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

Scheme 1

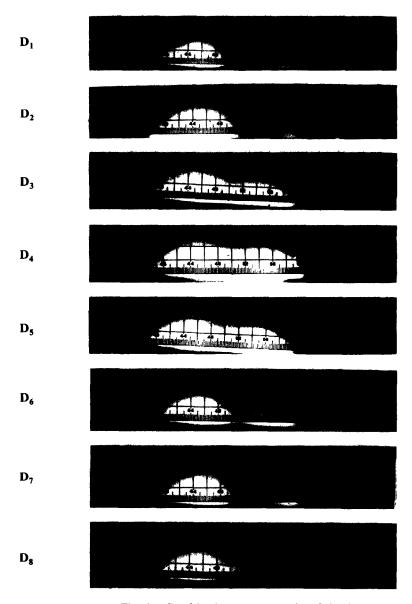


Fig. 1. Sensitisation spectrographs of the dyes.

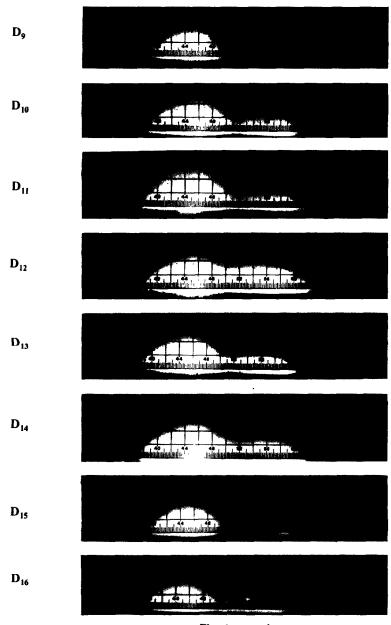


Fig. 1—contd.

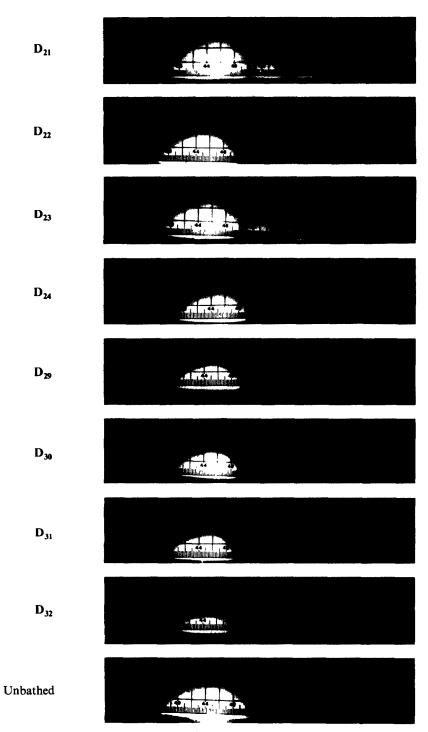


Fig. 1—contd.

chain β -substituted and β -unsubstituted analogues.^{4,5} The styryl cyanines have been examined extensively³⁻¹² 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, D_{21-24} of series 3 and D_{29-32} of series 4), with those analogues described previously^{1,2} (D_{17-20} of series 3, 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 m μ 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

gybase shape* cool and shape*	Dye	Methiodide	Dye as methiodide	Crystal	Yield	M.p.	Molecular	Foun	Found (%)	Calc. (%)	(%)
Q'Mel 2p-DMA(P-P)-S-QMel dvc 46 130 C ₂ 6,H ₂ 3,N ₂ I 6-CIQ'Mel 2p-DMA(P-P)-S-6-CIQMel sdvc 41 160 C ₂ 6,H ₂ 4,N ₂ CII 6-CIQ'Mel 2p-DMA(P-P)-S-6-CIQMel dvm 46 175 C ₂ 6,H ₂ 4,N ₂ CII 6-MCQ'Mel 2p-DMA(P-P)-S-6-RQMel ldvm 68 169 C ₂ 7,H ₂ N ₂ I) 6-MCQ'Mel 2p-DMA(P-P)-S-6-ROQMel ldvm 61 185 C ₂ 7,H ₂ N ₂ I) 6-ELQ'Mel 2p-DMA(P-P)-S-6-ROQMel dvc 51 212 C ₂ 8,H ₂ N ₂ I) 6-ELQ'Mel 2p-DMA(P-P)-S-6-ROQMel dvc 43 185 C ₂ 8,H ₂ N ₂ I) 6-ELQ'Mel 2p-DMA(P-NP)-S-6-ROQMel dvm 47 210 C ₂ 8,H ₂ N ₂ I) 6-ELQ'Mel 2p-DMA(P-NP)-S-6-ROQMel dvm 47 210 C ₂ 8,H ₂ N ₂ I) 6-ELQ'Mel 2p-DMA(P-NP)-S-6-ROQMel dvm 47 210 C ₂ 8,H ₂ N ₂ I) 6-ELQ'Mel 2p-DMA(P-NP)-S-6-ROQMel dvm 47 210 C ₂ 8,H ₂ N ₂ I) 6-ELQ'Mel	sympo	of pass		shape ^b	<u></u>	3	Jormann	N	Hal.	N	Hal.
6-CiQ'MeI 2-DMA(β-P)-S-6-CiQMeI sdv 41 160 C ₂ 6H ₂ M ₂ N ₂ CII 6-BrQMeI 2-p-DMA(β-P)-S-6-BrQMeI dvn 46 175 C ₂ 6H ₂ M ₂ N ₂ CII 6-IQMeI 2-p-DMA(β-P)-S-6-BrQMeI dvn 46 175 C ₂ 6H ₂ M ₂ N ₂ II 6-MeQ'MeI 2-p-DMA(β-P)-S-6-ReQMeI idvn 63 108 C ₂ H ₂ N ₂ N ₂ II 6-MeQ'MeI 2-p-DMA(β-P)-S-6-ReQMeI dvc 43 185 C ₂ H ₂ N ₂ N ₂ II 6-ERQ'MeI 2-p-DMA(β-P)-S-6-ReQMeI dvc 43 185 C ₂ H ₂ N ₂ N ₂ II 6-ERQ'MeI 2-p-DMA(β-P)-S-6-ReQMeI dvc 43 185 C ₂ H ₂ N ₂ N ₂ II 6-ERQ'MeI 2-p-DMA(β-H)P-S-6-ReQMeI dvn 47 210 C ₂ H ₂ N ₂ N ₂ IIO 6-MeQ'MeI 2-p-DMA(β-H)P-S-6-ReQMeI dvn 47 210 C ₂ H ₂ N ₂ N ₂ IIO 6-MeQ'MeI 2-p-DMA(β-H)P-S-6-ReQMeI dvn 47 214 C ₂ H ₂ N ₂ N ₂ IIO 6-MeQ'MeI 2-p-DMA(β-H)P-S-6-ReQMeI dvr 47 214 C ₂ H ₂ N ₂ N ₂ IIO	Δ	Q'MeI	2-p-DMA(β-P)-S-QMeI	dvc	\$	130	C ₂₆ H ₂₅ N ₂ I	5.63	25.76	69-5	25-81
6-BrQ'MeI 2-DMA(β-P)-S-6-BrQMeI dvnn 46 175 C ₂ eH ₂ N,BH 6-IQ'MeI 2-DMA(β-P)-S-6-IQMeI ivs'n 44 212 C ₂ eH ₂ N,JBH 6-IQ'MeI 2-DMA(β-P)-S-6-IQMeI idvtn 68 169 C ₂ H ₂ N,JI 6-MeQ'MeI 2-DMA(β-P)-S-6-BrOQMeI idvtn 68 169 C ₂ H ₂ N,JI 6-MeQ'MeI 2-DMA(β-P)-S-6-BrOQMeI idvtn 63 20 C ₂ H ₂ N,JI 5-G-BzQ'MeI 2-DMA(β-P)-S-6-BrOQMeI dvc 43 182 C ₂ H ₂ H ₂ N,JIO 6-GIQ'MeI 2-DMA(β-HNP)-S-6-BrOQMeI dvn 47 210 C ₂ H ₂ H ₃ N,JIO 6-BrO'MeI 2-DMA(β-HNP)-S-6-BrOQMeI dvn 47 214 C ₂ H ₂ H ₃ N,JIO 6-MeO'MeI 2-DMA(β-HNP)-S-6-BrOQMeI dvn 47 214 C ₂ H ₂ H ₃ N,JIO 6-MeO'MeI 2-DMA(β-HNP)-S-6-BrOQMeI dvn 47 214 C ₂ H ₂ H ₃ N,JIO 6-BEQ'MeI 2-DMA(β-HNP)-S-6-BrOQMeI dvn 47 214 C ₂ H ₂ H ₃ N,JIO 6-BEQ'MeI	Ď,	6-CIQ'MeI	2-p-DMA(\(\theta\)-S-6-CIQMeI	sdvc	4	99	$C_{26}H_{24}N_2CII$	5.28	30-81	5.32	30.86
6-IQ'Mel 2-DMA(B-P)-S-6-IQMel ivs'n 44 212 C ₂ eH ₄ N ₁ 1 ₂ 6-MeO'Mel 2-DMA(B-P)-S-6-MeOMel ivs'n 64 12 C ₂ eH ₄ N ₁ 1 ₂ 6-MeO(Mel 2-DMA(B-P)-S-6-MeOMel idvm 63 208 C ₂ H ₂ N ₂ N ₃ 10 5-6-BZQ'Mel 2-DMA(B-P)-S-6-NiQMel dvc 51 212 C ₂ H ₂ N ₃ N ₃ 10 5-6-BZQ'Mel 2-DMA(B-NP)-S-6-NiQMel dvc 43 185 C ₂ H ₂ N ₃ N ₃ 10 6-CIQ'Mel 2-DMA(B-NP)-S-6-NiQMel dvn 47 210 C ₂ H ₂ N ₃ N ₃ 10 6-RQ'Mel 2-DMA(B-NP)-S-6-NiQMel dvn 47 210 C ₂ H ₂ N ₃ N ₃ 10 6-MeQ'Mel 2-DMA(B-NP)-S-6-NiQMel dvn 47 210 C ₂ H ₂ N ₃ N ₃ 10 6-MeQ'Mel 2-DMA(B-NP)-S-6-NeQMel dvn 47 21 C ₂ H ₂ N ₃ N ₃ 10 6-MeQ'Mel 2-DMA(B-NP)-S-6-NeQMel dvn 47 21 C ₂ H ₂ N ₃ N ₃ 10 6-MeQ'Mel 2-DMA(B-NP)-S-6-NeQMel dvn 47 21 C ₂ H ₂ N ₃ N ₃ 10 6-M	ď	6-BrQ'MeI	2-p-DMA(B-P)-S-6-BrQMeI	dvtn	4	175	C2, H, N, BrI	4.85	36.17	4.90	36.25
6-MeQ'MeI 2-DMA(\(\beta\)-P.S-6-MeQMeI Idvm 68 169 C ₂ H ₂ T ₃ N ₃ I 6-MeQ'MeI 2-p-DMA(\(\beta\)-P.S-6-MeQMeI gdvmn 61 185 C ₂ H ₂ T ₃ N ₃ IO 5.6-BeQ'MeI 2-p-DMA(\(\beta\)-P.S-6-EtQMeI dvc 51 212 C ₂ H ₂ S ₃ N ₃ IO 5.6-BeQ'MeI 2-p-DMA(\(\beta\)-P.S-6-EtQMeI dvc 43 185 C ₂ H ₂ S ₃ N ₃ IO 6-CIQ'MeI 2-p-DMA(\(\beta\)-P.S-6-CIQMeI dvc 43 185 C ₂ H ₂ S ₃ N ₃ IO 6-CIQ'MeI 2-p-DMA(\(\beta\)-P.S-6-CIQMeI dvn 47 210 C ₂ H ₂ S ₃ N ₃ IO ₂ 6-EIQ'MeI 2-p-DMA(\(\beta\)-P.S-6-EIQMeI dvn 47 210 C ₂ H ₂ S ₃ N ₃ IO ₂ 6-EIQ'MeI 2-p-DMA(\(\beta\)-P.S-6-EIQQMeI dvn 47 210 C ₂ H ₂ S ₃ N ₃ IO ₂ 6-MeQ'MeI 2-p-DMA(\(\beta\)-P.S-6-EIQQMeI dvn 47 214 C ₂ H ₂ S ₃ N ₃ IO ₃ 6-MeQ'MeI 2-p-DMA(\(\beta\)-P.S-6-EIQQMeI dvn 47 214 C ₂ H ₂ S ₃ N ₃ IO ₃ 6-MeQ'MeI 2-p-DMA(\(\beta\)-P.S-6-MeQMeI dvn <td>Ď.</td> <td>6-IQ'MeI</td> <td>2-p-DMA(B-P)-S-6-IQMeI</td> <td>ivs'n</td> <td>4</td> <td>212</td> <td>$C_{26}H_{24}N_2I_2$</td> <td>4.48</td> <td>41.23</td> <td>4.53</td> <td>41.10</td>	Ď.	6-IQ'MeI	2-p-DMA(B-P)-S-6-IQMeI	ivs'n	4	212	$C_{26}H_{24}N_2I_2$	4.48	41.23	4.53	41.10
6-MeOQ'MeI 2-p-DMA(P-P)-S-6-MeOQMeI gdwmn 61 185 C ₂ H ₂ N ₂ N ₂ IO 6-EtOQ'MeI 2-p-DMA(P-P)-S-6-FtOQMeI dvc 51 212 C ₂₈ H ₂ N ₂ IO 5.6-BZQ'MeI 2-p-DMA(P-P)-S-6-FtOQMeI dvc 51 212 C ₂₈ H ₂ N ₂ IO 6-EtOQ'MeI 2-p-DMA(P-P)-S-6-FtOQMeI dvc 43 185 C ₂₈ H ₂ N ₂ IO 6-CIQ'MeI 2-p-DMA(P-N-P)-S-6-CIQMeI dvn 47 210 C ₂₈ H ₂ N ₃ IO 6-RQ'MeI 2-p-DMA(P-N-P)-S-6-RQMeI dvn 47 210 C ₂₈ H ₂ N ₃ IO 6-RQ'MeI 2-p-DMA(P-N-P)-S-6-RQMeI dvn 47 214 C ₂₇ H ₂ S ₃ N ₃ IO 6-MeQ'MeI 2-p-DMA(P-N-P)-S-6-RQMeI dvn 47 214 C ₂₈ H ₂ S ₃ N ₃ IO 6-MeQ'MeI 2-p-DMA(P-N-P)-S-6-RQMeI dvn 47 214 C ₂₈ H ₂ S ₃ N ₃ IO 6-MeQ'MeI 2-p-DMA(P-N-P)-S-6-RQMeI dvn 47 214 C ₂₈ H ₂ S ₃ N ₃ IO 6-MeQ'MeI 2-p-DMA(P-N-P)-S-6-RQMeI dvn 47 214 C ₂₈ H ₂ S ₃ N ₃ IO	ď	6-MeQ'MeI	2-p-DMA(B-P)-S-6-MeQMeI	ldvtn	89	169	C_2, H_2, N, I	5.47	25-05	5.53	25.10
6-E1QQ'MeI 2-p-DMA(β-P)-S-6-E1QQMeI ldvn 63 208 C ₂₈ H ₃ ,N ₂ IO 5.6-BZQ'MeI 2-p-DMA(β-P)-S-β-NtQMeI dvc 51 212 C ₂₈ H ₃ ,N ₂ IO 6-CIQ'MeI 2-p-DMA(β-H)P-S-G-NtQMeI dvc 43 185 C ₂₈ H ₃ N ₂ IO 6-CIQ'MeI 2-p-DMA(β-H)P-S-G-CIQMeI dvn 47 210 C ₂₈ H ₃ N ₃ IO 6-RQ'MeI 2-p-DMA(β-H)P-S-G-RQMeI dvn 47 210 C ₂₈ H ₃ N ₃ IO 6-RQ'MeI 2-p-DMA(β-H)P-S-G-RQMeI dvn 47 210 C ₂₈ H ₃ N ₃ IO 6-RQ'MeI 2-p-DMA(β-H)P-S-G-RQQMeI dvn 47 214 C ₂₇ H ₂ N ₃ IO 6-RQ'MeI 2-p-DMA(β-H)P-S-G-RQQMeI dvn 47 214 C ₂₇ H ₂ N ₃ IO 6-RQ'MeI 2-p-DMA(β-1NP-S-G-RQQMeI dvn 47 214 C ₂₇ H ₂ N ₃ IO 6-RQ'MeI 2-p-DMA(β-2-NP)-S-G-RQQMeI dvn 47 214 C ₂₇ H ₂ N ₃ IO 6-RQ'MeI 2-p-DMA(β-2-NP)-S-G-RQQMeI dvn 47 214 C ₂₇ H ₂ N ₃ IO 6-RQ'MeI </td <td>ď</td> <td>6-MeOQ'MeI</td> <td>2-p-DMA(B-P)-S-6-MeOQMeI</td> <td>gdvmn</td> <td>19</td> <td>185</td> <td>$C_{27}H_{27}N_2IO$</td> <td>5.31</td> <td>24.39</td> <td>5.36</td> <td>24.33</td>	ď	6-MeOQ'MeI	2-p-DMA(B-P)-S-6-MeOQMeI	gdvmn	19	185	$C_{27}H_{27}N_2IO$	5.31	24.39	5.36	24.33
5,6-B2Q'MeI 2-p-DMA(β-P)-S-P.NtQMeI dv 51 212 C ₃ θH ₂ /N ₂ II Q'MeI 2-p-DMA(β-4-NP)-S-QMeI dvc 43 185 C ₂ eH ₂ A ₃ N ₃ IO ₂ 6-CIQ'MeI 2-p-DMA(β-4-NP)-S-GTQMeI dvn 47 210 C ₂ eH ₂ A ₃ N ₃ IO ₂ 6-BCQ'MeI 2-p-DMA(β-4-NP)-S-GTQMeI dvn 47 210 C ₂ eH ₂ A ₃ N ₃ IO ₂ 6-BCQ'MeI 2-p-DMA(β-4-NP)-S-GTQMeI dvn 47 210 C ₂ H ₂ A ₃ N ₃ IO ₂ 6-MeQ'MeI 2-p-DMA(β-4-NP)-S-GTQQMeI dvn 47 214 C ₂ H ₂ A ₃ N ₃ IO ₂ 6-BCQ'MeI 2-p-DMA(β-4-NP)-S-GTQQMeI dvn 47 214 C ₂ H ₂ B ₃ N ₃ IO ₂ 6-BCQ'MeI 2-p-DMA(β-4-NP)-S-GTQQMeI dvtm 47 214 C ₂ H ₂ B ₃ N ₃ IO ₂ 6-BCQ'MeI 2-p-DMA(β-2-NP)-S-G-BCQMeI dvtm 47 214 C ₂ H ₂ B ₃ N ₃ IO ₂ 6-BCQ'MeI 2-p-DMA(β-2-NP)-S-G-BCQMeI dvtm 45 23 C ₂ H ₂ B ₃ N ₃ IO ₂ 6-BCQ'MeI 2-p-DMA(β-2-NP)-S-G-BCQQMeI dvtm 42 25 <t< td=""><td>Ď,</td><td>6-EtOQ'MeI</td><td>2-p-DMA(B-P)-S-6-EtOQMcI</td><td>ldvn</td><td>63</td><td>208</td><td>C₂₈H₂₉N₂IO</td><td>5.14</td><td>23.62</td><td>5.22</td><td>23.69</td></t<>	Ď,	6-EtOQ'MeI	2-p-DMA(B-P)-S-6-EtOQMcI	ldvn	63	208	C ₂₈ H ₂₉ N ₂ IO	5.14	23.62	5.22	23.69
Q'Mel 2-DMA(β-4NP)-S-QMel dvc 43 185 C ₂₆ H ₂ N ₃ 1O ₃ 6-CIQ'Mel 2-PDMA(β-4NP)-S-6-IQMel sdvs"n 45 204 C ₂₆ H ₂ N ₃ IO ₂ 6-RQ'Mel 2-PDMA(β-4NP)-S-6-IQMel dvn 47 210 C ₂₆ H ₂ N ₃ IO ₂ 6-RQ'Mel 2-PDMA(β-4NP)-S-6-IQMel dvn 47 210 C ₂₆ H ₂ N ₃ IO ₂ 6-MeQ'Mel 2-PDMA(β-4NP)-S-6-ReQMel dvn 47 214 C ₂₇ H ₂₆ N ₃ IO ₂ 6-MeQ'Mel 2-PDMA(β-4NP)-S-6-ReQMel dvn 47 214 C ₂₇ H ₂₆ N ₃ IO ₂ 5-EIOQ'Mel 2-PDMA(β-4NP)-S-6-ReQMel dvn 47 214 C ₂₇ H ₂₆ N ₃ IO ₂ 6-MeQ'Mel 2-PDMA(β-2NP)-S-6-ReQMel dvn 47 214 C ₂₇ H ₂₆ N ₃ IO ₂ 6-MeQ'Mel 2-PDMA(β-2-NP)-S-6-ReQMel dvn 47 214 C ₂₇ H ₂₆ N ₃ IO ₂ 6-MeQ'Mel 2-PDMA(β-2-NP)-S-6-ReQMel dvn 45 23 C ₂₈ H ₂₆ N ₃ IO ₂ 6-MeQ'Mel 2-PDMA(β-2-NP)-S-6-ReQMel dvs 44 26 C ₂₇ H ₂₆ N ₃ IO ₂	D ₈	5,6-BzQ'MeI	2-p-DMA(\theta-P)-S-\theta-NtQMcI	dvc	51	212	$C_{30}H_{27}N_2I$	4.98	23-23	5.02	23.29
6-CIQ'MeI 2-p-DMA(β-4-NP)-S-6-CIQMeI sdws"n 45 204 C ₂₆ H ₂₃ N ₃ CIIO ₂ 6-BrQ'MeI 2-p-DMA(β-4-NP)-S-6-RQMeI dvn 47 210 C ₂₆ H ₂₃ N ₃ BrIO ₂ 6-IQ'MeI 2-p-DMA(β-4-NP)-S-6-RQMeI drvg 46 197 C ₂₇ H ₂₆ N ₃ IO ₂ 6-MeQ'MeI 2-p-DMA(β-4-NP)-S-6-MeQMeI dvn 47 214 C ₂₇ H ₂₆ N ₃ IO ₂ 6-MeQ'MeI 2-p-DMA(β-4-NP)-S-6-MeQMeI dvn 47 214 C ₂₇ H ₂₆ N ₃ IO ₂ 5-EIQQ'MeI 2-p-DMA(β-4-NP)-S-6-MeQMeI dvn 47 214 C ₂₇ H ₂₆ N ₃ IO ₂ 6-MeQ'MeI 2-p-DMA(β-2-NP)-S-6-MeQMeI dvn 62 22 C ₂₈ H ₂₈ N ₃ IO ₂ 6-MeQ'MeI 2-p-DMA(β-2-NP)-S-6-MeQMeI dvn 63 211 C ₂₇ H ₂₆ N ₃ IO ₂ 6-MeQ'MeI 2-p-DMA(β-2-NP)-S-6-MeQMeI dvs 45 236 C ₂₈ H ₂₈ N ₃ IO ₂ 5-6-BZQ'MeI 2-p-DMA(β-2-NP)-S-6-MeQMeI dvs 44 256 C ₂₉ H ₂₈ N ₃ IO ₂ 6-MeQ'MeI 2-p-DMA(β-3-DNP)-S-6-MeQMeI dvs 69 172	ď	Q'MeI	2-p-DMA(\$-4-NP)-S-QMeI	dvc	43	185	C26H24N31O2	7.76	23.59	7.82	23-65
6-BrQ'MeI 2-p-DMA(β-4NP)-S-6-BrQMeI dvn 47 210 C ₂₆ H ₂₃ N ₃ BrIO ₂ 6-IQ'MeI 2-p-DMA(β-4NP)-S-6-IQMeI dvn 50 241 C ₂₆ H ₂₃ N ₃ I ₂ O ₂ 6-MeQ'MeI 2-p-DMA(β-4NP)-S-6-MeQMeI dvn 47 214 C ₇ ·H ₂₆ N ₃ IO ₂ 6-MeQ'MeI 2-p-DMA(β-4NP)-S-6-EIQQMeI dvn 47 214 C ₇ ·H ₂₆ N ₃ IO ₂ 5-EIQQ'MeI 2-p-DMA(β-4NP)-S-6-EIQQMeI dvn 47 214 C ₇ ·H ₂₆ N ₃ IO ₂ 6-MeQ'MeI 2-p-DMA(β-2NP)-S-6-MeQMeI dvn 45 237 C ₂₆ H ₂₆ N ₃ IO ₂ 6-MeQ'MeI 2-p-DMA(β-2-NP)-S-6-MeQMeI dvn 45 23 C ₂₇ H ₂₆ N ₃ IO ₂ 6-MeQ'MeI 2-p-DMA(β-2-NP)-S-6-MeQMeI dvs 45 236 C ₂₇ H ₂₆ N ₃ IO ₂ 5-EIQQ'MeI 2-p-DMA(β-2-NP)-S-6-MeQMeI dvs 45 25 C ₂₇ H ₂₆ N ₃ IO ₂ 5-EBQ'MeI 2-p-DMA(β-3-DNP)-S-6-MeQMeI dvs 45 25 C ₂₇ H ₂₆ N ₃ IO ₂ 6-MeQ'MeI 2-p-DMA(β-3-DNP)-S-6-MeQMeI dvs 25 C ₂₇ H ₂₆ N ₃ IO ₃ </td <td>Dio</td> <td>6-CIQ'MeI</td> <td>2-p-DMA(\$-4-NP)-S-6-CIQMeI</td> <td>sdvs"n</td> <td>45</td> <td>2 4</td> <td>C26H23N3CIIO2</td> <td>7-31</td> <td>28-42</td> <td>7-35</td> <td>28-45</td>	Dio	6-CIQ'MeI	2-p-DMA(\$-4-NP)-S-6-CIQMeI	sdvs"n	45	2 4	C26H23N3CIIO2	7-31	28-42	7-35	28-45
6-IQ'MeI 2-p-DMA(β-4-NP)-S-6-IQMeI dvm 50 241 C ₂ H ₂ N ₁ J ₂ O ₂ 6-MeQ'MeI 2-p-DMA(β-4-NP)-S-6-MeQMeI dvm 47 214 C ₂ H ₂ 6 _N J ₁ O ₂ 6-MeO'MeI 2-p-DMA(β-4-NP)-S-6-MeQMeI dvm 47 214 C ₂ H ₂ 6 _N J ₁ O ₂ 5,6-BcQ'MeI 2-p-DMA(β-4-NP)-S-6-MeQMeI dvm 45 237 C ₃ 0-H ₂ 6 _N J ₁ O ₂ 6-MeQ'MeI 2-p-DMA(β-2-NP)-S-6-MeQMeI dvmvrrf 63 211 C ₂ H ₂ 6 _N J ₁ O ₂ 6-MeQ'MeI 2-p-DMA(β-2-NP)-S-6-MeQMeI gdvm 55 219 C ₂ H ₂ 6 _N J ₁ O ₂ 6-BcQ'MeI 2-p-DMA(β-2-NP)-S-6-MeQMeI dvs 45 236 C ₃ H ₂ 6 _N J ₁ O ₂ 5,6-BcQ'MeI 2-p-DMA(β-2-NP)-S-6-MeQMeI dvs 44 265 C ₃ H ₂ 6 _N J ₁ O ₂ 6-MeQ'MeI 2-p-DMA(β-3-3-DNP)-S-6-MeQMeI dvs 67 168 C ₂ 7H ₂ 8 _N J ₁ O ₂ 6-MeQ'MeI 2-p-DMA(β-3-5-DNP)-S-6-MeQMeI gdvs 70 181 C ₃ H ₂ 3 _N J ₁ O ₂ 6-BcQ'MeI 2-p-DMA(β-3-5-DNP)-S-6-MeQOMeI gdvs 70	D	6-BrQ'MeI	2-p-DMA(\$-4-NP)-S-6-BrQMeI	dvn	47	210	C26H23N3BrIO2	6.78	33-65	6.82	33.62
6-MeQ'Mel 2-p-DMA(β-4-NP)-S-6-MeQMel drug in 46 197 C ₇ H ₂ kN ₃ 1O ₂ 6-MeQ'Mel 2-p-DMA(β-4-NP)-S-6-MeQMel dvm 47 214 C ₇ H ₂ kN ₃ 1O ₂ 5,6-BCQ'Mel 2-p-DMA(β-4-NP)-S-6-EtOQMel dvm 62 222 C ₂₈ H ₂₈ N ₃ 1O ₃ 5,6-BCQ'Mel 2-p-DMA(β-4-NP)-S-6-NtQMel dvtmvrt' 63 211 C ₂₇ H ₂₆ N ₃ 1O ₂ 6-MeQ'Mel 2-p-DMA(β-2-NP)-S-6-MeQMel gdvmn 55 219 C ₇₇ H ₂₆ N ₃ 1O ₂ 6-MeQ'Mel 2-p-DMA(β-2-NP)-S-6-MeQMel dvsn 45 236 C ₂₈ H ₂₈ N ₃ 1O ₂ 5,6-BCQ'Mel 2-p-DMA(β-2-NP)-S-6-MeQMel dvsn 45 236 C ₂₉ H ₂₈ N ₃ 1O ₂ 6-MeQ'Mel 2-p-DMA(β-2-NP)-S-6-MeQMel dvs"w'c' 44 265 C ₂₉ H ₂₈ N ₃ 1O ₂ 6-MeQ'Mel 2-p-DMA(β-3-DNP)-S-6-MeQMel dvs"w'c' 44 265 C ₂₉ H ₂₈ N ₃ 1O ₂ 6-MeQ'Mel 2-p-DMA(β-3-DNP)-S-6-MeQMel gdvs'n 69 172 C ₂₇ H ₂₃ N ₃ 1O ₃ 6-EtOQ'Mel 2-p-DMA(β-3-DNP)-S-6-EtOQMel gdvs'n 69	D ₁₂	6-IQ'MeI	2-p-DMA(B-4-NP)-S-6-IQMeI	dvtn	20	241	$C_{26}H_{23}N_{3}I_{2}O_{2}$	6.29	38.36	6.33	38-31
6-MeOQ'MeI 2-p-DMA(β-4-NP)-S-6-MeOQMeI dvm 47 214 C ₂₇ H ₂₆ N ₃ IO ₃ 6-EtQQ'MeI 2-p-DMA(β-4-NP)-S-6-EtQQMeI dvm 62 22 C ₂₈ H ₂₈ N ₃ IO ₃ 5,6-BZQ'MeI 2-p-DMA(β-4-NP)-S-6-RtQQMeI dvmvrt' 63 21 C ₂₇ H ₂₆ N ₃ IO ₂ 6-MeQ'MeI 2-p-DMA(β-2-NP)-S-6-MeQMeI gdvmn 55 219 C ₂₇ H ₂₆ N ₃ IO ₂ 6-MeQ'MeI 2-p-DMA(β-2-NP)-S-6-MeQMeI dvs 45 26 C ₂₈ H ₂₈ N ₃ IO ₂ 5,6-BZQ'MeI 2-p-DMA(β-2-NP)-S-6-MeQMeI dvs 44 265 C ₂₉ H ₂₆ N ₃ IO ₂ 6-MeQ'MeI 2-p-DMA(β-3-NP)-S-6-MeQMeI dvs 67 168 C ₂₇ H ₂₃ N ₃ IO ₄ 6-MeQ'MeI 2-p-DMA(β-3-DNP)-S-6-MeQMeI gdvs 69 172 C ₇₇ H ₂₃ N ₃ IO ₄ 6-EtOQ'MeI 2-p-DMA(β-3-DNP)-S-6-EtOQMeI gdvs 70 18I C ₅₈ H ₂₇ N ₃ IO ₄ 5-6-BZQ'MeI 2-p-DMA(β-3-5-DNP)-S-6-RtOQMeI gdvs 70 18I C ₅₇ H ₂₇ N ₃ IO ₄ 5-6-BZQ'MeI 2-p-DMA(β-3-5-DNQMeI gdvs 70 <t< td=""><td>D</td><td>6-MeQ'MeI</td><td>2-p-DMA(p-4-NP)-S-6-MeQMeI</td><td>drvg'n</td><td>4</td><td>197</td><td>C_2,$H_2$6$N_3$$IO_2$</td><td>7.57</td><td>22.98</td><td>7.62</td><td>23.05</td></t<>	D	6-MeQ'MeI	2-p-DMA(p-4-NP)-S-6-MeQMeI	drvg'n	4	197	C_2 , H_2 6 N_3 IO_2	7.57	22.98	7.62	23.05
6-E1QQ'MeI 2-PDMA(β-4NP)-S-6-E1QQMeI dvm 62 222 C ₂₈ H ₂₈ N ₃ IO ₃ 5,6-B2Q'MeI 2-p-DMA(β-4NP)-S-β-NtQMeI dvs"cwrt' 46 237 C ₃₀ H ₂₆ N ₃ IO ₂ 6-MeQ'MeI 2-p-DMA(β-2-NP)-S-6-MeQMeI gdvmn 55 219 C ₂₇ H ₂₆ N ₃ IO ₂ 6-MeOQ'MeI 2-p-DMA(β-2-NP)-S-6-EtOQMeI dvsn 45 236 C ₂₈ H ₂₈ N ₃ IO ₂ 5,6-B2Q'MeI 2-p-DMA(β-2-NP)-S-6-EtOQMeI dvs"w'c' 44 265 C ₃₀ H ₂₆ N ₃ IO ₂ 6-MeQ'MeI 2-p-DMA(β-3,5-DNP)-S-6-MeQMeI dvtm 67 168 C ₂₇ H ₂₃ N ₃ IO ₄ 6-MeOQ'MeI 2-p-DMA(β-3,5-DNP)-S-6-MeOQMeI gdvs'n 69 172 C ₂₇ H ₂₃ N ₃ IO ₄ 6-EtOQ'MeI 2-p-DMA(β-3,5-DNP)-S-6-EtOQMeI gdvs'n 69 172 C ₂₇ H ₂₃ N ₃ IO ₄ 5,6-BZQ'MeI 2-p-DMA(β-3,5-DNP)-S-6-RtOQMeI gdvs'n 65 203 C ₃₀ H ₂₅ N ₃ IO ₄ 5,6-BZQ'MeI 2-p-DMA(β-3,5-DNP)-S-6-RtOQMeI gdvs'n 65 203 C ₃₀ H ₂₅ N ₃ IO ₄	D.	6-MeOQ'MeI	2-p-DMA(8-4-NP)-S-6-MeOQMeI	dvtn	47	214	C27H26N3IO3	7.36	22:34	7-41	22:40
5,6-BQ'MeI 2-p-DMA(β-4-NP)-S-β-NtQMeI dvs"cwrt' 46 237 C ₃₀ H ₂₆ N ₃ IO ₂ 6-MeQ'MeI 2-p-DMA(β-2-NP)-S-6-MeQMeI gdvmn 55 219 C ₂₇ H ₂₆ N ₃ IO ₂ 6-MeOQ'MeI 2-p-DMA(β-2-NP)-S-6-EtOQMeI gdvmn 55 219 C ₂₇ H ₂₆ N ₃ IO ₂ 5,6-BQ'MeI 2-p-DMA(β-2-NP)-S-6-EtOQMeI dvs"w'c' 44 265 C ₃₀ H ₂₆ N ₃ IO ₂ 6-MeQ'MeI 2-p-DMA(β-3-DNP)-S-6-MeQMeI dvtm 67 168 C ₂₇ H ₂₃ N ₄ IO ₄ 6-MeQ'MeI 2-p-DMA(β-3,5-DNP)-S-6-MeOQMeI sdvs"n 69 172 C ₂₇ H ₂₃ N ₄ IO ₄ 6-EtOQ'MeI 2-p-DMA(β-3,5-DNP)-S-6-EtOQMeI gdvs'n 70 181 C ₃₈ H ₂₇ N ₄ IO ₄ 5,6-BQ'MeI 2-p-DMA(β-3,5-DNP)-S-6-RtOQMeI gdvs'n 65 203 C ₃₀ H ₂₅ N ₄ IO ₄ 5,6-BQ'MeI 2-p-DMA(β-3,5-DNP)-S-6-RtOQMeI gdvs'n 65 203 C ₃₀ H ₂₅ N ₄ IO ₄	DIS	6-EtOQ'MeI	2-p-DMA(p-4-NP)-S-6-EtOQMeI	dvtn	62	222	$C_{28}H_{28}N_3IO_3$	7.18	21.81	7.23	21.86
6-MeQ'MeI 2-p-DMA(β-2.NP)-S-6-MeQMeI dvinwrt 63 211 C ₂ -H ₂ 6N ₃ 10 ₂ 6-MeQ'MeI 2-p-DMA(β-2.NP)-S-6-MeQMeI gdwnn 55 219 C ₂ H ₂ 8N ₃ 10 ₂ 5,6-BZQ'MeI 2-p-DMA(β-2-NP)-S-6-EtOQMeI dvsn 45 236 C ₂₈ H ₂₈ N ₃ 10 ₂ 5,6-BZQ'MeI 2-p-DMA(β-2-NP)-S-6-NtQMeI dvm 67 168 C ₂ +H ₂ N ₃ 10 ₄ 6-MeQ'MeI 2-p-DMA(β-3,5-DNP)-S-6-MeQMeI sdvs'n 69 172 C ₂ +H ₂ N ₃ 10 ₄ 6-EtOQ'MeI 2-p-DMA(β-3,5-DNP)-S-6-EtOQMeI gdvs'n 70 181 C ₂₈ H ₂ 2,N ₃ 10 ₄ 5,6-BZQ'MeI 2-p-DMA(β-3,5-DNP)-S-6-RtOQMeI gdvs'n 65 203 C ₃₀ H ₂ 3,N ₃ 10 ₄	D16	5,6-BzQ'MeI	2-p-DMA(\$-4-NP)-S-\$-NtQMeI	dvs"cwrt'	4	237	$C_{30}H_{26}N_3IO_2$	7.09	21.57	7.17	21-63
6-MeOQ'MeI 2-p-DMA(β-2-NP)-S-6-MeOQMeI gdvmn 55 219 C ₇ H ₂₆ N ₃ IO ₃ 6-EIOQ'MeI 2-p-DMA(β-2-NP)-S-6-EIOQMeI dvsn 45 236 C ₂₈ H ₂₈ N ₃ IO ₃ 5,6-BZQ'MeI 2-p-DMA(β-2-NP)-S-β-NIQMeI dvm 67 168 C ₃ γH ₂₈ N ₃ IO ₄ 6-MeQ'MeI 2-p-DMA(β-3,5-DNP)-S-6-MeQMeI sdvs'n 69 172 C ₃ γH ₂₃ N ₃ IO ₄ 6-EIOQ'MeI 2-p-DMA(β-3,5-DNP)-S-6-EIOQMeI gdvs'n 70 181 C ₂₈ H ₂₇ N ₃ IO ₄ 5,6-BZQ'MeI 2-p-DMA(β-3,5-DNP)-S-β-NIQMeI gdvtn 65 203 C ₃₀ H ₂₃ N ₄ IO ₄	\mathbf{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
6-EIOQ'MeI 2-p-DMA(β-2-NP)-S-6-EIOQMeI dvsn 45 236 C ₁₉ H ₂₈ N ₃ IO ₃ 5,6-BZQ'MeI 2-p-DMA(β-2-NP)-S-β-NIQMeI dvs"w'c' 44 265 C ₃₀ H ₂₆ N ₃ IO ₂ 6-MEQ'MeI 2-p-DMA(β-3,5-DNP)-S-6-MEQMeI dvm 67 168 C ₁₇ H ₂₃ N ₃ IO ₄ 6-MEOQ'MeI 2-p-DMA(β-3,5-DNP)-S-6-MEOQMeI gdvs'n 69 172 C ₁₇ H ₂₃ N ₃ IO ₄ 6-EIOQ'MeI 2-p-DMA(β-3,5-DNP)-S-6-EIOQMeI gdvs'n 65 203 C ₃₀ H ₂₃ N ₃ IO ₄ 5,6-BZQ'MeI 2-p-DMA(β-3,5-DNP)-S-β-NIQMeI g'dvtn 65 203 C ₃₀ H ₂₃ N ₄ IO ₄	\mathbf{D}_{22}	6-McOQ'MeI	2-p-DMA(\theta-2-NP)-S-6-MeOQMeI	gdvmn	55	219	C27H26N3IO3	7.36	22-33	7:41	22:40
5,6-B2Q'MeI 2-p-DMA(p-2-NP)-S-p-NtQMeI dvs"w'c' 44 265 C ₃₀ H ₂₆ N ₃ IO ₂ 6-MeQ'MeI 2-p-DMA(p-3,5-DNP)-S-6-MeQMeI dvtn 67 168 C ₂₇ H ₂₃ N ₄ IO ₄ 6-MeOQ'MeI 2-p-DMA(p-3,5-DNP)-S-6-MeOQMeI gdvs'n 69 172 C ₂₇ H ₂₃ N ₄ IO ₄ 6-EtOQ'MeI 2-p-DMA(p-3,5-DNP)-S-6-EtOQMeI gdvs'n 70 181 C ₂₈ H ₂₇ N ₄ IO ₅ 5,6-B2Q'MeI 2-p-DMA(p-3,5-DNP)-S-p-NtQMeI g'dvtn 65 203 C ₃₀ H ₂₃ N ₄ IO ₄	D_{23}	6-EtOQ'MeI	2-p-DMA(\theta-2-NP)-S-6-EtOQMeI	dvsn	45	236	C28H28N3IO3	7.17	21.82	7.23	21.86
6-MeQ'Mel 2-p-DMA(#3,5-DNP)-S-6-MeQMel 6vn 67 168 C ₁₇ +H ₂₃ N ₄ 1O ₄ 6-MeOQ'Mel 2-p-DMA(#3,5-DNP)-S-6-MeOQMel 8dvs'n 69 172 C ₁₇ +H ₂₃ N ₄ 1O ₄ 6-EtOQ'Mel 2-p-DMA(#3,5-DNP)-S-6-EtOQMel 8dvs'n 70 181 C ₁₈ H ₂₇ N ₄ 1O ₄ 5,6-B2Q'Mel 2-p-DMA(#-3,5-DNP)-S-6-NtQMel g'dvtn 65 203 C ₃₀ H ₂₃ N ₄ 1O ₄	Dz	5,6-BzQ'MeI	2-p-DMA(β-2-NP)-S-β-NtQMeI	dvs"w'c'	4	592	C30H26N3IO2	7.11	21.58	7.17	21.63
6-MeOQ'MeI 2-p-DMA(\$4.3,5-DNP)-S-6-MeOQMeI sdvs"n 69 172 C ₂₇ H ₂₅ N ₄ IO ₅ 6-EtOQ'MeI 2-p-DMA(\$4.3,5-DNP)-S-6-EtOQMeI gdvs'n 70 181 C ₂₈ H ₂₇ N ₄ IO ₅ 5,6-BZQ'MeI 2-p-DMA(\$4.3,5-DNP)-S-\$-\$-NtQMeI g'dvtn 65 203 C ₃₀ H ₂₅ N ₄ IO ₄	D_{29}	6-MeQ'MeI	2-p-DMA(p-3,5-DNP)-S-6-MeQMeI	dvtn	29	168	C27H25N4104	9-35	21.27	9.40	21.31
6-EtOQ'Mei 2-p-DMA(p-3,5-DNP)-S-6-EtOQMei gdvs'n 70 181 C ₁₈ H ₂ N ₄ IO ₅ 5,6-BZQ'Mei 2-p-DMA(p-3,5-DNP)-S-p-NtQMei g'dvtn 65 203 C ₃₀ H ₂₅ N ₄ IO ₄	D	6-McOQ'MeI	2-p-DMA(β-3,5-DNP)-S-6-MeOQMeI	sdvs"n	69	172	C27H25N4IO5	9.07	20-71	9.15	20.75
5,6-BZQ'MeI 2-p-DMA(B-3,5-DNP)-S-β-NtQMeI g'dytn 65 203 C ₃₀ H ₂₅ N ₄ IO ₄	D31	6-EtOQ'MeI	2-p-DMA(\$-3,5-DNP)-S-6-EtOQMeI	gdvs'n	20	181	C ₁₈ H ₂₇ N ₄ IO 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	98.8	20:03

*Q, quinoline; Q', quinaldine; P, phenyl; S, styryl; Bz, Benz; NP, nitrophenyl; Nt, naphthyl; DMA, dimethylamino; DNP, dinitrophenyl.

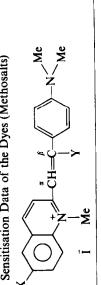
b c, Crystals; c', clusters; d, dark; g, glistening; g', glazing; i, intense; l, lustrous; m, minute; n, needles; r, reddish; s, shining; s', slender; s", small; t, tiny; t', tinge; v, violet; w, with; w', woolly.

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

	ork	Н		<i>Series 6</i> (<i>refs 4, 5</i>)	λ_{max} $(m\mu)$	530	550	552				
	Reported work	-(0)-	Me Z-	Series 5 (ref. 2)	λ_{max} $(m\mu)$	568	579	585	578	580	581	575
Me Me		NO ₂		Series 4	λ_{max} $(m\mu)$	569	280	584	574	578	583	576
Ž		Z		Seri	Дуе	*D ₂₅	*D*	*D28	D_{29}	Ü,	\mathbf{D}_{31}	\mathbf{D}_{32}
H=C	Present work ^a	-NO ₂	Series 3	es 3	λ_{max} $(m\mu)$	564	579	583	268	577	579	574
₩-Z-Z+		$-\langle 0 \rangle$		Seri	Dye	*D ₁₇	* 0 *	*D20	$\mathbf{D}_{\mathbf{n}}$	\mathbf{D}_{22}	ը	D_{2d}
<i>-</i>	Presen		NO ₂	Series 2	λ_{max} $(m\mu)$	563	575	584	695	575	2/8	573
*			Z	Seri	Dye	מ מ	ם מ	$\mathbf{D_{12}}$	D_{13}	D ₁₄	D ₁₅	D16
				Series 1	λ_{max} $(m\mu)$	562	575	582	545	248 8 5	, 56 (6)	571
		<u> </u>		Ser	Дуе	ם ת	ິດິ	D4	D,	മ്	Ď,	D,
		*			× →	Н	B G	I	Me	OMe	OEt	5,6-Benz

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

TABLE 3 Sensitisation Data of the Dyes (Methosalts)



ŀ		i	, _ 1	_		_				1
Reported work	H Series 6 (refs 4, 5)	Атах (ти)	580 595	595	96					
	F. Seri (refs		Range (mµ)	630	959	650				
	7 We	λ _{max} * (mμ)	580 540up	240w 280 %	540 580mi	280	540vw 580w	540vw 580w	525up 550	
	-{()}-z	Me M Series 5 (ref. 2)	Range ^b (mµ)	630	(2 600w) 680 (2 600w)	680 (≥600mi)	019	680 (>600wt)	680 (>600vwt)	046
	NO ₂	1	λ m ax (mμ)	11	1	l	1	1		1
	Series 4	Series 4	Range' (mµ)	2 2	5 0	D	Ď,	Ď	Ds	å
	Z	1-	Dye	.0.s	*D2	*D28	D29	D30	D31	D32
	Series 1 Series 3		Remarks	w, dc, ibvr mi, c	m, c	i, ic	mi, lc	w, k	mi, c	w, aı
		ies 3	λmax (mμ)	995 360	990	290	530	\$40w	3, 8	580up
		Range (mµ)	620	630	059	620	620	620	620	
			Dye	*D ₁₇	*D19	*D*	D ₂₁	D22	D23	D24
Present work			Remarks	w, ai mi, aı	m, ac	ı, c	mı, ub	mi, ub	w, as	w, aı
		NO ₂	λmax (mμ)	570 540w	570m 580	280	999	265	99	I
		_ &	Range (mµ)	630	8	650	630	95	₹	2
ļ		Dye	ų ų	D ₁₁	Dız	D ₁₃	D ₁₄	Dıs	D ₁₆	
		Remarks	w, dc w, dc, mp	i, au	i, au	i, au	m, c	m, c	mi, c	
		λmax (mμ)	580	540	260	550	530	530	\$ 52 S	
		Range (mµ)	D ₁ 600 580 v D ₂ 610 580 v	620	970	019	019	620	009	
			Dye	5 5	ũ	ď	á	å	Ď,	å
	<u>†</u>		` >< →	≖ 5	Æ		Me	ОМе	OEt	5,6-Benz Dg

* Values marked with an asterisk have been taken from Ref 1
* a., Almost continuous; ai, almost isolated; au, almost uniform, c, continuous; dc, disconnected; i, intense, ibw, unlet 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.
* Ds, Desenstiser

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:

$$6-I > 6-Br > 6-Cl > 6-H$$

and also

$$6-OEt > 6-OMe > 6-Me > 6-H$$

[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 ($\mathbf{D_6}$ – $\mathbf{D_8}$, $\mathbf{D_{10}}$ and $\mathbf{D_{21}}$ – $\mathbf{D_{23}}$) 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

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

and

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

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

and

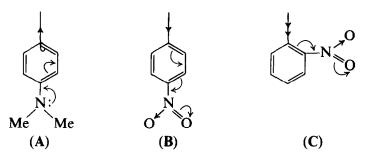
$$OEt \ge OMe \ge Me \ge H$$

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, with regard to the range of extrasensitisation, 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 dyes² (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



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 dyes² (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**)],

$$\begin{array}{c|c}
H & & & \\
C & & & \\
C & & & \\
O_2N & & \\
\hline
(D) & & \\
\end{array}$$

thus inhibiting resonance delocalisation. Even so, the absorption and sensitisation properties of these dyes lie between those for the β -4-dimethylaminophenyl² (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 Banerji¹) 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 2h 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 (1/50000 = 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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