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Studies on the Synthesis and Solvatochromic Behaviour of Mono- and Tri-methine Cyanines: Methine Cyanine Dyes, Synthesis and Solvatochromism

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ABSTRACT

New asymmetrical 6[2(or 4)]-monomethine cyanines, and bis{2,6-[2 (or 4)]-monomethine}, 6[or 2]-trimethine and bis(2,6[or 2]-trimethine) cyanines incorporating a 4-aryl-1,2,3,4,5,6-hexahydroimidazolo[3,4-c] pyrimidine residue (pyrimidinium-2-yl salt) were prepared. Structural confirmation was carried out by spectral analyses. The solvatochromic behaviour of selected cyanines was investigated and their ionisation constants were determined.

INTRODUCTION

Methine cyanine dyes find extensive application as photosensitisers for silver halide emulsion in blue–green light[1–6] and as inhibitors of cell growth and division.[7] In the present work, new imidazolopyrimidine cyanines (**4a–4f, 5a–5f, 6, 9, 10a–10c**) were prepared in order to study their spectral and solvatochromic behaviour on the basis that such dyes might exhibit a photosensitisation effect. Furthermore, the absorption spectra in buffer solution were utilised for the determination of the acid dissociation constants for some of these compounds in order to permit selection of a suitable pH when the compounds are applied as photosensitisers.

RESULTS AND DISCUSSION

The synthesis of the desired imidazolo[3,4-*c*]pyrimidine mono(tri)-methine cyanines started with the 4-aryl-1,2,3,4,5,6-hexahydroimidazolo[3,4-*c*]-pyrimidine-2,6-diones (**2a–2c**), which were prepared by interaction of

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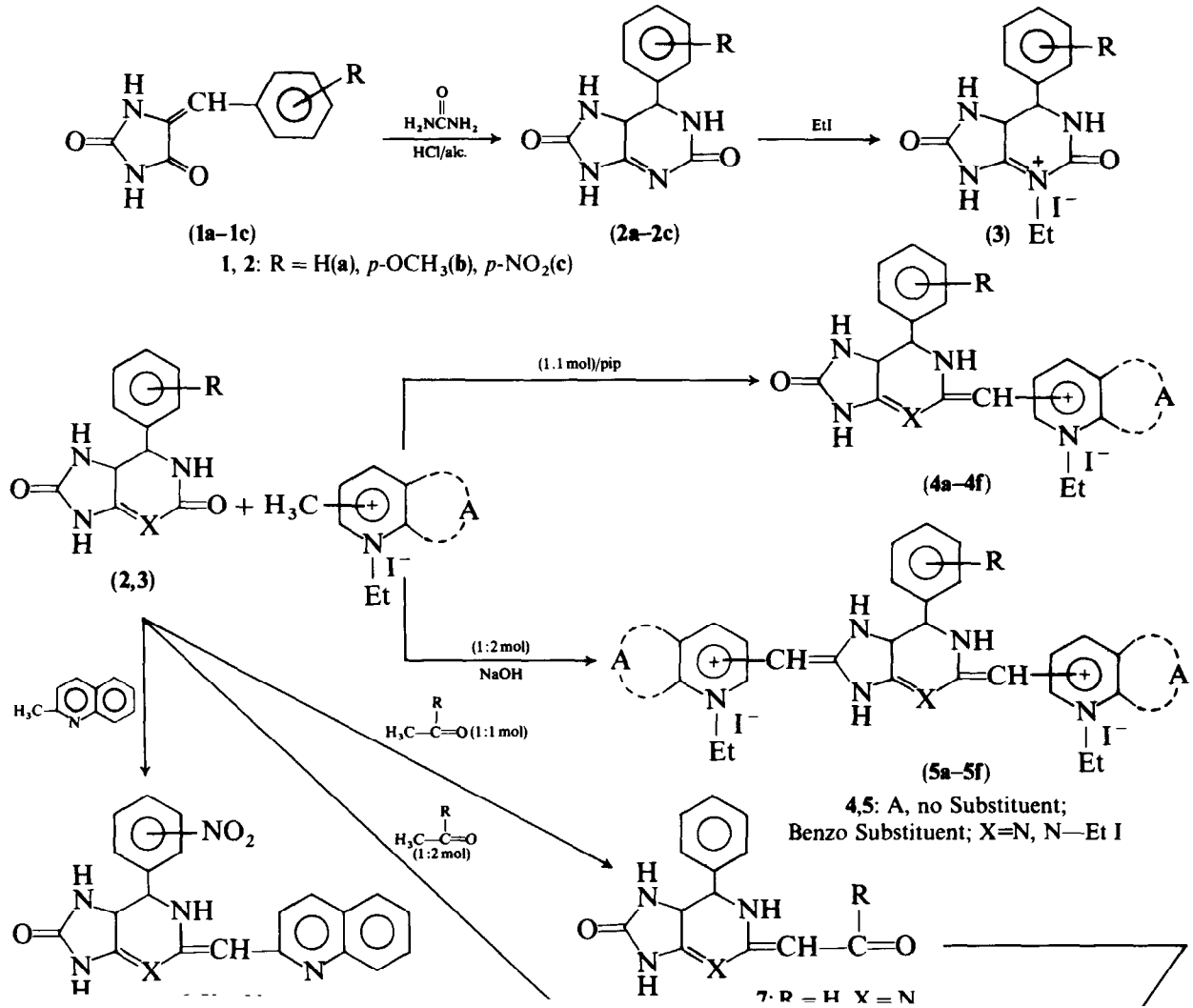
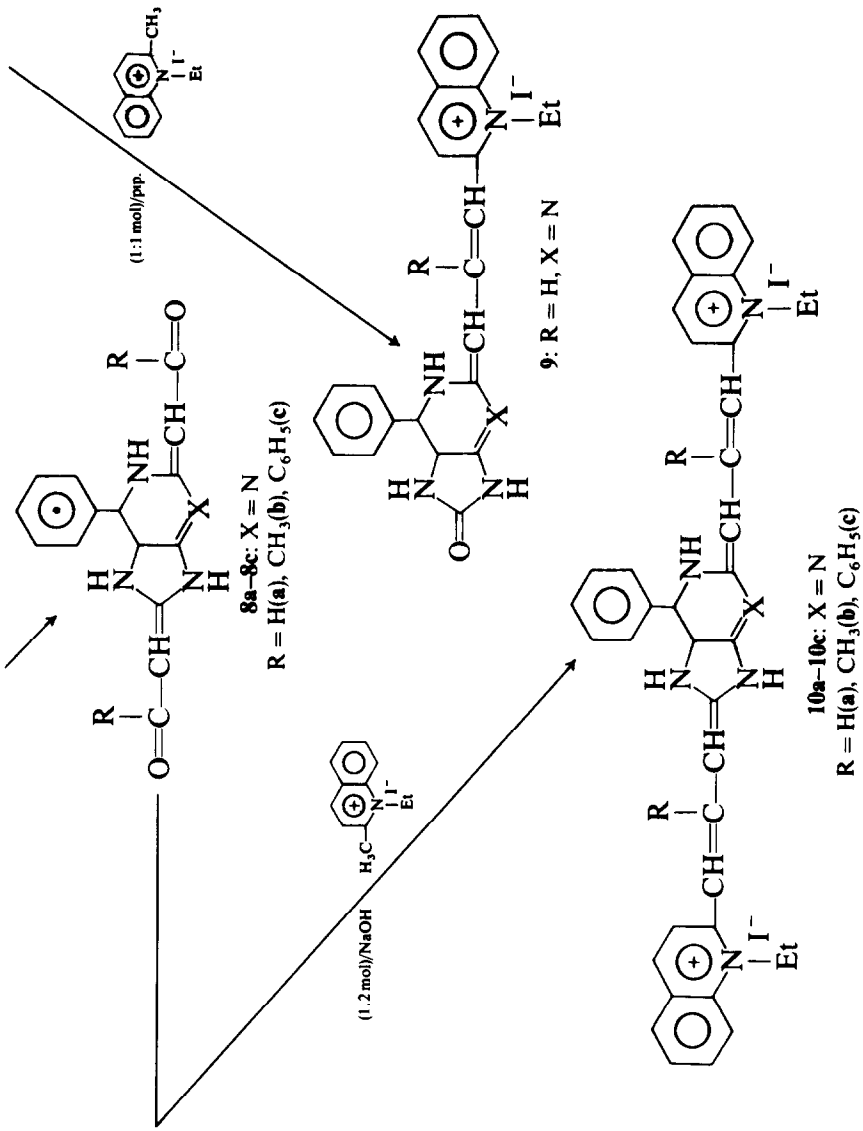

(1a–1c)
(2a–2c)
(3)
1, 2: R = H(a), p-OCH3(b), p-NO2(c)
(1.1 mol)/pip
(4a–4f)
(2,3)
(1:2 mol)
NaOH
(5a–5f)
4,5: A, no Substituent;
Benzo Substituent; X=N, N—Et I
(1:1 mol)
(1:2 mol)
7: R = H, X = N


(1:1 mol)/pip.
8a–8c: X = N
R = H(a), CH3(b), C6H5(c)
9: R = H, X = N
(1.2 mol)/NaOH
10a–10c: X = N
R = H(a), CH3(b), C6H5(c)

Scheme 1

equimolar amounts of 4-arylidenohydantoin (**1a–1c**)[8] and urea in absolute ethanol containing conc. hydrochloric acid. Quaternisation of **2a** with ethyl iodide gave the corresponding 4-phenyl-1,2,3,4,5,6-hexahydroimidazolo-[3,4-*c*]pyrimidinium-2-yl salt 2,6-dione (**3a**).

The structures of the compounds were established by elemental analyses and IR data. Thus, the IR spectra of **2a–2c** showed well-defined absorption bands at 1510 cm^{-1} [ν(C=N)] 1665–1750 cm^{-1} [ν(C=O)] and 3500–3580 cm^{-1} [ν(NH)]. Compound **3a** showed a characteristic IR band at 3000 cm^{-1} due to the ethiodide heterocyclic residue.

The ^{1}H-NMR spectra of **2a–2c** in $CDCl_3$ showed, in addition to the multiplet at δ 7·4–7·7 ppm (5H, aromatic), signals at δ 3·2 (br, 3H, 3NH exchangeable with D_2O) and at δ 6·4(d, 2H, dihydropyrimidine). Compound **3a** showed signals at δ 3·4 ppm (q, 2H, NCH_2) and δ 3·0 (t, 3H, CH_3I) in addition to the above signals obtained with compounds **2a–2c**.[9]

Reaction of compounds **2a–2c** or **3a** with an equimolar amount of 2- or 4-methyl quaternary salts such as 1-ethyl-2-methylpyridinium iodide, 1-ethyl-2-methylquinolinium iodide and 1-ethyl-4-methylpyridinium iodide in the presence of piperidine as catalyst, afforded the corresponding asymmetrical imidazolo[3,4-*c*]pyrimidine (pyrimidinium-2-yl salt)-6[2-(or 4-)]-monomethine cyanines (**4a–4f**). On the other hand, reaction of **2a–2c** or **3a** with bimolar amounts of the 2- or 4-methyl quaternary salts gave the corresponding asymmetrical imidazolo[3,4-*c*]pyrimidine (pyrimidinium-2-yl salt)-bis-2,6[2-(or 4-)]-monomethine (**5a–5f**) (see Scheme 1).

The structure of the compounds were established by elemental analyses, IR and ^{1}H-NMR data. IR and ^{1}H-NMR spectral data are listed in Table 4. Further evidence for the structure of compounds (**5a–5f**) is given by the interaction of **4a–4f** with an equimolar amount of 2- or 4-methyl quaternary salts in the presence of sodium hydroxide (Scheme 1).

The asymmetrical imidazolo[3,4-*c*]pyrimidine (pyrimidinium-2-yl salt)-6[2-(or 4-)]-monomethines (**4a–4c**) and their bis{2,6-[2-(or 4-)]-monomethine (**5a–5f**) had different colours ranging from reddish violet to intense violet and were soluble in polar organic solvents and in conc. sulphuric acid, by which iodine was liberated on heating. They exhibited a strong green fluorescence in solution depending on the type of substituents, and their ethanolic solution gave a yellow colour in acidic medium which turned violet on basification with an alkali. This reversible change in colour gives an indication to their possible use as acid–base indicators in protometric titrations.

In the visible absorption spectra of compounds **4a–4f** in 95% ethanol, the position and molar extinction coefficients of the bands was influenced by the nature of the heterocyclic quaternary residue (A). Thus the absorption spectra of **4a** (R = H, A = 2-(1-ethylpyridinium-2-yl salt), had λ_{max} at 480,

580 nm (ε_{max} 8400, 460 mol^{-1} cm^2); substituting the 1-ethylquinolinium-2-yl salt moiety (**4b**) for A increased the number and intensity of the absorption bands (λ_{max} 510, 560, 605 nm; ε_{max} 3100, 2000, 15 800 mol^{-1} cm^2). On the other hand, the absorption band of **4c** (A = 1-ethylpyridinium-4-yl) underwent a blue shift of 95 nm (λ_{max} 420, 485 nm; ε_{max} 2500, 1650 mol^{-1} cm^2) compared with **4a**.

Additionally, the position of the bands was influenced by the nature of the aryl substituents (R). Thus, substituting R = 4-OCH_3 for R = H gave a red shift of 55 nm in the C-T band (**4d**, R = 4-OCH_3, A = 1-ethylquinolinium-2-yl salt; λ_{max} 455, 505, 500, 602, 660 nm; ε_{max} 2950, 2650, 2550, 2350, 1450 mol^{-1} cm^2). This red shift is attributed to an increase in both the mass of the molecule and its coplanarity. Introduction of a nitro group (compound **4e**) caused a blue shift (R = 4-NO_2, A = 1-ethylquinolinium-2-yl salt; λ_{max} 515, 570 nm; ε_{max} 9400, 8600 mol^{-1} cm^2), Table 1.

Comparing the absorption spectra of **4b** and **4f**, it is evident that quaternisation not only brings about a bathochromic shift of 85 nm, but also enhances the intensity of the band (Table 1).

Similarly, the absorption bands in the electronic spectra of compounds **5a–5f** in 95% ethanol also underwent bathochromic or hypsochromic shifts depending on the nature of the heterocyclic quaternary residue A, of the aryl substituent R and by quaternisation of the pyrimidine moiety X (Table 2).

The reaction of **2a** with non-quaternised heterocyclic compounds for a prolonged period in the presence of piperidine as catalyst gave the corresponding asymmetrical 2-monomethine bases **6** (Scheme 1). The electronic spectrum of **6** in 95% ethanol showed a single broad absorption at 370 nm (ε_{max} 5000 mol^{-1} cm^2). On comparing the absorption spectra of **4e** and **6**, it can be seen that the quaternisation gives a bathochromic shift of 200 nm, and also increases the band intensity.

Interaction of compound **2a** with equimolar or bimolar amounts of methyl carbonyl compounds such as acetaldehyde, acetone and acetophenone in the presence of piperidine or sodium hydroxide afforded the corresponding 6-acylmethylideno- or 2,6-diacylmethylideno derivatives (**7**, **8a–8c**). The reaction of compounds **7** and **8a–8c** with equimolar or bimolar amounts of 1-ethylquinolinium-2-yl salt gave the corresponding 6[2]- or bis{2,6[2(2)]-trimethine}cyanines, **9**, **10a–10c** (Scheme 1).

The structures of these compounds were established by elemental analyses and by IR and ^{1}H-NMR data. The IR spectra of **7** and of **8a–8c** showed a well-defined band at 1660 cm^{-1} (C=C conjugated with C=O). The IR spectra of 6[2]- or bis{2,6[2(2)]-trimethine} cyanines (**9**, **10a–10c**) showed no such absorption but a characteristic absorption at 2860–2940 cm^{-1} [ν(ethiodide of heterocyclic residue)]. The ^{1}H-NMR spectra of **9** and of

TABLE 1

Characterisation Data for 4-Aryl-1,2,3,4,5,6-hexahydroimidazolo-[3,4-*c*]pyrimidine-2,6-diones (**2a–2c**, **3a**) and Their Monomethine Cyanines (**4a–4f**)

Compound no.	*m.p.* (°C)	*Yield* (%)	*Molecular formula* (*mol wt*)	*Nature of products*	*Analysis (%) calcd (found)*			*Absorption spectra*	
					C	*H*	*N*	λ_{max} (*nm*)	ε_{max} ($mol^{-1}\,cm^2$)
2a	220	61	$C_{11}H_{10}O_2N_4$ (230)	White crystals	57·39 (57·45)	4·34 (4·38)	24·34 (24·41)	—	
2b	235	53	$C_{12}H_{12}O_3N_4$ (260)	Pale yellow crystals	55·38 (55·43)	4·61 (4·70)	21·53 (21·63)	—	
2c	247	56	$C_{11}H_9O_4N_5$ (275	Yellow crystals	48·0 (48·12)	3·27 (3·35)	25·45 (25·60)	—	
3a	200	67	$C_{13}H_{15}O_2N_4I$ (386)	Brown crystals	40·41 (40·49)	3·88 (3·93)	14·50 (14·57)	—	
4a	235	42	$C_{19}H_{20}N_5OI$ (461)	Reddish crystals	49·45 (49·59)	4·33 (4·41)	15·18 (15·21)	480 580	8 400 4 600
4b	195	55	$C_{23}H_{22}N_5OI$ (511)	Violet crystals	54·01 (54·10)	4·30 (4·40)	13·69 (13·75)	510 510 605	3 100 2 000 1 580
4c	228	47	$C_{19}H_{20}N_5OI$ (461)	Brownish violet crystals	49·45 (49·61)	4·33 (4·38)	15·18 (15·25)	420 485	2 500 1 650
4d	230	60	$C_{24}H_{24}N_5O_2I$ (541)	Intense violet crystals	53·23 (53·28)	4·43 (4·50)	12·93 (13·00)	455 505 560 602 660	2 950 2 650 2 550 2 350 1 450
4e	220	63	$C_{23}H_{21}N_6O_3I$ (556)	Intense bluish violet crystals	49·64 (49·77)	3·77 (3·91)	15·10 (15·25)	515 570	9 400 8 600
4f	235	62	$C_{25}H_{27}N_5OI_2$ (667)	Intense violet crystals	44·47 (45·01)	4·04 (4·10)	10·49 (10·55)	510 587 690	2 500 2 250 1 100

TABLE 2

Characterisation Data for Symmetrical and asymmetrical Imidazolo[3,4-*c*]pyrimidine Bis{2,6(2,2)-monomethine} Cyanines (**5a–5i**)

Compound no.	*m.p.* (°C)	*Yield* (%)	*Molecular formula* (*mol wt*)	*Nature of products*	*Analysis (%) calcd (found)*			*Absorption spectra*	
					C	*H*	*N*	λ_{max} (*nm*)	ε_{max} ($mol^{-1}\,cm^2$)
5a	242	53	$C_{27}H_{30}N_6I_2$ (692)	Intense reddish crystals	46·82	4·33	12·13	420	11 600
					(46·97)	(4·50)	(12·23)	485	9 800
5b	215	60	$C_{35}H_{34}N_6I_2$ (792)	Shiny violet crystals	53·03	10·60	4·29	510	3 900
					(53·15)	(10·73)	(4·40)	585	5 700
5c	236	57	$C_{27}H_{30}N_6I_2$ (692)	Brownish violet crystals	46·82	4·33	12·13	483	14 600
					(46·90)	(4·60)	(12·38)		
5d	210	62	$C_{36}H_{36}N_6OI_2$ (822)	Intense violet crystals	52.55	4·37	10·21	510	2 550
					(52·71)	(4·49)	(10·40)	560	2 650
								600	2 600
5e	190	65	$C_{35}H_{33}N_7O_2I_2$ (837)	Bluish violet crystals	50·17	3·94	11·70	515	4 000
					(50·27)	(4·08)	(11·85)	560	4 600
5f	205	58	$C_{37}H_{39}N_6I_3$ (948)	Intense violet crystals	46·83	4·11	8·86	515	2 450
					(46·92)	(4·18)	(8·90)	560	1 700
								600	1 900
5g	233	23	$C_{31}H_{32}N_6I_2$ (742)	Brownish violet crystals	50·13	4·31	11·32	485	6 600
					(50·25)	(4·53)	(11·60)	510	6 600
								555	5 500
5i	250	26	$C_{31}H_{32}N_6I_2$ (742)	Brownish violet crystals	50·13	4·31	11·32	530	7 700
					(50·33)	(4·40)	(11·57)	582	5 600

TABLE 3
IR and ^{1}H-NMR Spectral Data of Selected Imidazolo-[3,4-*c*]-pyrimidine Pyrimidinium-2-yl Salt Cyanines

Compound no.	*IR*: $\nu_{max}^{KBr}(cm^{-1})$	^{1}*H-NMR* ($CDCl_3$): δ (*ppm*)[a]
4a–4e	2945 [ν(ethiodide of heterocyclic residue)] 3320–3580 [ν(NH)] 1665 [ν(C=C)] 1750 [ν(C=O imidazolone)]	7·5, 7·8 (m, 10H, aromatic and heterocyclic) 6·5 (a, 1H, olefinic) 3·95 (q, 2H, NCH_2) 3·4 (b, 2H, 2NH exchangeable with D_2O) 1·3, 2·1 (t, 3H, CH_3I) 1·3, 6·5 (d, 2H, dihydropyrimidine)
4f	2945 [ν(ethiodide of heterocyclic residue)] 3320–3580 [ν(NH)] 1665 [ν(C=C)] 1750 [ν(C=O imidazolone)]	7·35 (m, aromatic, heterocyclic) 3·25 (s, 3H(3NH), 1H(olefinic), 4H ($2NCH_2$) 1·2 6H($2CH_3I$), 2H(dihydropyrimidine)
5a–5e	2945 [ν(ethiodide of heterocyclic residue)] 3490–3590 [ν(NH)] 1665 [ν(C=C)]	6·9, 7·4–7·65 (m, 15H, aromatic and heterocyclic) 3·85 (b, 3H, 3NH) 6·42 (s, 2H, olefinic) 1·5–2(d, 2H, dihydropyrimidine) 3·35 (q, 4H, $2NCH_2$) 2·8 (t, 6H, $2CH_3I$)
5f	3500 [ν(NH)] 1760 [ν(*sec*-NH in conjugation with C=C)] 2940 [ν(ethiodide of heterocyclic residue)]	7·4 (m, 15H, aromatic, heterocyclic) 3·3 3H(3NH), 3H 4·5 (s, 2H, olefinic) 1·5 (d, 2H, dihydropyrimidine) (9H, $3CH_3I$)
9	3440–3560 [ν(NH)] 1740 [ν(C=O)] 1665 [ν(C=C in conjugation)] 2940 [ν(ethiodide of heterocyclic residue)]	7·45, 7·6 (m, 10H, aromatic and heterocyclic) 3–3·8 3H(3NH), 2H(NCH_2) 6·45 (3H, conjugate olefinic) 2–2·8 (3H, CH_3I)
10	3540 [ν(NH)] 1665 [ν(C=C in conjugation)] 2860–2940 [ν(ethiodide of heterocyclic residue)]	7·3, 7·7 (15H, aromatic, heterocyclic) 3·1 (3H, 3NH) 3·7 (4H, $2NCH_2$) 6·3 (4H, olefinic) 0·5, 1·2 (2H, dihydro) 1·95 (6H, $2CH_3I$)

[a] Abbreviations: s, singlet; m, multiplet; q, quartet; t, triplet.

TABLE 4

Characterisation Data for 6-Acylmethylideno- and 2,6-Diacylmethylideno Derivatives (**7**, **8a–8c**) and Their 6[2]-Methine or Bis{2,6[2(2)]-trimethine Cyanines (**9**, **10a–10c**)

Compound no.	*M.p.* (°C)	*Yield* (%)	*Molecular formula* (*mol wt*)	*Nature of products*	*Analysis* (%) *calcd* (*found*)			*Absorption spectra*	
					C	*H*	*N*	λ_{max} (*nm*)	ε_{max} ($mol^{-1}\ cm^2$)
7	197	21	$C_{13}H_{12}N_4O_2$ (256)	Brown crystals	60·93 (61·01)	4·68 (4·73)	21·87 (21·99)		—
8a	212	25	$C_{15}H_{14}N_4O_2$ (282)	Intense brown crystals	63·82 (63·95)	4·96 (5·20)	19·85 (20·23)		—
8b	180	29	$C_{17}H_{18}N_4O_2$ (310)	Brown crystals	65·80 (66·07)	5·80 (6·03)	18·06 (18·22)		—
8c	190	32	$C_{27}H_{22}N_4O_2$ (434)	Brown crystals	74·63 (74·99)	5·06 (5·18)	12·90 (13·16)		—
9	205	30	$C_{25}H_{24}N_5OI$ (537)	Intense violet crystals	55·86 (55·90)	4·46 (4·52)	13·03 (13·11)	510 590	5 300 5 100
10a	185	33	$C_{39}H_{38}N_6I_2$ (844)	Intense violet crystals	55·45 (55·60)	4·50 (4·77)	9·95 (10·05)	480 sh 510 560 585 sh	6 600 7 800 6 300 5 800
10b	193	41	$C_{41}H_{42}N_6I_2$ (872)	Deep violet crystals	56·42 (56·47)	4·81 (4·93)	9·63 (9·80)	460 515 sh 562 605	9 000 8 800 12 400 16 000
10c	216	39	$C_{51}H_{46}N_6I_2$ (996)	Bluish violet crystals	61·44 (61·66)	4·61 (4·84)	8·43 (8·70)	455 520 565 602	10 000 11 000 15 600 19 400

10a–10c in $CDCl_3$ showed characteristic signals due to aromatic, heterocyclic protons, olefinic and other protons and these are listed in Table 3.[9]

The trimethine cyanines **9** and **10a–10c** had colours ranging from violet to intense violet and were soluble in polar organic solvents and in conc. sulphuric acid, by which iodine was liberated on heating. They exhibited a strong green fluorescence in solution and their ethanolic solution gave interchangeable colour in acidic and basic media.

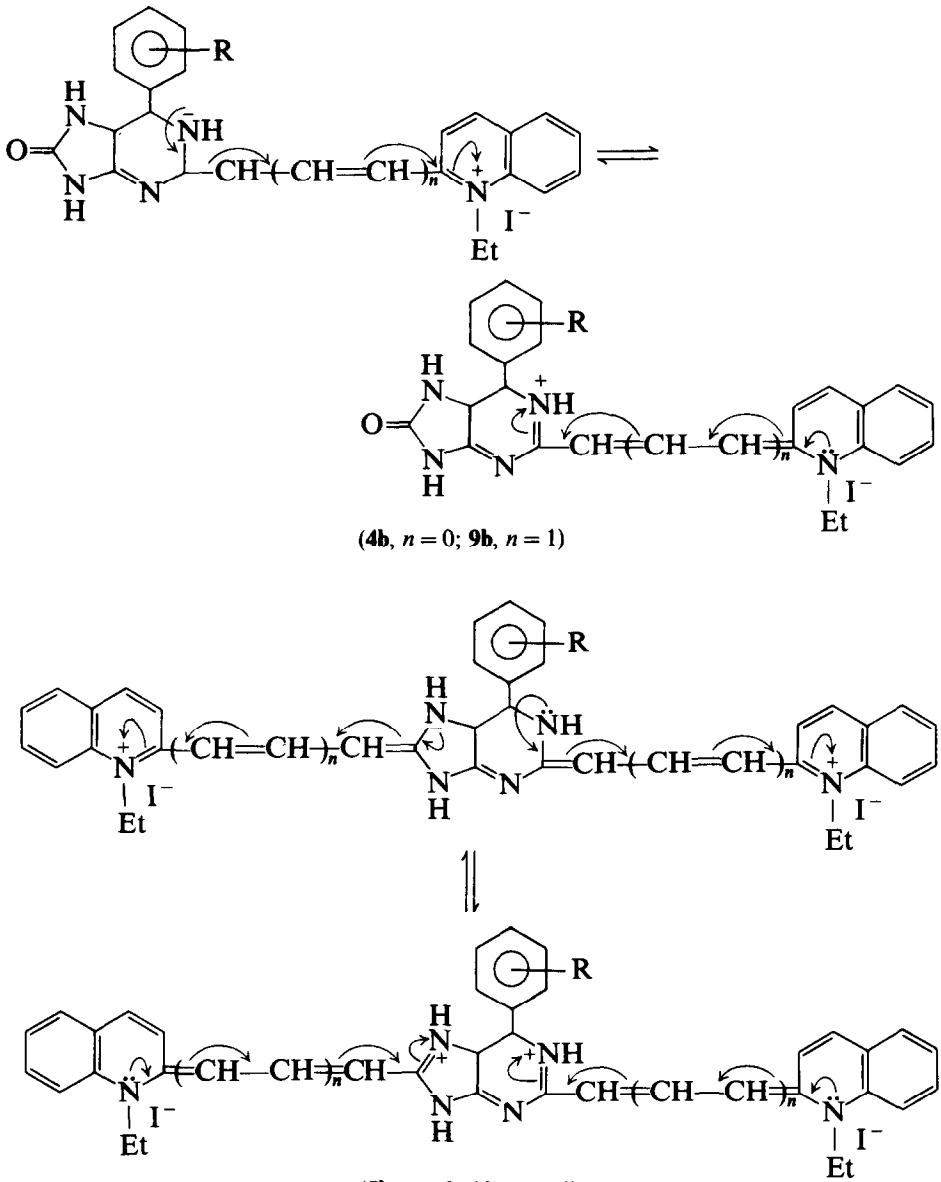
The visible absorption spectra of **10a–10c** in 95% ethanol showed absorption bands which became more intense and underwent a red shift on increasing the inductive character of the the β-substituents (R). For example, compound **10a** (R = H) showed absorptions at 480(sh), 510, 560, 585(sh) (ε_{max} 6600, 7800, 6300, 5800 mol^{-1} cm^2). Replacing the β-hydrogen atom by a methyl group caused a red shift of 20 nm (**10b**, R = CH_3), λ_{max} 400, 515(sh), 562, 605 nm (ε_{max} 9000, 8800, 12 400, 16 000 mol^{-1} cm^2), and where R was phenyl, a red shift of 17 nm relative to **10a** was observed (**10c**, R = C_6H_5), λ_{max} 455, 520, 565, 602 nm; ε_{max} 10 000, 11 000, 15 600, 19 400 mol^{-1} cm^2.

Comparison of the absorption spectra of the 6(2)-monomethine (**4b**) and 6(2)-trimethine cyanine (**9**) shows that increasing the number of methine groups in the cyanine residue causes a strong red shift of 30 nm with increase in intensity of the absorption band (Tables 1 and 4).

Solvents effects

The broadness of the absorption bands can be considered as evidence of their C—T nature. Such charge-transfer may takes place from the NH of the pyrimidine moieties as the donor to the heterocyclic quaternary residue as the acceptor centre for 6(2)-mono- and tri-methine cyanines (**4b**, **9**) and from the NH of each pyrimidine and imidazoline moiety as donor to the heterocyclic quaternary residue as acceptor centre for bis{2,6[2,2]-mono- and tri-methine} cyanine (**5b**, **10**). This can be represented schematically as shown opposite.

The absorption of imidazolo[3,4-*c*]pyrimidine-6(2)-monomethine cyanine (**4b**), bis-2,6-(2,2)-monomethine (**5b**), 6(2)-trimethine (**9**) and bis{2,6(2,2)-trimethine} cyanine (**10**) in the wavelength range 400–800 nm were studied in different solvents, i.e. isobutanol, $CHCl_3$, DMF and benzene. Results of the solvatochromic behaviour of these compounds (λ_{max} and ε_{max} values of the intramolecular and intermolecular C-T bands) are given in Table 5. Generally, it is observed that increase of solvent polarity in the sequence benzene → chloroform → ethanol → isobutanol → DMF resulted in an increase in the extinction of the absorption bands (i.e. a higher concentration of the mesomeric forms). This behaviour indicates that the polar excited states of these compounds are stabilised by polarisation of the



(**4b**, $n = 0$; **9b**, $n = 1$)

(**5b**, $n = 0$; **10a**, n = 1)

interaction forces as the polarisability of the solvent increases (i.e. lower excitation energy is required).

Strong evidence for the existence of these compounds in a mesomeric equilibrium is provided by the two well-defined isobestic points on studying the dependence of the visible spectra of, for example, compound **4b** in $CHCl_3$–ethanol mixture (Fig. 1).

TABLE 5
Absorption Spectra of Imidazolopyrimidine Cyanines in Organic Solvents

Compound no.	*Benzene*		*$CHCl_3$*		*Ethanol*		*Isobutanol*		*DMF*	
	λ_{max} (*nm*)	ε_{max} (mol^{-1} cm^2)	λ_{max} (*nm*)	ε_{max} (mol^{-1} cm^2)	λ_{max} (*nm*)	ε_{max} (mol^{-1} cm^2)	λ_{max} (*nm*)	ε_{max} (mol^{-1} cm^2)	λ_{max} (*nm*)	ε_{max} (mol^{-1} cm^2)
4a		—	480 sh	2000	480 sh	2800	480 sh	3000	480 sh	2720
	515	1340	510	2440	510	3400	510	3700	510	3360
		—	560	1860	560	2400	560	3100	565	2400
	595	1040	610	1600	600	2100	605	3040	605	2240
	640	760	710	560	695	940	680	920	700	960
4b		—	470 sh	1280	465	1532	465	1532	508	1372
	515	460	515	1180	505	1448	505	1328	545	1328
		—	560	1132	558	1456	545 sh	1276	560	1320
		—	610	992	600	1304	560	1280	608	1184
	640	288	665	672	660	832	605	1152	665	780
	715	280	700	592	690	752	630	716	700 sh	668
4c	480	1500	485	4600	480	5000		—		—
	520	1848	518	5640	515	6240	515	3360	515	7440
	555	1482	565	4260	563	5880	665	4120	570	7000
	598	1812	590	4160	585	5700	585	4040		—
	640	660	670	1760	665	2200	600 sh	3600	670	2660
	715	822	700	1400	695	2160	680	1040	700	2320
5b	475	2016	480	2496	475	2528	475	1736		—
	515	2304	515	2704	515	2960	515	2040	515	2880
	555	2720	555	3040	550	3328	545	2280	560	3440
	595	3840	595	4112	585	4320	585	3280	588	4128
	690	944	700	800	710	736	680	664	700	832
9		—	485	2200	485	1800		—	485	2200
		—	515	2790	510	2370		—	512	2700
		—	560	2350	560	2080		—	560	2350
		—	595	2810	585	2320		—	590	2630
		—	710	660	690	590		—	700	620
10a	465	3408	470	5520	463	4260	468	3120	465	4208
	520	2704	515	4800	510	3780	505	2300	510	3568
	565	2720	570	5120	560	4200	545	2040	565	3968
	625	2576	610	5408	603	4340	515	2000	610	4320
	673	1600	665	3200	660	2440	605	1800	665	2352
	710	1360	710	2240	695	1840	685	1120	705	1520

However, the unexpected blue shift observed in the λ_{max} of the longer-wavelength visible band, as well as the higher extinction on increasing the alcohol content in chloroform, can be mainly ascribed to the possible interaction of ethanol molecules with the lone pair electrons of the NH of the pyrimidine nucleus through their greater tendency than chloroform

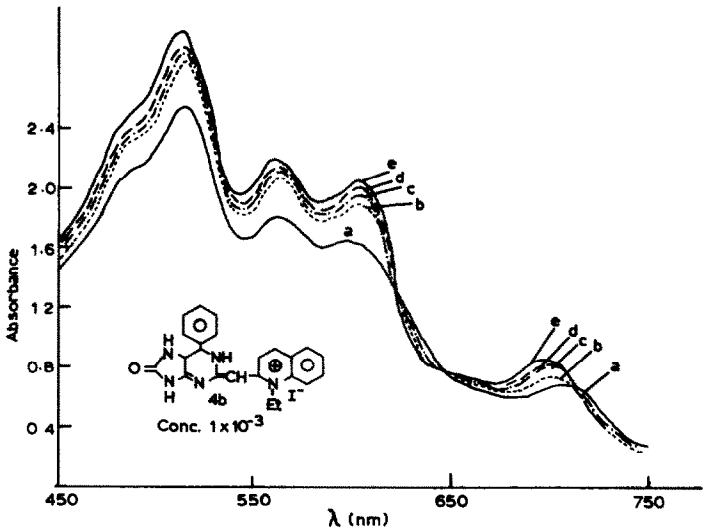


Fig. 1. Electronic absorption spectra of **4b** in $CHCl_3$–EtOH mixtures.

molecules to form hydrogen bonds. This results in a difficult charge transfer from the NH group to the quinolinium iodide, thus causing the blue shift.

Effect of aqueous universal buffers

The ethanolic solutions of pyrazolo[3,4-*c*]pyrimidine-6(2)-monomethine, bis{2,6-(2,2)-monomethine}, 6(2)-trimethine and bis{2,6(2,2)-trimethine} cyanines (**4b**, **5b**, **9** and **10**) were violet in basic medium and turned to yellow or were discharged on acidification. This prompted us to study the effect of different aqueous universal buffer solutions on the spectral behaviour to permit selection of the suitable pH when the compounds are applied as photosensitisers.

The absorbance of the C-T band in compounds **4b**, **5b**, **9** and **10** increased with increasing pH. This is due to the gradual liberation of the proton from the NH group as the pH of the medium is increased. This in turn results in an easier intermolecular charge transfer from the NH of pyrimidine or imidazoline moieties depending on the type of the cyanine molecules. The variation of absorbance with pH can be utilised for the determination of the ionisation constant of organic compound.[10] By plotting the absorbance at λ_{max} versus pH, S-shaped curves were obtained (Fig. 2). The values are listed in Table 6. The horizontal portion of the S-curves corresponds to the acidic form of the compound, while the upper portion to the right corresponds to the basic form, since the pK_a is defined as the pH value for which one-half of

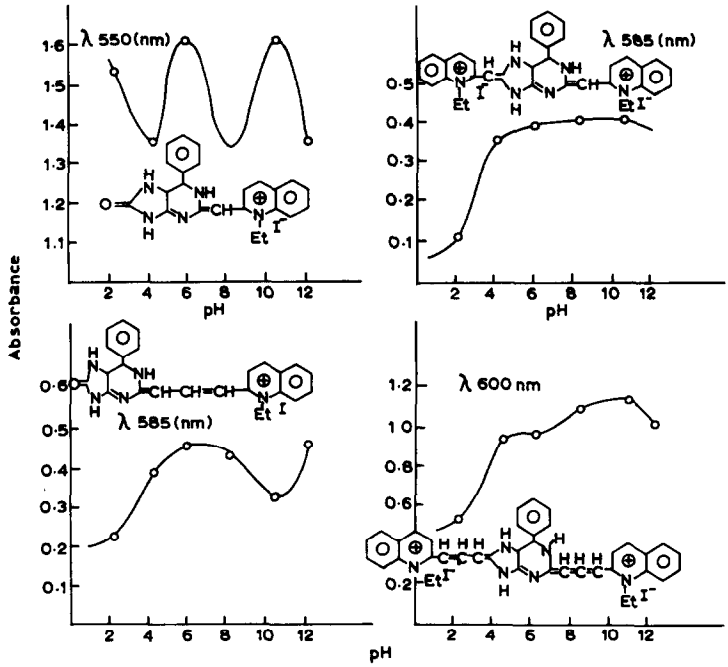


Fig. 2. S-shaped curves of absorbance versus pH of compounds.

the compound is in the basic form and the other half in the acidic form. This point is determined by the intersection of the curve with a horizontal line midway between the left and right segments.

From Fig. 2, the pK_a values for compounds **4d**, **5b**, **9** and **10a** are 5·3, 9·3; 3·5, 9·0; 3·5, 8·2 and 3·0, 7·0 respectively.

TABLE 6
Electronic Spectral Data for Some Dyes of Different pHs

pH	*Absorbance at* λ_{max}			
	Dye **4d** (*550 nm*)	*Dye* **5b** (*585 nm*)	*Dye* **9** (*585 nm*)	*Dye* **10a** (*600 nm*)
2·4	1·54	0·11	0·23	0·54
4·2	1·36	0·35	0·39	0·95
6·0	1·62	0·39	0·46	0·99
8·2	1·34	0·40	0·43	1·12
10·6	1·62	0·41	0·32	1·17
12·2	1·36	0·38	0·45	1·05

EXPERIMENTAL

IR spectra were recorded on a Unicam SP 1200 using the KBr technique. Absorption spectra in the visible region were recorded on a Shimadzu UV–Vis 240 recording spectrophotometer. The NMR spectra were determined with an EM-390 90 MHz NMR spectrometer. All melting points were uncorrected. 4-Arylidenohydantoin derivatives (**1a–1c**) were prepared by methods similar to those described earlier.[8]

Solutions

The organic solvents used for solvent effects (ethanol, isobutanol, benzene, $CHCl_3$, DMF) were all Spectrograde BDH or Merck products; 10^{-3}M stock solutions of selected cyanine derivatives were prepared by dissolving an accurate weight of the recrystallised product in the required solvent. Solutions of lower molarities, used in spectral measurements, were obtained by appropriate dilution.

The buffer solutions used were components of the modified universal series of Britton.[11]

Syntheses

*4-Aryl-1,2,3,4,5,6-hexahydroimidazolo[3,4-c]pyrimidine-2,6-dione (**2a–2c**)*
An alcoholic solution (10 ml) of 4-arylidenohydantoin[8] (0·02 mol) was refluxed with 2 g urea and 20 ml of conc. HCl on a water bath for 8–10 h. The reaction mixture was filtered hot and allowed to cool. The precipitated products, after neutralisation with 5M-NaOH, were filtered, washed several times with water and crystallised from ethanol to give compounds **2a–2c**.

*4-Phenyl-1,2,3,4,5,6-hexahydroimidazolo[3,4-c]pyrimidinium-2-yl salt-2,6-dione (**3a**)*
Equimolar ratios (0·01 mol) of **2a** and ethyl iodide were heated on a water bath for 10 h. The reaction mixture was triturated with ethanol, concentrated, cooled, precipitated with water and filtered. The residue was crystallised from ethanol to give **3a**.

Characterisation data for compounds **2a–2c** and **3a** are listed in Table 1.

*Asymmetrical imidazolo[3,4-c]pyrimidine (pyrimidinium-2-yl salt)-6[2(4)]-monomethine cyanines (**4a–4f**) and their bis 2,6-[2(4)]-monomethine derivatives (**5a–5f**)*
Equimolar ratios of **2a–2c** or **3a** and of the appropriate 2-methyl quaternary

salts (α-picoline, quinaldine, γ-picoline, 0·01 mol) were dissolved in ethanol (30 ml) and piperidine (2 ml) was added. The reaction mixture was refluxed for 15–20 h, filtered hot, concentrated, cooled and acidified with acetic acid. After dilution with water, the precipitated products were collected and crystallised from ethanol togive **4a–4f**.

Interaction of **2a–2c** or **3a** with bimolar ratios of 2-methyl quaternary salts (0·02 mol) gave the bis 2,6[2(4)]-monomethine derivatives (**5a–5f**).

The results are summarised in Tables 1 and 2.

*Asymmetrical imidazolo(3,4-c)pyrimidine 6(2)- monomethine base (**6**)*
Equimolar ratios of **2c** and quinaldine (0·01 mol) were dissolved in ethanol (30 ml) and piperidine (2 ml) was added. The reaction mixture was refluxed for 12–15 h, filtered hot, concentrated, cooled and acidified with acetic acid. After dilution with water, the precipitated product was collected and crystallised from ethanol to give **6**, m.p. 260°C, yield 40%.

$C_{21}H_{16}O_3N_6$ requires: C, 63·0; H, 4·0; N, 21·0.
Found: C, 63·1; H, 4·2; N, 21·2%.
λ_{max} 370 nm; ε_{max} 5000 M^{-1} cm^2).

*6-Acylmethylideno-bis(2,6-acylmethylideno)-4-phenylimidazolo [3,4-c]-pyrimidine (**7**, **8a–8c**)*
An ethanolic solution of **2a** (0·01 mol) and the appropriate carbonyl compound (acetaldehyde, acetone and/or acetophenone) (0·01 mol or 0·02 mol) were refluxed for 15–20 h in the presence of 1–2 g of sodium hydroxide. The reaction mixture was filtered while hot, concentrated and the resinous material was triturated with ether and then with water to give the corresponding 6-bis(2,6-acylmethylideno) derivatives (**7**, **8a–8c**) which were crystallised from aqueous ethanol (2:1). The results are listed in Table 4.

*Asymmetrical (Symmetrical)-4-phenyl-1,2,3,4,5,6-hexahydroimidazolo[3,4-c]-pyrimidine 6(2)-methine and/or bis{2,6[2,2]-trimethine} cyanines (**9**, **10a–10c**)*
A mixture of **7** or of **8a–8c** (0·01 mol) and equimolar or bimolar ratios of the 1-ethylquinolinium-2-yl salt (0·01 or 0·02 mol) was dissolved in ethanol (30 ml) and 0·5–1 g of sodium hydroxide was then added. The reaction mixture was heated at 70–80°C for 10 h, concentrated, cooled and diluted with water. The precipitated products were filtered, washed several times with water and crystallised from ethanol to give the trimethine cyanines **9** and **10a–10c**. The results are given in Table 4.

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