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Electronic Absorption Spectral Studies on New Dimethine Cyanine Dyes

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ABSTRACT

New asymmetrical dimethine cyanine dyes were prepared by the condensation of 4-benzylideno-oxazol-/imidazol-5-one-2-carboxaldehyde derivatives with 2-methylpyridinium(quinolinium)-2-yl salts. Cyclocondensation reaction of these dyes with urea gave new asymmetrical oxazolo(imidazo)-[4,5-d]-pyrimidine-2(2)-dimethine cyanines. The ultraviolet and visible absorption spectra of some selected dyes were investigated in single and mixed solvents, and also in aqueous buffer solutions. Molecular complex formation with ethanol was verified through mixed-solvent studies. Electronic transitions have been attributed to either locally excited or predominantly charge-transfer states. The spectral shifts are discussed in relation to molecular structure and in terms of medium effects. The variation of absorbance with pH is utilised for the determination of pKa values for some selected compounds.

1 INTRODUCTION

Dimethine cyanine dyes[1–5] find extensive application as photosensitisers for silver halide emulsions,[6–9] textile dyes[10] and as bacteriocidal agents.[11] In the present work, 4-benzylideno-oxazol(imidazol)-5-one-2-carboxaldehyde derivatives (**2a–2g**) were prepared as intermediates for the synthesis of a series of new asymmetrical dimethine cyanines (**3a–3h** and **4a–4e**). A correlation

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was established between molecular structure and spectral behaviour of the compounds.

2 RESULTS AND DISCUSSION

2.1 Synthesis

Selective oxidation of 4-benzylideno-2-methyl-oxazol(imidazol)-5-one[12] (**1a–1g**) using SeO_2[13] in dioxane gave the corresponding 2-carboxaldehyde derivatives (**2a–2g**) in satisfactory yields (Table 1, part I). Further reaction of equimolar ratios of **2a–2g** and methyl quaternary salts in the presence of alcohol and piperidine afforded the corresponding asymmetrical dimethine cyanines **3a–3h** (Table 1, part II). The condensation reaction took place through the acyclic aldehydic group, as outlined in Scheme 1.

The cyclocondensation reaction of the dimethine cyanines **3a–3c**, **3f** and **3h** with urea in ethanol containing conc. HCl produced the biheterocyclic dimethine cyanines, viz. oxazolo- or imidazo-[4,5-d]pyrimidine-2(2)-dimethine cyanines **4a–4e** (Table 1, part III). These dyes were also obtained by the direct interaction of oxazolo(imidazo)-[4,5-*d*]pyrimidine-2-carboxaldehyde **5a–5d**[13] with 2-methyl quaternary salts using piperidine as catalyst (Scheme 1).

The structures of compounds **3a–3h** and **4a–4e** were confirmed by elemental analysis (Table 1, parts II and III), IR and ^{1}H-NMR spectral data. Both series of compounds were deeply coloured and were partially soluble in non-polar solvents, in which they gave red to blue solutions with a green fluorescence. They were readily soluble in most polar solvents, giving reddish-violet or intense violet solutions with a slight or intense green fluorescence depending on the solvent. They were soluble in conc. H_2SO_4, liberating iodine vapour on warming. Their ethanolic solutions gave a violet colour in alkaline medium, discharged on acidification.

2.2 Relation between molecular structure and spectral behaviour of the cyanines

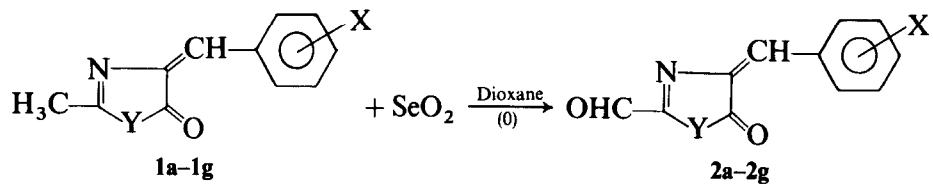
The λ_{max} and ε_{max} values for compounds **3a–3h** in ethanol are collated in Table 2. Substituting A = H in compound **3a** by A = C_6H_4-2-yl salt moiety in compound **3b** resulted in red shifts of 5 and 18 nm in the bands at 515 and 542 nm, respectively, accompanied by the appearance of two new shoulders at 593 and 658 nm. This could be attributed to the more extensive π-delocalisation in compound **3b**.

The visible absorption spectra of **3b–3g** depends on the nature of the

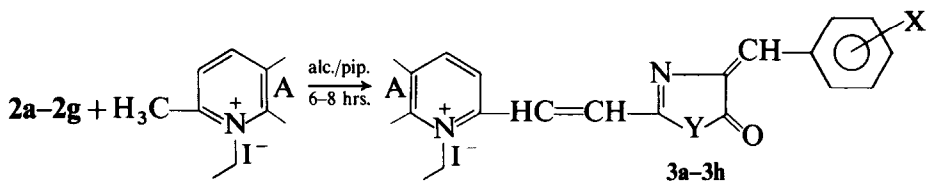
TABLE 1

Characterisation Data for 4-Benzylideno-oxazol(imidazo)-5-one-2-carboxaldehyde (**2a–2g**) and Dimethine Cyanine Dyes (**3g–3h** and **4a–4e**)

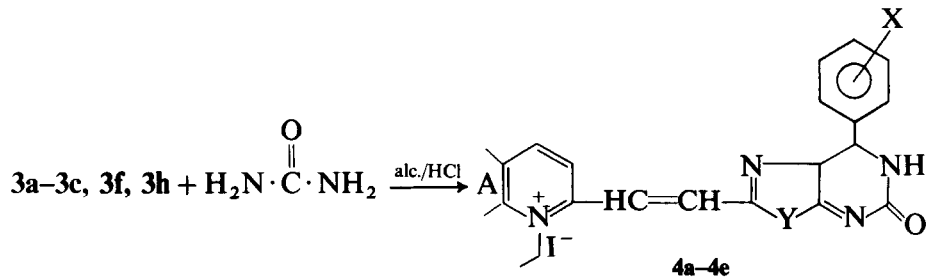
Compound no.	*M.p.* (°C)	*Yield* (%)	*Molecular formula* (*Mol. wt*)	*Colour of crystals*	*Elemental analysis, Calculated* (*Found*) (%)		
					C	*H*	*N*
I Compounds **2a–2g**							
2a	185	70	$C_{11}H_{17}NO_3$ (201)	Yellow	65·7 (65·5)	3·5 (3·7)	7·0 (6·7)
2b	195	65	$C_{12}H_9NO_4$ (231)	Yellow–orange	62·3 (62·3)	3·9 (3·7)	6·1 (6·1)
2c	118	50	$C_{11}H_6N_2O_5$ (246)	Orange	53·7 (53·9)	2·4 (2·1)	11·4 (11·3)
2d	125	55	$C_{11}H_6N_2O_5$ (246)	Yellow	53·7 (53·7)	2·4 (2·3)	11·4 (11·4)
2e	100	42	$C_{11}H_6N_2O_5$ (246)	Yellow	53·7 (53·7)	2·4 (2·4)	11·4 (11·3)
2f	205	53	$C_{11}H_7NO_4$ (217)	Pale yellow	60·8 (60·9)	3·2 (3·2)	6·45 (6·5)
2g	110	62	$C_{11}H_8N_2O_2$ (200)	Yellow	66·0 (65·9)	4·0 (3·7)	14·0 (13·95)
II Cyanine dyes **3a–3h**							
3a	200	17	$C_{19}H_{17}N_2O_2I$ (432)	Scarlet violet	52·8 (52·8)	3·9 (3·9)	6·5 (6·5)
3b	185	70	$C_{23}H_{19}N_2O_2I$ (482)	Intense violet	57·3 (57·3)	3·9 (3·9)	5·8 (6·0)
3c	180	62	$C_{24}H_{21}N_2O_3I$ (512)	Bluish violet	56·25 (56·3)	4·1 (4·1)	5·5 (5·5)
3d	150	69	$C_{23}H_{18}N_3O_4I$ (527)	Intense violet	52·4 (52·4)	3·4 (3·4)	8·0 (8·0)
3e	225	78	$C_{23}H_{18}N_3O_4I$ (527)	Intense violet	52·4 (52·5)	3·4 (3·4)	8·0 (8·0)
3f	175	65	$C_{23}H_{18}N_3O_4I$ (527)	Intense violet	52·4 (52·5)	3·4 (3·45)	8·0 (7·9)
3g	170	73	$C_{23}H_{19}N_2O_3I$ (598)	Violet	55·4 (55·45)	3·8 (3·9)	5·6 (5·6)
3h	178	71	$C_{23}H_{20}N_3OI$ (481)	Bluish violet	57·4 (57·4)	4·2 (4·15)	8·7 (8·8)
III Cyanine dyes **4a–4e**							
4a	218	30	$C_{20}H_{19}N_4O_2I$ (474)	Brown	50·6 (50·7)	4·0 (4·1)	11·8 (11·8)
4b	177	65	$C_{24}H_{21}N_4O_2I$ (524)	Intense violet	55·0 (55·0)	4·0 (4·0)	10·7 (10·7)
4c	182	75	$C_{25}H_{23}N_4O_3I$ (554)	Bluish violet	54·15 (54·2)	4·15 (4·15)	10·1 (10·1)
4d	195	70	$C_{24}H_{21}N_5O_4I$ (569)	Bluish violet	50·6 (50·7)	3·7 (3·7)	12·3 (12·3)
4e	168	68	$C_{24}H_{22}N_5OI$ (523)	Intense violet	55·1 (55·1)	4·2 (4·2)	13·4 (13·4)



Compound	$1_a, 2_a$	$1_b, 2_b$	$1_c, 2_c$	$1_d, 2_d$	$1_e, 2_e$	$1_f, 2_f$	$1_g, 2_g$
Y =	O	O	O	O	O	O	NH
X =	H	*p*-OCH_3	*p*-NO_2	*o*-NO_2	*m*-NO_2	*p*-OH	H

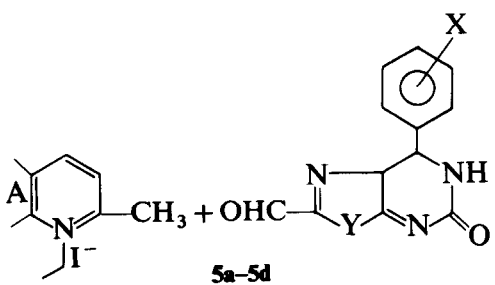


Compound	3_a	3_b	3_c	3_d	3_e	3_f	3_g	3_h
Y =	O	O	O	O	O	O	O	NH
A =	H-2yl-salt	C_6H_4-2yl-salt	C_6H_4-2yl-salt	C_6H_4-2yl-salt	C_6H_4-2yl-salt	C_6H_4-2yl-salt	C_6H_4-2yl-salt	C_6H_4-2yl-salt
X =	H	H	*p*-OCH_3	*p*-NO_2	*o*-NO_2	*m*-NO_2	*p*-OH	H



4a–4e

Compound	4_a	4_b	4_c	4_d	4_e
Y =	O	O	O	O	NH
A =	H-2yl-salt	C_6H_4-2yl-salt	C_6H_4-2yl-salt	C_6H_4-2yl-salt	C_6H_4-2yl-salt
X =	H	H	*p*-OCH_3	*m*-NO_2	H



5a–5d

Compound	5_a	5_b	5_c	5_d
Y =	O	O	O	NH
X =	H	*p*-OCH_3	*m*-NO_2	H

Scheme 1

TABLE 2

Visible Absorption Spectral[a] Characteristics of the Dimethine Cyanine Dyes **3a–3h** and **4a–4e** in Ethanol at 27°C

I Cyanine dyes ***3a–3h***

3a	***3b***	***3c***	***3d***	***3e***	***3f***	***3g***	***3h***
490 sh (10·564)	490 sh (12·460)	490 sh (9·751)	—	473 (12·510)	—	490 sh (10·022)	—
515 sh (14·356)	520 (15·065)	520 (11·490)	532 sh (13·544)	—	525 sh (10·970)	519 (9·961)	521 sh (8·803)
542 (18·961)	560 (18·961)	560 (19·286)	567 (20·134)	567 (15·732)	563 (17·531)	561 (14·492)	561 (13·826)
—	593 sh (14·356)	595 sh (11·918)	—	576 sh (16·929)	587 sh (15·575)	596 sh (12·460)	590 (13·116)
—	658 sh (4·416)	658 sh (4·310)	663 (4·720)	658 sh (6·400)	663 sh (3·802)	658 sh (4·430)	658 sh (3·310)

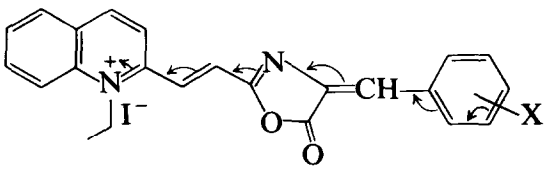
II Cyanine dyes ***4a–4e***

4a	***4b***	***4c***	***4d***	***4e***
465 (14·285)	480 sh (3·896)	—	—	480 sh (6·513)
—	520 (9·136)	520 (8·956)	520 (8·736)	518 (9·256)
540 sh (9·090)	560 (13·351)	560 (13·311)	560 (12·691)	560 (13·311)
—	603 (17·016)	603 (16·216)	603 (14·996)	602 (17·151)

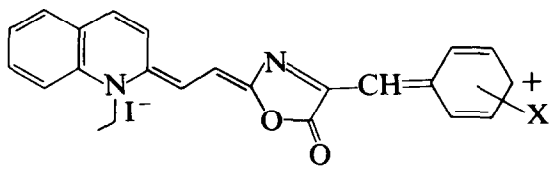
[a] Data shown are λ_{max}(nm) with ε_{max}(mol^{-1} cm^2) in parentheses; sh = shoulder.

substituent as well as its position within the benzylidene moiety (Table 2, part I).

The shoulder within the range 576–596 nm is influenced by the type of substituent (X), this being attributable to an electronic transition involving the whole molecule associated with intramolecular charge transfer. This charge transfer (CT) seems to originate from the 4-aryl residue as a source to the positively charged heterocyclic quaternary (N) atom as a sink. The CT taking place within the solute molecule can be represented schematically as follows:



Ground state



Excited state

The absorption band observed within the range 560–567 nm shows slight red shifts of 7, 3 and 7 nm on introducing a nitro group into the *o*-, *m*- and *p*-positions respectively, of the aryl residue. This shift can be attributed to the electronic effect of these substituents, i.e. an intramolecular CT to the pendant ring.

The visible absorption bands of the dimethine cyanine dyes **3a**–**3h** were slightly influenced by the nature of the heterocyclic moiety. Thus, the imidazolodimethine cyanine (**3h**) shows a CT band at 590 nm, hypsochromically shifted by 3 nm compared with the corresponding shoulder at 593 nm in the analogous oxazolodimethine derivative **3b**, (Table 2, part I). This may be attributed to the greater electron availability at the oxygen atom in the oxazolo moiety.

The visible absorption spectra of the biheterocyclic dimethine cyanines **4a**–**4e** in ethanol showed the absorption bands to be strongly red-shifted on increasing the conjugation of the quaternary heterocyclic residue (A). Thus the visible bands of the dimethine cyanine **4b**, incorporating A = C_6H_4-2yl salt, show larger red shifts (15–20 nm) than those of the analogue where A = H-2-yl salt (**4a**, Y = O, X = H), (Table 2, part II). This can be attributed to the more extensive π-delocalisation within the quaternary heterocyclic moiety of **4b**.

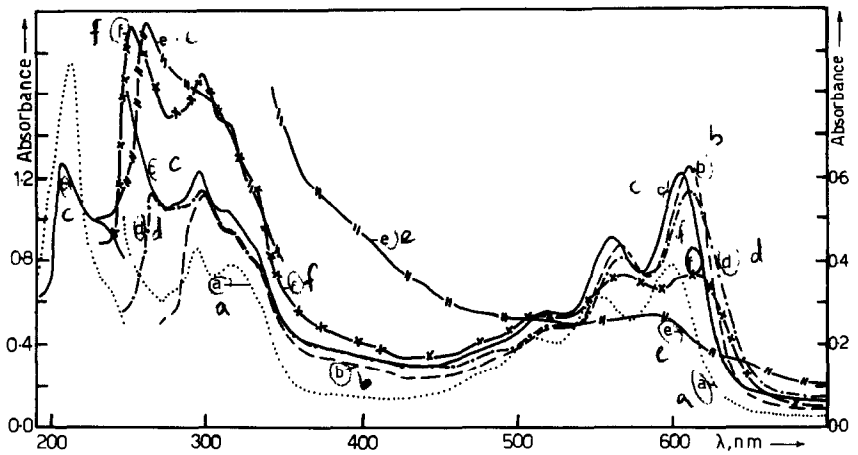


Fig. 1. Electronic absorption spectra of $3{\cdot}58 \times 10^{-5}$ M-**4b** in (a) H_2O; (b) DMF; (c) EtOH; (d) $CHCl_3$; (e) CCl_4; (f) dioxane, at 27°C.

It can be seen that the conjunction of the pyrimidine nucleus in **4b** causes a red shift of 10 nm with regard to the 593 nm band in the precursor **3b**, with increase in intensity of the band (cf. Table 2).

2.3 Solvatochromic behaviour of oxazolo[4,5-*d*]pyrimidine-2(2)-dimethine cyanine (4b) in pure solvents

The electronic absorption spectra of the dimethine cyanine **4b** in solvents of different polarities (H_2O, DMF, EtOH, $CHCl_3$, CCl_4 and dioxane) are shown in Fig. 1. The λ_{max} and ε_{max} values of the absorption bands are given in Table 3.

TABLE 3

Electronic Absorption Spectral[a] Characteristics of the Oxazolo[3,4-*d*]pyrimidine-2(2)-dimethine Cyanine **4b** in Single Solvents at 27°C

H_2O	*DMF*	*EtOH*	*$CHCl_3$*	*CCl_4*	*Dioxane*
211 (43·979)	—	208 (29·320)	—	—	—
230 sh (13·089)	—	230 sh (23·142)	—	—	—
294 (12·566)	297 (15·707)	295 (17·121)	297 (16·021)	295 sh (40·314)	297 (22·539)
315 (11·754)	314 sh (13·613)	314 (14·147)	314 sh (13·874)	314 sh (36·126)	313 (19·791)
512 (7·697)	528 sh (8·325)	520 (9·136)	526 (8·325)	515 sh (8·744)	513 (8·901)
553 (9·948)	566 (12·827)	560 (13·351)	567 (12·147)	—	568 (11·257)
598 (11·780)	610 (17·278)	603 (17·016)	610 (15·969)	630 sh (6·597)	612 (11·204)

[a] Data shown are λ_{max}(nm) with ε_{max}(mol^{-1} cm^2) in parentheses; sh = shoulder.

The spectrum in ethanol exhibits seven absorption bands. The UV bands, located at up to 314 nm, can be assigned to π–π^* transitions of the benzenoid and heterocyclic rings. These bands are little influenced by change in the solvent polarity. The other bands at longer wavelengths can be attributed to n–π^* transitions and to intramolecular charge-transfer (CT) interaction.[14] The observed spectral shifts are consistent with a CT across the chromogen.

The visible band at 603 nm in ethanol can be ascribed to an intramolecular CT transition. The good linear relationship, passing through the origin, obtained on plotting the absorbance of this band versus the molar concentration supports the idea that the transition of this band is intramolecular across the chromogen. Furthermore, the high molar extinction coefficient of this band is in accordance with its CT nature.

Examination of the results reported in Table 3 reveals that the bands corresponding to n–π^* and CT transitions show a slight red shift on changing the solvent from EtOH to DMF, $CHCl_3$, dioxane and CCl_4. The small blue shift observed in ethanol may be explained as a result of hydrogen bonding between the ethanol and the lone pair of electrons of the oxazolo-nitrogen atom. This results in a slight decrease in the electron density of the nitrogen atom, and consequently decreases to some extent the mobility of the attached π-electrons to the conjugated pathway. The slight blue shift observed in the λ_{max} of the CT band in H_2O (598 nm, 11 780 mol^{-1} cm^2) relative to ethanol (603, 17 016 mol^{-1} cm^2), 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 oxazolo-nitrogen atom through hydrogen bonding.

2.4 Spectral behaviour of oxazolo[4,5-*d*]pyrimidine-2(2)-dimethine cyanine (4b) 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 water. The visible spectrum of compound **4b** in $CHCl_3$ and H_2O containing progressively increasing quantities of EtOH, showed (Fig. 2) an increase in the absorbance of the CT band with increasing proportion of ethanol.

Evidence for hydrogen-bond formation between the solute molecules and ethanol or water can be obtained from data on the free energy change of formation (ΔG) of the molecular complex, calculated using the relationship (1).

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

The stability constant (K_f) of the complex can be determined from a

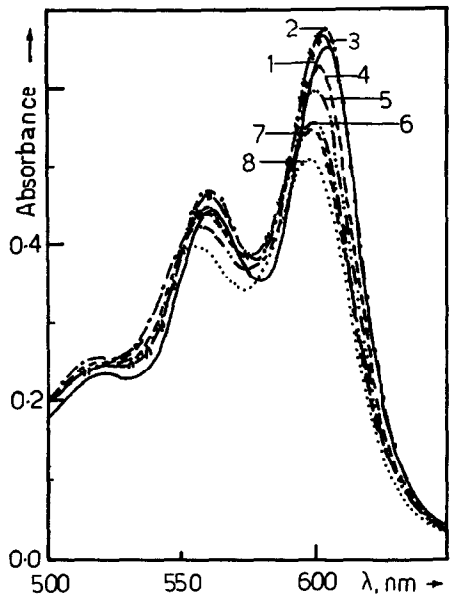


Fig. 2. Electronic absorption spectra of $3{\cdot}82 \times 10^{-5}$M dimethine cyanine **4b** in ethanol–water mixtures at 27°C. Water %(v/v): (1) 0·0; (2) 15·0; (3) 45·0; (4) 75·0; (5) 85·0; (6) 90·0; (7) 93·0; (8) 95·0.

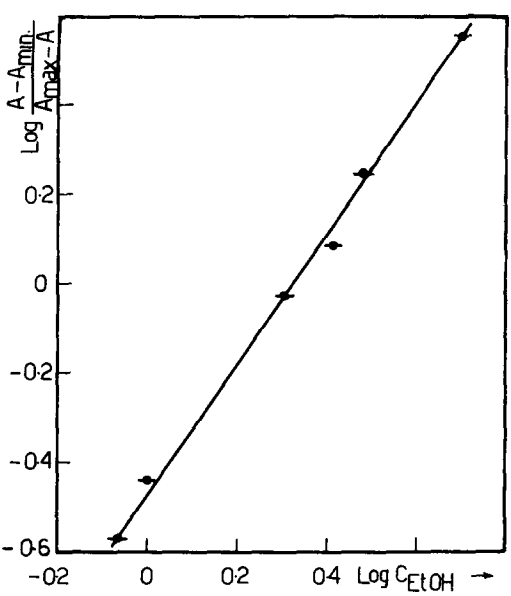


Fig. 3. Log $(A - A_{min}/A_{max} - A)$ versus log C_{EtOH} for compound **4b** in EtOH–$CHCl_3$ mixtures at 27°C.

TABLE 4
Data Obtained for the Cyanine Dye **4b** in Mixed Solvents at 27°C

System	*Excitation energy* ($kJ\,mol^{-1}$)		*Orientation energy* ($kJ\,mol^{-1}$)	*H-bond energy* ($kJ\,mol^{-1}$)	*n*	K_f	ΔG ($kJ\,mol^{-1}$)
	Pure solvent	*Pure EtOH*					
$CHCl_3$–EtOH	195·96 ($CHCl_3$)	197·92	0·33	1·00	1	0·474	1·860
H_2O–EtOH	199·89 (H_2O)	197·92	0·836	0·670	1	0·490	1·778

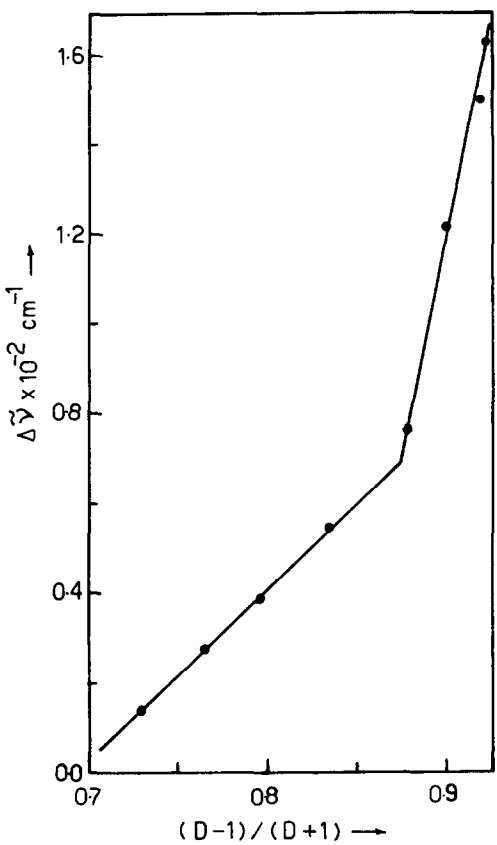


Fig. 4. CT band shifts ($\Delta\tilde{\nu}$) versus $(D-1)/(D+1)$ for compound **4b** in EtOH–$CHCl_3$ mixtures at 27°C.

consideration of the behaviour in mixed solvents[15,16] using the relationship (2)[17,18] (Fig. 3).

$$\log K_f = \log \frac{A - A_{min}}{A_{max} - A} - n \log C_{EtOH} \quad (2)$$

The values of K_f and ΔG of the hydrogen-bonded molecular complex liable to be formed in solution between the molecules of compound **4b** and EtOH or H_2O are given in Table 4. The values of K_f, ΔG and n (the number of EtOH or H_2O molecules which are complexed with the solute molecule) indicate that a 1:1 complex is formed.

The plot of $\Delta\tilde{\nu}$ of the CT band as a function of $(D-1)/(D+1)$ for compound **4b** is non-linear (Fig. 4).[19] Therefore, the CT band shift is governed by other factors in addition to the dielectric constant (D) of the medium. These factors include solute–solvent interaction.

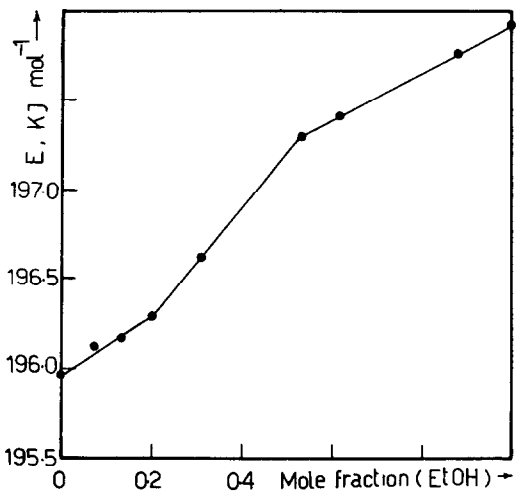


Fig. 5. CT band excitation energy (E) versus EtOH mole fraction for compound **4b** in EtOH–$CHCl_3$ mixtures at 27°C.

On plotting the excitation energy (E) of the CT band in the mixed solvent versus the ethanol mole fractions (Fig. 5), a broken line with three segments is obtained. The first segment indicates the orientation of the solvent molecules around the solute molecule.[18] The second segment represents the molecular complex formation, while the third segment represents the steady state of the energy attained after the complete formation of the molecular complex.[18] The values of orientation and hydrogen-bond energies are given in Table 4.

2.5 Acid–base properties of 4-benzylideneoxazol-5-one-2(2)-quinolinium-2-yl salt dimethine cyanine and its oxazolo[4,5-*d*]pyrimidine dimethine derivative (3b and 4b respectively) in aqueous universal buffers

The electronic absorption spectra of compounds **3b** and **4b** in aqueous buffer solutions of varying pH values (1·80–11·58) show regular changes with increase in the pH of the medium [Fig. 6(A) and (B)]. Increasing the pH results in an increase in the absorbance of the n–π^* and the CT bands for both compounds. In addition, the n–π^* bands show a red shift in their λ_{max}. As the pH of the medium decreases, the extinction coefficient of these bands becomes lower and the n–π^* bands show a blue shift in λ_{max}. This behaviour

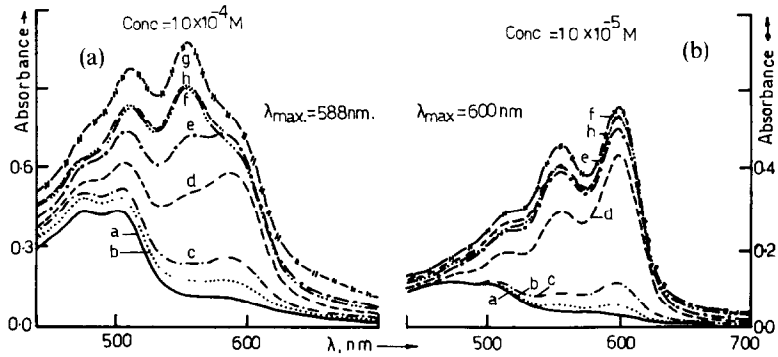


Fig. 6. Absorption spectra of dimethine cyanines (a) **3b** and (b) **4b** in aqueous universal buffer solutions of various pH values at 27°C: a, 1·80; b, 2·16; c, 3·29; d, 4·78; e, 5·60; f, 7·03; g, 10·14; h, 11·58.

can be interpreted on the basis that the hetero-nitrogen atom becomes protonated at low pH and therefore the CT interaction is inhibited and the protonated form does not absorb in the visible. As the pH increases, the oxazolo and oxazolo[4,5-*d*]pyrimidine become deprotonated and therefore mesomeric interaction with the rest of the molecule is enhanced and, consequently, CT interaction within the free base is facilitated, and the free base absorbs in the visible.

The visible absorption spectra of compounds **3b** and **4b** in aqueous buffer solutions of varying pH values were used in the spectrophotometric determination of the pK_a values of these compounds. The absorbance–pH curves are typical dissociation curves, supporting the acid–base equilibrium. The acid dissociation constants (pK_a) of the compounds were determined from the variation of absorbance with pH using the spectrophotometric half-height, limiting absorbance and Colleter methods.[20–23] The results obtained are listed in Table 5. The pK_a value of compound **4b** is higher than

TABLE 5
pK_a Values for Compounds **3b** and **4b** at 27°C

Compound	*Method*[a]			*Mean* pK_a
	a	*b*	*c*	
3b	4·20	4·15	4·25	4·20
4b	4·60	4·65	4·70	4·65

[a] Methods: a, Half-height: b, limiting absorbance; c, Colleter.

that of **3b** and this is in accord with the expected increase in electron-withdrawing power of the biheterocyclic moiety in **4b** relative to that of the heterocyclic moiety in **3b**.

3 EXPERIMENTAL

3.1 General

All melting points are uncorrected. The IR spectra (KBr) were determined on a Perkin–Elmer Infrared 127B spectrophotometer. The electronic absorption spectra were recorded on a Shimadzu UV–VIS recording spectrophotometer UV-240 and the ^{1}H-NMR on an EM-390 90 MHz NMR spectrometer.

4-Benzylideno-2-methyloxazol(imidazol)-5-one derivatives (**1a–1g**) were prepared in a way similar to that described earlier.[12]

Stock solutions of the dyes ($1{\cdot}0 \times 10^{-3}$M) were prepared. The solutions used in spectral measurements were obtained by appropriate dilution. For mixed-solvent studies, an accurate volume of $1{\cdot}0 \times 10^{-3}$M-ethanolic solution of the dye was added to the required volume of ethanol and the solution made up to 10 ml with the other solvent ($CHCl_3$ or H_2O). For pH studies, an accurate volume of $1{\cdot}0 \times 10^{-3}$M-ethanolic solution of the dye was added to 5 ml of the buffer solution in a 10-ml measuring flask. A modified buffer series derived from that of Britton[24] was used.

3.2 Synthesis of 4-benzylideno-oxazol/imidazol-5-one-2-carboxaldehyde (2a–2g)

Compounds **1a–1g** (0·01 mol) and selenium dioxide (0·013 mol) were dissolved in dioxane or acetic acid (20 ml) and the mixture refluxed for 8 h. The liquor was filtered from deposited selenium metal and the products

which precipitated after concentration and cooling of the filtrate were collected and recrystallised from ethanol. The results are listed in Table 1, part I.

IR for **2f**: 1750–1700 cm^{-1} [ν(CHO)].

3.3 Synthesis of asymmetrical dimethine cyanine dyes (3a–3h)

Equimolar amounts of compounds **2a–2g** and 2-methyl quaternary salts (α-picoline or quinaldine ethiodide) (0·01 mol) were dissolved in ethanol (30 ml) and piperidine (3–5 drops) added. The reaction mixture was refluxed for 6–8 h, filtered hot, concentrated, cooled and acidified with acetic acid. The precipitated products after dilution with water were collected and recrystallised from aqueous ethanol. The results are listed in Table 1, part II).

IR for **3g**: 2990–2985 cm^{-1} [ν(EtI)], 1900 cm^{-1} [ν(C=O) of oxazol-5-one], 1625–1585 cm^{-1} [ν(CH=CH)], 1380 cm^{-1} [$\nu(CH_3)$].

^{1}H-NMR ($CDCl_3$) for **3b**: δ 7·2–6·5 ppm (m, 13H, arom. + heter. + olefinic protons), 6·4 ppm (s, 1H, =CH), 2·2 ppm (t, 3H, CH_3) and 3·2 ppm (q, 2H, CH_2 joined to immonium centre).

3.4 Synthesis of 3a 4-di(H)-4-aryloxazolo/imidazo[4,5-*d*]pyrimidine-6(5*H*)-one-2-carboxaldehyde (5a–5d)

These compounds were prepared in a way similar to that described previously.[14]

3.5 Synthesis of oxazolo/imidazo[4,5-*d*]pyrimidine-2(2)-dimethine cyanine (4a–4e)

These compounds were prepared via two routes, from the cyclo-condensation reaction of the arylidino-dimethines **3a–3c**, **3f** or **3h** with urea, and from direct interaction of the 2-carboxaldehyde pyrimidine derivatives **5a–5d** with the 1-ethylpyridinium(or quinolinium)-2-yl salt.

3.5.1 Route (a)

An alcoholic solution (10 ml) of the appropriate 4-arylidino-dimethine **3a–3c**, **3f** or **3h**; 0·02 mol) was refluxed with 2g urea and conc. HCl (20 ml) for 8–10 h. The reaction mixture was filtered hot and allowed to cool. The precipitated products, after neutralisation with 5M-NaOH, were filtered off, washed with water and recrystallised from alcohol. The results are listed in Table 1, part III).

3.5.2 Route (b)

Equimolar ratios of compounds **5a–5d** and the appropriate methyl quaternary salts (α-picoline or quinaldine ethiodide) (0·01 mol) were refluxed for 8–10 h in ethanol (30 ml) containing piperidine (3 drops). After filtering and cooling, the precipitated products were collected and recrystallised from aqueous ethanol.

IR for **4e**: 3000–2850 cm^{-1} [ν(EtI)], 1730 cm^{-1} [ν(C=O) of pyrimidinone], 1610–1580 cm^{-1} [ν(C=C)] and 3600–3400 cm^{-1} [ν(NH)].

^{1}H-NMR ($CDCl_3$) for **4b**: δ6·7–6·2 ppm (m, 13H, arom. + heter. + olefinic protons), 5·6 ppm (s, 1H, NH exchangeable with D_2O), 3·4 ppm (q, 2H, CH_2 joined to immonium centre) and 1·9 ppm (t, 3H, CH_3), 1·5 ppm (dd, 2H, 3a,4-di(H) of pyrimidinone).

REFERENCES

1. Osman, A. M. & Khalil, Z. H., *J. Appl. Chem. Biotechnol.*, **25** (1975) 683.
2. Osman, A. M., Hassan, K. M., Khalil, Z. H. & Turin, V. D., *J. Appl. Chem. Biotechnol.*, **26** (1976) 71.
3. Osman, A. M., Khalil, Z. H., Khalaf, A. A. & Ibrahim, A., *J. Appl. Chem. Biotechnol.*, **26** (1976) 517.
4. Osman, A. M., Youssef, M. S. K. & Khalil, Z. H., *J. Appl. Chem. Biotechnol.*, **26** (1976) 762.
5. Hillers, S., Lidaks, M. & Sukhova, N. M., USSR Patent 333835 (1976).
6. Centre National de la Recherche Scientifique, French Patent 1 545 577 (1968).
7. Itek Corp., US Patent 3592648 (1971).
8. Eastman Kodak Co., US Patent 3598602 (1971).
9. Eastman Kodak Co., German Offen. 1950779 (1970).
10. Ilford, British Patent 797144 (1955).
11. Takeda Chemical Industries Ltd, German Offen. 2919447 (1979).
12. Vogel, A. I., *A Text-Book of Practical Organic Chemistry*, 3rd edn, Longman, London, 1975.
13. Koraiem, A. I. M., Khalil Z. H. & Abu El-Hamd, R. M., *J. Chem. Technol. Biotechnol.*, **36** (1986) 473.
14. Bhutra, M. P. & Tandon, S. P., *Z. Naturforsch.*, **25B** (1970) 36.
15. Issa, R. M., Ghoneim, M. M., Idriss, K. A. & Harfoush, A. A., *Z. Phys. Chem.*, **94**(5) (1975) 135.
16. El-Ezaby, M. S., Salem, I. M., Zewail, A. H. & Issa, R. M., *J. Chem. Soc. B* (1970) 1293.
17. El-Shahawy, A. S., Girgis, M. M. & Khalil, Z. H., *Croat. Chem. Acta*, **60** (1987) 613.
18. El-Shahawy, A. S., Girgis, M. M. & Khalil, Z. H., *Z. Phys. Chem. (Leipzig)*, accepted for publication.
19. Abd El-Mottaleb, M. S. A. & Khalil, Z. H., *Z. Phys. Chem. (Leipzig)*, **260** (1979) 650.
20. Issa, I. M., Issa, R. M. & Abdel-Aal, M. S., *Egypt J. Chem.*, **14** (1971) 25.

21. Issa, I. M., Issa, R. M., El-Ezaby, M. S. & Ahmed, Y. Z., *Z. Phys. Chem.*, **242** (1969) 169.
22. Issa, R. M., El-Ezaby, M. S. & Zewail, A. H., *Z. Phys. Chem.*, **244** (1970) 157.
23. Colleter, J. C., *Ann. Chim. (France)*, **5** (1960) 415.
24. Britton, H. T. S., *Hydrogen Ions*, 4th edn, Chapman & Hall, London, 1952, p. 313.