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Chromophoric Chain β-(Styryl-Substituted Styryl and Phenyl-Substituted Butadienyl) Cyanines: Effect of β-Substituents and Chain Lengthening on the Visible Absorption Spectra, Photosensitisation Properties and Antimicrobial Activity

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SUMMARY

In continuation of our previous studies, a number of hemicyanines, viz. chromophoric chain β-styryl-substituted (CCBSS) styryl cyanines and chromophoric chain β-phenyl-substituted (CCBPS) butadienyl cyanines have been synthesised by condensing two new isomeric chalcones namely (i) 4-dimethylaminophenyl styryl ketone and (ii) 4-dimethylaminostyryl phenyl ketone, with quaternised bases of variously substituted quinaldines. These hemicyanines were prepared with a view to studying the effect of the nature of the chain β-substituents and the length of the prime

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chromophoric chain of the dye molecules on their visible absorption and on their spectral sensitisation of photographic silver halide emulsions.

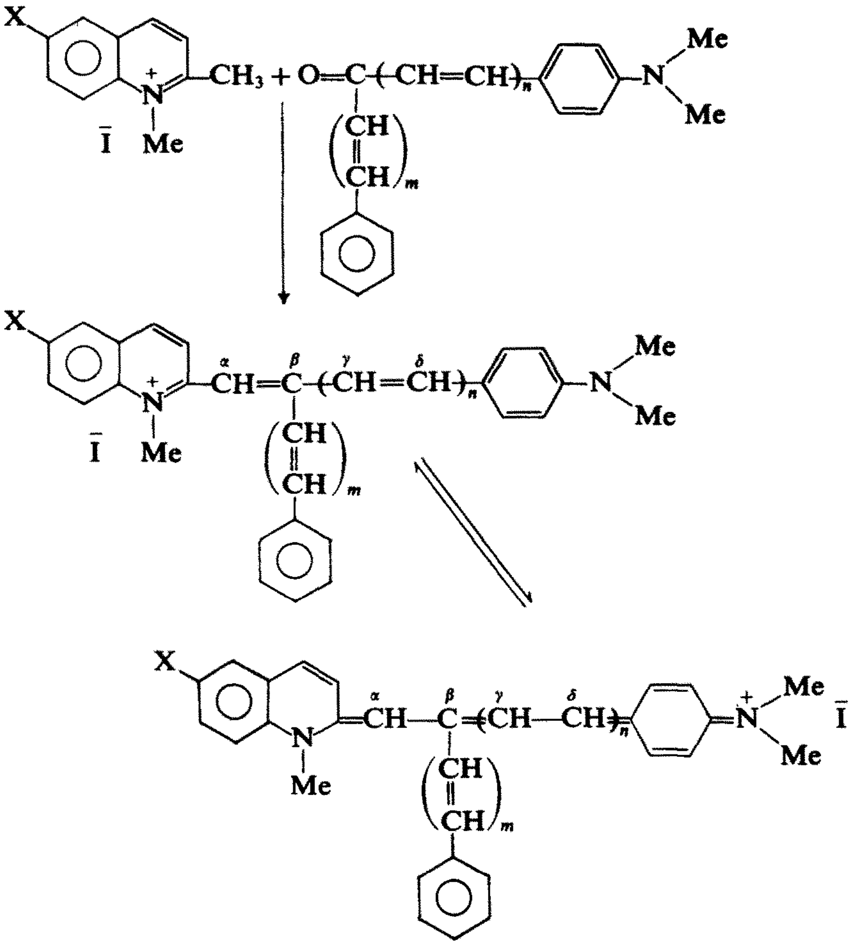
All the dyes obtained showed uniform bathochromic shifts in their absorption maxima compared with analogues having no substituent in the chain, and in accord with previously reported results. CCBSS styryl cyanines absorb at longer wavelengths than their β-phenyl and β-4-nitrophenyl derivatives and at lower wavelengths than their β-4 dimethylaminophenyl analogues, while the CCBPS butadienyl dyes exhibit hypsochromic shifts relative to various β-substituted styryl analogues. The butadienyl series of dyes, however, are better photosensitisers than the corresponding dyes of the styryl series.

The compounds have also been screened with respect to their microbial activity on the basis of previous studies reported in the literature.

1. INTRODUCTION

The synthesis of styryl cyanine dyes by the condensation of quaternised heterocyclic bases and various carbonyl compounds has been extensively reported[1-16] and the dyes have also been studied with respect to their absorption spectra and photosensitisation properties.[1-10,13-16] It has been reported that, in styryl cyanines, substitution in the prime chromophoric chain at positions either α- or β- to the heterocyclic moiety leads to hypsochromic shifts in the absorption maxima (λ_{max})[17-22] compared to the chain unsubstituted analogues, and the object of this present work is to study the effect of such substitution, as well as the effect of elongation of the conjugated chain of the dye molecules, on the basis of optical properties. For this purpose, two new isomeric chalcones, 4-dimethylaminophenyl styryl ketone and 4-dimethylaminostyryl phenyl ketone, were prepared and condensed with substituted quinaldine methiodides to give CCBSS styryl and CCBPS butadienyl cyanine dyes respectively, as shown in Scheme 1.

The visible absorption maxima and the range of extra sensitisation data of these CCBSS styryl dyes and CCBPS butadienyl dyes have been collated and analysed, and comparison has been made with the corresponding chain β-substituted and chain unsubstituted quinaldine analogues. The dyes absorb at longer wavelengths than their chain unsubstituted analogues and show uniform bathochromic shifts, which corroborate previous observations.[1-4] Irrespective of the nature of the β-substituents, the dyes carrying increasingly higher molecular weight



Dye	*X*	*n*	*m*	*Dye*	*X*	*n*	*m*
D_{45}	H	0	1	D_{53}	H	1	0
D_{46}	Cl	0	1	D_{54}	Cl	1	0
D_{47}	Br	0	1	D_{55}	Br	1	0
D_{48}	I	0	1	D_{56}	I	1	0
D_{49}	Me	0	1	D_{57}	Me	1	0
D_{50}	OMe	0	1	D_{58}	OMe	1	0
D_{51}	OEt	0	1	D_{59}	OEt	1	0
D_{52}	5,6-benzo	0	1	D_{60}	5,6-Benzo	1	0

Scheme 1

substituents in the heterocyclic nucleus show enhanced bathochromic shifts in λ_{max} and also exhibit extra extended photosensitisation characteristics.

Since the unsubstituted β-phenyl, the electron-attracting β-4-nitrophenyl and the electron-donating β-4-dimethylaminophenyl substituents have a strong resonance effect,[1-3] it is possible that chromophoric chain β-substitution of such types, may affect the resonance stabilisation of these dye molecules. However, steric hindrance to the resonance stabilisation in the prime chromophoric chain of styryl and butadienyl cyanines due to bulkiness of the β-substituents may also be an important factor.

It has been reported that quinoline and chalcone derivatives possess a broad range of therapeutic activities, especially, antiseptic,[23] analgesic,[24] anti-serotonin,[25] antimitotic[26] and antimicrobial,[27,28] such as, anti-amoebic,[29] antimalarial,[30] anthelmintic[31,32] and antitubercular[33] actions. A study of the clinical aspects of the newly prepared hemicyanines showed them to have antibacterial activity.

2. RESULTS AND DISCUSSION

The absorption maxima of the quinaldinium iodide salts in ethanol are listed in Table 1. The sensitisation spectrographs of the photographic plates bathed in dye solution were obtained and compared with that of an undyed plate, as shown in Fig. 1, and the sensitisation data are recorded in Table 3. Comparisons of some of these optical properties are shown in Tables 2 and 4.

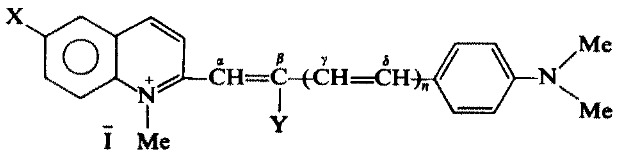
2.1. Visible absorption spectra

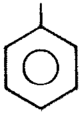
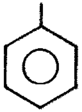
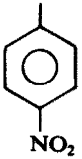
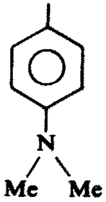
A study of the absorption maxima of the CCBSS styryl dyes (series **1**) and the CCBPS butadienyl dyes (series **2**) with those of analogous dyes previously reported[1-3] (series **3–5**) and of β-unsubstituted dyes[6,8] quoted from the literature (series **6**) leads to some interesting generalisations.

The chain β-phenyl substituents uniformly result in bathochromic shifts in absorption maxima relative to their corresponding β-unsubstituted analogues,[6,8] irrespective of the nature of additional groups attached to the β-phenyl ring, i.e. whether they are electron-attracting, such as NO_2, or electron-donating, such as NMe_2 or whether

TABLE 1

Absorption Data of CCBSS Styryl and CCBPS Butadienyl Dyes (Metho Salts in Absolute Ethanol)



	Present work				Reported work			
	Y = 		Y = 		Y = 	Y = 	Y = 	Y = H
	n = 0 Series 1		n = 1 Series 2		n = 0 Series 3 (Refs. 1, 3)	n = 0 Series 4 (Refs. 1, 3)	n = 0 Series 5 (Ref. 2)	n = 0 Series 6 (Refs. 6, 8)
X	*Dye*	λ_{max} ($m\mu$)	*Dye*	λ_{max} ($m\mu$)	λ_{max} ($m\mu$)	λ_{max} ($m\mu$)	λ_{max} ($m\mu$)	λ_{max} ($m\mu$)
H	D_{45}	564	D_{53}	532	562	563	568	530
Cl	D_{46}	576	D_{54}	550	570	570	577	548
Br	D_{47}	578	D_{55}	554	575	575	579	550
I	D_{48}	583	D_{56}	572	582	584	585	552
Me	D_{49}	571	D_{57}	523	545	569	578	
OMe	D_{50}	581	D_{58}	525	548	575	580	
OEt	D_{51}	582	D_{59}	529	569	578	581	
5,6-Benzo	D_{52}	576	D_{60}	524	571	573	575	

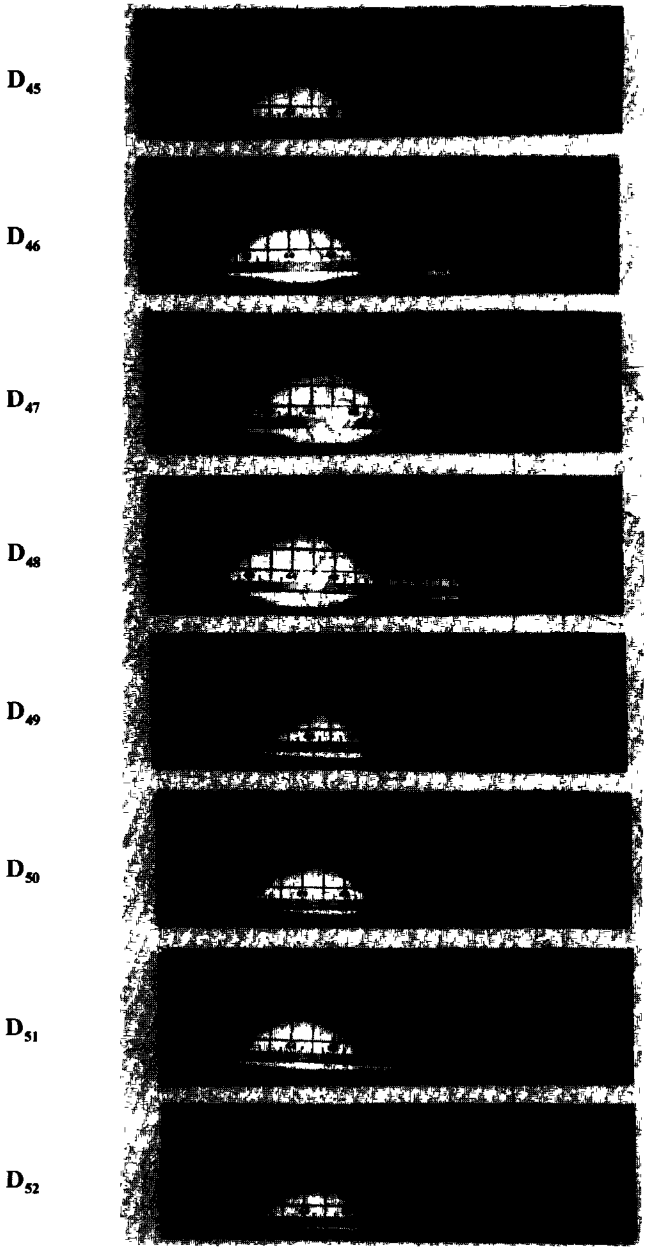


Fig. 1. Sensitisation spectrographs of the dyes.

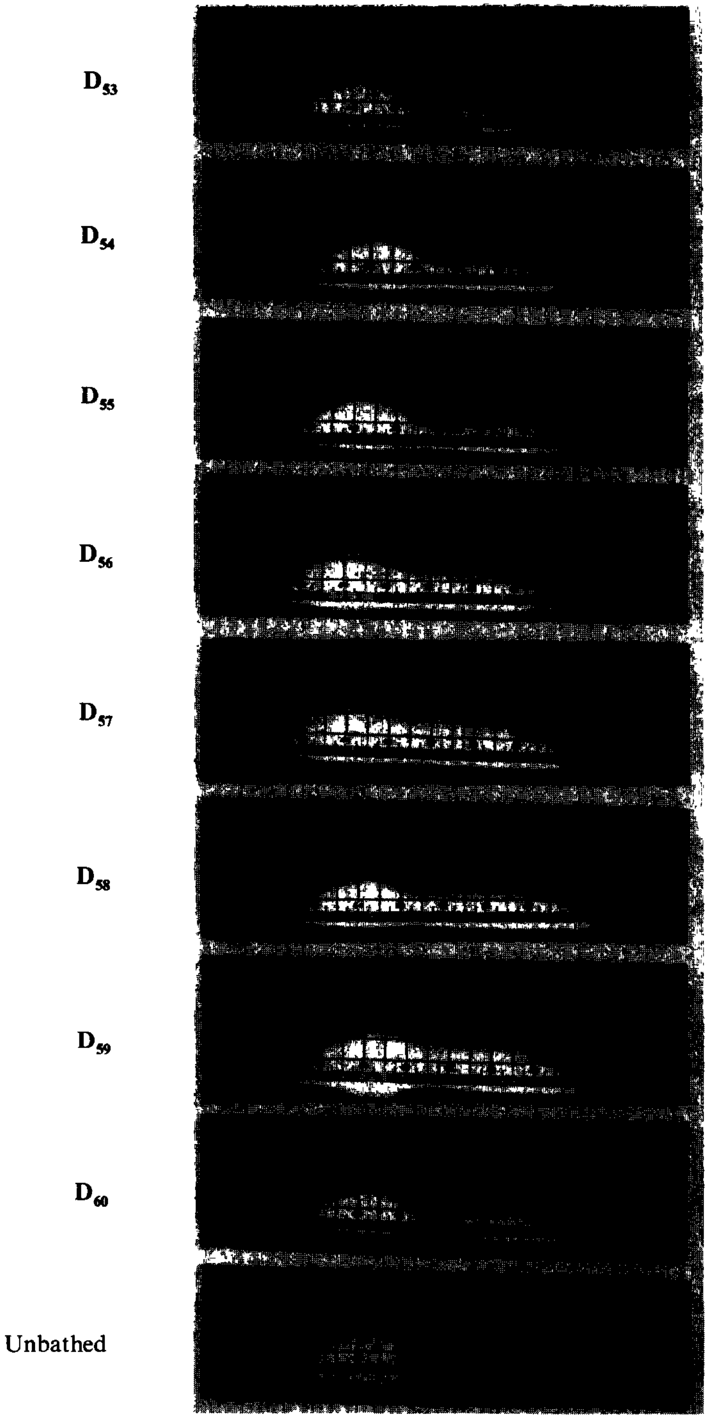
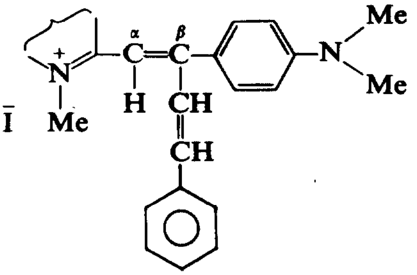


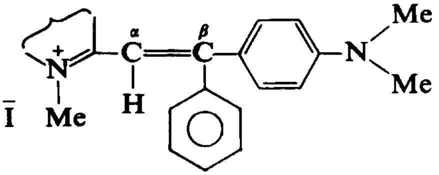
Fig. 1—*contd.*

the β-phenyl group is replaced by a β-styryl group. The bathochromic shifts are more pronounced with the β-phenyl styryl dyes[1-3] and CCBSS styryl dyes (about 20–40 μm) than CCBPS butadienyl dyes (about 2–20 μm). It is also seen that with either β-substitution to variously substituted phenyl groups or to a phenyl group linked with a conjugated chain, as in the β-styryl group, both types of substitution result in very similar bathochromic shifts (Table 1). This observation is in accord with previously reported data.[1-4]

The conclusion that the close proximity of bulky substituent may lead to bathochromic shifts seems untenable when the absorption data of CCBSS styryl dyes (series **1**) and β-phenyl-substituted dyes (series **3**) are considered. If steric crowding is operative in causing bathochromic shifts, then the CCBSS styryl dyes **2a**, which have less strain (the phenyl group being two C-atoms away from the prime chromophoric chain), should absorb at shorter wavelengths than the more strained β-phenyl substituted dyes **2b**. The results are, however, the reverse of this, the CCBSS styryl dyes absorb at longer wavelengths than the corresponding β-phenyl substituted styryl dyes.



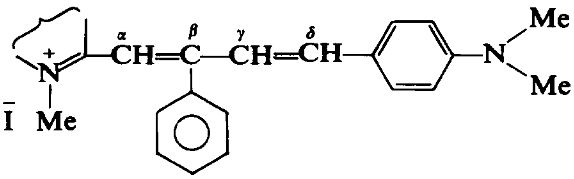
2a



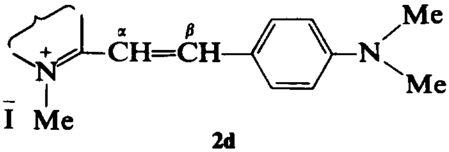
2b

It would thus appear from the above results that no consistent theory can be put forward correlating absorption splits with the character of the β-substituent, other than that any β-substitution causes bathochromic shifts in styryl cyanine dyes.[1-4]

The CCBPS butadienyl dyes **2c** differ from the 4-dimethylaminostyryl dyes **2d** in two ways: they have a longer conjugated chain and also a chromophoric chain β-phenyl substituent. However, the CCBPS butadienyl dyes **2c** differ from the β-phenyl substituted styryl dyes **2b** only in the increased length of the conjugated chain, the phenyl substituent being attached to the identical carbon atom of the chromophoric chain, but the steric effect of the β-substituent in the butadienyl dyes **2c** is not



2c



2d

likely to be the same as that of the same substituent in β-phenyl substituted styryl dyes **2b**. The two phenyl groups are directly linked to the sp^2 C-atom in the dyes **2b**, whilst in the dyes **2c**, one of the phenyl groups is two C-atoms away. The dyes **2b**, due to the bulky β-phenyl group adjacent to the dimethylaminobenzene nucleus, may suffer an out-of-plane twisting; such influence is absent in the dyes **2c**. Further, the dyes **2c** may also be expected to have added resonance stabilisation due to additional π-orbital interaction between the two N-atoms involved in the resonance.

The dyes **2a** have the same separation of the two phenyl groups attached to sp^2 C-atoms but the additional π-orbital stabilisation is absent in these dyes. However, the CCBPS butadienyl dyes (series **1**) absorb at lower wavelengths than their β-phenyl styryl analogues (series **3**), as shown in Table 1. Lengthening of the conjugated chain has not, therefore, led to the greater than expected bathochromic shifts in absorption maxima, at least in the case where the chromophoric chain is β-substituted. On the contrary, β-substitution in butadienyl dyes results in a hypsochromic shift in comparison to β-phenyl-substituted styryl dyes, as is also reported in the literature[17-22] for styryl dyes.

Data for the CCBPS butadienyl dyes (series **2**) and the chain unsubstituted styryl dyes (series **6**) confirm established results. It is known that bathochromic shifts are frequently discernible in the absorption of cyanine dyes with lengthening of the conjugated chain of C-atoms between polyvalent atoms involved in the resonance system.[5,16] The butadienyl dyes (series **2**) exhibit small, but definite, bathochromic shifts in λ_{max} compared to their corresponding chain unsubstituted dyes (series **6**), as shown in Table 2. This bathochromic shift may be attributed to

TABLE 2
Comparison of λ_{max} of the Butadienyl and the Chain Unsubstituted Styryl Dyes (mμ)

	H	*Cl*	*Br*	*I*	*Ref.*
CCBPS butadienyl dyes	532	550	554	572	Present work
Chain unsubstituted styryl dyes	530	548	550	552	6, 8
Bathochromic shift	2	2	4	20	

intramolecular protonation of the methylenic N-atom, with a consequent stabilisation of the delocalised polyenic cation.[34]

In the heterocyclic moiety, the influence of the 6-substituents in λ_{max}, although small, is consistent and systematic for the series **1** and **2**. Thus, progressive increase in molecular weight of the substituent causes progressive bathochromic shifts in both the present series and also in all the preceding series,[1-3] the sequence being generally in the order:

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

and

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

The present results confirm earlier observations that the nature and position of the substituents in the heterocyclic terminal residue of the dye molecule may affect both the visible absorption band and the photosensitisation properties.[35-38]

The spectroscopic absorption of the dyes, based on the condensed β-naphthaquinaldine system, is anomalous but, even in this case, the effect of β-phenyl groups is clearly operative, the dyes showing bathochromic shifts in most of the series (except series **2**) compared to the β-unsubstituted analogues[6,8] and thus supporting the previous observations.[1-4]

2.2. Photosensitisation

A study of the sensitisation data does not permit any definite generalisation to be made. CCBSS styryl dyes (series **1**) are slightly better sensitisers than the β-phenyl styryl dyes (series **3**), but are inferior sensitisers to the corresponding other β-substituted dyes, whether they carry an electron-attracting group (series **4**), an electron-donating group (series **5**) or even are chain unsubstituted dyes (series **6**). Thus the chromophoric chain β-substitution has no beneficial effect. The ranges of extra sensitisation of the β-substituted styryl dyes (except series **5**) are in general lower than those for β-unsubstituted analogues. This may be related to steric effects since the CCBPS and CCBSS groups of styryl cyanines are probably projecting above and below the plane of the conjugated planar molecules.[3,38]

CCBPS butadienyl dyes (series **2**) are superior sensitisers to most of the previously studied β-substituted styryl dyes,[1,3,4] with respect to their extension, range, maximum and distinct uniform intensity (Table 3). In this series several dyes ($\mathbf{D_{55}}$, $\mathbf{D_{56}}$, $\mathbf{D_{57}}$ and $\mathbf{D_{59}}$) have high extra sensitisation, the λ_{max} having shifted towards the longer wavelengths by 0·160 mμ (1600 Å). The photosensitising properties of this series of dyes are more or less comparable with those of β-4-dimethylaminostyryl dyes (series **5**) but are definitely superior to their corresponding isomeric CCBSS styryl dyes (series **1**). Presumably the lengthening of a conjugated chain between the two N-atoms (hetero- and exo-cyclic) is responsible for such enhancement in spectral sensitisation. There is little possibility of steric hindrance to the planarity of the resonating system and consequently the delocalisation of π molecular orbitals is not hindered.

It is also noticeable that the extension of optical sensitisation conferred by 6-substituents in the heterocyclic system follows a similar sequence to that observed in absorption characteristics, i.e.

$$I > Br > Cl > H$$

and

$$Me \geq OEt \geq OMe > H > \beta\text{-naphthyl}$$

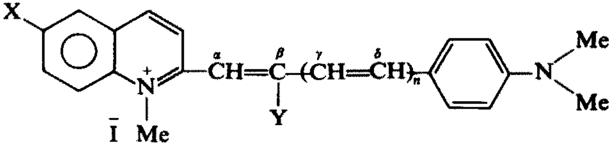
in both the series **1** and **2**.

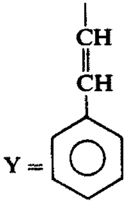
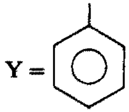
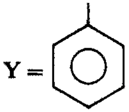
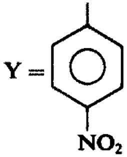
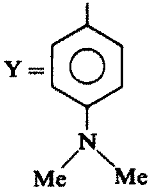
2.3. General comparative observations

A preliminary observation may thus be made that any substitution at the β-position in the chromophoric chain of styryl dyes leads to bathochromic shifts in absorption maxima and to enhanced sensitisation as is shown by a comparison of the data for the chain unsubstituted dyes quoted in the literature[1-3,6,8,39] (Tables 1 and 3).

Considering the two optical properties of the β-substituted styryl dyes,

TABLE 3
Sensitisation Data of CCBSS Styryl and CCBPS Butadienyl Dyes (Metho Salts)



Present work		*Reported work*			
					Y = H
n = 0 Series **1**	n = 1 Series **2**	n = 0 Series **3** (Refs. 1, 3)	n = 0 Series **4** (Refs. 1, 3)	n = 0 Series **5** (Ref. 2)	n = 0 Series **6** (Refs. 6, 8)

X	*Dye*	*Range* (*mμ*)	λ_{max}[a] (*mμ*)	*Remarks*[a]	*Dye*	*Range* (*mμ*)	λ_{max}[a] (*mμ*)	*Remarks*[a]	*Range* (*mμ*)	λ_{max} (*mμ*)	*Range* (*mμ*)	λ_{max} (*mμ*)	*Range* (*mμ*)	λ_{max} (*mμ*)	*Range* (*mμ*)	λ_{max} (*mμ*)
H	$\mathbf{D_{45}}$	615	560vw 585w	vw lc	$\mathbf{D_{53}}$	630	560u	mi c	600	580	630	570	630	580	630	580
Cl	$\mathbf{D_{46}}$	630	585u	w ac	$\mathbf{D_{54}}$	550	585u	fi c	610	580	640	540 570	680 ≥ 600	540 580	650	595
Br	$\mathbf{D_{47}}$	630	585w	w ac iibvi	$\mathbf{D_{55}}$	680	585u	fi c	620	540	640	580	680 ≥ 600	540 580 660	650	595
I	$\mathbf{D_{48}}$	630	585w	w ac iibvi	$\mathbf{D_{56}}$	680	600s	vi c	620	560	650	580	680 ≥ 600	540 580 660	650	600
Me	$\mathbf{D_{49}}$	630	540vw 585w	wbc	$\mathbf{D_{57}}$	680	580u	vi ac	610	550	630	560	610	580		
OMe	$\mathbf{D_{50}}$	620 600t	580vw	vw nu	$\mathbf{D_{58}}$	640	585u	fi c	610	530 550	640	565	680 ≥ 600	540 580		
OEt	$\mathbf{D_{51}}$	620 600t	580w	vw nu	$\mathbf{D_{59}}$	680	560u	i au	620	530 550	640	600	680 600	540 580		
 5,6-Benzo	$\mathbf{D_{52}}$	620 600t	590w	vw nu	$\mathbf{D_{60}}$	640	580	i ac	600	525 550	640	—	≥ 640	525 550		

[a] Abbreviations: ac, almost continuous; au, almost uniform; bc, but continuous; c, continuous; fi, fairly intense; i, intense; iibvi, intense in blue violet increased; lc, loosely connected; nu, not uniform; mi, moderately intense; t, trace; u, unpronounced; vi, very intense; vw, very weak; w, weak.

TABLE 4
Relationship Between Absorption and Sensitisation Maxima of CCBSS Styryl Dyes (mμ)

Dye	*Absorption* λ_{max}	*Sensitisation* λ_{max}	*Difference*
D_{45}	564	560	+4
D_{46}	576	585	−9
D_{47}	578	585	−7
D_{48}	583	585	−2
D_{50}	581	580	+1
D_{51}	582	580	+2

no general relationship between them can be made. However, in the case of the CCBSS styryl dyes, absorption and sensitisation maxima closely approximate in most cases (Table 4), supporting the view of earlier workers.[14,40-42]

CCBSS styryl dyes (series **1**) have absorption maxima at longer wavelengths than the β-phenyl-substituted analogues (series **3**). Though the former have greater extension of sensitisation, they are weaker sensitisers, so far as intensity of sensitisation is concerned (Tables 1 and 3).

Comparison of the spectral data (absorption and sensitisation) of the CCBPS butadienyl dyes (series **2**) shows that, the absorption maxima of these dyes are shifted towards the red, corresponding to a similar shift to the extra sensitisation maxima, which is in accord with the general observation of the earlier workers[7,14,40] and of the authors[1-4] in the case of butadienyl cyanines. In this series, sensitisation maxima are at relatively longer wavelengths than the corresponding absorption maxima.

3. EXPERIMENTAL

3.1. The chalcones

(i) 4-Dimethylaminophenyl styryl ketone (chalcone)

The general procedure for the synthesis of ketones described by Shah *et al.*[43] was adopted with suitable modifications.

The starting material, cinnamalanilide, was reached according to the process as previously described.[1] The precaution of temperate heating obviated tar formation and the chalcone obtained was recrystallised from ethanol–benzene (3:1) in small fibrous yellow crystals; yield 35%, m.p. 164–165 °C.

> Found: C, 81·24; H, 6·72; N, 5·52; $C_{17}H_{17}ON$ requires: C, 81·27; H, 6·77; N, 5·58%. IR spectra: ν_{max}^{KBr} (cm^{-1}), 1165(C—N—C); 1310(CH═CH); 1590(C═C); 1740(C═O).

(*ii*) *4-Dimethylaminostyryl phenyl ketone* (*chalcone*)

This compound was obtained by a method similar to that used[44] for the preparation of 2′-nitrochalcone. Refluxing 4-dimethylaminobenzaldehyde and acetophenone in the presence of sodium acetate afforded the chalcone, which was recrystallised from aqueous ethanol as glistening yellow leaflets; yield 70%, m.p. 100 °C.

> Found: C, 81·23; H, 6·73; N, 5·52; $C_{17}H_{17}ON$ requires: C, 81·27; H, 6·77; N, 5·58%. IR spectra: ν_{max}^{KBr} (cm^{-1}), 1160(C—N—C); 1310(CH═CH); 1590(C═C); 1690(C═O).

3.2. The substituted quinaldine methiodides

The quaternised quinaldinium salts were obtained by the method of Johnson and Adams[45] with slight modifications as described earlier.[1]

3.3. The styryl and butadienyl dyes

Condensations to form the dyes were effected by the previously reported general method.[1,2] A solution of the chalcone and the quaternary salt (1:1 molar) in absolute ethanol, together with a few drops of piperidine, was refluxed for about 2h. The dye, which separated on cooling, was purified by recrystallisation from methanol.

Analytical data, yield, m.p. (uncorrected) and other characteristics of the dyes are summarised in Table 5.

3.4. Absorption and photosensitisation spectra

Absorption maxima were recorded on a Beckmann spectrometer, model DU, and photosensitisation on an Adam Hilger wedge spectrograph, using process plates (N40, Ilford Ltd) in the manner described previously.[1-3]

TABLE 5
Analytical Data of CCBSS Styryl and CCBPS Butadienyl Dyes

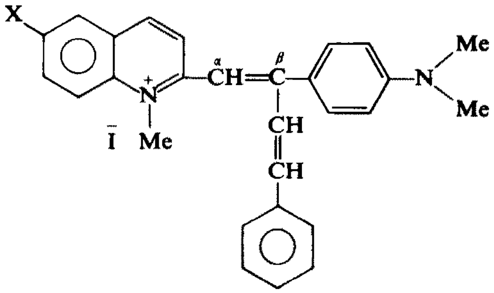
Dye	*Quaternised base*[a]	*Dye name*[a]	*Crystal colour and shape*[b]	*Yield (%)*	*M.p. (°C)*	*Molecular formula*	*Found (%)*		*Calc. (%)*	
							N	*Hal*	*N*	*Hal*
D_{45}	Q'MeI	2-*p*-DMA(*β*-S)-S-QMeI	dvsc	60·5	194	$C_{28}H_{27}IN_2$	5·34	24·46	5·40	24·52
D_{46}	6-ClQ'MeI	2-*p*-DMA(*β*-S)-S-6-ClQMeI	dvs'n	67·8	210	$C_{28}H_{26}ClIN_2$	5·02	29·35	5·07	29·41
D_{47}	6-BrQ'MeI	2-*p*-DMA(*β*-S)-S-6-BrQMeI	dvtnwrr'	68·8	225	$C_{28}H_{26}BrIN_2$	4·62	34·65	4·69	34·69
D_{48}	6-IQ'MeI	2-*p*-DMA(*β*-S)-S-6-IQMeI	dvlmn	69·8	243	$C_{28}H_{26}I_2N_2$	4·27	39·39	4·36	39·43
D_{49}	6-MeQ'MeI	2-*p*-DMA(*β*-S)-S-6-MeQMeI	dvl'wbgr'	57·4	221	$C_{29}H_{29}IN_2$	5·21	23·82	5·26	23·87
D_{50}	6-OMeQ'MeI	2-*p*-DMA(*β*-S)-S-6-OMeQMeI	dvc	61·5	238	$C_{29}H_{29}IN_2O$	5·05	23·09	5·11	23·18
D_{51}	6-OEtQ'MeI	2-*p*-DMA(*β*-S)-S-6-OEtQMeI	dvs"w'c'	63·4	253	$C_{30}H_{31}IN_2O$	4·91	22·51	4·98	22·59
D_{52}	5,6BzQ'MeI	2-*p*-DMA(*β*-S)-S-*β*-NtQMeI	dvg'c	47·3	267	$C_{32}H_{29}IN_2$	4·85	22·30	4·93	22·36
D_{53}	Q'MeI	2-*p*-DMA(*β*-P)-BDE-QMeI	dvnwgr'	87·6	207	$C_{28}H_{27}IN_2$	5·36	24·47	5·40	24·52
D_{54}	6-ClQ'MeI	2-*p*-DMA(*β*-P)-BDE-6-ClQMeI	dvs'''tn	89·5	217	$C_{28}H_{26}ClIN_2$	5·01	29·36	5·07	29·41
D_{55}	6-BrQ'MeI	2-*p*-DMA(*β*-P)-BDE-6-BrQMeI	dvln	88·7	230	$C_{28}H_{26}BrIN_2$	4·62	34·71	4·69	34·69
D_{56}	6-IQ'MeI	2-*p*-DMA(*β*-P)-BDE-6-IQMeI	dvg'cwgr'	88·5	239	$C_{28}H_{26}I_2N_2$	4·28	39·38	4·36	39·43
D_{57}	6-MeQ'MeI	2-*p*-DMA(*β*-P)-BDE-6-MeQMeI	dvtnwrr'	84·0	226	$C_{29}H_{29}I_2N$	5·19	23·83	5·26	23·87
D_{58}	6-OMeQ'MeI	2-*p*-DMA(*β*-P)-BDE-6-OMeQMeI	dvs"f	90·1	235	$C_{29}H_{29}IN_2O$	5·03	23·07	5·11	23·18
D_{59}	6-OEtQ'MeI	2-*p*-DMA(*β*-P)-BDE-6-OEtQMeI	dvsn	91·3	242	$C_{30}H_{31}IN_2O$	4·89	22·52	4·98	22·59
D_{60}	5,6-BzQ'MeI	2-*p*-DMA(*β*-P)-BDE-*β*-NtQMeI	dvlmn	84·5	252	$C_{32}H_{29}IN_2$	4·84	22·28	4·93	22·36

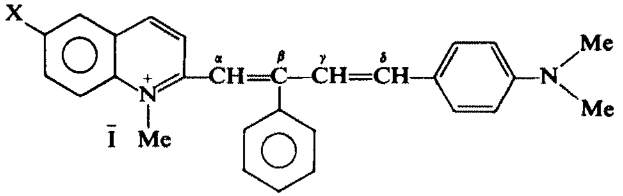
[a] Abbreviations: Q, quinoline; Q', quinaldine; S, styryl; Bz, benzo; Nt, naphthyl; BDE, butadienyl; DMA, dimethylamino.

[b] Abbreviations: b, bottle; c, crystals; c', clusters; d, dark; f, flakes; g, green; g', glistening; l, lustrous; l', leaflets; n, needles; m, minute; r, reddish; r', reflux; s, small; s', slender; s", scintillating; s''', shining; t, tiny; v, violet; w, with; w', woolly.

TABLE 6

Antimicrobial Activity of CCBSS Styryl and CCBPS Butadienyl Compounds (Test Solution 0·5 mg)





X	*Dye*	*Diameter of inhibitory zone (mm)*		*Dye*	*Diameter of inhibitory zone (mm)*	
		S. aureus 24 h	*E. coli 24 h*		*S. aureus 24 h*	*E. coli 24 h*
H	D_{45}	30	24	D_{53}	34	28
Cl	D_{46}	40	34	D_{54}	45	36
Br	D_{47}	40	32	D_{55}	45	35
I	D_{48}	36	29	D_{56}	40	33
Me	D_{49}	23	18	D_{57}	30	22
OMe	D_{50}	28	23	D_{58}	33	27
OEt	D_{51}	26	22	D_{59}	32	26
5,6-Benzo	D_{52}	15	10	D_{60}	22	16

3.5. Antimicrobial activity

The purified and screened cyanines were tested for antibacterial activity against *S. aureus* and *E. coli* by the cup–plate method,[46] using ethanol as a solvent (concn 10 mg ml^{-1}). The test solution (containing 0·5 mg) was used for 24 h to study the action. The results are recorded in Table 6.

The halogen derivatives (**D_{54}–D_{56}** and **D_{46}–D_{48}**) of CCBPS butadienyl and CCBSS styryl compounds were found highly active against *S. aureus* (ZI: 36–45 mm) and against *E. coli* (ZI: 29–36 mm), whilst the phenyl and alkoxy derivatives (**D_{53}**, **D_{58}**, **D_{59}** and **D_{45}**, **D_{50}**, **D_{51}**) showed moderate activity against *S. aureus* (ZI: 26–34 mm) and against *E. coli* (ZI: 22–28 mm). Thus, the halide-substituted compounds exhibit more pronounced antibacterial activity than the other derivatives studied, although the above range of activity is less as compared to antibiotics like tetracyclines, chloramphenicol, sulpha drugs, penicillins, etc.

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