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Heterocyclic halide moieties in the synthesis and study of some conjugated oxazine methine cyanine dyes

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Abstract. New asymmetrical/symmetrical styryl cyanines (3a–d, 4a–d), monomethine cyanine dyes (5a–d, 6a–d) and trimethine cyanine dyes (11a–g, 12a–g) incorporating *bis* pyrazolo-[2,3-*b*;2′,3′-*b*′] oxazine and/or pyrazolo [2,3-*b*]-oxazolo [2′,3′-*b*] oxazine were prepared. The new synthesised cyanines were identified by elemental and spectral analyses. The uv–visible absorption spectra of some selected dyes were investigated in pure and mixed solvents as well as in aqueous buffer solutions. Molecular complex formation with ethanol was verified by mixed solvent studies. Electronic transitions were attributed to either locally excited or predominantly charge transfer states. The spectral shifts were discussed in relation to molecular structure and in terms of medium effects. The variation of absorbance with *p*H was utilized for the determination of the *pKa* values for some selected compounds.

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

1. Introduction

Methine cyanines, comprising the styryl, mono- and tri-methine types, play a vital role in various applications such as photosensitisers in blue-green light (Broker and Keyes 1935), and as inhibitors of cell-growth and division (Zigman and Gilman 1980) and can be used for the determination of the sensitivity of micro-organisms to antibiotics (Lykov *et al* 1987). In this investigation, new asymmetrical/symmetrical styryl cyanines (3a–d and 4a–d) monomethine cyanines (5a–d and 6a–d) and trimethine cyanines (11a–g and 12a–g) were prepared to study the photosensitisation effect on their spectral behaviour. Solvatochromic and acid-base properties of some selected dyes were studied for use as photosensitisers.

2. Results and discussion

2.1 *Synthesis*

Reaction of 4-amino-3-methyl-1-phenyl pyrazol-5-one with 4-bromo-3(2)-methyl-1-phenyl pyrazol (oxazol)-5-one (Khaikin *et al* 1965) in ethanolic solutions under basic catalysis (pyridine) afforded the corresponding 3,5-dimethyl-1,7-diphenyl-*bis*-pyrazolo [2,3-*b*;2′,3′-*b*′] oxazine (1a) and 3,6-dimethyl-1-phenyl pyrazolo [2,3-*b*]

*For correspondence

oxazolo [2′,3′-*b*′] oxazine (1b) respectively. The structures of (1a,b) were confirmed by elemental analyses (table 1), IR and ^{1}H NMR (Scheinmann 1970) spectral data (table 2).

Direct quaternisation of (1a,b) using excess amount of ethyl iodide under controlled conditions gave 3,5-dimethyl *bis*-pyrazolium [2,3-*b*,2′,3′-*b*′] oxazine *bis*-2,6-yl salt (2a) and 3,6-dimethyl pyrazolium [2,3-*b*] oxazolium [2′,3′-*b*′]-oxazine *bis*-2,5yl salt (2b) respectively (scheme 1). The structures of (2a,b) were established by elemental analyses, IR and ^{1}H NMR spectral data (tables 1,2).

Reaction of equimolar ratios of (2a,b) and equi-(bi-)molar ratios of aromatic aldehydes such as benzaldehyde, *p*-methoxy and *p*-nitro-benzaldehyde under piperdine catalysis achieved the corresponding *bis*-pyrazolium-2,6-yl [2,3-*b*;2′,3′-*b*′] oxazine-3-(*bis*-3,5-) styryl (*bis*-styryl) cyanine dyes and pyrazolium-2-yl [2,3-*b*]-oxazolium-5-yl [2′,3′-*b*′]oxazine-6-(*bis*-3,6-)styryl (*bis*-styryl)cyanine dyes 3a–d and 4a–d (scheme 1).

The structure of styryl and *bis*-styryl dyes (3a–d) and (4a–d) were confirmed by elemental analyses (table 3), IR and ^{1}H NMR spectral data (table 2). Both series of compounds were coloured and were partially soluble in nonpolar solvents, in which they gave red solutions. They were readily soluble in most polar solvents, giving reddish-violet solutions. They were soluble in conc. H_2SO_4, liberating iodine vapour on warming. Their ethanolic solutions gave a red colour in alkaline medium which discharged on acidification.

Other new types of asymmetrical N-ethyl pyrazolo-(oxazolo)-[2,3-*b*] pyrazolium-2-yl[2′,3′-*b*′] oxazine-3(6)[4(1)]-monomethine dyes (5a–d) and/or symmetrical N,N′-ethyl *bis*-pyrazolo [2,3-*b*;2′,3′-*b*′]-oxazine-, N-ethyl pyrazolo [2,3-*b*] N-ethyl oxazolo-[2′,3′-*b*′]oxazine -3,5(3,6)[4(1)] monomethine cyanine dyes (6a–d) were synthesised through the interaction of equimolar ratios of (2a,b) and equi-(bi-) molar ratios of 1-methyl pyridinium/quinolinium or isoquinolinium iodide under piperidine catalysis (scheme 1).

The structure of monomethine cyanine dyes (5a–d) and (6a–d) were confirmed by elemental analysis (table 3), IR and ^{1}H NMR spectral data (table 2). These compounds are partially soluble in nonpolar solvents and fairly soluble in polar organic solvents. They exhibit coloured solution with slight or intense green fluorescence depending upon either inserting heterocyclic quaternary salts or synthesised triheterocyclic moieties. They are soluble in conc. H_2SO_4 releasing iodine vapour on heating. Their ethanolic solutions gave permanent colour in basic medium which faded on acidification with interchangeable changes in colour.

The condensation of equimolar ratios (2a,b) with equi-(bi-) molar ratios of ethylorthoformate and/or acid amide (acetamide, trifluoroacetamide and benzamide) afforded the corresponding asymmetrical (symmetrical) intermediate compounds 7a,b; 8a–d (9a,b and 10a–d) respectively.

The nature of condensation reactions depend upon the type of catalyst used. Thus, reactions involving ethylorthoformate were carried out under piperidine catalysis and ethanol as solvent, while those containing acid amide were carried out under fusion conditions followed by extraction with ethanol. The latter asymmetrical (symmetrical) intermediate compounds are considered key intermediates for the synthesis of asymmetrical and symmetrical tri-/meso-substituted tri-methine cyanines (11a–g and 12a–g) when reacted with equi-(bi-) molar ratios of 2-methyl quaternary salts in the presence of piperidine as basic catalyst (scheme 1).

Table 1. The characterization of starting materials (1a,b and 2a,b) and intermediate compounds (7a,b; 8a–d; 9a,b and 10a–d).

Compound	m.p. (°C)	Yield (%)	Mol. formula (Mol. wt.)	Colour	R =	X(A)	Analysis (%): Calcd.(found) C	H	N
1a	196–8	75	$C_{20}H_{17}N_5O$ (343)	Red	–	3[1-Phenyl pyrazole]	69·97 (70·10)	4·96 (4·67)	20·41 (19·91)
1b	185	73	$C_{14}H_{12}N_4O_2$ (268)	Orange	–	6[Oxazole]	62·69 (62·51)	4·48 (4·73)	20·90 (21·13)
2a	210–2	78	$C_{24}H_{27}N_5OI_2$ (655)	Brown	–	3[1-Phenyl pyrazolium 2-yl-salt]	43·97 (44·29)	4·12 (4·52)	10·69 (11·01)
2b	173–5	74	$C_{18}H_{22}N_4O_2I_2$ (580)	Brown	–	6[Oxazolium-5-yl-salt]	37·24 (36·81)	3·79 (4·11)	9·66 (10·03)
7a	146–8	73	$C_{29}H_{37}N_5O_3I_2$ (757)	Orange	H	3[1-Phenyl pyrazolium 2-yl-salt]	45·97 (46·23)	4·89 (4·67)	9·25 (9·51)
7b	156–8	63	$C_{23}H_{32}N_4O_4I_2$ (682)	Red	H	6[Oxazolium-5-yl-salt]	40·47 (40·71)	4·69 (4·33)	8·21 (8·61)
8a	175	68	$C_{26}H_{29}N_5O_2I_2$ (697)	Red	CH_3	3[1-Phenyl pyrazolium 2-yl-salt]	44·76 (45·10)	4·16 (3·91)	10·04 (10·19)
8b	185	59	$C_{26}H_{26}N_5O_2I_2F_3$ (784)	Brownish red	CF_3	3[1-Phenyl pyrazolium 2-yl-salt]	41·55 (41·32)	3·46 (3·76)	9·32 (9·65)

(*Continued*)

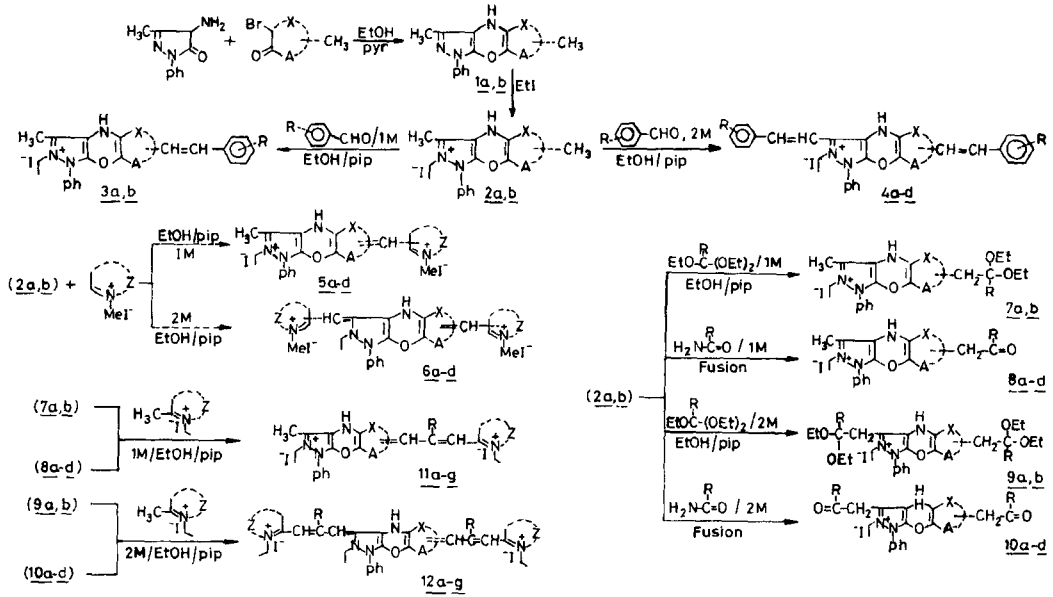
Table 1. (*Continued*)

Compound	m.p. (°C)	Yield (%)	Mol. formula (Mol. wt.)	Colour	R =	X(A)	Analysis (%): Calcd.(found) C	H	N
8c	123–5	62	$C_{31}H_{31}N_5O_2I_2$ (759)	Red	C_6H_5	3[1-Phenyl pyrazolium 2-yl-salt]	49·01 (48·77)	4·08 (4·22)	9·22 (9·43)
8d	210–2	55	$C_{20}H_{24}N_4O_3I_2$ (622)	Brown	CH_3	6[Oxazolium-5-yl-salt]	38·59 (38·65)	3·86 (4·14)	9·00 (9·06)
9a	162–4	77	$C_{34}H_{47}N_5O_5I_2$ (859)	Orange	H	3[1-Phenyl pyrazolium 2-yl-salt]	47·50 (47·66)	5·47 (5·11)	8·15 (8·49)
9b	187–9	69	$C_{28}H_{42}N_4O_6I_2$ (752)	Red	H	6[Oxazolium-5-yl-salt]	42·86 (43·13)	5·36 (5·44)	7·14 (7·55)
10a	192–4	72	$C_{28}H_{31}N_5O_3I_2$ (739)	Brown	CH_3	3[1-Phenyl pyrazolium 2-yl-salt]	45·47 (45·33)	4·20 (4·15)	9·47 (9·61)
10b	156–8	63	$C_{28}H_{25}N_5O_3I_2F_6$ (847)	Brown	CF_3	3[1-Phenyl pyrazolium 2-yl-salt]	39·67 (40·11)	2·95 (3·14)	8·27 (7·98)
10c	168	67	$C_{38}H_{35}N_5O_3I_2$ (863)	Brown	C_6H_5	3[1-Phenyl pyrazolium 2-yl-salt]	52·84 (52·53)	4·06 (3·96)	8·11 (8·40)
10d	218	52	$C_{22}H_{26}N_4O_4I_2$ (664)	Red	CH_3	6[Oxazolium-5-yl-salt]	39·76 (39·67)	3·92 (4·11)	8·43 (8·38)

Table 2. IR and ^1H NMR spectral data of some selected starting compounds and their styryl, monomethine, trimethine cyanine derivatives

Compound	IR spectrum, ν_{max}^{KBr} (cm^{-1})	^1H NMR ($CDCl_3$) spectrum, δ(ppm)[a]
1a	3100–2900 (*v* satd. CH) 3400–3200 (*v*-NH) 1775–1740 (*v*-cyclic *sec* NH) 1650–1620 (*v*-C=C) 1595–1520 (*v*-C=N) 1020–1050 (*v*-C–O–C) 760–675 (*v*-Ar.monosub.)	7·4–8·2 (*m*, 10(H), Ar–H) 5·4 (*s*, 1(H), NH) 2·4 (*s*, 6(H), $2CH_3$ of pyrazole)
1b	3400–3200 (*v*-NH) 1775–1740 (*v*-cyclic *sec* NH) 1650–1630 (*v*-C=C) 1590–1520 (*v*-C=N) 1010–1050 (*v*-C–O–C) 760–675 (*v*-Ar.monosub)	7·3–8·5 (*m*, 5(H), Ar–H) 5·48 (*s*, 1(H), NH) 2·4 (*s*, 3(H), CH_3 of pyrazole) 3·15 (*s*, 3(H), CH_3 of oxazole)
2a	2980–2940 (*v* ethiodide) 1775–1740 (*v*-cyclic *sec* NH) 1640–1600 (*v*-C=C) 1560–1510 (*v*-C=N) 760–675 (*v*-Ar.monosub.)	7·4–8·5 (*m*, 10(H), Ar–H) 5·5 (*s*, 1(H), NH) 3·9–4·1 (*q*, 4(H), 2 CH_2–N^+) 3·2 (*s*, 6(H), $2CH_3$ of pyrazoles) 2·8–2·9 (*t*, 6(H), $2CH_3$ of ethiodide)
2b	3100–2900 (*v* sat. CH) 3400–3200 (*v*-NH) 2980–2930 (*v* ethiodide) 1575–1510 (*v*-C=N) 1020–1050 (*v*-C–O–C)	7·5–8·5 (*m*, 5(H), Ar–H) 5·6 (*s*, 1(H), NH) 5·0–5·2 (*q*, 2(H), CH_2N^+ of oxazole) 3·9–4·1 (*q*, 2(H), CH_2–N^+ of pyrazoles) 3·6 (*s*, 3(H), CH_3 of oxazole); 3·1 (*s*, 3(H), CH_3 of pyrazoles); 3·2–3·4 (*t*, 3(H), CH_3 ethiodide of oxazole); 2·7–2·9 (*t*, 3(H), CH_3 ethiodide of pyrazoles)
3b	1620–1600 (*v*-C=C) 1580–1520 (*v*-CH=CH) 2980–2940 (*v* ethiodide) 1775–1750 (*v sec* NH)	7·2–8·2 (*m*, 16(H), Ar–H and CH=CH) 5·3 (*s*, 1(H), NH) 4·0–4·2 (*q*, 4(H), $2CH_2$–N^+) 3·6 (*s*, 3(H), OCH_3 gp); 3·2 (*s*, 3(H), CH_3 of pyrazole); 2·6–2·9 (*m*, 6(H), $2CH_3$ of ethiodide)
5b	1620–1600 (*v*-C=C) 2980–2940 (*v* ethiodide) 1775–1740 (*v sec.* NH) 1590–1510 (*v*-C=N)	7·2–8·2 (*m*, 17(H), Ar-(het.)H and CH=) 5·6 (*s*, 1(H), NH) 5·1 (*s*, 3(H), methiodide) 4·0–4·1 (*q*, 2(H), CH_2–N^+ of pyrazole, ethiodide); 3·1–3·4 (*m*, 5(H), CH_2–N and CH_3 of pyrazole); 2·75–2·9 (*t*, 3(H), CH_3 of ethiodide); 1·1–1·3 (*t*, 3(H), CH_3^* CH_2–N)
5d	2980–2930 (*v* ethiodide) 1620–1600 (*v* C=C) 1020–1010 (*v*-C–O–C) 3400–3200 (*v*-NH) 1590–1510 (*v*-C=N)	7·4–8·5 (*m*, 12(H), Ar-(het.)H and CH=) 5·65 (*s*, 1(H), NH) 5·3 (*s*, 3(H), methiodide) 4·0–4·1 (*q*, 2(H), CH_2–N^+ of pyrazole) 3·5–3·7 (*q*, 2(H), CH_2–N); 3·2 (*s*, 3(H), CH_3 of pyrazole); 2·7–2·9 (*t*, 3(H), CH_3 of ethiodide); 1·2–1·4 (*t*, 3(H), CH_3^* CH_2–N)
7a	1620–1600 (*v*-cyclic C=C) 2980–2940 (*v* ethiodide) 1760–1720 (*v sec.* NH) 1550–1500 (*v*-cyclic C=N)	7·0–8·0 (*m*, 10(H), Ar–H) 5·0 (*s*, 1(H), NH) 4·1–4·3 (*q*, 2(H), CH_2–N^+) 3·5–3·8 (*m*, 7(H), CH, $2CH_2$–O, CH_2N^+); 3·2 (*s*, 3(H), CH_3 of pyrazole); 3·0 (*d*, 2(H), CH_2^* CH); 2·6–2·8 (*t*, 3(H), CH_3 of ethiodide); 2·4–2·5 (*t*, 3(H), CH_3 of ethiodide); 1·1–1·3 (*t*, 6(H), $2CH_3$ of ethoxy)
11b	2980–2930 (*v* ethiodide) 3400–3200 (*v*-NH) 1770–1710 (*v-sec.* NH) 1550–1500 (*v*-cyclic C=N) 1620–1600 (*v*-C=C) 1380 (*v*-CH=CH–CH)	7·5–8·5 (*m*, 19(H), Ar-(het.)H and CH=CH–CH) 5·63 (*s*, 1(H), NH) 5·1–5·3 (*q*, 2(H), CH_2N^+ of quinoline) 4·0–4·2 (*q*, 2(H), CH_2N^+ of pyrazole) 3·3–3·6 (*m*, 5(H), CH_2–N and CH_3 ethiodide of quinoline) 3·1 (*s*, 3(H), CH_3 of pyrazole); 2·7–2·9 (*t*, 3(H), CH_3 of ethiodide); 1·2–1·4 (*t*, 3(H), CH_3 CH_2 N)

[a]Abbreviations; *s*, singlet; *d*, doublet; *t*, triplet; *m*, multiplet



(1a,b):X(A) = 3[1-phenyl pyrazole] (a), X(A) = 6-oxazole (b)
(2a,b):X(A) = 3[1-phenyl pyrazolium-2-yl-salt] (a), X(A) = 6[oxazolium-5yl-salt] (b).
(3a–d) and (4a–d):X(A) = 3[1-phenyl pyrazolium-2yl-salt]; R = H (a), R = p-OCH_3 (b), R = p-NO_2 (c) X(A) = 6[oxazolium-5yl-salt]; R = p-OCH_3 (d)
(5a–d) and (6a–d):X(A) = 3[N-ethyl pyrazole], Z = 1-methyl pyridinium-4yl-salt (a); X(A) = 3[N-ethyl pyrazole], Z = 1-methyl quinolinium-4yl-salt (b); X(A) = 3[N-ethyl pyrazole], Z = 2-methyl iso-quinolinium-1yl-salt (c); X(A) = 6[N-ethyl oxazole], Z = 1-methyl quinolinium-4yl-salt (d)
(7a,b) and (9a,b):X(A) = 3[1-phenyl pyrazolium-2yl-salt], R = H (a); X(A) = 6[oxazolium-5yl-salt], R = H (b)
(8a–d) and (10a–d):X(A) = 3[1-phenyl pyrazolium-2yl-salt], R = CH_3 (a); R = CF_3 (b); R = C_6H_5 (c). X(A) = 6[oxazolium-5yl-salt], R = CH_3 (d)
(11a–g) and (12a–g):X(A) = 3[N-ethyl pyrazole], R = H, Z = 1-ethyl pyridinium-2yl-salt (a); X(A) = 3[N-ethyl pyrazole], R = H, Z = 1-ethyl quinolinium-2yl-salt (b); X(A) = 6[N-ethyloxazole], R = H, Z = 1-ethyl quinolinium-2yl-salt (c); X(A) = 3[N-ethyl pyrazole], R = CH_3 Z = 1-ethyl quinolinium-2yl-salt(d); X(A) = 3[N-ethyl pyrazole], R = CF_3 Z = 1-ethyl quinolinium-2yl-salt (e); X(A) = 3[N-ethyl pyrazole], R = C_6H_5, Z = 1-ethyl quinolinium-2yl-salt (f); X(A) = 6 [N-ethyl oxazole], R = CH_3, Z = 1-ethyl quinolinium-2yl-salt (g)

Scheme 1. Derivative substituents

The structures of the intermediates and the resultant dyes were confirmed by elemental analysis (tables 1,3), IR and ^{1}H NMR spectral data (table 2). Both asymmetrical (symmetrical)-tri-and/or meso-substituted tri-methine cyanine dyes (11a–g and 12a–g) are highly coloured in solution, exhibiting intense green to blue fluorescence depending upon the solvent used. They are soluble in conc. H_2SO_4, liberating iodine vapour on warming. Their ethanolic solutions give a violet colour in alkaline medium, discharged on acidification.

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

The λ_{max} and ε_{max} for newly synthesised styryl cyanines (3a–d and 4a–d), monomethine cyanines (5a–d and 6a–d) and tri-(mesosubstituted tri-) methine cyanines (11a–g and 12a–g) in ethanol are collected in table 3. The visible absorption spectra of asymmetrical (symmetrical) styryl-(*bis*-styryl) cyanines 3a–d (4a–d) in ethanol exhibit a single and broad band located at wavelength range 415–510 nm (table 3). This band is influenced by the type of substituent (R). Thus, substituting R = H (3a, 4a) by R = *p*-OH_3 (3b, 4b) causes a bathochromic shift (5–15 nm), while substituting R = H by an electron acceptor group R = *p*-NO_2 (3c, 4c), causes a hypsochromic shift (5nm). Charge transfer (CT) seems to occur from the 4-aryl residue (source) to the positively charged heterocyclic nitrogen atom (sink). The CT taking place within the solute molecule (4b for example) can be represented as in scheme 2.

The absorption bands of asymmetrical (symmetrical) styryl (*bis*-styryl) cyanines 3a–d (4a–d) are influenced by the nature of the condensed triheterocyclic moiety X(A). Thus, the pyrazolo-oxazine-oxazole dyes (3d, 4d) are more bathochromically shifted by 40–45 nm than the analogous (3b, 4b) which include the *bis*-pyrazolo-oxazine nucleus (cf table 3). Also, asymmetrical styryl cyanines 3a–d have absorption bands bathochromically shifted by 5–15 nm than the symmetrical *bis*-styryl cyanines 4a–d. This is due to the free electronic charge transfer pathways in asymmetrical dyes (table 3).

The electronic spectra of both asymmetrical (symmetrical) monomethine cyanines 5a–d (6a–d) and/or trimethine cyanines 11a–c (12a–c) in 95% ethanol showed absorption bands in the visible region 370–690 nm which undergo bathochromic or hypsochromic shift depending on the nature of both the heterocyclic quaternary residue (Z) and the tri-condensed heterocyclic X(A), table 3. Substituting Z = pyridinium-4-yl in compound 5a by Z = quinolinium-4-yl in compound 5b resulted in red shifts of 45 nm, accompanied by the appearance of two new absorption bands. This could be attributed to the more extensive π-delocalisation within quinolinium-4-yl salt of 5b. Similar behaviour can be shown in symmetrical monomethine cyanines (6a–d) and in asymmetrical (symmetrical) trimethine cyanines 11a–c (12a–c).

Changing the linkage position of quinoline residue from 4-yl to 1-yl in both asymmetrical (symmetrical) monomethine cyanine dyes 5b, c (6b, c) resulted in slight hypsochromic shifts of 25–50 nm. This is due to increase in the conjugation of the quinoline moiety in the 4-yl linkage (table 3).

The *bis*-pyrazolo oxazine dyes show CT bands hypsochromically shifted compared to those incorporating pyrazolo-oxazine-oxazole analogues (cf table 3). This is attributed to greater electron availability at the oxygen atom in the oxazole moiety.

Table 3. The characterization of styryl (*bis*-styryl) cyanine, mono-(*bis*-mono-) methine cyanine and tri-(*bis*-tri-) methine cyanine dyes (3a–d; 4a–d; 5a–d; 6a–d; 11a–g and 12a–g).

Compound	m.p. (°C)	Yield (%)	Mol. formula (Mol.wt.)	Colour	Z or R	X(A)	Analysis (%): Calcd. (found) C	H	N	Absorption spectra in 95% ethanol λ_{max} (nm)	ε_{max} (m^{-1} cm^2)
3a	160	35	$C_{31}H_{31}N_5OI_2$ (743)	Brown	R:H	3[1-Phenyl pyrazolium-2-yl-salt]	50·07 (49·81)	4·17 (4·11)	9·42 (9·56)	455	2260
3b	135–7	46	$C_{32}H_{33}N_5O_2I_2$ (773)	Reddish violet	R:p-OCH_3	3[1-Phenyl pryazolium-2-yl-salt]	49·68 (49·35)	4·27 (4·51)	9·06 (9·17)	470	2720
3c	210–2	32	$C_{31}H_{30}N_6O_3I_2$ (788)	Brown	R:p-NO_2	3[1-Phenyl pyrazolium-2-yl-salt]	47·21 (46·89)	3·81 (4·13)	10·66 (10·45)	450	2099
3d	133–5	49	$C_{26}H_{28}N_4O_3I_2$ (698)	Red	R:p-OCH_3	6[Oxazolium-5-yl-salt]	44·70 (45·10)	4·01 (3·78)	8·02 (8·16)	420,510	5600,3000
4a	140–2	42	$C_{38}H_{35}N_5OI_2$ (831)	Brown	R:H	3[1-Phenyl pyrazolium-2-yl-salt]	54·87 (55·21)	4·21 (4·15)	8·42 (8·53)	450	2730
4b	110–2	49	$C_{40}H_{39}N_5O_3I_2$ (891)	Reddish violet	R:p-OCH_3	3[1-Phenyl pyrazolium-2-yl-salt]	53·87 (54·13)	4·38 (4·19)	7·86 (8·16)	455	2100
4c	95	34	$C_{38}H_{33}N_7O_5I_2$ (921)	Brown	R:p-NO_2	3[1-Phenyl pyrazolium-2-yl-salt]	49·51 (49·33)	3·58 (3·98)	10·64 (10·75)	445	3550
4d	146–8	54	$C_{34}H_{34}N_4O_4I_2$ (816)	Brownish violet	R:p-OCH_3	6[Oxazolium-5-yl-salt]	50·00 (49·78)	4·17 (4·33)	6·86 (7·13)	415,500*sh*	63200,50400
5a	140–2	42	$C_{30}H_{32}N_6OI_2$ (746)	Brown	Z:pyridinium-4-yl salt	3[N-Ethyl pyrazole]	48·27 (48·55)	4·29 (4·62)	11·26 (11·11)	480	4600
5b	166–8	69	$C_{34}H_{34}N_6OI_2$ (796)	Orange	Z:quinolinium-4-yl salt	3[N-Ethyl pyrazole]	51·26 (50·96)	3·86 (3·45)	10·55 (10·73)	350,445, 525	73000,68000, 49000

(Continued)

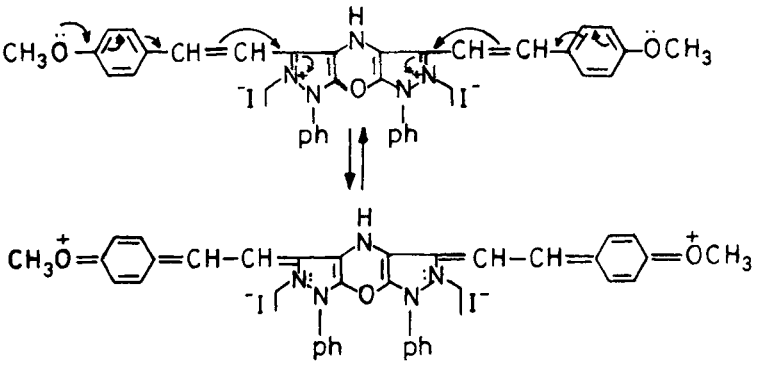
Table 3. (*Continued*)

Compound	m.p. (°C)	Yield (%)	Mol. formula (Mol.wt.)	Colour	Z or R	X(A)	Analysis (%): Calcd. (found) C	H	N	Absorption spectra in 95% ethanol λ_{max} (nm)	ε_{max} (m^{-1} cm^2)
5c	150–2	54	$C_{34}H_{34}N_6OI_2$ (796)	Brownish red	Z: iso-quinolinium-1-yl salt	3[N-Ethyl pyrazole]	51·26 (51·55)	3·86 (3·48)	10·55 (10·78)	460,520*sh*	3840,3000
5d	185	62	$C_{28}H_{29}N_5O_2I_2$ (721)	Reddish violet	Z: quinolinium-4-yl salt	6[N-Ethyl oxazole]	46·60 (47·03)	4·02 (3·88)	9·71 (10·16)	440,540	4198,3130
6a	180	45	$C_{36}H_{37}N_7OI_2$ (837)	Brown	Z: pyridinium-4-yl-salt	3[N-Ethyl pyrazole]	51·61 (51·75)	4·42 (4·35)	11·71 (12·11)	475	4920
6b	204–6	69	$C_{44}H_{41}N_7OI_2$ (937)	Red	Z: quinolinium-4-yl-salt	3[N-Ethyl pyrozole]	56·35 (56·17)	4·38 (4·56)	10·46 (10·62)	425,500	5000,4198
6c	184–6	58	$C_{44}H_{41}N_7OI_2$ (937)	Brown	Z: iso-quinolinium-1-yl-salt	3[N-Ethyl pyrazole]	56·35 (55·98)	4·38 (4·16)	10·46 (10·41)	390,500	7200,6420
6d	205–7	67	$C_{38}H_{36}N_6O_2I_2$ (862)	Brown	Z: quinolinium-4-yl-salt	6[N-Ethyl oxazole]	52·90 (53·13)	4·18 (4·25)	9·75 (10·09)	435,510*sh*	5900,4320
11a	230	49	$C_{33}H_{36}N_6OI_2$ (786)	Brownish violet	R: H,Z: pyridinium-2-yl-salt	3[N-Ethyl pyrazole]	50·38 (49·91)	4·85 (4·63)	10·69 (10·71)	465,550*sh*	4480,2360
11b	178	68	$C_{37}H_{38}N_6OI_2$ (836)	Intense violet	R: H, Z: quinolinium-2-yl-salt	3[N-Ethyl pyrazole]	53·11 (52·86)	4·55 (4·32)	10·05 (9·78)	520,559 600*sh*,657	10800,11040, 5200,2120
11c	228	62	$C_{31}H_{33}N_5O_2I_2$ (761)	Deep violet	R: H, Z: quinolinium-2-yl-salt	6[N-Ethyl oxazole]	48·88 (49·13)	4·34 (4·18)	9·20 (9·67)	395,500 590,690	7806,15120, 4800,1194
11d	218	68	$C_{38}H_{40}N_6OI_2$ (850)	Intense violet	R: CH_3,Z: quinolinium-2-yl-salt	3[N-Ethyl pyrazole]	53·65 (53·41)	4·71 (4·31)	9·88 (10·12)	385,500, 600,695	199700,371000, 115000,30000
11e	230	55	$C_{38}H_{37}N_6OI_2F_3$ (904)	Violet	R:CF_3,Z:quinolinium-2-yl-salt	3[N-Ethyl pyrazole]	50·44 (50·61)	4·09 (3·92)	9·29 (8·93)	395,500	229900,359900

(*Continued*)

Table 3. (*Continued*)

Compound	m.p. (°C)	Yield (%)	Mol. formula (Mol.wt.)	Colour	Z or R	X(A)	Analysis (%): Calcd. (found) C	H	N	Absorption spectra in 95% ethanol λ_{max} (nm)	ε_{max} (m^{-1} cm^2)
11f	165	67	$C_{43}H_{42}N_6OI_2$ (912)	Deep violet	R:C_6H_5,Z:quinolinium-2-yl-salt	3[N-Ethyl pyrazole]	56·58 (56·41)	4·61 (4·75)	9·21 (8·98)	525,560, 598,660,690*sh*	140000,210000, 139000,54000,2230
11g	190	70	$C_{32}H_{35}N_5O_2I_2$ (775)	Deep violet	R:CH_3,Z:quinolinium-2-yl-salt	6[N-Ethyl oxazole]	49·55 (49·71)	4·52 (4·21)	9·03 (8·91)	390,500, 600*sh*,698	95400,16800, 64200,15000
12a	215	54	$C_{42}H_{45}N_7OI_2$ (917)	Brownish violet	R:H,Z:pyridinium-2-yl-salt	3[N-Ethyl pyrazole]	54·96 (55·15)	4·91 (4·68)	10·69 (10·53)	395,485, 550*sh*	11840,18760, 4800
12b	235	72	$C_{50}H_{49}N_7OI_2$ (1017)	Violet	R:H, Z:quinolinium-2-yl-salt	3[N-Ethyl pyrazole]	59·00 (59·16)	4·82 (4·53)	9·64 (9·75)	520,557, 597,655	6800,11080, 7080,2040
12c	210	69	$C_{44}H_{44}N_6O_2I_2$ (942)	Intense violet	R:H, Z:quinolinium-2-yl-salt	6[N-Ethyl oxazole]	56·05 (55·81)	4·67 (4·29)	8·92 (9·11)	390,500, 585,690	29000,125400, 678000,10800
12d	233–5	72	$C_{52}H_{53}N_7OI_2$ (1045)	Intense violet	R:CH_3,Z:quinolinium-2-yl-salt	3[N-Ethyl pyrazole]	59·71 (59·26)	5·07 (4·81)	9·38 (9·62)	520,560, 595,660	128000,150000, 94000,45000
12e	185	62	$C_{52}H_{47}N_7OI_2F_6$ (1153)	Violet	R:CF_3,Z:quinolinium-2-yl-salt	3[N-Ethyl pyrazole]	54·12 (53·80)	4·08 (3·76)	8·50 (8·88)	355,420, 440,485	270000,249900, 329990,10000
12f	220	72	$C_{62}H_{57}N_7OI_2$ (1169)	Intense violet	R:C_6H_5,Z:quinolinium-2-yl-salt	3[N-Ethyl pyrazole]	63·64 (63·29)	4·88 (5·12)	8·38 (8·49)	505,560*sh* 595	4060,2400, 1598
12g	215	75	$C_{46}H_{48}N_6O_2I_2$ (970)	Deep violet	R:CH_3,Z:quinolinium-2-yl-salt	6[N-Ethyl oxazole]	56·91 (57·13)	4·95 (4·66)	8·66 (8·75)	390,515, 555,595, 695	80400,115800, 126000,78000, 29400



Scheme 2. CT transition for dye 4b.

Absorption bands in the electronic absorption spectra of asymmetrical (symmetrical) meso-substituted trimethine cyanines 11d–g (12d–g) in 95% ethanol (visible region 355–698) undergo bathochromic or hypsochromic shift depending on the diene side chain substituent (R). Thus, the absorption bands of asymmetrical (symmetrical) meso-substituted trimethine 11d–g (12d–g), substituted with $R=CH_3$ or C_6H_5 are bathochromically shifted by 35–60 nm with an increase in the number of absorption bands than those substituted with $R=CF_3$. This is due to the hyperconjugation and mesomeric effects of methyl and phenyl groups, while the CF_3 group causes a more powerful inductive effect. Also, these dyes are influenced by the nature of the condensed triheterocyclic system and the symmetry of cyanine molecules (cf table 3).

The meso-substituted trimethine cyanines 11d–g (12d–g) show strong bathochromic shift of 5–30 nm when compared to trimethine cyanine analogues 11a–c (12a–c). This is attributed to the hyperconjugation and mesomeric effects of meso-substituted trimethine dyes. (cf table 3).

2.3 *Solvatochromic behaviour of asymmetrical mono(tri)methine cyanine dye 5b(11c) in pure solvents*

The absorption bands (λ_{max}, ε_{max} values) of the title compounds (5b, 11c) owing to electronic transitions obtained in pure solvents of different dielectric constants (Weast and Astle 1981) (viz. H_2O, DMF, EtOH, $CHCl_3$, CCl_4 and dioxane), are represented in table 4a and figure 1.

The spectrum in ethanol consists of three and four significant absorption bands respectively. The shorter bands can be assigned to π–π^* transitions within the benzenoid and heterocyclic rings. These bands are influenced to a small extent by changing the polarity of the medium. The other bands at longer wavelengths can be attributed to n–π^* transitions and to intramolecular charge-transfer (CT) interaction (Bhutra and Tandon 1970). The intramolecular CT transition for dye 11c (as example) can be represented as in scheme 3.

The visible absorption band for 5b (11c), located at 447 (500 nm), was attributed to an intramolecular CT transition originating from the oxazine oxygen/pyrazolo nitrogen (5b) or the oxazolo oxygen/nitrogen (11c) as a source to the positively charged heterocyclic quaternary (N) atom as a sink.

Careful examination of the results reported in table 4a reveals that bands corresponding to CT transitions show bathochromic shifts on changing the organic solvents from ethanol to dioxane, DMF, $CHCl_3$ and CCl_4. The hypsochromic shifts observed in the λ_{max} of CT bands for two compounds (5b, 11c) in ethanol can be mainly explained as a result of intermolecular H-bond formation between ethanol and the lone pair of electrons of the oxazine-oxygen/pyrazolo-nitrogen (5b) and/or oxazolo oxygen/nitrogen for 11c. Thus, the mobility of the attached π-electrons to the conjugated pathway is decreased and consequently the observed high excitation energy needed in an ethanolic medium is relative to the other organic solvents used. The hypsochromic shift observed in the λ_{max} of the CT band of dyes (5b, 11c) in water relative to ethanol, as well as the lower extinction coefficient, can be mainly ascribed to the stronger interaction of the H_2O molecule with the lone pair of electrons of the oxazine-oxygen/pyrazolo-nitrogen (5b) and/or oxazolo-oxygen/nitrogen (11c) atoms through hydrogen bonding.

2.4 *Spectral behaviour of N-ethyl pyrazolo (pyrazolium-2yl) [2,3-b; 2',3'-b'] oxazine-3(4)-monomethine cyanine dye (5b) in mixed solvents*

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 ethanol or DMF. The visible spectrum of dye (5b) in DMF/ethanol mixture showed a gradual hypsochromic shift and an increase in the absorbance of the CT band with increasing proportion of ethanol, while in DMF/CCl_4 mixture, it showed hypsochromic shift and the existence of a well-defined isobestic point with increasing proportion of ethanol (figure 2). Appearance of the isobestic point is convincing evidence for the existence of compound 5b in tautomeric equilibrium.

It is interesting to verify H-bond formation between the solute 5b and ethanol or DMF by calculating the free energy change of formation (ΔG) of the molecular complex using the relation,

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

The stability constant (K_f) of the complex can be determined from a consideration of the behaviour in mixed solvents (El-Shahawy *et al* 1987; Koraiem *et al* 1991) using the relation (figure 3),

$$\log K_f = \log \frac{A - A_{min}}{A_{max} - A} - n \log C_{EtOH}. \tag{2}$$

The values of K_f, ΔG and n (the number of EtOH or DMF molecules which are complexed with the solute molecule) indicate that a 1:1 complex is formed (table 4b).

The plot of the spectral shifts ($\Delta\nu$) of the CT band as a function of $(D-1)/(D+1)$ (Abd El-Mottaleb and Khalil 1979) is nonlinear (figure 4). Therefore, the CT band shift is governed by other factors in addition to the dielectric constant (D) of the medium (Idriss *et al* 1985). These factors include solute–solvent interaction.

On plotting the excitation energy (E) of the CT band in the mixed solvent vs the solvent mole fraction, a broken line with three segments is obtained (figure 5). The first segment indicates the orientation of the solvent molecules around the solute molecule. The second segment represents molecular complex formation, while the third

Table 4(a). Electronic absorption spectra [λ_{max} nm (ε_{max} mol^{-1} cm^2) characteristic of mono- and tri-methine cyanine dyes (5b, 11c) in different single solvents.

Compound	Water	DMF	EtOH	$CHCl_3$	CCl_4	Dioxane
5b	350(5700)	350(8660)	350(7300)	375(4800)	370(4680)	370(5000)
	442(6600)	—	447(6800)	448(8460)	449(9500)	448(8600)
	—	539(3500)	525(4900)	—	—	—
11c	395(4000)	415(4798)	395(7806)	410(6060)	415(4840)	415(7060)
	490(6080)	509(7600)	500(15120)	507(9600)	507(6760)	505(9000)
	595(2400)	590(3200)	590(4800)	585(4400)	588(3240)	585(4560)
	—	690(0960)	690(1194)	690(1900)	—	—

Table 4(b). Commutative data obtained for monomethine cyanine dye (5b) in mixed solvents.

Compound	Mixed-solvent systems	Excitation energy single	solvents	Orientation energy*	H-bond energy*	Total energy*	n	LogK_f	K_f	ΔG (kcal mol^{-1})
5b	(DMF–EtOH)	53·96 (DMF)	56·63 (EtOH)	0·5	0·34	0·84	1	0·78	6·03	0·97
	(CCl_4–DMF)	63·70 (CCl_4)	60·85 (DMF)	−0·2	−0·6	−0·8	1	1·11	12·88	1·39

*kcal mol^{-1}

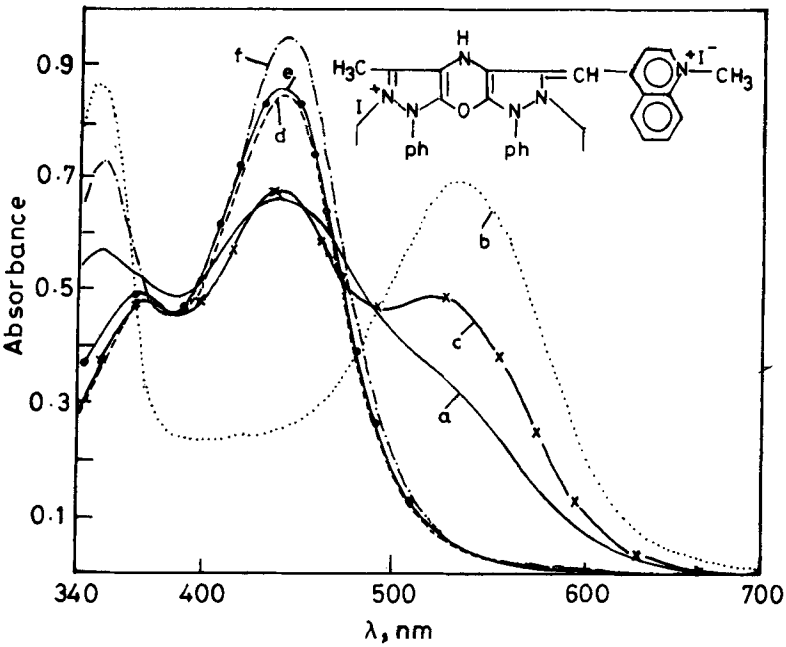
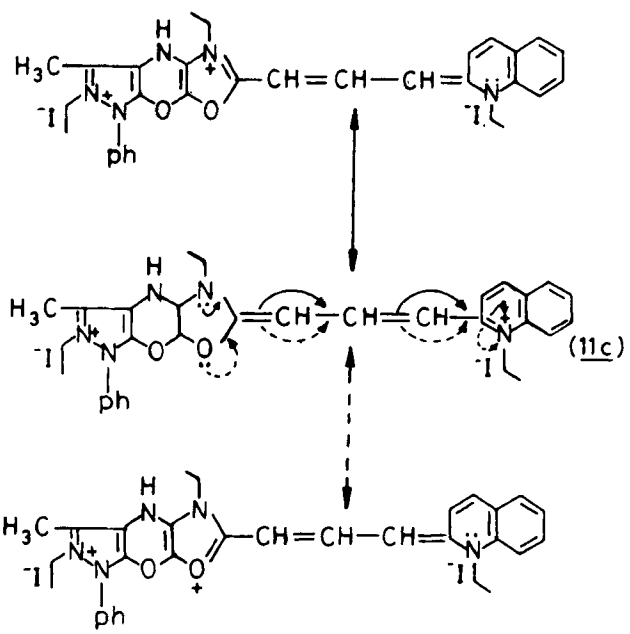


Figure 1. Electronic absorption spectra of 1×10^{-4} M monomethine cyanine 5b at 27°C in (a) H_2O, (b) DMF, (c) EtOH, (d) $CHCl_3$, (e) CCl_4 and (f) dioxane.



Scheme 3. CT transition for dye 11c

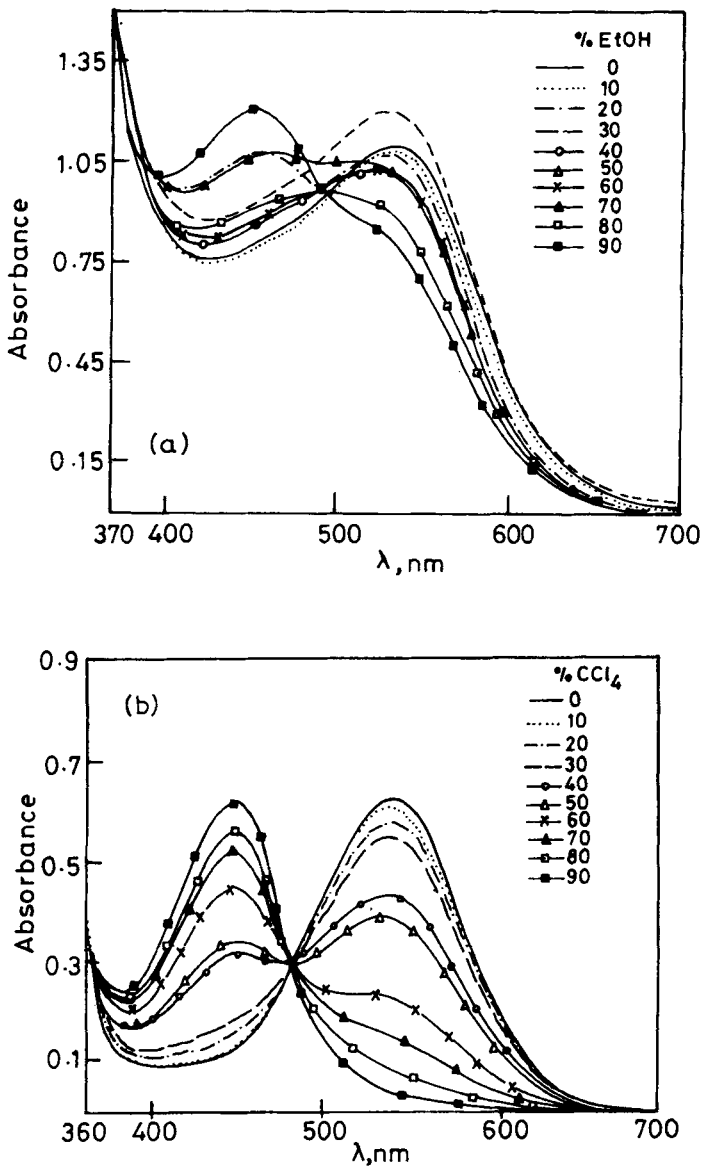


Figure 2. Electronic absorption spectra of 1×10^{-5} M monomethine cyanine 5b at 27°C in DMF/EtOH (**a**) and DMF/CCl_4 (**b**) mixtures.

represents the steady state of the energy attained after the complete formation of the molecular complex. Values of orientation and H-bond energies are given in table 4b.

2.5 *Acid-base properties of some selected newly synthesised cyanine dyes (5b, 11c and 11g) in aqueous universal buffer solution*

The ethanolic solutions of some selected monomethine cyanines (5b) and trimethine cyanines (11c and 11g) gave a permanent colour in basic medium which discharged

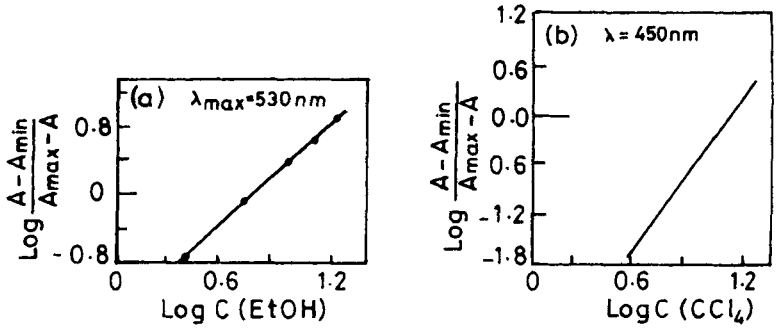


Figure 3. $\text{Log}[(A - A_{min})/(A_{max} - A)]$ vs. $\log C_{EtOH}$ (**a**), and vs. $\log C_{ccl_4}$ (**b**), at 27°C, for 5b in DMF/EtOH and DMF/CCl_4 mixtures respectively.

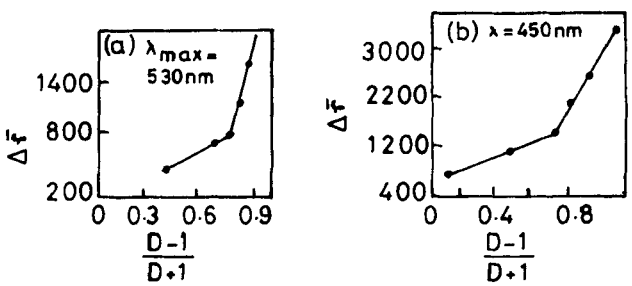


Figure 4. CT band shifts ($\Delta\bar{\nu}$) vs. $(D-1)/(D+1)$ at 27°C for 5b in DMF/EtOH (**a**) and DMF/CCl_4 (**b**) mixtures.

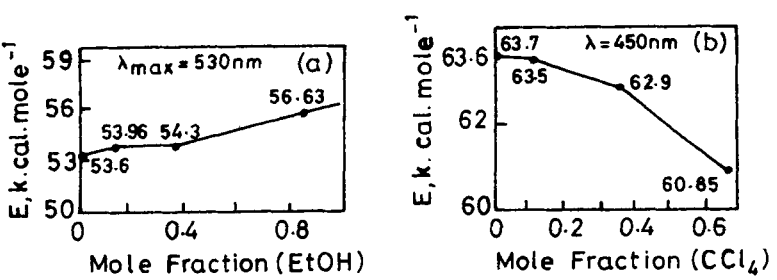


Figure 5. CT band excitation energy E_{vs}. EtOH (CCl_4) mole fraction at 27°C for 5b in DMF/EtOH (DMF/CCl_4) mixtures (**a**(**b**)).

on acidification. This prompted us to study their spectral behaviours in different aqueous buffer solutions in order to ensure optimal *p*H in their application. The effectiveness of the compounds as photosensitizers increases when they are present in ionic form, which has a higher planarity (Mahmoud *et al* 1975).

The electronic absorption spectra of cyanine dyes (5b, 11c and 11g) in aqueous buffer solutions of varying *p*H values (1·8–12·00) show regular changes with increasing *p*H of the medium, especially the CT bands (table 5). Increasing the *p*H of the medium results in an increase in absorbance of the CT bands. As the *p*H of the medium decreases, the extinction of these bands become lower and disappear at *p*H < 4·54. This behaviour can be interpreted on the principle that the oxazine-oxygen and/or oxazole-oxygen (nitrogen) atoms become protonated in solutions of

Table 5. The variation of absorbance in λ_{max} characteristics of selected compounds in different aqueous universal buffer solutions. Values in parentheses in column headings are λ_{max} values.

Compound *p*H	5b (530)	11c (500)	11g (560)
1·84	0·27	0·40	0·20
2·30	0·39	0·50	0·23
3·50	—	0·69	0·36
4·54	0·42	0·76	0·40
7·00	0·77	0·73	0·42
8·62	0·78	0·74	0·41
9·57	0·78	0·71	0·43
10·30	0·77	—	—
10·98	0·75	—	—
11·40	0·73	0·67	0·41
12·00	0·68	—	—
pK_a	8·5	5·25	4·7, 8·8

low *p*H and therefore, the CT interaction within the protonated form is expected to be difficult, i.e. the protonated form does not absorb energy in the visible region. On the other hand, as the *p*H of the medium increases ($pH > 7{\cdot}00$), the protonated compounds become deprotonated and therefore, their mesomeric interactions with the rest of the molecule are intensified. Consequently, the CT interaction within the free base is facilitated, i.e. the free base absorbs energy in the visible region.

The recorded visible absorption spectra of dyes (5b, 11c, 11g) in aqueous buffer solutions of different *p*H values were applied to the spectrophotometric determination of the pK_a values. The absorbance-*p*H curves are typical dissociation curves, supporting the acid–base equilibrium. The acid dissociation constant (pK_a) was determined from the variation of absorbance with *p*H using spectrophotometric half-height, limiting absorbance and Colleter methods (Colleter 1960; Issa *et al* 1970).

The ionic (non-protonated) form of monomethine cyanine dye (5b) at $pH > 4{\cdot}54$ reveal pK_a (8·5). While the trimethine cyanine (11c) and meso-substituted trimethine cyanine (11g) have ionic forms at *p*H values $> 3{\cdot}5$ and $> 2{\cdot}3$ and reveal $pK_a = 5{\cdot}25$ and 4·7 at *p*H 8·8 respectively. The higher planarity in case of trimethine cyanines (11c, 11g) appears in the lower *p*H values of their ionic (non-protonated) forms. This is due to the mesomeric effect of the increasing number of methine groups in dye (11c) and the hyperconjugative effect of the meso-substituted group in the dye (11g).

3. Experimental

3.1 *General*

All melting points are uncorrected. The IR spectra were determined with a Perkin–Elmer Infrared 127β spectrophotometer. The UV-visible absorption spectra were recorded on a Shimadzu UV-vis recording spectrophotometer UV-240. The ^{1}H NMR spectra were recorded with a EM-390 90 HHZ NMR spectrometer.

4-Amino-(bromo)-3-methyl-1-phenyl pyrazolone and 4-bromo-oxazole were prepared as described earlier (Khaikin *et al* 1965).

3.2 *Solutions*

Stock solutions of the dyes were of the order 10^{-3} M. Solutions of low molarities used in spectral measurements were obtained by accurate dilution.

An accurate volume of 10^{-3} M DMF solution of the dye was placed in a 10 ml measuring flask containing the required volume of DMF, then made up to the required volume with the other solvent (EtOH or CCl_4) to study the spectral behaviour in mixed solvents.

An accurate volume of 10^{-3} M ethanolic solution of the dye was added to 5 ml of buffer solution in a 10 ml measuring flask and then made up to the required volume with redistilled water. The *p*H of this solution was checked before making spectral measurements. A modified buffer series derived in a way similar to that of Britton (1952) was prepared.

3.3 *Synthesis of 3,5-dimethyl-1,7-diphenyl pyrazolo [2,3-b; 2',3'-b'] oxazine and/or 3,6-dimethyl-1-phenyl pyrazolo [2,3-b] oxazole [2',3'-b'] oxazine moieties (1a and 1b)*

Equimolar ratios of 4-amino-3-methyl-1-phenyl pyrazolone (0·01 M) and 4-bromo-3(2)-methyl-1-phenyl pyrazol(oxazole)-5-one (0.01 M) were dissolved in ethanol and 5–7 drops of pyridine was added. The reaction mixture was refluxed for 10–12 h, filtered hot and then cooled. The precipitated products were separated after dilution with water and crystallised from ethanol (table 1).

3.4 *Synthesis of 3,5-dimethyl-bis pyrazolium-2,6-yl [2,3-b; 2',3'-b'] oxazine and/or 3,6-dimethyl pyrazolium-2yl [2,3-b] oxazolium-5yl [2',3'-b']-oxazine moieties (2a and 2b)*

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

3.5 *Synthesis of asymmetrical/symmetrical bis-pyrazolium-2,6yl [2,3-b; 2',3'-b'] oxazine and pyrazolium-2yl [2,3-b] oxazolium-5yl [2',3'-b'] oxazine 3-/6- or bis-3,5/3,6-styryl/bis-styryl cyanines (3a–d and 4a–d)*

A mixture of (2a, 2b; 0·01 M) and aromatic aldehydes (benzaldehyde, *p*-methoxy benzaldehyde and *p*-nitrobenzaldehyde, 0·01/0·02 mol) were dissolved in ethanol (50 ml) and 3–5 drops of piperidine was added. The reaction mixture was refluxed for 12–14 h, filtered hot, concentrated and cooled, and then acidified with acetic acid. The products were precipitated on dilution with water and crystallized from ethanol to give the corresponding compounds (3a–d) and (4a–d) respectively. Relevant data for them are given in table 3.

3.6 *Synthesis of asymmetrical N-ethyl pyrazolo-/oxazolo-[2,3-b] pyrazolium-2yl [2',3'-b']oxazine 3(6)[4(1)]-monomethine cyanines (5a–d) and symmetrical bis-N,N-ethyl pyrazolo [2,3-b; 2',3'-b'] oxazine or N-ethyl pyrazolo [2,3-b]-N-ethyl oxazolo [2',3'-b'] oxazine bis 3,5(3,6)[4(1)]-monomethine cyanine dyes (6a–d)*

Equi-/bimolar amounts of methyl quaternary salts (pyridinium, quinolinium and isoquinolinium iodide, 0·01/0·02 mol) and compounds (2a, 2b; 0.01 M) were dissolved in ethanol (30 ml) and 3–5 drops of piperidine was added. The reaction mixture was refluxed for 8–10 h, filtered hot, concentrated and cooled, and then acidified

with acetic acid. The precipitated products after dilution with water were collected and recrystallised from aqueous ethanol. The results are listed in table 3.

3.7 *Synthesis of asymmetrical N-ethyl pyrazolo-/oxazolo-[2,3-b]pyrazolium-2yl[2',3'-b']oxazine-3(6)[2(2)] tri-/meso substituted tri-methine cyanine dyes (11a–g) and/or symmetrical bis-N,N-ethyl pyrazolo [2,3-b;2',3'-b']oxazine, N-ethyl pyrazolo[2,3-b]-N-ethyl oxazolo[2,'3'-b']oxazine bis 3,5(3,6)[2(2)] tri-/meso substituted tri-methine cyanine dyes (12a–g)*

(a) A mixture of (2a, 2b; 0·01M) and equi-/bimolar ratios of ethylorthoformate and/or acid amide (acetamide, trifluoroacetamide and benzamide, 0·01/0·02 mol) were refluxed in ethanol (30 ml) containing piperidine (3–6 drops) for 6–8 h. The reaction mixture was filtered hot, allowed to cool and the precipitated products were collected and recrystallized from aqueous ethanol to give the intermediate compounds (7a, b, 8a, b, 9a, b and 10a, b), table 1.
(b) To a mixture of the latter, the intermediate compounds (0·01M) and equi-/bi molar ratios of 2-methyl quaternary salts in ethanol (40 ml) and a few drops of piperidine were added. The reaction mixture was refluxed for 8–10 h, filtered hot and cooled. The products (11a–g and 12a–g) were separated out on dilution with water and recrystallised from absolute ethanol (table 3).

4. Conclusions

The spectral behaviour of the newly synthesised cyanine dyes (3a–d, 4a–d, 5a–d, 6a–d, 11a–g and 12a–g) reveals a criterion for the direct relation between the absorption spectra and photosensitization effects. The results of such behaviour showed that the position of absorption bands and their molar extinction coefficients are influenced by heterocyclic quaternary residue (their linkage position), nature of the involved condensed triheterocyclic moieties and type of cyanine molecules. Thus, the quinolinium-4-yl in both asymmetrical (symmetrical) dyes incorporating the same condensed triheterocyclics are more sensitive as photosensitizers than those of quinolinium-1-yl or pyridinium-4-yl cyanine analogues especially of the monomethine type.

Additionally, it is obvious that asymmetrical (symmetrical) dyes involving quinolinium-2-yl salt are more photosensitive than those of the trimethine series involving pyridinium-2-yl salt (11a–g, 12a–g) as they have high absorption values in their spectra.

The results also show that absorption values of the newly synthesised dyes incorporating condensed tri-heterocyclics are influenced by the nature of such heterocyclic moieties. Thus, the oxazole conjugated with pyrazolo [2,3-*b*] oxazine in the asymmetrical (symmetrical) styryl, mono-, tri- and meso-substituted tri-methine type of compounds might exhibit greater photosensitization than conjugated pyrazole analogues as they have high spectral absorption values.

Also, all asymmetrical styryl, mono-, tri- and meso-substituted tri-methine cyanines might be more photosensitive than their symmetrical analogues.

Further, it is obvious that increasing the number of methine groups in both asymmetrical (symmetrical) trimethine types increases their absorption values and makes them more photosensitive than their monomethine analogues. On the other hand, diene side chain substitution in meso-trimethine types with electron-donating

groups (e.g. CH_3, C_6H_5) makes them more photosensitive than the unsubstituted compounds or those substituted with electron-withdrawing group (e.g.CF_3).

The solvatochromic behaviour of some selected cyanine dyes (5b, 11c), in pure organic solvents of different polarities (H_2O, DMF, EtOH, $CHCl_3$, CCl_4 and dioxane) showed that the CT bands exhibit a hypsochromic shift in ethanol and water media relative to DMF, $CHCl_3$, CCl_4 and dioxane media. This is due to both increase in solvent polarity and solute–solvent interaction through H-bonding.

Also, the solvatochromic behaviour of selected monomethine cyanine dyes (5b) in mixed solvents reveals the possibility of the formation of H-bond solvated complexes.

In view of the mediachromic behaviour of some selected newly synthesised cyanine dyes (5b, 11c and 11g)—in aqueous universal buffer solution and the values of their dissociation (protonation) constant (pK_a), it is concluded that they possess basic character and may be used as photosensitizers in both acidic and basic media. The degree of the basic character of such dyes is of the order of 11g > 11c > 5b.

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