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Synthesis, Visible Absorption, Photosensitisation and Antimicrobial Activity of Some Butadienochromophoric Chain-Substituted Asymmetric Cyanines

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ABSTRACT

Some butadienochromophoric chain-substituted asymmetric cyanines (BCCSAC) have been synthesised by the catalytic condensation of three chalcones, viz. 4-dimethylaminostyryl phenyl ketone, 4-dimethylaminostyryl 4′-nitrophenyl ketone and 4-dimethylaminostyryl 4′-hydroxyphenyl ketone, separately, with 6-substituted quinaldinium ethiodides.

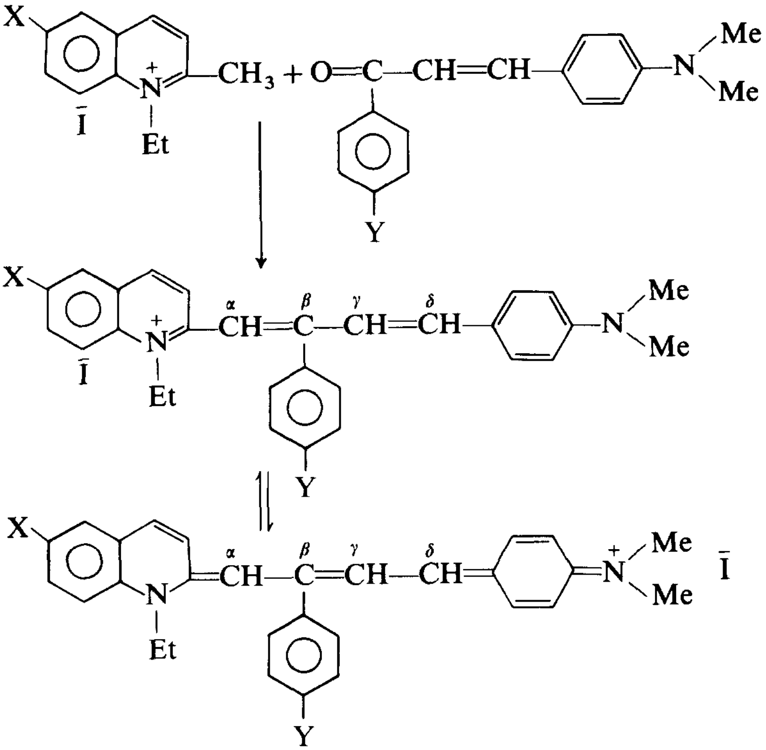
These BCCSAC were prepared with the object of studying the effects of electron donor and acceptor substituents at the 4′-position in the chain β-phenyl nucleus, of elongation of the chromophoric chain on the visible absorption maxima and spectral photosensitivity, and of investigating their antimicrobial efficacy.

The dyes were found to absorb at longer wavelengths and to show uniform bathochromic shifts compared with analogues having no substituents in the chain and in the β-phenyl nucleus. These BCCSAC are concluded to be superior sensitisers than the corresponding arylidenologues, in accord with the authors' previous observations.

Purified samples were also subjected to in vitro *antimicrobial screening to evaluate their bactericidal activity on the basis of inhibitory zone data, collected at different concentrations, and many of them were found to exhibit antistaphylococcal and antiescherichial activities.*

1 INTRODUCTION

Novel applications[1-5] of some polyenic cyanines and infrared dyes, especially in optical information storage devices, solar energy conversion systems, histological staining, antimicrobial operations and also as tools for lasers, have been described. The hemicyanines have been the subject of several investigations[5-15] and some data have been reported on the effect of



Dye	X	Y	Dye	X	Y	Dye	X	Y
$^1C_1$	H	H	$^2C_1$	H	NO_2	$^3C_1$	H	OH
$^1C_2$	Cl	H	$^2C_2$	Cl	NO_2	$^3C_2$	Cl	OH
$^1C_3$	Br	H	$^2C_3$	Br	NO_2	$^3C_3$	Br	OH
$^1C_4$	I	H	$^2C_4$	I	NO_2	$^3C_4$	I	OH
$^1C_5$	Me	H	$^2C_5$	Me	NO_2	$^3C_5$	Me	OH
$^1C_6$	OMe	H	$^2C_6$	OMe	NO_2	$^3C_6$	OMe	OH
$^1C_7$	OEt	H	$^2C_7$	OEt	NO_2	$^3C_7$	OEt	OH

Scheme 1

substituents[16-19] in the main chromophoric chain and on the effect of elongation of the chain, based on optical absorption data and on photosensitisation properties.[2,3]

In this present investigation three substituted chalcones, namely (i) 4-dimethylaminostyryl phenyl ketone, (ii) 4-dimethylaminostyryl 4′-nitrophenyl ketone and (iii) 4-dimethylaminostyryl 4′-hydroxyphenyl ketone, were prepared and each condensed catalytically with 6-substituted quinaldinium ethiodides, affording a series of BCCSAC, as summarised in Scheme 1; λ_{max} and photosensitisation data of the dyes were recorded and the effect of the nature of the β-substituents and of elongation of the prime chain is discussed on the basis of collated data, and a comparison is made with the corresponding chain-unsubstituted and non-elongated chain analogues.

The BCCSAC absorb at longer wavelengths than their chain-unsubstituted and corresponding chain-substituted styrylogues, which corroborates previous observations.[2,3,18-20] Irrespective of the nature of the β-substituent in the butadienyl chain, increase in molecular size of the 6-substituent in the heterocyclic moiety results in bathochromic shifts. The butalogues are also better sensitisers, exhibiting more extended photosensitisation characteristics than the lower homoderivatives.

Since, in styryl cyanines, the unsubstituted β-phenyl, the electron-attracting β-4′-nitrophenyl and the electron-donating β-4′-dimethylaminophenyl substituents have a strong resonance effect, [16-18] it is possible that similar β-substitution in the butadienochromophoric chain may affect the resonance stabilisation of the dye molecules, in a similar manner. However, steric factors may also be an important factor.

2 RESULTS AND DISCUSSION

The absorption maxima of the dyes in ethanol are listed in Table 1. The sensitisation spectrographs obtained from emulsified silver halide photographic plates bathed in dye solution are shown in Fig. 1, together with one undyed plate for comparison. Photosensitisation data are given in Table 4 and some comparative observations in Tables 2, 3 and 5.

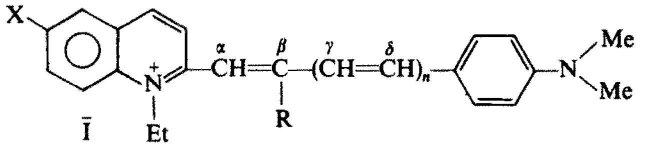
2.1 Absorption maxima

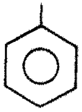
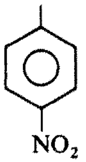
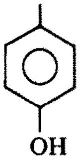
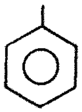
Comparison was made of the λ_{max} of the BCCSAC (series **1–3**) together with those of their styrylogues[16-18] (series **4–6**) and the chain-unsubstituted homoderivatives[7,9] (series **7**).

The β-phenyl substituents cause, in general, bathochromic shifts in

TABLE 1

Absorption Data of BCCSAC (Etho Salts in Absolute Ethanol)



	Present work/etho salts						Reported work/metho salts			
R	 *n* = *1* *Series* **1**		 *n* = *1* *Series* **2**		 *n* = *1* *Series* **3**		 *n* = *0* *Series* **4** (*Refs 16, 18*)	 *n* = *0* *Series* **5** (*Refs 16, 18*)	 *n* = *0* *Series* **6** (*Ref. 17*)	*H* *n* = *0* *Series* **7** (*Refs 7, 9*)
X	*Dye*	λ_{max} (*nm*)	*Dye*	λ_{max} (*nm*)	*Dye*	λ_{max} (*nm*)	λ_{max} (*nm*)	λ_{max} (*nm*)	λ_{max} (*nm*)	λ_{max} (*nm*)
H	$^1C_1$	563	$^2C_1$	573	$^3C_1$	566	562	563	568	530
Cl	$^1C_2$	572	$^2C_2$	581	$^3C_2$	575	570	570	577	548
Br	$^1C_3$	576	$^2C_3$	585	$^3C_3$	579	575	575	579	550
I	$^1C_4$	582	$^2C_4$	590	$^3C_4$	583	582	584	585	552
Me	$^1C_5$	566	$^2C_5$	575	$^3C_5$	572	545	569	578	—
OMe	$^1C_6$	568	$^2C_6$	583	$^3C_6$	579	548	575	580	—
OEt	$^1C_7$	572	$^2C_7$	587	$^3C_7$	581	569	578	581	—

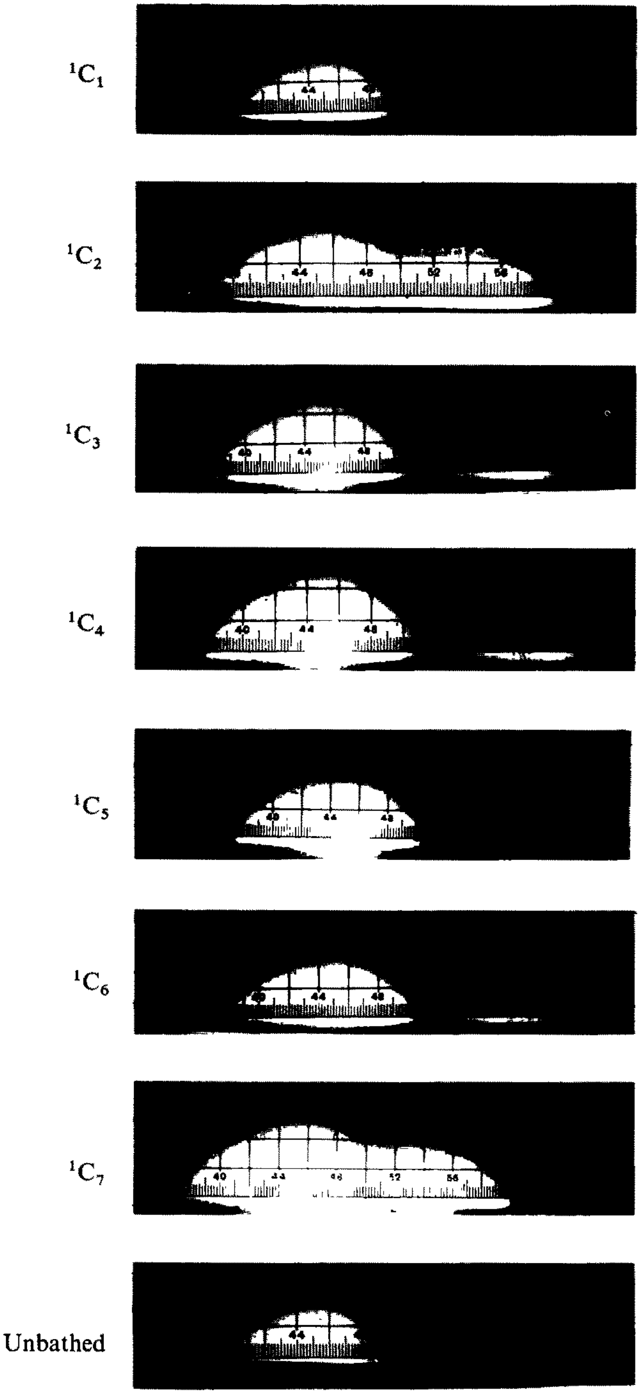


Fig. 1. Sensitisation spectrographs of the dyes.

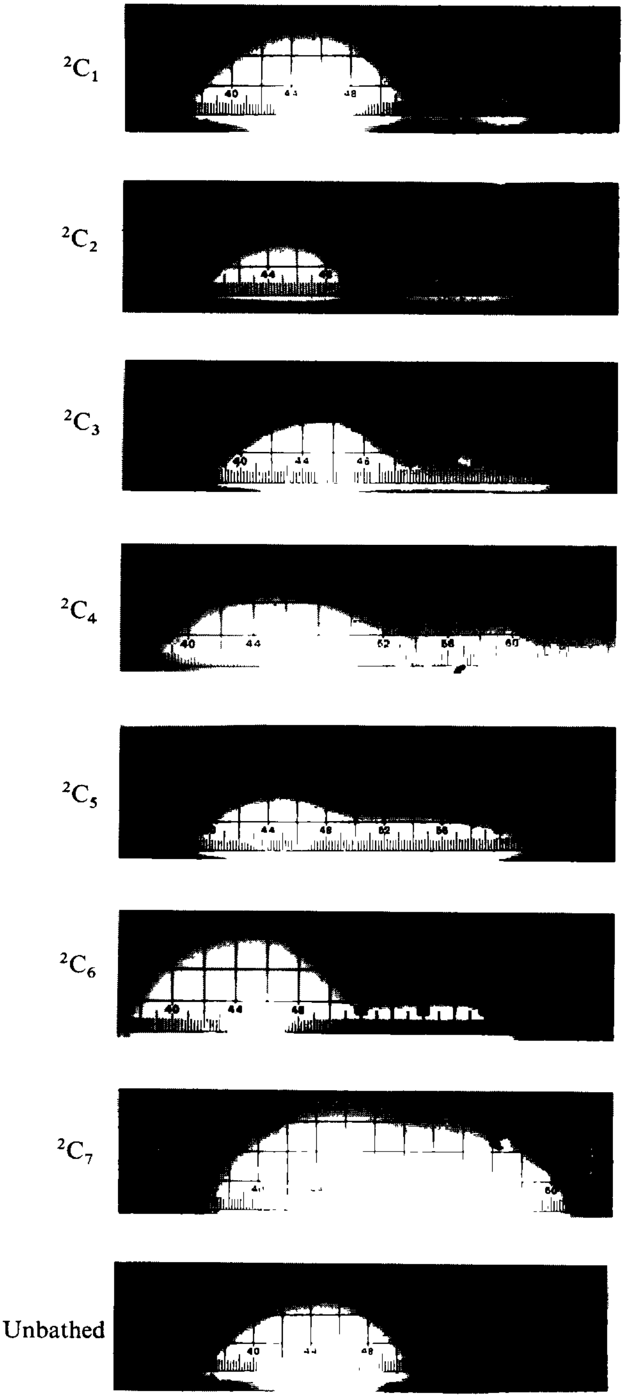


Fig. 1.—*contd.*

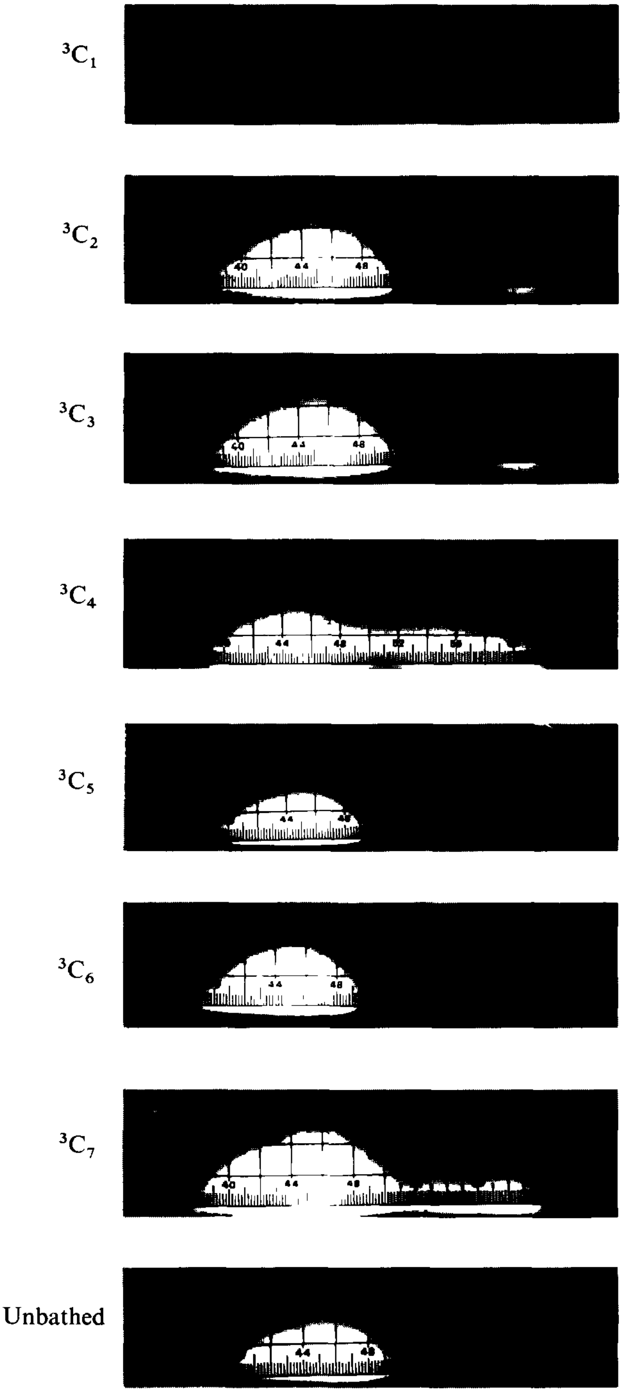
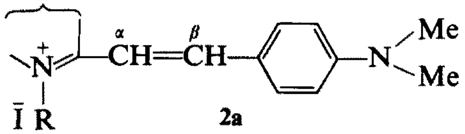
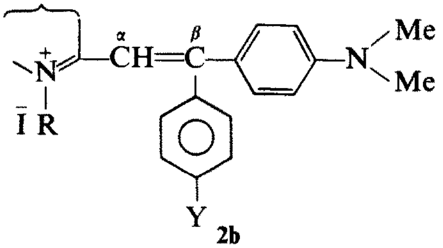


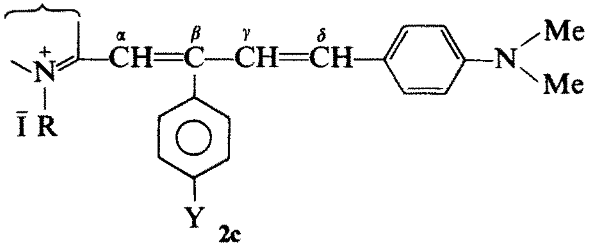
Fig. 1.—*contd.*

absorption of a similar order, viz. between 24 and 43 nm relative to the corresponding β-unsubstituted methostyrylogues,[7,9] irrespective of the polar nature of the substituent at the 4′-position of the β-phenyl ring. The bathochromic shifts are more pronounced with the β-4′-nitrophenyl (33–43 nm) and β-4′-hydroxyphenyl (27–36 nm) dyes than with the β-phenyl derivatives (24–33 nm). Among the dyes investigated (series **1**–**3**), the electron attracting β-4′-nitrophenyl derivatives absorb at longer wavelength than the butalogues containing the electron-donating β-4′-hydroxyphenyl or the β-phenyl substituent. Thus, β-substitution to various 4′-substituted phenyl groups, or to the phenyl group itself linked with a conjugated chain, as in the β-substitution in styrylogues,[2,3,16–20] both result in very similar bathochromic shifts, but more enhanced in the former case (Table 1), except for powerful electron-releasing substituents such as NMe_2 in the styrylogues. These results (Tables 1, 2 and 3) are in accord with previous reports.[2,3,16–20]

The conclusion that close proximity of bulky substituents may lead to bathochromic shifts[21] seems tenable, when the λ_{max} values of BCCSA cyanines (series **1**–**3**) and β-phenyl-substituted styrylogues (series **4**–**6**) are considered. Probably steric crowding is operative in causing the bathochromic shifts.[22–25]


2a


2b


2c

The BCCSA cyanine dyes **2c** differ from the chain-unsubstituted dyes[7,9] **2a** in two ways: they have a longer conjugated chain (one more vinyl group) and also a chromophoric chain β-homophenyl substituent, while the BCCSA cyanine dyes **2c** differ from the corresponding styrylogues[16–20] **2b** only in the increased length of the conjugated chain, the homophenyl substituent being attached to the identical C-atom of the chromophoric chain. The steric effect in the butadienyl dyes **2c** is not likely to be the same as that of the same substituent in the identical β-position of the styryl dyes **2b**. The two aryl groups are directly attached to the sp^2 C-atom in the dyes **2b**, whilst in the dyes **2c** one of the aryl groups is two C-atoms away. The cyanines **2b**, due to the bulky β-aryl/β-4′-substituted aryl group adjacent to the dimethylaminophenyl residue, may suffer out-of-plane twisting. Such an influence is absent in the cyanines **2c** and in addition, the dyes **2c** may also be expected to have added resonance stabilisation[26] due to additional π-orbital interaction between the two N-atoms (one heterocyclic and the other exocyclic) involved in the resonance. Thus, lengthening of the conjugated chain leads to the expected enhanced bathochromic shifts[6,15,26] in absorption maxima (Table 1).

The λ_{max} values of the butadienyl dyes (series **1–3**), the styryl dyes (series **4–6**) and the chain-unsubstituted dyes (series **7**) confirm the conclusion that bathochromic shifts are frequently observed in the adsorption of cyanine dyes with lengthening of the conjugated chain of C-atoms between the polyvalent atoms involved in the resonance system.[6,15] In fact these butadienyl dyes exhibit large bathochromic shifts compared with the corresponding styrylogues and the chain-unsubstituted dyes as shown in Tables 2 and 3. The bathochromic shift may be attributed to intramolecular protonation of the methylene N-atom, with a consequent stabilisation of the delocalised polyenic cation.[27]

According to Brooker, λ_{max} values increase for each additional vinyl group and the increments are non-convergent.[26] In such cases, there is no bond alternation, and resonance only stabilises the ground states of the dye molecules. Substitution in the β-aryl ring is presumed to perturb the benzene nucleus both by inductive and resonance effects,[21,28–30] resonance effects giving greater changes in spectra than inductive effects.[21,28,29]

In the heterocyclic quinolinic system, the influence of the 6-substituents on λ_{max}, although small, is consistent and systematic for all the dyes (series **1–3**). Progressive increase in the molecular weight of the 6-substituents causes a progressive bathochromic shift in all three series and also in other series previously reported,[2,3,16–20] the sequence generally following the orders:

$$\text{6-I} > \text{6-Br} > \text{6-Cl} > \text{6-H}$$

and

$$\text{6-OEt} > \text{6-OMe} > \text{6-Me} > \text{6-H}$$

TABLE 2
Comparison of BCCSAC (Ethosalts) and Their Styrylogues (Methosalts)

Set	*Dyes*	*H*	*Cl*	*Br*	*I*	*Me*	*OMe*	*OEt*	*Refs*
(i)	β-Phenyl derivatives of BCCSAC (series **1**), λ_{max}(nm)	563	572	576	582				Present work
	Chain-unsubstituted styrylogues (series **7**), λ_{max} (nm)	530	548	550	552				7, 9
	Bathochromic shift (nm)	+33	+24	+26	+30				
(ii)	β-Phenyl derivatives of BCCSAC (series **1**), λ_{max} (nm)	563	572	576	582	566	568	572	Present work
	β-Phenyl-substituted styrylogues (series **4**), λ_{max} (nm)	562	570	575	582	545	548	569	16, 18
	Bathochromic shift (nm)	+1	+2	+1	0	+21*	+20*	+3	
(iii)	β-4′-Nitrophenyl derivatives of BCCSAC (series **2**), λ_{max} (nm)	573	581	585	590	575	583	587	Present work
	β-4′-Nitrophenylsubstituted styrylogues (series **5**), λ_{max} (nm)	563	570	575	584	569	575	578	16, 18
	Bathochromic shift (nm)	+10	+11	+10	+6	+6	+8	+9	

* Abnormal shift.

TABLE 3
Comparison of Analogues of BCCSAC (Ethosalts)

Set	*Dyes*	*H*	*Cl*	*Br*	*I*	*Me*	*OMe*	*OEt*
(i)	β-4′-Nitrophenyl derivatives (series **2**), λ_{max} (nm)	573	581	585	590	575	583	587
	β-4′-Hydroxyphenyl derivatives (series **3**), λ_{max} (nm)	566	575	579	583	572	579	581
	Bathochromic shift (nm)	+7	+6	+6	+7	+3	+4	+6
(ii)	β-4′-Nitrophenyl derivatives (series **2**), λ_{max} (nm)	573	581	585	590	575	583	587
	β-Phenyl derivatives (series **1**), λ_{max} (nm)	563	572	576	582	566	568	572
	Bathochromic shift (nm)	+10	+9	+9	+8	+9	+5	+5
(iii)	β-4′-Hydroxyphenyl derivatives (series **3**), λ_{max} (nm)	566	575	579	583	572	579	581
	β-Phenyl derivatives (series **1**), λ_{max} (nm)	563	572	576	582	566	568	572
	Bathochromic shift (nm)	+3	+3	+3	+1	+6	+11	+9

These results thus confirm earlier observations that the nature and position of the substituent in the heterocyclic terminal residue of the dye molecule may influence both the visible absorption band and the photosensitisation spectra.[2,3,31-34]

2.2 Photosensitisation

The sensitisation data permit a few generalisations to be made. BCCSAC (series **1**–**3**) are fairly good sensitisers as regards their extended range and distinct uniform intensity of sensitisation, compared with most of the styrylogues (series **4** and **5**) previously studied,[2,3,16,18-20] except for the β-4′-dimethylaminostyryl dyes[17] (series **6**). The β-4′-nitrophenyl-substituted dyes (series **2**) have the highest extra sensitisation, λ_{max} having shifted towards longer wavelength by around 160 nm, and in some cases ($^2C_3$, $^2C_4$, $^2C_6$ and $^2C_7$) two peaks are discernible. Further, the photosensitisation properties of this series of dyes are more or less comparable with those of β-4′-dimethylaminostyryl dyes (series **6**).

It is also apparent that the β-4′-substituted phenyl dyes (series **2** and **3**), irrespective of whether they contain an electron-attracting or donating group, are somewhat better sensitisers than the β-phenyl dyes (series **1**) and thus the chromophoric chain β-4′-substitution in the phenyl ring of the butadienyl dyes has a beneficial effect.

The extension of optical sensitisation induced by 6-substituents in the heterocyclic moiety of all the dyes studied (series **1**–**3**) follows a similar sequence to that observed in absorption characteristics, i.e.

$$I > Br > Cl > H$$

and

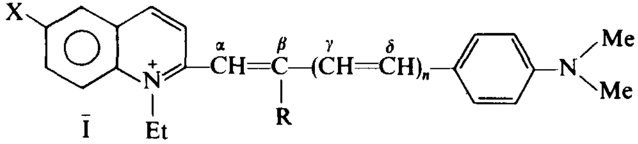
$$OEt > OMe > Me > H$$

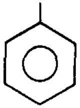
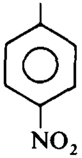
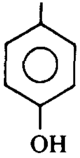
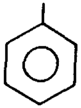
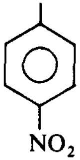
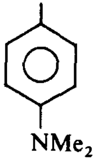
Previous studies have shown that an increase in length of the conjugated chain augments extra sensitisation.[15,26,31] This present work also shows that lengthening of the conjugated chain between two N-atoms in butadienyl dyes (series **1**–**3**) relative to the corresponding styryl dyes (series **4** and **5**) gives an enhancement in spectral sensitisation in accord with the above. This may be due to the fact that there is little possibility of steric hindrance to the planarity of the resonating system and consequently the delocalisation of the π-molecular orbitals is not hindered.

2.3 General comparative observations

A preliminary observation may thus be made that any substitution at the 4′-position of the β-phenyl ring in butadienyl dyes, more so than the

TABLE 4
Sensitisation Data of BCCSAC (Etho Salts)



	Present work/etho salts									Reported work/metho salts							
R																*H*	
	n = 1 *Series* ***1***			*n = 1* *Series* ***2***			*n = 1* *Series* ***3***			*n = 0* *Series* ***4*** (*Refs 16, 18*)		*n = 0* *Series* ***5*** (*Refs 16, 18*)		*n = 0* *Series* ***6*** (*Ref. 17*)		*n = 0* *Series* ***7*** (*Refs* 7, 9)	
X	*Dye*	*Range* (*nm*)	λ_{max} (*nm*)	*Dye*	*Range* (*nm*)	λ_{max} (*nm*)	*Dye*	*Range* (*nm*)	λ_{max} (*nm*)	*Range* (*nm*)	λ_{max} (*nm*)	*Range* (*nm*)	λ_{max} (*nm*)	*Range* (*nm*)	λ_{max} (*nm*)	*Range* (*nm*)	λ_{max} (*nm*)
H	$^1C_1$	600	550	$^2C_1$	630	580	$^3C_1$	620	560	600	580	630	570	630	580	630	580
Cl	$^1C_2$	610	560	$^2C_2$	640	585	$^3C_2$	630	570	610	580	640	540	680	540	650	595
													570	≥600	580		
Br	$^1C_3$	620	570	C_3	680	550	$^3C_3$	640	580	620	540	640	580	680	540	650	595
						590								≥600	580		
I	$^1C_4$	620	570	$^2C_4$	680	560	$^3C_4$	650	580	620	560	650	580	680	540	650	600
						590								≥600	580		
Me	$^1C_5$	610	550	$^2C_5$	660	580	$^3C_5$	620	560	610	550	630	560	610	580	—	—
OMe	$^1C_6$	620	560	$^2C_6$	660	550	$^3C_6$	640	580	610	530	640	560	680	540	—	—
						585					550			≥600	580		
OEt	$^1C_7$	620	560	$^2C_7$	680	550	$^3C_7$	650	580	620	530	640	600	680	540	—	—
						585					550			600	580		

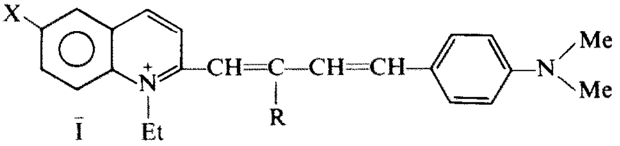
styrylogues,[2,16–18,20] leads to bathochromic shifts in absorption maxima and extended ranges as well as maxima in photosensitisation. This is shown by comparison of data for the chain β-phenyl-unsubstituted and the chain nonsubstituted derivatives[2,7,9,35] (Tables 1 and 4).

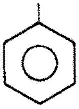
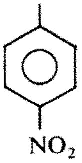
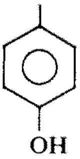
In most cases of BCCSAC, absorption and sensitisation maxima generally approximate with each other (Table 5), supporting the view of earlier workers.[2,3,26,36–38]

It is evident that with identical peripheral substituents in the heterocyclic system, the β-4′-nitrophenyl-substituted dyes (series 2) are uniformly the best sensitisers in respect of range (630–680 nm), maximum (550–580–590 nm) and intensity. They also absorb at longer wavelength and have the highest

TABLE 5

Relationship Between Absorption and Sensitisation Maxima (λ_{max}) of BCCSAC



R	*X*	*Dye*	*Absorption* λ_{max} *(nm)*	*Sensitisation* λ_{max} *(nm)*	*Difference (nm)*
	H	$^{1}C_1$	563	550	+13
	Cl	$^{1}C_2$	572	560	+12
	Br	$^{1}C_3$	576	570	+6
	I	$^{1}C_4$	582	570	+12
	Me	$^{1}C_5$	566	550	+16
	OMe	$^{1}C_6$	568	560	+8
	OEt	$^{1}C_7$	572	560	+12
	H	$^{2}C_1$	573	580	−7
	Cl	$^{2}C_2$	581	585	−4
	Br	$^{2}C_3$	585	590	−5
	I	$^{2}C_4$	590	590	0
	Me	$^{2}C_5$	575	580	−5
	OMe	$^{2}C_6$	583	585	−2
	OEt	$^{2}C_7$	587	585	+2
	H	$^{3}C_1$	566	560	+6
	Cl	$^{3}C_2$	575	570	+5
	Br	$^{3}C_3$	579	580	−1
	I	$^{3}C_4$	583	580	+3
	Me	$^{3}C_5$	572	560	+12
	OMe	$^{3}C_6$	579	580	+1
	OEt	$^{3}C_7$	581	580	+1

range (573–590 nm) among the dyes studied (series **1**–**3**). The electron displacement towards the nitro group due to polar effects augments the bathochromic shift and the extension of the sensitisation range. Probably, where there is electron displacement to the nitro group, this facilitates free rotation and the β-phenyl-substituted ring is thus likely to lie in the same plane as the other rings and to participate in the resonance delocalisation, causing increased absorption and photosensitisation.

The β-4′-hydroxy-substituted dyes (series **3**) are somewhat less effective sensitisers (620–650 nm) and absorb at slightly lower wavelength (566–583 nm). Possibly the electron release from the hydroxy group to the conjugated system leads to enhancement of the bathochromic shift and extra sensitisation. It seems, therefore, that both electron acceptor and donor substituents in the 4′-position of the β-phenyl ring give an additive effect to the optical properties of the dyes, consistent with earlier views.[1,2,17,18,39,40]

3 EXPERIMENTAL

3.1 The chalcones

The preparation of chalcones has been described by Rout and co-workers,[41] and an alternative simpler method has been reported by Doshi & Ghiya,[42] viz. heating a substituted acetophenone and benzaldehyde in alkaline, DMF. Although the method is more convenient than the conventional method[43,44] high yields of pure product are not always obtained.

A new method of preparation of chalcones, which afforded almost theoretical yields of very high purity product, was developed and the three chalcones were thus obtained.

Equimolar amounts of a substituted acetophenone and a benzaldehyde (or a cinnamaldehyde) were dissolved in the minimum quantity of pure methanol and to the solution were added dry pulverised caustic alkali. The mixture was shaken briskly for 25–30 min, and left for a further 1 h at room temperature. The separated product was filtered, washed, dried and recrystallised from a suitable solvent (ethanol, toluene, petroleum ether, etc.).

3.1.1 4-Dimethylaminostyryl phenyl ketone

This chalcone has recently been reported by Jha *et al.*[2] adopting the preparative method of earlier workers.[41] In this present work it was obtained by the above general method.

Yield 87%, m.p. 110°C (lit.[2] yield 70%, m.p. 110°C).

TABLE 6
Analytical Data of BCCSAC

Dye	*Quaternised base*[a]	*Dye name*[a]	*Yield* (%)	*M.p.* (°*C*)	*Molecular formula*	*Found* (%)		*Calc.* (%)	
						N	*Hal*	*N*	*Hal*
$^{1}C_{1}$	2-MeQEtI	2-*p*-DMAP (β-P) BDEQEtI	78·0	179	$C_{29}H_{29}IN_2$	5·2	23·8	5·3	23·9
$^{1}C_{2}$	2-Me-6-ClQEtI	2-*p*-DMAP (β-P) BDE6-ClQEtI	78·4	187	$C_{29}H_{28}ClIN_2$	4·9	28·65	4·9	29·7
$^{1}C_{3}$	2-Me-6-BrQEtI	2-*p*-DMAP (β-P) BDE-6-BrQEtI	79·2	199	$C_{29}H_{28}BrIN_2$	4·5	33·8	4·6	33·9
$^{1}C_{4}$	2-Me-6-IQEtI	2-*p*-DMAP (β-P) BDE-6-IQEtI	80·5	207	$C_{29}H_{28}I_2N_2$	4·2	38·5	4·25	38·6
$^{1}C_{5}$	2,6-DiMeQEtI	2-*p*-DMAP (β-P) BDE-6-MeQEtI	72·7	184	$C_{30}H_{31}IN_2$	5·1	23·2	5·1	23·3
$^{1}C_{6}$	2-Me-6-OMeQEtI	2-*p*-DMAP (β-P) BDE-6-OMeQEtI	76·0	206	$C_{30}H_{31}IN_2O$	4·9	22·5	5·0	22·6
$^{1}C_{7}$	2-Me-6-OEtQEtI	2-*p*-DMAP (β-P) BDE-6-OEtQEtI	81·3	211	$C_{31}H_{33}IN_2O$	4·8	22·0	4·9	22·05
$^{2}C_{1}$	2-Me QEtI	2-*p*-DMAP (β-4′-NP) BDEQEtI	63·8	193	$C_{29}H_{28}IN_3O_2$	7·2	21·9	7·3	22·0
$^{2}C_{2}$	2-Me-6-ClQEtI	2-*p*-DMAP (β-4′-NP) BDE-6-ClQEtI	64·2	207	$C_{29}H_{27}ClIN_3O_2$	6·8	26·5	6·9	26·6
$^{2}C_{3}$	2-Me-6-BrQEtI	2-*p*-DMAP (β-4′-NP) BDE6-BrQEtI	65·7	223	$C_{29}H_{27}BrIN_3O_2$	6·4	31·5	6·4	31·55
$^{2}C_{4}$	2-Me-6-IQEtI	2-*p*-DMAP (β-4′-NP) BDE6-IQEtI	66·0	241	$C_{29}H_{27}I_2N_3O_2$	5·9	36·1	6·0	36·1

$^2C_5$	2,6-DiMeQEtI	2-*p*-DMAP (*β*-4′-NP) BDE6-MeQEtI	61·7	194	$C_{30}H_{30}IN_3O_2$	7·0	21·45	7·1	21·5
$^2C_6$	2-Me-6-OMeQEtI	2-*p*-DMAP (*β*-4′-NP) BDE-6-OMeQEtI	69·3	227	$C_{30}H_{30}IN_3O_3$	6·9	20·9	6·9	20·9
$^2C_7$	2-Me-6-OEtIQEtI	2-*p*-DMAP (*β*-4′-NP) BDE-6-OEtQetI	72·4	249	$C_{31}H_{32}IN_3O_3$	6·7	20·4	6·8	20·45
$^3C_1$	2-MeQEtI	2-*p*-DMAP (*β*-4′-HP) BDEQEtI	66·5	173	$C_{29}H_{29}IN_2O$	5·05	23·1	5·1	23·2
$^3C_2$	2-Me-6-ClQEtI	2-*p*-DMAP (*β*-4′-HP) BDE6-ClQEtI	71·3	184	$C_{29}H_{28}CLIN_2O$	4·8	27·8	4·8	27·9
$^3C_3$	2-Me-6-BrQEtI	2-*p*-DMAP (*β*-4′-HP) BDE-6-BrQEtI	73·6	196	$C_{29}H_{28}BrIN_2O$	4·4	33·0	4·5	33·0
$^3C_4$	2-Me-6-IQEtI	2-*p*-DMAP (*β*-4′-HP) BDE-6-IQEtI	74·7	217	$C_{29}H_{28}I_2N_2O$	4·1	37·6	4·15	37·7
$^3C_5$	2,6-DiMeQEtI	2-*p*-DMAP (*β*-4′-HP) BDE-6-MeQEtI	65·7	170	$C_{30}H_{31}IN_2O$	4·95	22·55	5·0	22·6
$^3C_6$	2-Me-6-OMeQEtI	2-*p*-DMAP (*β*-4′-HP) BDE6-OMeQEtI	74·3	187	$C_{30}H_{31}IN_2O_2$	4·8	21·9	4·8	22·0
$^3C_7$	2-Me-6-OEtQEtI	2-*p*-DMAP (*β*-4′-HP) BDE-6-OEtQEtI	75·2	210	$C_{31}H_{33}N_2O_2$	4·65	21·4	4·7	21·45

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[a] Abbreviations: P, phenyl; Q, quinoline; HP, hydroxyphenyl; NP, nitrophenyl; BDE, butadienyl; DMAP, dimethylaminophenyl.

3.1.2 4-Dimethylaminostyryl 4'-nitrophenyl ketone

Recrystallised from petroleum ether (80–110°C) as shining red crystals; yield 82%, m.p. 118–119°C.

Analysis: Found: C, 68·9; H, 5·4; N, 9·4. $C_{17}H_{16}N_2O_3$ requires: C, 68·9; H, 5·4; N, 9·5%.

IR spectra (KBr) (cm^{-1}): 1310 (CH=CH); 1680 (C=O); 1600 (C=N); 1465 (NO_2).

3.1.3 4-Dimethylaminostyryl 4'-hydroxyphenyl ketone

Recrystallised from alcohol as yellow crystals; yield 77%, m.p. 165°C.

Analysis: Found: C, 76·3; H, 6·3; N, 5·2. $C_{17}H_{17}NO_2$ requires: C, 76·4; H, 6·4; N, 5·2%.

IR spectra (KBr) (cm^{-1}): 1315 (CH=CH); 1700 (C=O); 1620 (C=N); 3400 (phenolic OH).

3.2 The quaternised bases

The 6-substituted quinaldinium ethiodides were prepared according to the general method of Johnson & Adams,[45] with slight modification as described earlier.[2,16]

3.3 The substituted butadienyl dyes

For the dye condensation, the general method of preparation previously reported[16,17] was used.

A mixture of the quaternary base and the chalcone dissolved in absolute alcohol was refluxed in the presence of a basic catalyst for about 2 h. The separated crude product was recrystallised from methanol.

Analytical data, yield, m.p. (uncorrected), etc., of the dyes are summarised in Table 6.

3.4 Absorption and photosensitisation spectra

The absorption maxima (λ_{max}) were recorded on a Beckmann spectrophotomer, model DU, and the photosensitisation spectra on an Adam Hilger wedge spectrograph, using process plates (N40, Ilford Ltd, UK) in the manner described earlier.[16–18]

3.5 Antimicrobial activity

The purified and screened samples of the cyanines were tested for bactericidality at different concentrations in ethanolic medium, using the 'disc sensitivity technique'[46] against *Staphylococcus aureus* [Gram-positive cocci] and *Escherichia coli* [Gram-negative bacilli] in nutrient agar medium and McConkey's medium respectively at an optimum temperature (35–37°C).

The β-haloaryl derivatives particularly the chloro derivative, were found to be highly active against *S. aureus* and *E. coli*, whilst the alkyl and alkoxy derivatives were moderately effective. The antimicrobiality of the compounds was less pronounced than that of known antibiotics.

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