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Synthesis and Characterization of Unsymmetrical Benzimidazoloindo-Carbocyanines

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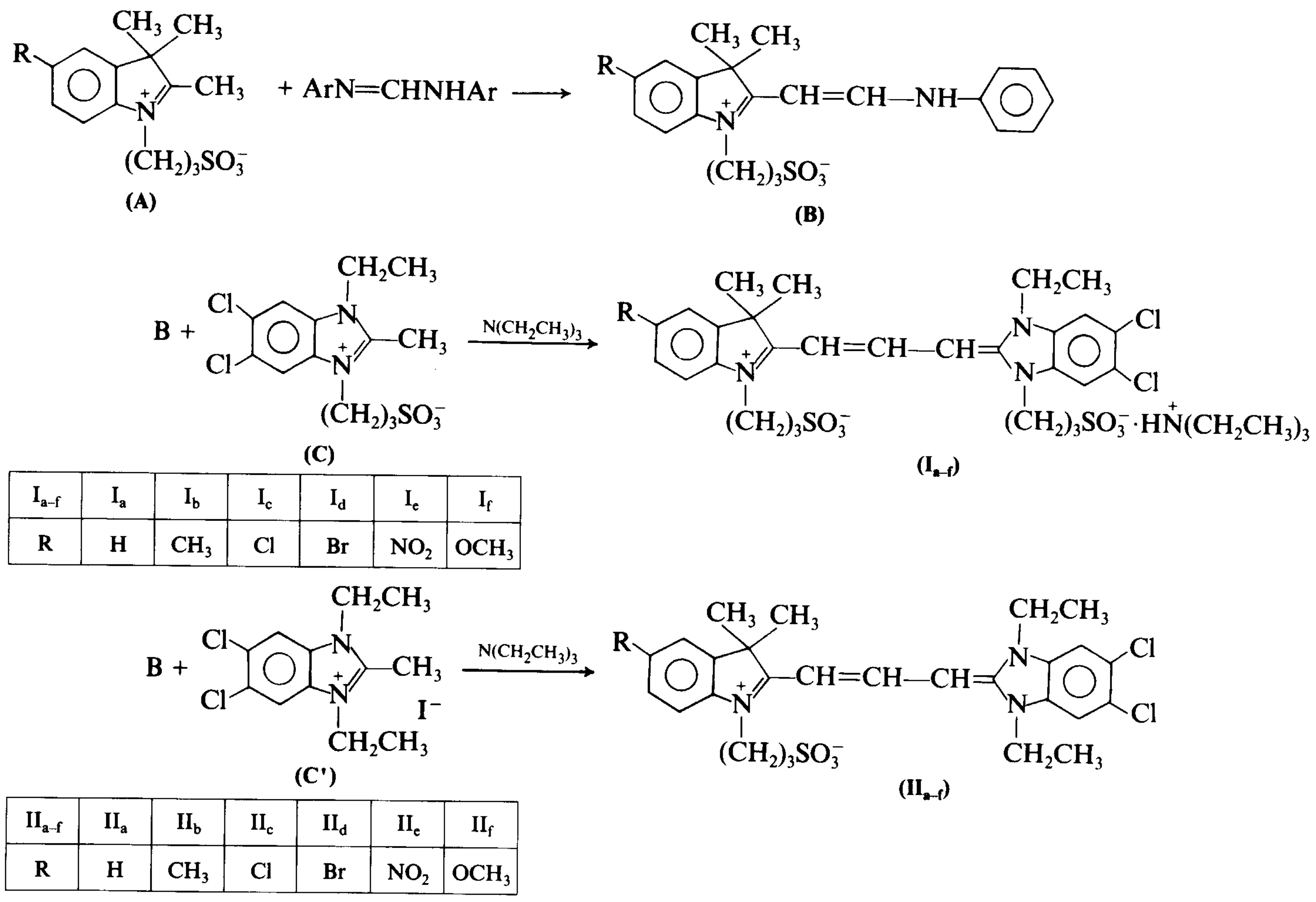
ABSTRACT

A series of unsymmetrical trimethinecyanine dyes were synthesized by condensation of 1-sulfopropyl-2-β'-anilinovinyl-3,3-dimethyl-5-(un)substituted indolenine betaines with 2'-methylbenzimidazolium derivatives, with the purpose of evaluating their potential application as green-sensitizing photographic colorants. The dyes were characterized by elemental analysis, ^1H *NMR and IR spectroscopy, and an attempt was made to correlate colorant structure with IR/visible absorption and the fluorescence of the dyes.*

1 INTRODUCTION

Whilst unsymmetrical benzimidazolindo-carbocyanines have been described as good orthochromatic sensitizers and excellent supersensitizers for silver halide emulsions in some patent specifications,[1–3] a systematic study of such compounds has not been reported. Although this type of dye was initially reported in 1957,[4] synthetic methods and the physical and chemical properties of the products have not been extensively described. The introduction of a sulfoalkyl group onto the heterocyclic nitrogen atom leads to changes in the solubility of the intermediates, and in the condensation conditions (including solvent options), but also renders the separation (purification) of the dyes from unreacted intermediates more difficult. This present paper reports the synthesis and characterization of a series of (un)substituted benzimidazoloindo-carbocyanine dyes, the structures of which are given by the general formulae I_{a-f}, II_{a-f}, III_{a-c} shown in Fig. 1. The variations in the structure of the dyes make it possible to investigate the structural influence on the physicochemical properties.



I_{a-f}	I_a	I_b	I_c	I_d	I_e	I_f
R	H	CH_3	Cl	Br	NO_2	OCH_3

II_{a-f}	II_a	II_b	II_c	II_d	II_e	II_f
R	H	CH_3	Cl	Br	NO_2	OCH_3

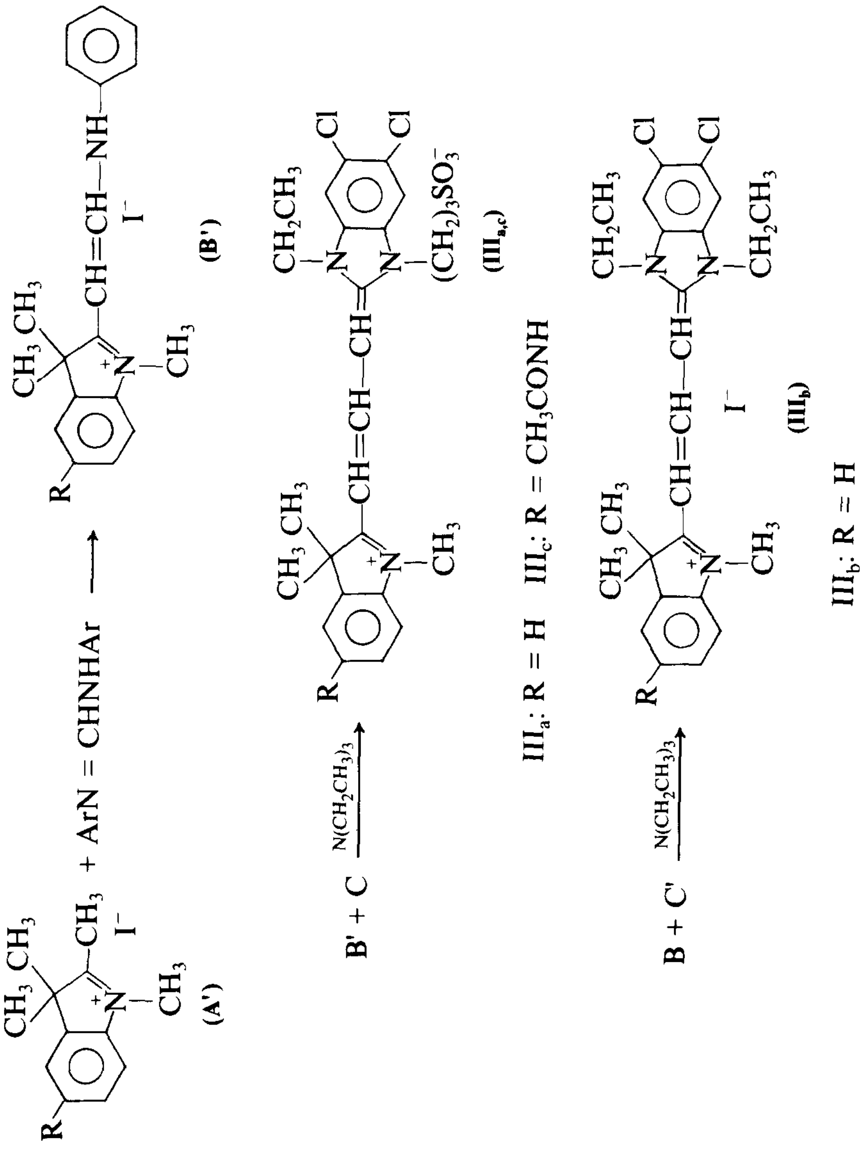


Fig. 1. Synthetic reactions for dyes I_{a-f}, II_{a-f}, III_{a-c}.

TABLE 1
Characterisation Data of Dyes (I_{a-f}, II_{a-f}, III_{a-c})

Dye	*M.P. (°C)*	*Yield (%)*	*M.F.*	*E.A. (%)*		
				C	*H (calculated)*	*N*
I_a	220–3	25	$C_{34}H_{48}N_4S_2O_6Cl_2$	54·22 (54·86)	6·87 (6·25)	7·52 (7·54)
I_b	>320	26	$C_{35}H_{50}N_4S_2O_6Cl_2$ $2H_2O$	52·76 (52·92)	6·63 (6·80)	6·80 (7·05)
I_c	232–5	28	$C_{34}H_{47}N_4S_2O_6Cl_3$ $2H_2O$	49·72 (50·11)	5·98 (6·26)	6·62 (6·87)
I_d	275–8	30	$C_{34}H_{47}N_4S_2O_6BrCl_2$ H_2O	48·29 (48·54)	5·60 (5·64)	6·45 (6·67)
I_e	>320	32	$C_{34}H_{47}N_5S_2O_8Cl_2$	51·21 (51·73)	5·94 (6·02)	8·29 (8·88)
I_f	307–10	61	$C_{35}H_{50}N_4S_2O_7Cl_2$ $2H_2O$	51·34 (51·87)	6·80 (6·73)	6·90 (6·92)
II_a	317–9	52	$C_{27}H_{31}N_3SO_3Cl_2$ H_2O	56·86 (57·20)	5·84 (5·82)	7·41 (7·41)
II_b	>320	60	$C_{28}H_{33}N_3SO_3Cl_2$	59·44 (59·74)	5·99 (5·93)	7·49 (7·47)
II_c	>320	67	$C_{27}H_{30}N_3O_3Cl_3S$ H_2O	53·85 (53·92)	5·40 (5·40)	6·84 (6·99)
II_d	>320	69	$C_{27}H_{30}N_3O_3BrCl_2S$	51·66 (51·65)	4·56 (4·83)	6·45 (6·70)
II_e	>320	66	$C_{27}H_{30}N_4O_5Cl_2S$ H_2O	53·33 (53·00)	5·17 (5·23)	8·76 (9·15)
II_f	>320	67	$C_{28}H_{33}N_3O_4Cl_2S$	57·44 (58·09)	5·70 (5·70)	7·14 (7·26)
III_a	267–7	51	$C_{26}H_{29}N_3O_3Cl_2S$	55·80 (56·37)	5·90 (5·90)	7·75 (7·60)
III_b	270–4	72	$C_{25}H_{28}N_3Cl_2I$	52·18 (52·79)	5·00 (4·98)	7·25 (7·40)
III_c	281–3	54	$C_{28}H_{32}N_4O_4Cl_2S$	56·57 (56·85)	5·18 (5·41)	8·28 (9·48)

2 RESULTS AND DISCUSSION

2.1 Synthesis

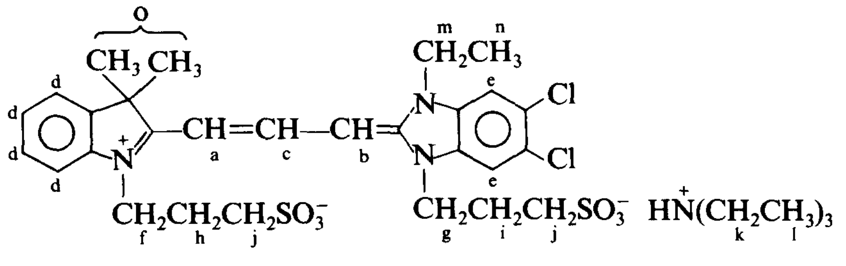
Equimolar amounts of the appropriate 2,3,3-trimethyl indolenine salt (A or A') were reacted with diphenyl formamide to produce the corresponding 2-anilinovinyl derivative (B or B'); further reaction of B (or B') with a selected benzimidazolium salt (C or C') containing an active methyl group then gave the corresponding unsymmetrical trimethine cyanines. Figure 1 shows the synthetic pathway to dyes I_{a-f}, II_{a-f}, III_{a-c}.

The indolenine salts represented by formula A or A' were prepared in a multi-stage reaction, via the *p*-(un)substituted aniline derivatives, as reported previously.[5-7] The anilinovinyl compounds were purified by recrystallization. The crude dyes (I_{a-f}, II_{a-f}, III_{a-c}) were separated and purified by column chromatography, precipitated with ether and recrystallized from methanol. Their purities were established by thin layer chromatography and elemental analysis. Good yields of the dyes were obtained from the reactions of various anilinovinyl compounds (B or B') with the benzimidazolium salts (C or C'); data are shown in Table 1.

2.2 Characterization

The structure of compounds I_{a-f}, II_{a-f}, III_{a-c} was established by IR spectroscopy and ^{1}H NMR. The IR spectra showed typical aromatic absorption (C=C, 1600–1610, 1500, 1400 (s) cm^{-1}; δ_{CH}, 700–900 cm^{-1}), resonance-conjugated unsaturated stretching modes in the chromophore (C=C, C=N, 1380–1480 cm^{-1} (s)), chromophoric CH out-of-plane bending (CH, 940–1030 cm^{-1}) and bands for the appropriate functional groups. The ^{1}H NMR spectra provide chemical shift data in accordance with the structure of the dyes.

For example, the chemical shifts in ppm of dye I_a are:



(Scheme 1)

a,	6·10 (d, 1H)	b,	6·45 (d, 1H)
c,e	8·10–8·30 (m, 3H)	d,	7·1–7·5 (m, 4H)
f,	4·20 (t, 2H)	g,	4·65 (t, 2H)
h,	2·25 (f, 2H)	i,	2·50 (f, 2H)
j,	3·10 (m, 4H)	k,	3·25 (q, 6H)
l,	1·35 (t, 9H)	m,	4·55 (q, 2H)
n,	1·60 (t, 3H)	o,	1·75 (s, 6H)

Relevant IR and ^{1}H NMR data for dyes I_{a-f}, II_{a-f}, III_{a-f} are shown in Table 2.

2.3 Absorption and fluorescence spectra

The absorption and fluorescence spectra of the dyes in methanolic solution showed hypsochromic or bathochromic shifts, depending on the nature of the substituents *R*. Absorption maxima of the dyes varied from 474 to 510 nm. Dyes I_c, I_d, I_e, II_c, II_d, II_e, having electron-withdrawing chloro, bromo or nitro groups in the indolenine ring, were hypsochromic with respect to dyes I_a and II_a, respectively; whilst dye III_c, carrying an electron-donating acetamido group substituent in the indolenine ring, showed a bathochromic shift of 8 nm. Dyes I_b, II_b, with the electron-donating

TABLE 2
IR and ^{1}H NMR Spectroscopy Data of Dyes

Dye	*IR data (cm^{-1})*			*^{1}H NMR data (ppm)*
I$_a$	1612	1559	1440	6·45 (d, 1H) 7·1–7·5 (m, 4H) 8·1–8·3 (m, 3H) 6·1 (d, 1H)
	1392	1272	1340	2·25 (f, 2H) 2·50 (f, 2H) 3·1 (m, 4H) 4·2 (t, 2H) 4·65 (t, 2H)
	1108	928	792	3·25 (q, 6H) 1·35 (t, 9H) 1·75 (s, 6H) 4·55 (q, 2H) 1·65 (t, 3H)
I$_b$	1559	1440	1381	7·9–8·15 (m, 3H) 7·0–7·25 (f, 3H) 6·2 (d, 1H) 6·4 (d, 1H) 2·25
	1318	1276	966	(f, 2H) 2·35 (f, 2H) 4·5 (q, 2H) 1·6 (t, 3H) 3·0 (f, 4H) 4·2 (t, 2H)
	810		723	3·25 (q, 6H) 1·35 (t, 9H) 4·6 (t, 2H) 2·15 (s, 3H) 1·7 (s, 6H)
I$_c$	1564	1445	1380	7·9–8·2 (f, 3H) 7·1–7·4 (f, 3H) 6·15 (d, 1H) 6·45 (d, 1H)
	1317	1206	1148	2·2–2·4 (m, 4H) 3·0 (f, 4H) 4·1 (t, 2H) 4·6 (t, 2H)
	966		669	3·3 (t, 6H) 1·3 (t, 9H) 4·5 (q, 2H) 1·65 (t, 3H) 1·7 (s, 6H)
I$_d$	1564	1445	1150	7·9–8·2 (m, 3H) 7·0–7·5 (f, 3H) 6·2 (d, 1H) 6·45 (d, 1H)
				2·25–2·4 (m, 4H) 2·9–3·05 (f, 4H) 4·65 (t, 2H) 4·1 (m, 4H)
	966		742	3·25 (q, 6H) 1·35 (t, 9H) 4·55 (q, 2H) 1·65 (t, 3H) 1·75 (s, 6H)
I$_e$	1572	1483	1450	8·2–8·4 (m, 3H) 7·1–7·5 (f, 3H) 6·26 (d, 1H) 6·5 (d, 1H)
	1387	1270	1139	2·3–2·6 (m, 4H) 3·1 (f, 4H) 4·2 (t, 2H) 4·7 (t, 2H)
	967			3·4 (t, 6H) 1·35 (t, 9H) 4·50 (q, 2H) 1·60 (t, 3H) 1·70 (s, 6H)
I$_f$	1558	1437	1334	7·9–8·4 (m, 3H) 6·8–7·2 (f, 3H) 6·2 (d, 1H) 6·4 (d, 1H)
	1210	1147	1041	1·70 (s, 6H) 2·2–2·4 (m, 4H) 3·1 (f, 4H) 4·25 (t, 2H) 4·40 (q, 2H)
	966			1·65 (t, 3H) 4·5 (t, 2H) 3·9 (s, 3H) 3·4 (t, 6H) 1·35 (t, 9H)
II$_a$	1564	1447	1380	8·3–8·4 (s, 2H) 7·8–7·9 (m, 1H) 7·0–7·5 (m, 4H)
	1276	1194	966	6·35–6·45 (d, 1H) 6·1–6·2 (d, 1H) 4·4–4·5 (q, 4H) 4·0 (t, 2H)
	826		761	2·0 (f, 2H) 2·8 (t, 2H) 1·3–1·5 (t, 3H) 1·6–1·7 (s, 6H)
II$_b$	1561	1441	1380	8·0–8·1 (m, 3H) 7·0–7·25 (m, 3H) 6·37 (d, 1H) 6·2 (d, 1H)
	1273	1154	1040	4·41 (q, 4H) 4·1 (t, 2H) 2·9 (t, 2H) 2·2 (f, 2H)
	966		724	2·37 (s, 3H) 1·7 (s, 6H) 1·6 (t, 6H)
II$_c$	1567	1446	1380	8·3–8·4 (s, 2H) 7·8–7·9 (m, 1H) 7·15–7·4 (m, 3H)
	1318		1153	6·1 (d, 1H) 6·4 (d, 1H) 4·0 (t, 2H) 3·1 (t, 2H) 1·9–2·1 (f, 2H)
	966		868	1·3–1·6 (t, 6H) 1·7–1·8 (s, 6H) 4·4–4·5 (q, 4H)
II$_d$	1567	1445	1380	7·9–8·15 (m, 3H) 7·0–7·4 (f, 3H) 6·4 (d, 1H) 6·25 (d, 1H)
	1319		1189	4·5 (q, 4H) 4·15 (t, 2H) 2·97 (t, 2H) 2·25 (f, 2H)
	967		828	1·7 (s, 6H) 1·6 (t, 6H)
II$_e$	1570	1481	1450	8·5 (s, 2H) 8·2–8·35 (m, 2H) 7·8–7·9 (m, 1H) 7·3 (d, 1H)
	1387	1270	1139	6·3 (d, 1H) 6·6 (d, 1H) 4·5 (q, 4H) 4·0 (t, 2H) 3·1 (t, 2H)
	967	899	758	2·0 (f, 2H) 1·6–1·8 (s, 6H) 1·6–1·4 (t, 6H)
II$_f$	1561	1441	1318	8·2 (s, 2H) 7·8–7·9 (m, 1H) 7·1–7·3 (m, 2H) 7·1–7·2 (d, 1H)
	1273	1194	1152	6·1 (d, 1H) 6·3 (d, 1H) 4·4–4·5 (q, 4H) 4·0 (t, 2H) 3·70 (s, 3H)
	1022		966	3·1 (t, 2H) 2·0 (f, 2H) 1·7 (s, 6H) 1·6–1·4 (t, 6H)
III$_a$	1615	1564	1446	8·05–8·3 (m, 3H) 7·05–7·5 (m, 4H) 6·45 (d, 1H)
	1393	1356	1274	6·1 (d, 1H) 4·65–4·5 (q, 4H) 3·05 (t, 2H) 3·50 (s, 3H)
	966	849	754	2·42 (f, 2H) 1·75 (s, 6H) 1·68 (t, 3H)
III$_b$	1615	1567	1488	8·3 (s, 2H) 7·9 (m, 1H) 6·9–7·4 (m, 4H) 6·4 (d, 1H)
	1374	1273	1158	6·1 (d, 1H) 4·4 (q, 4H) 3·5 (s, 3H) 1·65 (s, 6H)
	967	862	742	1·50 (t, 6H)
III$_c$	1670		1622	1·5 (s, 3H) 2·14 (s, 3H) 3·17 (s, 3H) 5·92–6·08 (m, 1H)
	1569		1120	6·34–6·53 (m, 1H) 9·9 (m, 1H) 1·59 (s, 6H) 2·5 (s, 2H)
	1196		978	3·37 (s, 2H) 4·53 (s, 4H) 7·0–8·3 (m, 6H)

5-methyl group, and dyes I_f, II_f with the electron-donating 5-methoxy group as substituent in the indolenine ring, displayed bathochromic shifts of 6–7 and 12–15 nm respectively, compared with the analogues III_a, I_a and II_a (R = H).

The absorption maximum of dye I_a was very similar to those of dyes II_a, III_b, III_c, and the nature of the substituent on the heterocyclic nitrogen had only a very limited effect on the absorption maxima. The molar extinction coefficients of the dyes were essentially identical, but the molar extinction coefficient of dyes I_f, II_f, because of the presence of the methoxy group, was about three times greater than that of dyes I_a, II_a. The absorption maxima of the dyes (λ_{max}) were at 44–71 nm longer wavelength than their emission maxima (as shown in Table 3).

2.4 General properties

Among the dyes studied, the solubility of dyes of the sub-series I_{a-f} was the highest due to enhancement resulting from introduction of the sulfopropyl group onto the heterocyclic nitrogen atom. The melting points of these dyes are also higher (Table 1).

TABLE 3
Characteristic Data of Dyes[a]

Dye	λ_{max}^{ab} *(nm)*	ε*(l cm*$^{-1}$ *mol*$^{-1}$*)* $(\times 10^{-4})$	λ_{max}^{ex} *(nm)*	$\lambda_{max}^{ex} - \lambda_{max}^{ab}$ *(nm)*
I_a	498	2·71	543	45
I_b	505	3·26	550	45
I_c	485	2·60	543	58
I_d	486	3·01	543	57
I_e	478	4·02	544	66
I_f	510	7·43	570	60
II_a	495	3·19	539	44
II_b	501	3·59	547	46
II_c	484	2·89	540	56
II_d	482	2·94	543	61
II_e	474	5·02	545	71
II_f	510	9·29	568	58
III_a	496	5·95	543	47
III_b	495	6·15	539	44
III_c	504	8·30	565	61

[a] Concentration: 1·0–4·0 × 10^{-5} mol; solvent: CH_3OH.

3 EXPERIMENTAL

3.1 General

Melting points were determined on a micro-melting point apparatus and are uncorrected; IR spectra were run in KBr discs on a Perkin–Elmer 683 spectrometer, visible spectra on a Hitachi UV-8451 A spectrophotometer and fluorescence spectra on a Rini-MPF-4 spectrophotofluorimeter. The ^1H NMR spectra were recorded on a Bruker Ac-200, using TMS as internal standard and DMSO-d_6 as solvent.

3.2 Synthesis of (5,6-dichloro-1-ethyl-3-3'-sulfopropyl-2-benzimidazole) (5-chloro-3,3-dimethyl-1-3'-sulfopropyl-2-indolenine) trimethincyanine triethyl ammonium salt

A mixture of 5,6-dichloro-1-ethyl-2-methylbenzimidazole (7·83 g) and 1,3-propanesultone (4·17 g) was heated at 170°C for 3 h. The product was crystallized from ethanol to give 9·5 g of 5,6-dichloro-1-ethyl-2-methyl-3-3'-sulfopropyl-benzimidazole betaine (C): yield 79·2%, $C_{13}H_{16}N_2SCl_2O_3$; calculated C 44·2%, H 5·14%, N 7·93%; found C 43·56%, H 5·25%, N 7·33%.

Condensation of diphenylformamidine (0·6 g) with 1-3'-sulfopropyl-2,3,3-trimethyl-5-chloro-indolenine salt (0·5 g) gave 0·55 g of the 1-3'-sulfopropyl-2-β'-anilinovinyl-3,3-dimethyl-indolenine salt (B) (R = Cl). The resulting quaternary salt was reacted in nitrobenzene (6·5 ml) at 140°C for 1 h with 0·45 g of C, 0·5 ml of acetic anhydride and 1 ml of NEt_3; On pouring the cold reaction mixture into ether, an oil separated, which slowly solidified on stirring. The solid was filtered and chromatographed using silica, eluting with a mixture of acetone : ethanol : water (3 : 5 : 1). The principal reddish band was eluted, solvent removed, and on addition of ether, a solid was obtained. Relevant characterization data are given in Tables 1 and 2.

Other dyes were prepared using a similar procedure.

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