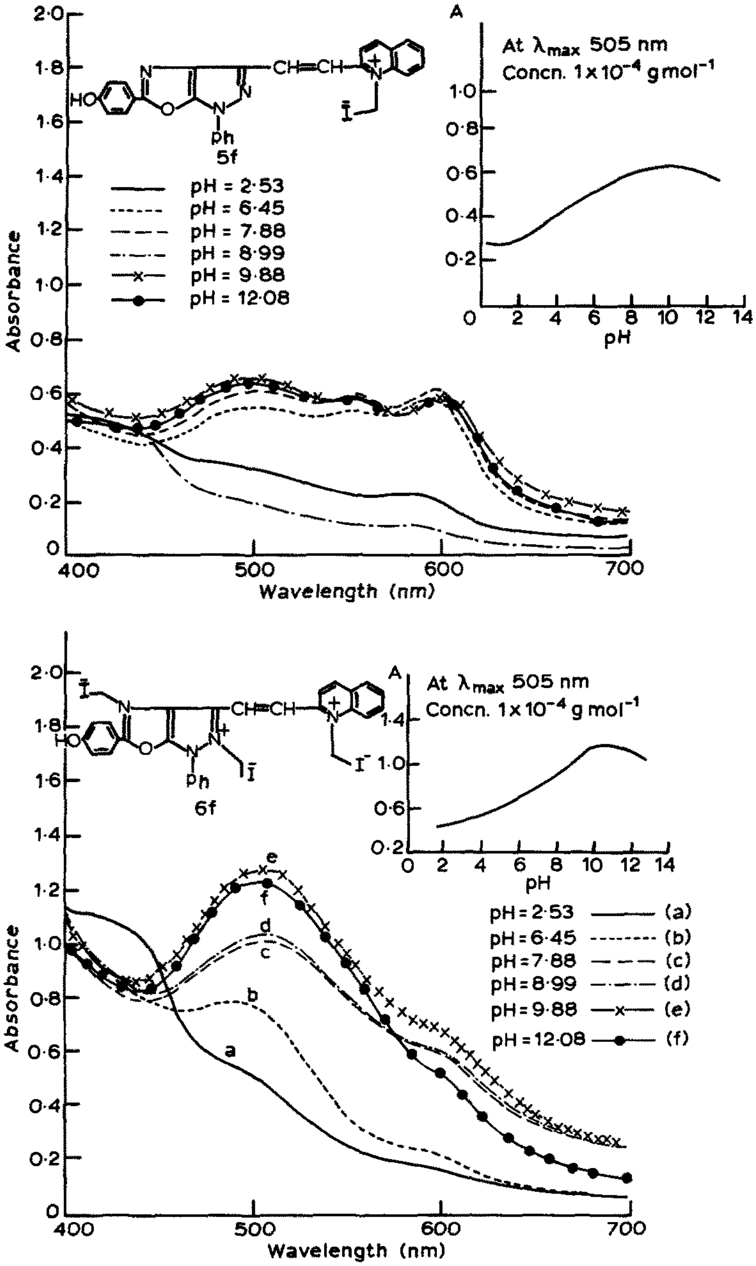


Fig. 2. The variation of absorption spectra of two selected cyanines (**5f** and **6f**) with changes in pH of the medium.

fluorescence. Their ethanolic solutions gave a violet colour in alkaline medium, discharged on acidification.

Absorption maxima of compounds **9a**–**9c** in 95% ethanol underwent bathochromic or hypsochromic shifts depending on the nature of the aryl substituent attached either to the polymethine chain or to the biheterocyclic system, i.e., the pyrazolo[3,4-*d*]oxazole moiety. Only small shifts were observed due to substitution of the β-aryl moieties with either electron-donating or -withdrawing groups. On changing the substitution in the aryl oxazole residue from an electron-withdrawing to an electron-donating group, bathochromic shifts of 25–27 nm resulted (Table 3).

The absorption spectra of two selected cyanines, viz., compounds **5f** and **6f** were recorded in ethanol/water mixtures (Fig. 1). The unexpected blue shift observed in the longer-wavelength band, as well as the lower extinction coefficient, on increasing the water content, can be mainly ascribed to possible hydrogen bonding between the water molecules and the OH group, thus leading to a decrease in the electron-donating character of the oxazolo[3,4-*d*]pyrazole system. In order to study the optimum pH for the application of these dyes as photosensitisers, the spectra of compounds **5f** and **6f** were recorded in aqueous solutions of varying pH. These showed a bathochromic shift in alkaline media due to a relatively increased negative charge density on the *N*-phenyl group or pyrazolo[3,4-*d*]aryloxazole or pyrazole moiety. The bands are hypsochromically shifted in acidic media due to protonation of the nitrogen hetero-atom of the nuclei or of the dimethine system at low pH, CT interaction within the protonated form thus being difficult. As the pH of the medium increases, on the other hand, deprotonation occurs and the CT interaction within the free base is facilitated (Fig. 2).

The ionisation constants of compounds **5f** and **6f** are relatable to the electron-accepting ability of the heterocyclic moieties.[15] This prompted us to determine the pK_a of the dyes in order to allow selection of suitable pH values when the dyes were applied as photosensitisers. The pK_a values of the compounds were obtained through spectrophotometric methods.[16,17] Thus by plotting the absorbance at λ_{max} vs pH, S-shaped curves were obtained (Fig. 2) from which the pK_a values of the cyanines **5f** and **6g** are 5·95 and 9·0, respectively.

3 EXPERIMENTAL

3.1 General

Melting points are uncorrected. The IR spectra were determined on a Unicam SP 1200 (KBr wafer). Electronic spectra were recorded on a

Shimadzu UV–Vis 240 recording spectrophotometer and the ^{1}H-NMR spectra on an EM-390 90 MHz NMR spectrometer.

Stock solutions (10^{-3} M) of selected cyanines were prepared by dissolving the recrystallised dyes in ethanol. Solutions of lower molarities used in spectra measurements were obtained by appropriate dilution. The aqueous universal buffer solutions of pH 2·53–12·08 were prepared and checked at 25°C using an Orion pH-meter model 60/A accurate to ±0·005 pH units.

3.2 Synthesis of 5-aryl-3-methyl-1-phenylpyrazolo[3,4-*d*]oxazoles (2a–2e)

Fusion of 4-amino-3-methyl-1-phenylpyrazol-5-one-hydrochloride[10] with equimolar ratios of aromatic aldehydes for 2–3 h in the presence of excess piperidine followed by diluting with ethanol, filtering while hot, concentrating and cooling gave coloured precipitates. These were filtered and crystallised from aqueous ethanol to give **2a–3e**. The results are listed in Table 1.

3.3 Synthesis of 5-aryl-1-phenylpyrazolo[3,4-*d*]oxazole-3-carboxaldehyde (3a–3e)

5-Aryl-3-methyl-1-phenylpyrazolo[3,4-*d*]oxazole (**2a–2e**; 0·01 mol) was refluxed for 14–16 h with SeO_2 (0·01 mol) in ethanol (40 ml). The reaction mixture was filtered hot from selenium metal and the filtrate cooled and refiltered. The filtrate was concentrated and the product which separated on cooling was filtered, washed and recrystallised from ethanol (see Table 1).

3.4 Synthesis of 5-aryl-1-phenylpyrazolium[3,4-*d*]oxazolium-3-carboxaldehyde 2,4-bis(ethyl iodide) (4d–4e)

Excess ethyl iodide was added to compounds **3a–3e** and the mixture refluxed for 3–5 h. The precipitate was washed with ether, triturated with ethanol by refluxing, filtering hot, concentrating and cooled. The products which precipitated after dilution with water were collected and recrystallised from ethanol (Table 1).

3.5 Synthesis of 5-aryl-1-phenylpyrazolo[3,4-*d*]oxazole-3[2- or 4-)]-mono- and tri-cationic dimethine cyanines (5a–5g, 6a–6g)

Equimolar amounts of compound **3a–3e** or **4a–4e** and the appropriate 2-(or 4-)methyl quaternary salt (α- or γ-picoline, quinaldine or lepidine ethiodide) (0·1 mol) was dissolved in ethanol (40 ml) and piperidine (3–5 drops) was added. The reaction mixture was refluxed for 9–11 h (**3a–3e**) or for 16–18 h (**4a–4e**), filtered hot, concentrated and cooled. The products were precipitated on dilution with water and were recrystallised from ethanol to give compounds **5a**–**5g** in a good yield and **6a**–**6g** in lower yield (Table 2).

3.6 Synthesis of 5-aryl-1-phenylpyrazolium[3,4-*d*]oxazolium-2- (or 4-)yl 3[2- (or 4-)]dicationic dimethine cyanines (7a–7c)

Equimolar amounts of compound **4b** and 2-(or 4-)methyl heterocyclic compounds, e.g. α- or γ-picoline or quinaldine (0·01 mol) were dissolved in ethanol (40 ml) and piperidine (3–5 drops) added. The reaction mixture was refluxed for 16–18 h, filtered hot, concentrated, cooled and diluted with water. The products were crystallised from ethanol to give compounds (**7a**–**7c**) in low yield (Table 3).

3.7 Synthesis of 5-aryl-1-phenylpyrazolo[3,4-*d*]oxazole-3-cinnamoyl derivatives (8a–8e)

Route 1
Equimolar amounts of **3a** or **3b** and the appropriate acetophenone derivatives (0·01 mol) were dissolved in ethanol (40 ml) and piperidine (5–6 drops). The mixture was refluxed for 5–7 h, filtered hot, concentrated, cooled and diluted with water. The products were crystallised from aqueous ethanol to give **8a**–**8c** (Table 3).

Route 2
Equimolar amounts of 3a or **3b** were stirred into ethanol (100 ml), 10% sodium hydroxide was added with stirring, followed by the acetophenone derivatives. After stirring for 5 h and standing overnight, the products were filtered and recrystallised from aqueous ethanol to give the identical product (m.p. and mixed m.p.) to those obtained above.

3.8 Synthesis of 3[β-substituted aryl] 3- and 2-tetramethine cyanine dyes (9a–9e)

Equimolar ratios of **8a**–**8e** and the 1-ethyl-2-methylquinolinium-2-yl salt (0·01 mol) were dissolved in ethanol and 2% sodium hydroxide was added. The reaction mixture was stirred at room temperature for 8–10 h. The precipitate was filtered, washed with water and recrystallised from ethanol to give the corresponding compound (**9a**–**9e**) (Table 3).

REFERENCES

1. Tomachev, A. I. & Karoben, E. F., *Ukr. Khim. Zh.*, **36**(5) (1970) 478.
2. Kozlov, N. S., Zhikhareva, O. D. & Batische, S. A., *Khim. Geterotski Soedin*, **12** (1972) 1619.

3. Brooker, L. G. S. & Keyes, G. H., *J. Amer. Chem. Soc.*, **57** (1935) 2488.
4. Fujirvara, M. S. & Masukawa, T. K. & Kawasaki, M., Ger. Offen. 2 734 335 (2 Feb. 1978); *Chem. Abstr.*, **88** (1978) 161442c.
5. Baba, S., Okubo, B. & Sakamoto, E., Ger. Offen. 2 600 968 (15 Jul. 1976); *Chem. Abstr.*, **86** (1977) 49175a.
6. Habu, T., Nakajima, T., Sakamoto, E., Fujimori, N. & Mine, K., Japan Kokai 76 140623 (3 Dec. 1976); *Chem. Abstr.*, **86** (1977) 163599s.
7. Moskalenko, Z. L., Kudryavskaya, N. V., Grechke, M. K., Timofeeva, R. V. & Tarasenko, I. P., USSR Patent 430747 (5 Oct. 1978); Patent Appln 1737698 (14 Jan. 1977); *Chem. Abstr.*, **90** (1979) 130621x.
8. Lea, B. A., Ger. Offen. 2817408 (26 Oct. 1978); *Chem. Abstr.*, **90** (1979) 144252 g.
9. Yoshida, A., Tanaka, A. & Tsubai, Y., US Patent 4134769 (16 Jan. 1979); *Chem. Abstr.*, **90** (1979) 213240y.
10. Khaikin, M. S., Levkoev, I. I. & Kukhtin, V. A., Zh. Org. Khim., **1**(1) (1965) 133–6; *Chem. Abstr.*, **62**, 16226c.
11. Osman, A. M., Mohamed, S. A., Abbady, M. A. & Mahmoud, A. M., *Indian J. Chem.*, **12** (1974) 48.
12. Osman, A. M. & Mohamed, S. A., *URA J. Chem.*, **14** (1971) 5.
13. Stein, C. W. C. & Day, A. R., *J. Amer. Chem. Soc.*, **64** (1942) 2567.
14. Khalil, Z. H., Koraiem, A. I. M., El-Maghraby, M. A. & Abu El-Hamd, R. M., *J. Chem. Tech. Biotechnol.*, **36** (1986) 379.
15. Mahmoud, M. R., Awad, A. M. & Shaker, A. M., *Spectrochim. Acta*, **41**(10) (1985) 1177.
16. Issa, I. M., Issa, R. M., El-Ezaby, M. S. & Ahmed, Y. Z., *Z. Phys. Chem.*, **242** (1969) 169.
17. Issa, R. M., El-Ezaby, M. S. & Zewall, A. H., *Z. Phys. Chem.*, **242** (1970) 155.