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Chromophoric Chain β-Aryl-Substituted Styryl Cyanines: Effect of Substituents on Visible Absorption Spectra and Photosensitisation Properties

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SUMMARY

A number of chromophoric chain β-aryl-substituted (CCBAS) styryl cyanines (hemicyanines) have been synthesised by condensing substituted quaternised quinaldine bases with substituted benzophenones, with a view to studying the effect of the aryl substituents on their visible absorption and silver halide photosensitisation properties.

The dyes absorb at longer wavelengths than the unsubstituted analogues, showing uniform bathochromic shifts and extra-photosensitisation properties, which corroborate the authors' previous findings.

Irrespective of the nature of the substituent attached to the chromophoric β-phenyl group, electron withdrawing and donating groups result in a bathochromic shift of the visible absorption band and extension of the extra-photosensitisation in most cases.

1. INTRODUCTION

We have reported recently the spectroscopic and sensitisation properties of a number of hemicyanines.[1–3] As a continuation of this work some

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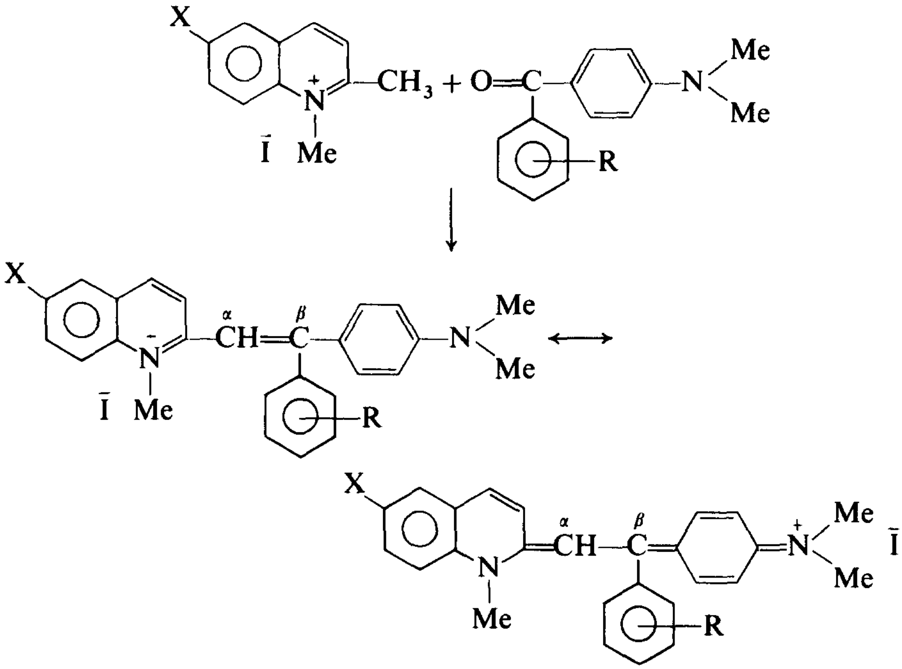
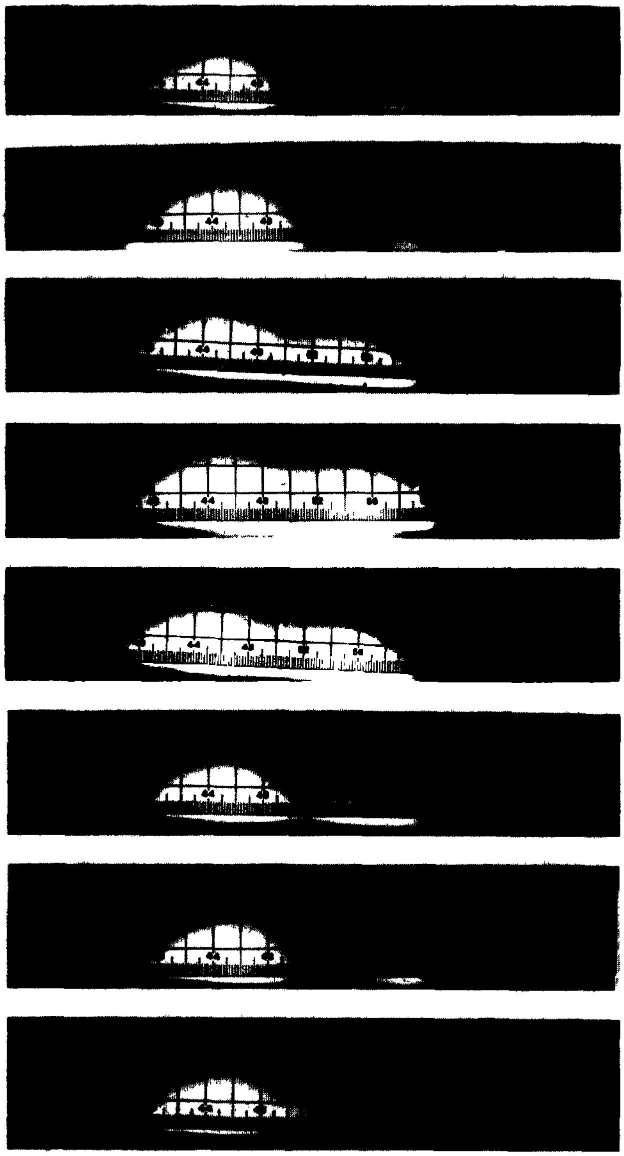
more CCBAS dyes have been prepared and the effect of the various β-aryl substituents on optical properties has been studied. These dyes were prepared by condensing 4-dimethylamino-, 4-dimethylamino-4′-nitro-, 4-dimethylamino-2′-nitro- and 4-dimethylamino-3′,5′-dinitro-benzophenones with different 6-substituted quinaldinium salts as summarised in Scheme 1.

Absorption maxima (λ_{max}) and the ranges of extra-sensitisation data have been recorded and comparison made between the corresponding



Dye	*X*	*R*	*Dye*	*X*	*R*	*Dye*	*X*	*R*
D$_1$	H	H	**D$_9$**	H	4-nitro	**D$_{21}$**	Me	2-nitro
D$_2$	Cl	H	**D$_{10}$**	Cl	4-nitro	**D$_{22}$**	OMe	2-nitro
D$_3$	Br	H	**D$_{11}$**	Br	4-nitro	**D$_{23}$**	OEt	2-nitro
D$_4$	I	H	**D$_{12}$**	I	4-nitro	**D$_{24}$**	5,6-Benz	2-nitro
D$_5$	Me	H	**D$_{13}$**	Me	4-nitro	**D$_{29}$**	Me	3,5-dinitro
D$_6$	OMe	H	**D$_{14}$**	OMe	4-nitro	**D$_{30}$**	OMe	3,5-dinitro
D$_7$	OEt	H	**D$_{15}$**	OEt	4-nitro	**D$_{31}$**	OEt	3,5-dinitro
D$_8$	5,6-Benz	H	**D$_{16}$**	5,6-Benz	4-nitro	**D$_{32}$**	5,6-Benz	3,5-dinitro

Scheme 1



D_1

D_2

D_3

D_4

D_5

D_6

D_7

D_8

Fig. 1. Sensitisation spectrographs of the dyes.

D_9

D_{10}

D_{11}

D_{12}

D_{13}

D_{14}

D_{15}

D_{16}

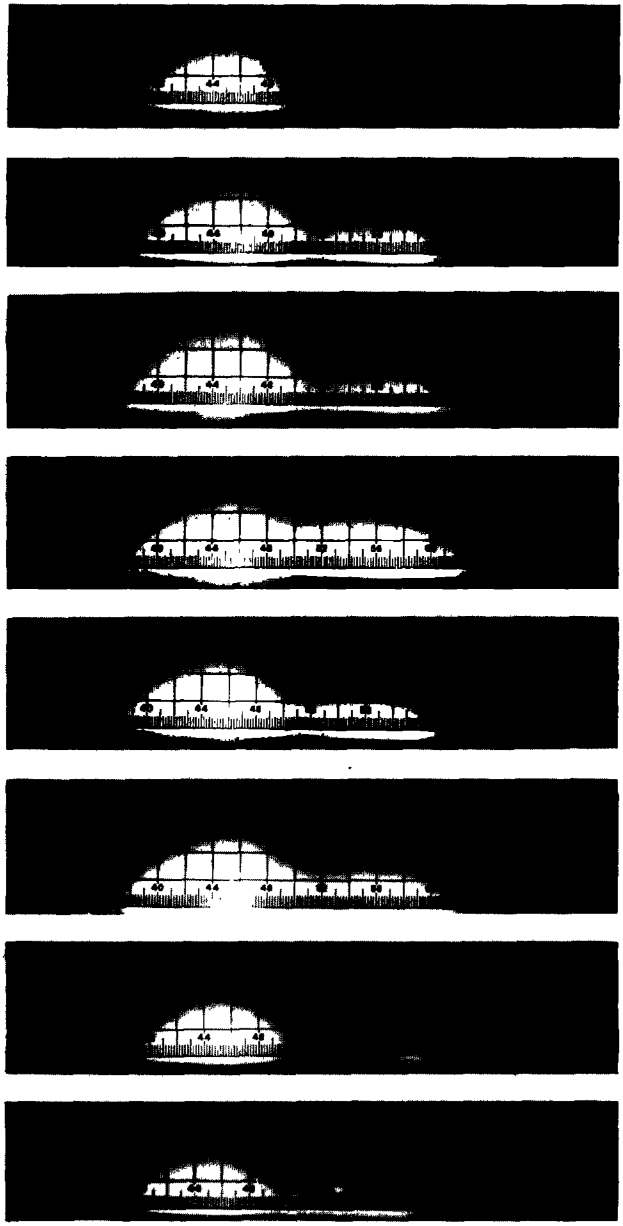


Fig. 1—*contd.*

D_{21}

D_{22}

D_{23}

D_{24}

D_{29}

D_{30}

D_{31}

D_{32}

Unbathed

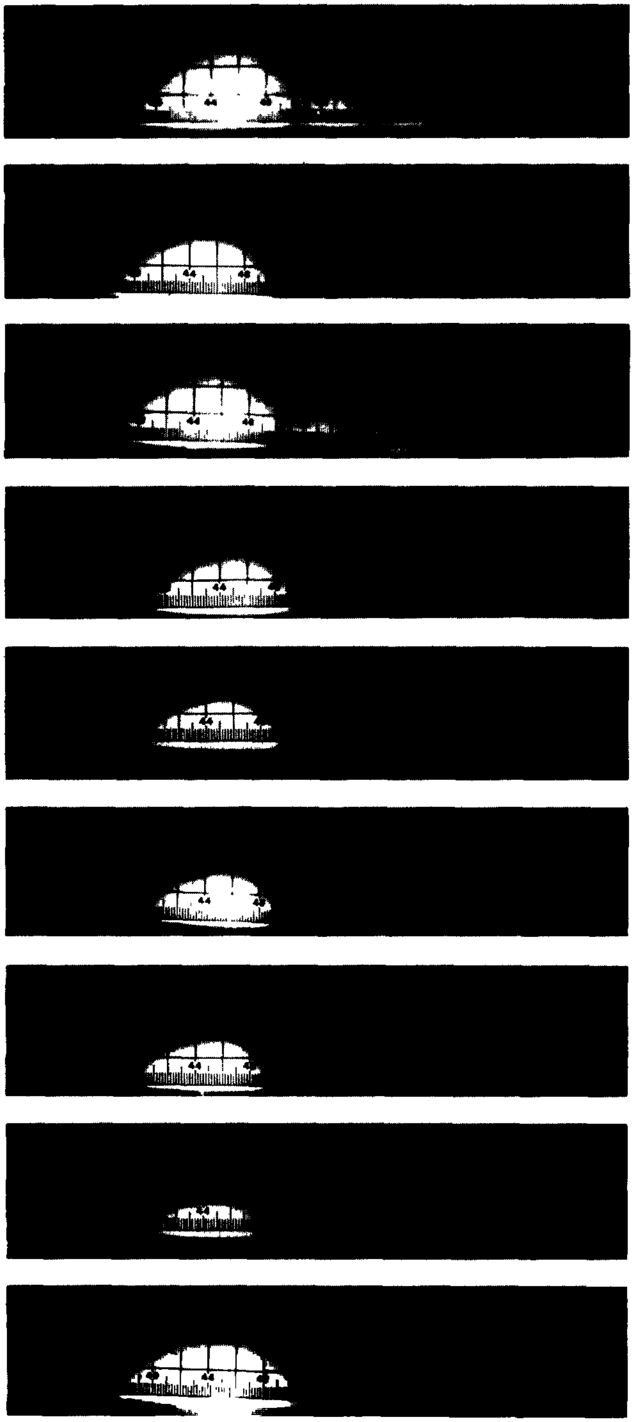


Fig. 1—*contd.*

chain β-substituted and β-unsubstituted analogues.[4,5] The styryl cyanines have been examined extensively[3-12] and earlier observations suggest that substituents attached to α- or β-carbon atom with respect to the heterocyclic end group in the chromophoric chain cause hypsochromic shifts of the absorption maxima compared with the unsubstituted analogues.[13-17]

However, the dyes now described show invariably bathochromic shifts which confirm the authors' previously reported work.[1-3]

Since the β-phenyl, β-4-nitrophenyl and β-2-nitrophenyl substituents have a strong resonance effect, it is possible that chromophoric chain β-substitution of this type may affect the resonance stabilisation of the dye molecule. However, the steric hindrance to the resonance stabilisation in the prime chromophoric chain due to the bulkiness of the β-substituents may also be an important factor to consider.

2. RESULTS AND DISCUSSION

Analytical and other experimental data for the dyes are summarised in Table 1. Sensitisation spectrographs of photographic plates treated with the dyes were obtained and compared with that of an undyed plate (Fig. 1). The absorption maxima (λ_{max}) of the iodide salts in ethanol are recorded in Table 2 and the extra-sensitisation data in Table 3.

2.1. Visible absorption spectra

Comparison of the absorption data for the present CCBAS styryl cyanine dyes (series 1, series 2, $\mathbf{D}_{21-24}$ of series 3 and $\mathbf{D}_{29-32}$ of series 4), with those analogues described previously[1,2] ($\mathbf{D}_{17-20}$ of series 3, $\mathbf{D}_{25-28}$ of series 4 and series 5) and with the β-unsubstituted dyes[4,5] (series 6) cited from the literature permits the following generalisations to be made.

A chain β-aryl substituent causes a general bathochromic shift of the absorption maximum of about 20–40 mμ relative to corresponding unsubstituted analogues,[4,5] irrespective of the nature of any additional groups attached to the phenyl ring, i.e., whether they are electron attracting or electron donating or whether they are just space occupying. This is in contrast to the earlier observations that either α- or β-substitution generally leads to hypsochromic shifts.[13-17] The present report also corroborates the authors' previous investigations.[1-3]

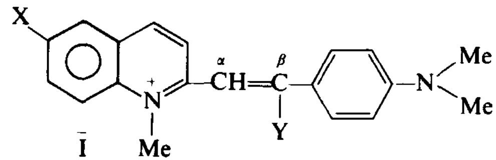
TABLE 1
Analytical Data of the Dyes

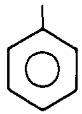
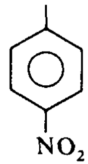
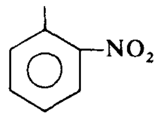
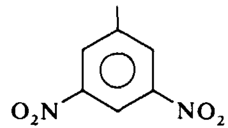
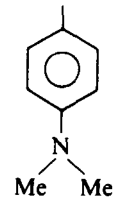
Dye symbol	*Methiodide of base*[a]	*Dye as methiodide*[a]	*Crystal colour and shape*[b]	*Yield (%)*	*M.p. (°C)*	*Molecular formula*	*Found (%)*		*Calc. (%)*	
							N	*Hal.*	*N*	*Hal.*
D_1	Q'MeI	2-*p*-DMA(β-P)-S-QMeI	dvc	46	130	$C_{26}H_{25}N_2I$	5·63	25·76	5·69	25·81
D_2	6-ClQ'MeI	2-*p*-DMA(β-P)-S-6-ClQMeI	sdvc	41	160	$C_{26}H_{24}N_2ClI$	5·28	30·81	5·32	30·86
D_3	6-BrQ'MeI	2-*p*-DMA(β-P)-S-6-BrQMeI	dvtn	46	175	$C_{26}H_{24}N_2BrI$	4·85	36·17	4·90	36·25
D_4	6-IQ'MeI	2-*p*-DMA(β-P)-S-6-IQMeI	ivs'n	44	212	$C_{26}H_{24}N_2I_2$	4·48	41·23	4·53	41·10
D_5	6-MeQ'MeI	2-*p*-DMA(β-P)-S-6-MeQMeI	ldvtn	68	169	$C_{27}H_{27}N_2I$	5·47	25·05	5·53	25·10
D_6	6-MeOQ'MeI	2-*p*-DMA(β-P)-S-6-MeOQMeI	gdvmn	61	185	$C_{27}H_{27}N_2IO$	5·31	24·39	5·36	24·33
D_7	6-EtOQ'MeI	2-*p*-DMA(β-P)-S-6-EtOQMeI	ldvn	63	208	$C_{28}H_{29}N_2IO$	5·14	23·62	5·22	23·69
D_8	5,6-BzQ'MeI	2-*p*-DMA(β-P)-S-β-NtQMeI	dvc	51	212	$C_{30}H_{27}N_2I$	4·98	23·23	5·02	23·29
D_9	Q'MeI	2-*p*-DMA(β-4-NP)-S-QMeI	dvc	43	185	$C_{26}H_{24}N_3IO_2$	7·76	23·59	7·82	23·65
D_{10}	6-ClQ'MeI	2-*p*-DMA(β-4-NP)-S-6-ClQMeI	sdvs″n	45	204	$C_{26}H_{23}N_3ClIO_2$	7·31	28·42	7·35	28·45
D_{11}	6-BrQ'MeI	2-*p*-DMA(β-4-NP)-S-6-BrQMeI	dvn	47	210	$C_{26}H_{23}N_3BrIO_2$	6·78	33·65	6·82	33·62
D_{12}	6-IQ'MeI	2-*p*-DMA(β-4-NP)-S-6-IQMeI	dvtn	50	241	$C_{26}H_{23}N_3I_2O_2$	6·29	38·36	6·33	38·31
D_{13}	6-MeQ'MeI	2-*p*-DMA(β-4-NP)-S-6-MeQMeI	drvg'n	46	197	$C_{27}H_{26}N_3IO_2$	7·57	22·98	7·62	23·05
D_{14}	6-MeOQ'MeI	2-*p*-DMA(β-4-NP)-S-6-MeOQMeI	dvtn	47	214	$C_{27}H_{26}N_3IO_3$	7·36	22·34	7·41	22·40
D_{15}	6-EtOQ'MeI	2-*p*-DMA(β-4-NP)-S-6-EtOQMeI	dvtn	62	222	$C_{28}H_{28}N_3IO_3$	7·18	21·81	7·23	21·86
D_{16}	5,6-BzQ'MeI	2-*p*-DMA(β-4-NP)-S-β-NtQMeI	dvs″cwrt′	46	237	$C_{30}H_{26}N_3IO_2$	7·09	21·57	7·17	21·63
D_{21}	6-MeQ'MeI	2-*p*-DMA-(β-2-NP)-S-6-MeQMeI	dvtnwrt′	63	211	$C_{27}H_{26}N_3IO_2$	7·58	23·01	7·62	23·05
D_{22}	6-MeOQ'MeI	2-*p*-DMA(β-2-NP)-S-6-MeOQMeI	gdvmn	55	219	$C_{27}H_{26}N_3IO_3$	7·36	22·33	7·41	22·40
D_{23}	6-EtOQ'MeI	2-*p*-DMA(β-2-NP)-S-6-EtOQMeI	dvsn	45	236	$C_{28}H_{28}N_3IO_3$	7·17	21·82	7·23	21·86
D_{24}	5,6-BzQ'MeI	2-*p*-DMA(β-2-NP)-S-β-NtQMeI	dvs″w′c′	44	265	$C_{30}H_{26}N_3IO_2$	7·11	21·58	7·17	21·63
D_{29}	6-MeQ'MeI	2-*p*-DMA(β-3,5-DNP)-S-6-MeQMeI	dvtn	67	168	$C_{27}H_{25}N_4IO_4$	9·35	21·27	9·40	21·31
D_{30}	6-MeOQ'MeI	2-*p*-DMA(β-3,5-DNP)-S-6-MeOQMeI	sdvs″n	69	172	$C_{27}H_{25}N_4IO_5$	9·07	20·71	9·15	20·75
D_{31}	6-EtOQ'MeI	2-*p*-DMA(β-3,5-DNP)-S-6-EtOQMeI	gdvs'n	70	181	$C_{28}H_{27}N_4IO_5$	8·87	20·24	8·94	20·29
D_{32}	5,6-BzQ'MeI	2-*p*-DMA(β-3,5-DNP)-S-β-NtQMeI	g'dvtn	65	203	$C_{30}H_{25}N_4IO_4$	8·81	20·03	8·86	20·09

[a] Q, quinoline; Q′, quinaldine; P, phenyl; S, styryl; Bz, Benz; NP, nitrophenyl; Nt, naphthyl; DMA, dimethylamino; DNP, dinitrophenyl.

[b] c, Crystals; c′, clusters; d, dark; g, glistening; g′, glazing; i, intense; l, lustrous; m, minute; n, needles; r, reddish; s, shining; s′, slender; s″, small; t, tiny; t′, tinge; v, violet; w, with; w′, woolly.

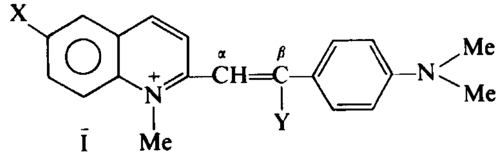
TABLE 2
Absorption Data of the Dyes (Methosalts in Absolute Ethanol)

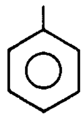
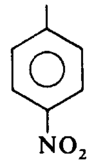
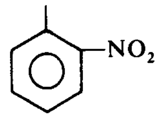
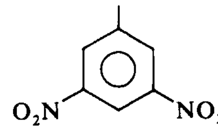
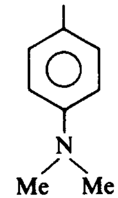


	Present work[a]								Reported work	
$Y \rightarrow$										H
	Series 1		Series 2		Series 3		Series 4		Series 5 (ref. 2)	Series 6 (refs 4, 5)
X ↓	Dye	λ_{max} ($m\mu$)	Dye	λ_{max} ($m\mu$)	Dye	λ_{max} ($m\mu$)	Dye	λ_{max} ($m\mu$)	λ_{max} ($m\mu$)	λ_{max} ($m\mu$)
H	D_1	562	D_9	563	$*D_{17}$	564	$*D_{25}$	569	568	530
Cl	D_2	570	D_{10}	570	$*D_{18}$	578	$*D_{26}$	578	577	548
Br	D_3	575	D_{11}	575	$*D_{19}$	579	$*D_{27}$	580	579	550
I	D_4	582	D_{12}	584	$*D_{20}$	583	$*D_{28}$	584	585	552
Me	D_5	545	D_{13}	569	D_{21}	568	D_{29}	574	578	
OMe	D_6	548	D_{14}	575	D_{22}	577	D_{30}	578	580	
OEt	D_7	569	D_{15}	578	D_{23}	579	D_{31}	583	581	
5,6-Benz	D_8	571	D_{16}	573	D_{24}	574	D_{32}	576	575	

[a] Values marked with an asterisk have been taken from Ref. 1.

TABLE 3
Sensitisation Data of the Dyes (Methosalts)



X ↓	Present work[a]															Reported work			
Y →																		H	
	Series 1				*Series 2*				*Series 3*				*Series 4*			*Series 5* (*ref. 2*)		*Series 6* (*refs 4, 5*)	
	Dye	*Range* (*mμ*)	*λ_{max}* (*mμ*)	*Remarks*[b]	*Dye*	*Range* (*mμ*)	*λ_{max}*[b] (*mμ*)	*Remarks*[b]	*Dye*	*Range* (*mμ*)	*λ_{max}*[b] (*mμ*)	*Remarks*[b]	*Dye*	*Range*[c] (*mμ*)	*λ_{max}* (*mμ*)	*Range*[b] (*mμ*)	*λ_{max}*[b] (*mμ*)	*Range* (*mμ*)	*λ_{max}* (*mμ*)
H	D_1	600	580	w, dc	D_9	630	570	w, ai	*D_{17}	620	560	w, dc, ibvr	*D_{25}	D^s	—	630	580	630	580
Cl	D_2	610	580	w, dc, mp	D_{10}	640	540w 570m	mi, ai	*D_{18}	630	590up	mi, c	*D_{26}	D^s	—	680 (≥ 600w)	540up 580w	650	595
Br	D_3	620	540	i, au	D_{11}	640	580	mi, ac	*D_{19}	630	590	mi, c	*D_{27}	D^s	—	680 (≥ 600w)	540w 580 660vw	650	595
I	D_4	620	560	i, au	D_{12}	650	580	i, c	*D_{20}	650	590	i, lc	*D_{28}	D^s	—	680 (≥ 600mi)	540 580mi 600	650	600
Me	D_5	610	550	i, au	D_{13}	630	560	mi, ub	D_{21}	620	530 580	mi, lc	D_{29}	D^s	—	610	580		
OMe	D_6	610	530 550	mi, c	D_{14}	640	565	mi, ub	D_{22}	620	540vw 580w	w, lc	D_{30}	D^s	—	680 (≥ 600vwt)	540vw 580w		
OEt	D_7	620	530 550	mi, c	D_{15}	640	600	w, ai	D_{23}	620	540 580	mi, c	D_{31}	D^s	—	680 (≥ 600vwt)	540vw 580w		
5,6-Benz	D_8	600	525 550	mi, c	D_{16}	640	—	w, ai	D_{24}	620	580up	w, ai	D_{32}	D^s	—	640	525up 550		

[a] Values marked with an asterisk have been taken from Ref 1

[b] ac, Almost continuous; ai, almost isolated; au, almost uniform, c, continuous; dc, disconnected; i, intense, ibvr, intense blue violet range; il, isolated; lc, loosely connected; m, moderate; mi, moderately intense; mp, more pronounced; ub, uniform band, up, unpronounced; vw, very weak; vwt, very weak trace; w. weak.

[c] D^s, Desensitiser

It can also be seen that the nature of the β-phenyl substituent (where R = H, 4-nitro or 2-nitro) has little effect on the absorption maximum. It is interesting that the recently reported 4-dimethylaminophenyl substituted dyes carrying electron donating substituents at the β-position have, in all cases, λ_{max} at longer wavelengths than the corresponding β-aryl dyes containing electron withdrawing groups or no group in the phenyl ring. The effect of the 4-dimethylaminophenyl group is almost equivalent to the space occupying, but electronically ineffective, β-3,5-dinitrophenyl group.

The influence of 6-substituents in the heterocyclic moiety on λ_{max} is small but consistent for most of the series (1–3). Thus the progressive bathochromic shifts in various series and in the series already reported[1,2] follow the sequence:

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

and also

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

[except in series 1, where $D_1 >$ both D_6 and D_5].

The present results also confirm the earlier observations[18,19] that the nature and position of the substituents in the heterocyclic terminal residue of the dye molecule can influence both the visible absorption band and the sensitisation properties.

Absorption spectrographic properties of the dyes based on the condensed β-naphthaquinaldine system are anomalous, but even here, the effect of β-aryl groups is clearly operative and the dyes again absorb at longer wavelengths than the β-unsubstituted analogues.[4,5]

2.2. Photosensitisation

Analysis of the sensitisation data does not permit any definite generalisation to be made. Although most of the newly prepared dyes (series 1, 2 and 3) except the β-3,5-dinitrophenyl dyes (series 4) are fairly good sensitisers, the effect of the chromophoric chain β-substitution has no appreciable beneficial effect. The ranges of extra-sensitisation are in general lower than those for the β-unsubstituted analogues. This may be a steric effect, due to the CCBAS group projecting above and below the plane of the conjugated planar molecule.[20]

The β-4-nitrophenyl dyes (series 2) are slightly better sensitisers when compared with the β-2-nitrophenyl (series 3) and β-phenyl (series 1) dyes. In some cases (**D_6–D_8**, **D_{10}** and **D_{21}–D_{23}**) two peaks can even be observed. In contrast the β-3,5-dinitrophenyl dyes (series 4) are desensitisers, and the intensity of the silver halide plates in the blue–violet range is decreased. The desensitising property varies in the order

$$\mathbf{D_{28} < D_{27} < D_{26} < D_{25}}$$

and

$$\mathbf{D_{29} < D_{31} < D_{30} < D_{32}}$$

It can also be seen that the extension of optical sensitisation induced by 6-substituents in the heterocyclic moiety follows the sequence:

$$I > Br > Cl > H$$

and

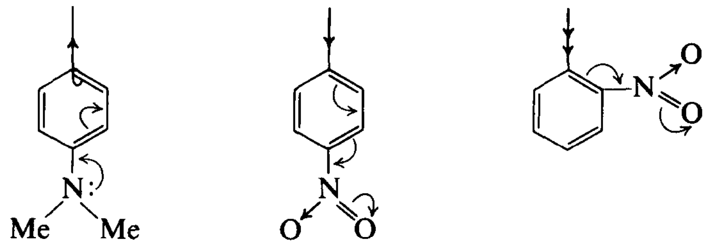
$$OEt \geq OMe \geq Me \geq H$$

Moreover, it was also found that the present dyes were inferior sensitisers in comparison with the β-4-dimethylaminophenyl dyes (series 5), recently reported by the authors,[2] with regard to the range of extra-sensitisation, the extension of the sensitisation maxima, number of peaks and intensity of extra-sensitisation. Of the electron attracting chromophore, —NO_2, and the electron donating auxochrome, —NMe_2, the latter is more effective than the former.

2.3. General comparative conclusion

Comparison of the absorption data of the variously β-substituted styryl dyes leads to some interesting observations.

The recently reported β-4-dimethylaminophenyl substituted dyes[2] (series 5) have consistently longer λ_{max} values than the corresponding β-4-nitrophenyl substituted dyes (series 2). The suggestion that the opposite mesomeric effect of the two substituents (**A**) and (**B**) is responsible for the comparatively lower bathochromic shifts in the case of (**B**), does not appear to be valid. For, if this were the case, the β-2-nitrophenyl substituted dyes (series 3) should have shown significant hypsochromic shifts, the 2-nitrophenyl group (**C**) being more strongly electron attracting than the 4-nitrophenyl group (**B**), because of combined mesomeric and inductive effects. It may, however, be argued that the bulky β-2-substituent causes out-of-plane twisting of the phenyl group, thus



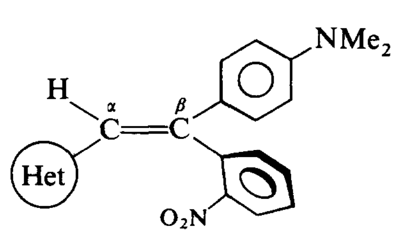
(A) (B) (C)

annulling the mesomeric effect and leaving only the inductive effect operative.

The enhanced bathochromic shifts conferred by the β-3,5-dinitrophenyl substituent (series 4) suggests that steric effects are probably more important than electronic effects. In this case the 3,5-dinitrophenyl group will have no mesomeric effect and only an insignificant inductive effect as a substituent.

It can also be seen for a given terminal hetero substituent that the β-4-dimethylaminophenyl substituted dyes[2] (series 5) are the best sensitisers among those dyes studied by the authors. The obvious conclusion is that the strong electron donating effect to the conjugated system causes an enhanced bathochromic shift and a correspondingly enhanced sensitisation. On the other hand, the β-4-nitrophenyl substituted dyes (series 2) are less effective sensitisers and absorb at a slightly shorter wavelength. The β-4-nitro substituted ring is not likely to lie exactly in the same plane and thus does not fully participate in resonance delocalisation, and consequently its electron withdrawing effect is reduced.

The optical properties of the β-2-nitrophenyl dyes (series 3) are more interesting. Although in the β-2-nitrophenyl compounds, the nitro group causes electron withdrawal due to both mesomeric and inductive effects, the mesomeric effect of the 2-nitrophenyl substituent is likely to be insignificant, as steric interference would, in all probability, twist the benzene ring out of the plane of the main conjugated system [model (**D**)],



(**D**)

thus inhibiting resonance delocalisation. Even so, the absorption and sensitisation properties of these dyes lie between those for the β-4-dimethylaminophenyl[2] (series 5) and the β-phenyl dyes (series 1) and close to the β-4-nitrophenyl dyes (series 2).

3. EXPERIMENTAL

3.1. Chain substituted styryl cyanines

4-Dimethylaminobenzophenone, 4-dimethylamino-4′-nitrobenzophenone, 4-dimethylamino-2′-nitrobenzophenone and 4-dimethylamino-3′,5′-dinitrobenzophenone (reported by Jha and Banerji[1]) were obtained by adaptation of the method of Shah *et al.*[21] The quaternary salts were prepared by the general procedure suggested by Johnson and Adams.[22]

Condensation to give the dyes was effected, using the method reported earlier.[1,2] A mixture of the ketone and the quinaldinium salt (M:M) dissolved in the requisite volume of absolute ethanol/pyridine, was refluxed for about 2 h in the presence of piperidine as catalyst. The dye which precipitated after concentration was purified by recrystallisation from methanol.

3.2. Absorption and sensitisation spectra

The absorption maxima (λ_{max}) of ethanolic solutions (1/1000 = w/v) of the dyes were recorded on a Beckmann Spectrophotometer Model DU, adjusting the transmission of the dye solutions to between 40 and 60 %. The sensitisation spectra were recorded on an Adam Hilger Wedge Spectrograph, using process plates (N40, Ilford Ltd) and a 150 cp point-o-lite AC lamp, as light source. The plates were previously dipped in dye solutions (1/50 000 = w/v in 30 % ethanol) for 4 min, drained and dried. Exposures of 4 min were given and plates were developed by the usual procedure. The spectrograph of an unbathed plate was also recorded for comparison (Fig. 1).

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