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# Chromophoric Chain β-Substituted Hemicyanines: Effect of the Nature of Substituents on Optical Properties

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## *SUMMARY*

*As a part of the project undertaken to study the effect of substitution, a number of chain β-substituted hemicyanines have been synthesised by condensing 4,4'-bis(dimethylamino)benzophenone with variously 6-substituted quinaldinium alkyl iodides. Absorption and photosensitisation of the dyes have been recorded*

*Contrary to the earlier observation that chain β-substitution in hemicyanine causes hypsochromic shifts in absorption,*[1–6] *the dyes under report have shown uniform bathochromic shifts, which confirms the authors' previous findings.*[7–9] *Further, these dyes absorb at longer wavelengths and are better sensitisers than their β-phenyl and β-*p*-nitrophenyl analogues*[8,9]

*Progressively weightier hetero-6-halosubstitutions have led to progressive bathochromic shifts and extended extrasensitisations, irrespective of the nature of the β-substituents.*[7–9] *Ethoquaternised hemicyanines have been found to absorb at longer wavelengths and to exhibit greater photosensitisation than their methoquaternised analogues*

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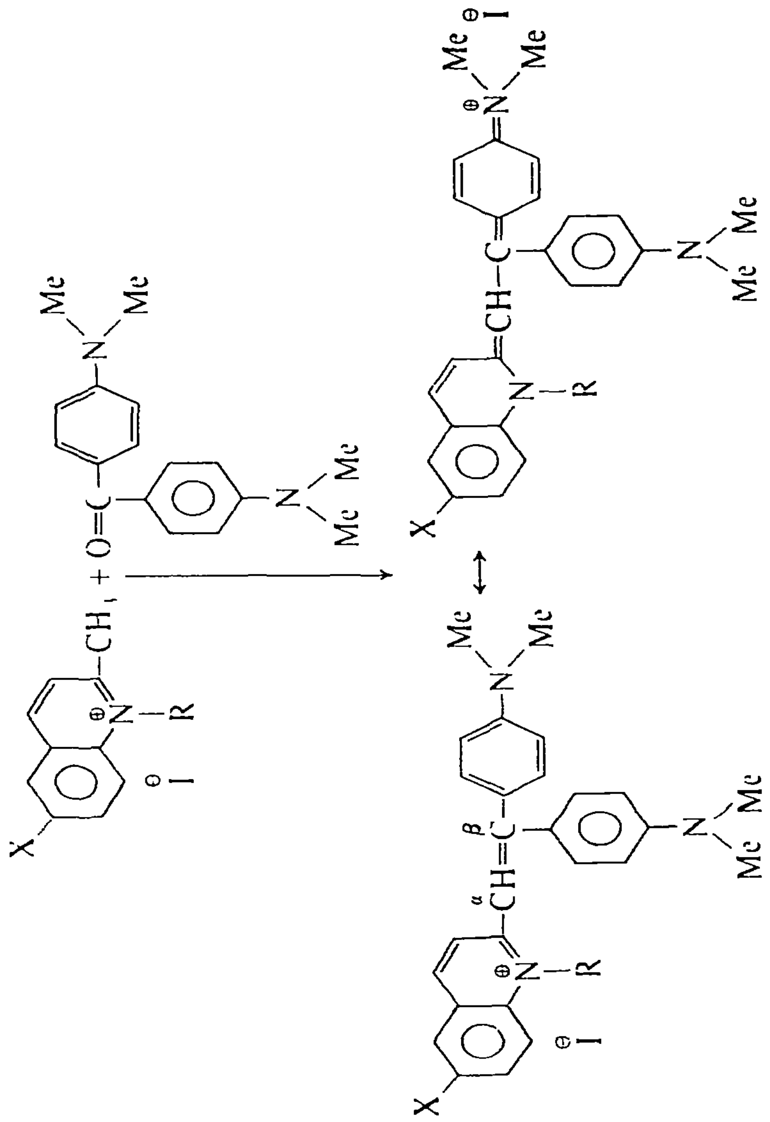


$D_{33}$ X = H, R = Me
$D_{34}$ X = Cl, R = Me
$D_{35}$ X = Br, R = Me
$D_{36}$ X = I, R = Me
$D_{37}$ X = Me, R = Me
$D_{38}$ X = OMe, R = Me

$D_{39}$ X = OEt, R = Me
$D_{40}$ X = 5,6-Benz, R = Me
$D_{41}$ X = H, R = Et
$D_{42}$ X = Cl, R = Et
$D_{43}$ X = Br, R = Et
$D_{44}$ X = I, R = Et

Scheme 1

# 1. INTRODUCTION

A survey of the relevant literature reveals that chromophoric chain substitutions in styrylcyanines, at positions either α- or β- to the heterocyclic nucleus, cause hypsochromic shifts in absorption maxima as compared with their chain unsubstituted analogues,[1-4] but the extent of hypsochromic shift is more pronounced in the former case.[5,6] As the reported observations did not appear to be based on extensive investigations, it was considered worthwhile to undertake a project for the synthesis of a reasonable number of chromophoric chain β-substituted hemicyanines and to study the effect of the nature of the various substituents on absorption and photosensitisation. In previous investigations the authors also reported the preparation and properties of chain β-substituted cyanines.[7-9]

Although the hemicyanines have been extensively studied[10-16] from different points of view—the effect of diverse substitutions in the heterocyclic moiety being the one most studied—very little work has been carried out to study the effect of substituents in the prime chromophoric chain of the dye molecules. The present communication deals with the synthesis of 12 chain β-substituted hemicyanines and a study of their optical properties. The dyes have been obtained by the condensation of 6-substituted quinaldinium alkyl iodides with 4,4′-bis(dimethylamino)-benzophenone as shown under Scheme 1.

The data for absorption maxima ($\lambda_{max}$) and ranges of extrasensitisation have been recorded and compared with those of their corresponding β-phenyl, β-*p*-nitrophenyl and chain β-unsubstituted analogues;[11,14] wherever possible reasonable conclusions have been drawn.

# 2. RESULTS AND DISCUSSION

Analytical data and some other characteristics of the dyes are given in Table 1. The sensitisation spectrographs of the dyes and of an unbathed plate are shown in Fig. 1. The absorption data are presented in Table 2 and extrasensitisation data in Table 3.

## 2.1. Optical absorption

Scrutiny of the absorption data of the chromophoric chain β-substituted dyes (series 1) of the present investigation together with those of the

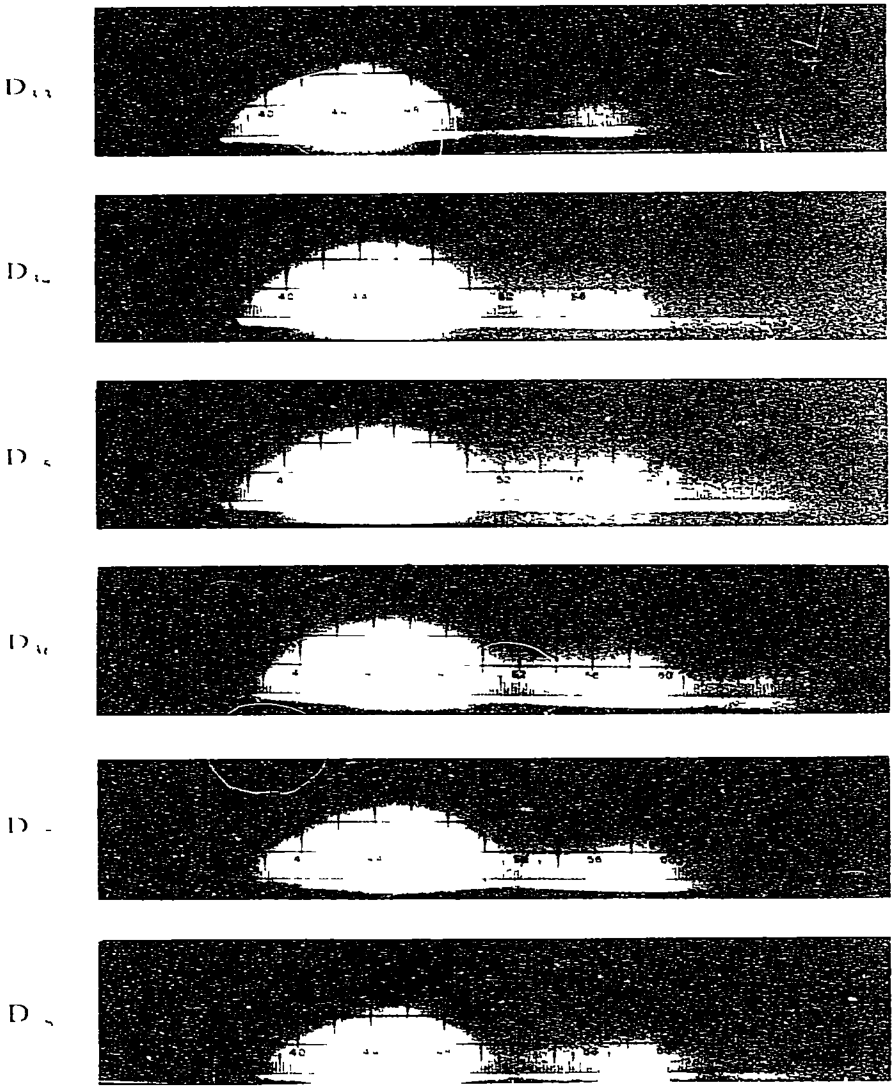


Fig 1 Sensitisation spectrographs of the dyes

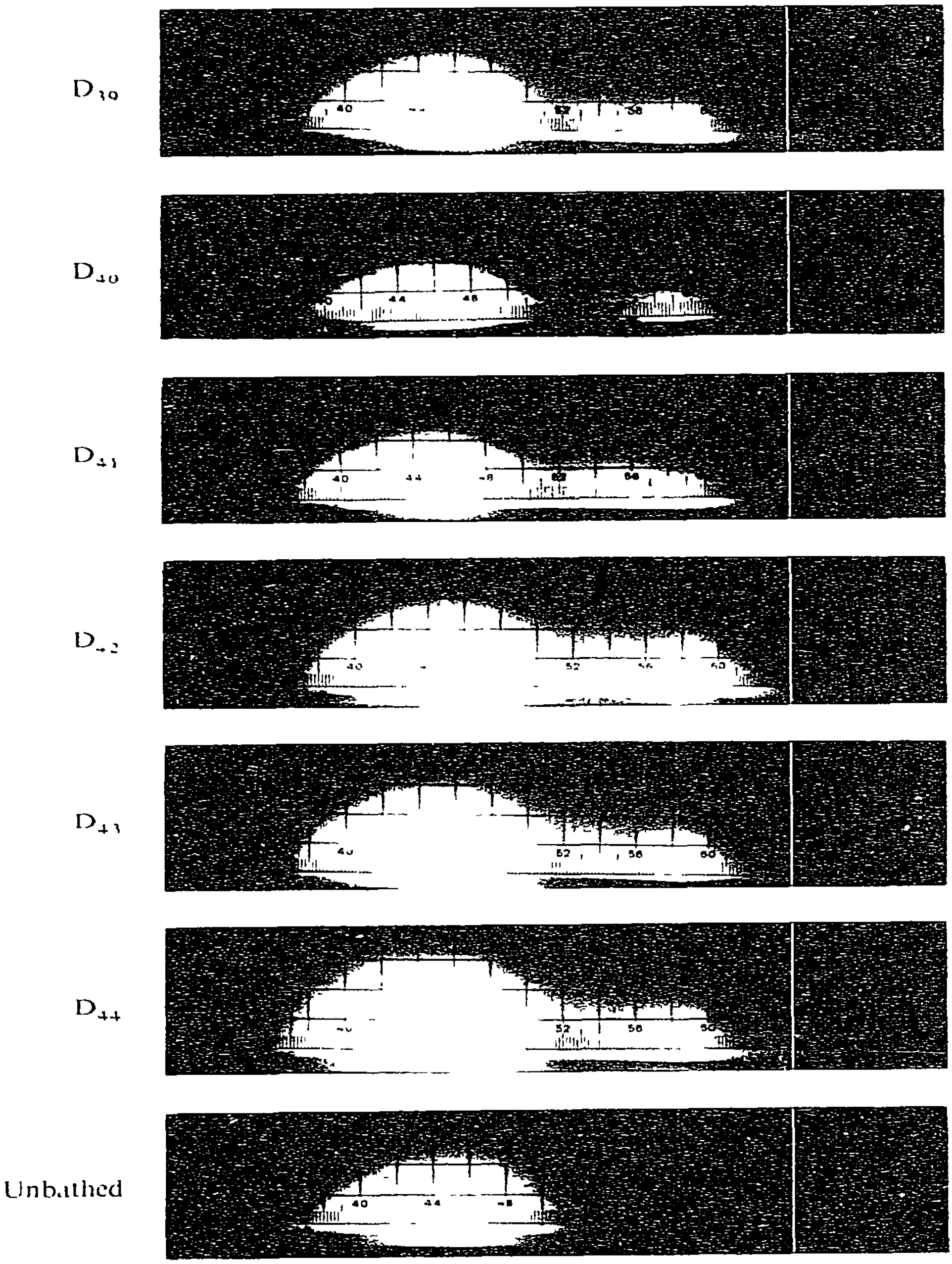

$D_{39}$
40
52
56
$D_{40}$
44
48
$D_{41}$
40
44
48
52
56
$D_{42}$
40
52
56
60
$D_{43}$
40
52
56
60
$D_{44}$
52
56
60
Unbathed
40
44
48

**Fig. 1.**—*contd*

## TABLE 1
Analytical Data of the Dyes

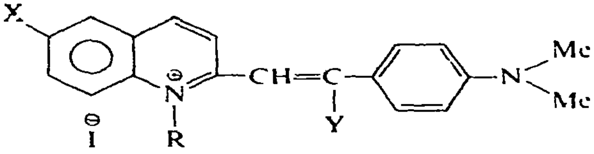
| *Dye symbol* | *Alkyl iodide of base*[a] | *Dye as alkyl iodide*[a] | *Crystal colour and shape*[b] | *Yield (%)* | *M p (°C)* | *Molecular formula* | *Found (%)* |  | *Calc (%)* |  |
|---|---|---|---|---|---|---|---|---|---|---|
|  |  |  |  |  |  |  | *N* | *Hal* | *N* | *Hal* |
| **D**$_{33}$ | Q'MeI | 2-*p*-DMA(*β*-4-DMAP)-S-QMeI | vc | 61 | 169 | $C_{28}H_{30}N_3I$ | 7·81 | 23·67 | 7·85 | 23·73 |
| **D**$_{34}$ | 6-ClQ'MeI | 2-*p*-DMA(*β*-4-DMAP)-S-6-ClQMeI | sivtn | 70 | 174 | $C_{28}H_{29}N_3ClI$ | 7·32 | 28·49 | 7·37 | 28·53 |
| **D**$_{35}$ | 6-BrQ'MeI | 2-*p*-DMA(*β*-4-DMAP)-S-6-BrQMeI | vnwrl | 49 | 204 | $C_{28}H_{29}N_3BrI$ | 6·79 | 33·77 | 6·84 | 33·83 |
| **D**$_{36}$ | 6-IQ'MeI | 2-*p*-DMA(*β*-4-DMAP)-S-6-IQMeI | s'c'sc | 67 | 232 | $C_{28}H_{29}N_3I_2$ | 6·31 | 38·45 | 6·35 | 38·41 |
| **D**$_{37}$ | 6-MeQ'MeI | 2-*p*-DMA(*β*-4-DMAP)-S-6-MeQMeI | svtn | 42 | 170 | $C_{29}H_{32}N_3I$ | 7·62 | 23·06 | 7·65 | 23·11 |
| **D**$_{38}$ | 6-MeOQ'MeI | 2-*p*-DMA(*β*-4-DMAP)-S-6-MeOQMeI | dvgs''n | 61 | 189 | $C_{29}H_{32}N_3IO$ | 7·37 | 22·52 | 7·43 | 22·48 |
| **D**$_{39}$ | 6-EtOQ'MeI | 2-*p*-DMA(*β*-4-DMAP)-S-6-EtOQMeI | dvl'n | 51 | 206 | $C_{30}H_{34}N_3IO$ | 7·19 | 21·87 | 7·25 | 21·93 |
| **D**$_{40}$ | 5,6-BzQ' | 2-*p*-DMA(*β*-4-DMAP)-S-*β*-NTQMeI | dvtn | 44 | 229 | $C_{32}H_{32}N_3I$ | 7·12 | 21·67 | 7·18 | 21·72 |
| **D**$_{41}$ | Q'EtI | 2-*p*-DMA(*β*-4-DMAP)-S-QEtI | svc | 36 | 171 | $C_{29}H_{32}N_3I$ | 7·56 | 23·07 | 7·65 | 23·13 |
| **D**$_{42}$ | 6-ClQ'EtI | 2-*p*-DMA(*β*-4-DMAP)-S-6-ClQEtI | dvtn | 45 | 178 | $C_{29}H_{31}N_3ClI$ | 7·13 | 27·78 | 7·20 | 27·84 |
| **D**$_{43}$ | 6-BrQ'EtI | 2-*p*-DMA(*β*-4-DMAP)-S-6-BrQEtI | dvsmn | 50 | 214 | $C_{29}H_{31}N_3BrI$ | 6·61 | 33·02 | 6·69 | 33·08 |
| **D**$_{44}$ | 6-IQ'EtI | 2-*p*-DMA(*β*-4-DMAP)-S-6-IQEtI | dvgs''n | 50 | 251 | $C_{29}H_{31}N_3I_2$ | 6·17 | 37·57 | 6·23 | 37·62 |

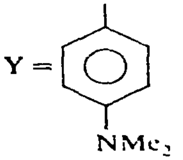
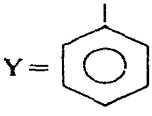
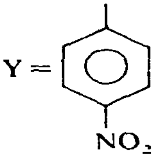
[a] Q, quinoline, Q', quinaldine, S, styryl, Bz, benz, NT, naphthyl, DMA, dimethylamino, DMAP, dimethylaminophenyl

[b] Crystals, c', coloured d, dark, g, glazing, l, lustre, l', lustrous, m, minute, n, needles, r, reddish, s, shining, s', sky, s'', small, t, tiny, v, violet, w, with

TABLE 2

Absorption Data of the Dyes (Metho and Etho Salts in Absolute Ethanol)



| | | | | | | |
|---|---|---|---|---|---|---|
| | |  | |  |  | Y = H |
| | | *Series 1* (*present work*) | | *Series 2* (*ref 8*) | *Series 3* (*ref 8*) | *Series 4* (*refs 11, 14*) |
| *X* | *R* | *Dye symbol* | $\lambda_{max}$ (*mμ*) | $\lambda_{max}$ (*mμ*) | $\lambda_{max}$ (*mμ*) | $\lambda_{max}$ (*mμ*) |
| H | Me | $D_{33}$ | 568 | 562 | 563 | 530 |
| Cl | Me | $D_{34}$ | 577 | 570 | 570 | 548 |
| Br | Me | $D_{35}$ | 579 | 575 | 575 | 550 |
| I | Me | $D_{36}$ | 585 | 582 | 584 | 552 |
| Me | Me | $D_{37}$ | 578 | 545 | 569 | |
| OMe | Me | $D_{38}$ | 580 | 548 | 575 | |
| OEt | Me | $D_{39}$ | 581 | 569 | 578 | |
| 5,6-Benz | Me | $D_{40}$ | 575 | 571 | 573 | |
| H | Et | $D_{41}$ | 570 | | | |
| Cl | Et | $D_{42}$ | 578 | | | |
| Br | Et | $D_{43}$ | 580 | | | |
| I | Et | $D_{44}$ | 585 | | | |

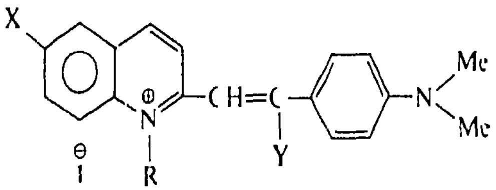
authors' previous work[8,9] (series 2 and 3) and of the β-unsubstituted dyes[11,14] (series 4) quoted from the literature leads to the following generalisations.

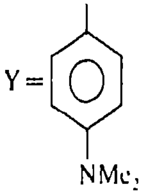
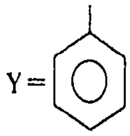
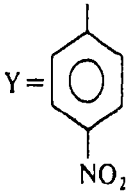
The chromophoric chain β-substitution has uniformly resulted in bathochromic shifts in absorption maxima ($\lambda_{max}$) of about 30 mμ, over their β-unsubstituted analogues, contrary to the earlier observations that both α- and β-substitutions lead to hypsochromic shifts. This also corroborates the authors' previous observations.[7–9]

The study of the effect of the nature of the chain β-substituent reveals

TABLE 3

Sensitisation Data of the Dyes (Metho and Etho Salts)



| | | Y =  NMe$_2$ | | | | Y =  | | Y =  NO$_2$ | | Y = H | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | | *Series 1*<br>*(present work)* | | | | *Series 2*<br>*(ref 8)* | | *Series 3*<br>*(ref 8)* | | *Series 4*<br>*(refs 11, 14)* | |
| | | *Extrasensitisation* | | | | *Extra-sensitisation* | | *Extra-sensitisation* | | *Extra sensitisation* | |
| *X* | *R* | *Dye symbol* | *Range*$^a$ *(mμ)* | $\lambda_{max}$ *(mμ)* | *Remarks*$^a$ | *Range (mμ)* | $\lambda_{max}$ *(mμ)* | *Range (mμ)* | $\lambda_{max}$ *(mμ)* | *Range (mμ)* | $\lambda_{max}$ *(mμ)* |
| H | Me | **D$_{33}$** | 630 | 580 | w, lc | 600 | 580 | 630 | 570 | 630 | 580 |
| Cl | Me | **D$_{34}$** | 680<br>(≥600vw) | 540up<br>580w | w, lc | 610 | 580 | 640 | 540w<br>570m | 650 | 595 |

| | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| Br | Me | $D_{35}$ | 680<br>(≥600w) | 540w<br>580<br>660vw | mc | 620 | 540 | 640 | 580 | 650 | 595 |
| I | Me | $D_{36}$ | 680<br>(≥600mi) | 540<br>580mi<br>660w | mc | 620 | 560 | 650 | 580 | 650 | 600 |
| Me | Me | $D_{37}$ | 610 | 580 | mi, c | 610 | 550 | 630 | 560 | | |
| OMe | Me | $D_{38}$ | 680<br>(≥600vwt) | 540vw<br>580w | w, il | 610 | 530<br>550 | 640 | 565 | | |
| OEt | Me | $D_{39}$ | 680<br>(≥600vwt) | 540vw<br>580w | w, il | 620 | 530<br>550 | 640 | 600 | | |
| 5,6-Benz | Me | $D_{40}$ | 640 | 525up<br>550 | m, ac | 600 | 525<br>550 | 640 | | | |
| H | Et | $D_{41}$ | 640 | 550up<br>570up | m, ac | | | | | | |
| Cl | Et | $D_{42}$ | 640 | 550up<br>585 | fi, c | | | | | | |
| Br | Et | $D_{43}$ | 680<br>(≥600vw) | 540up<br>585<br>650vw | fi ≤ 620<br>ac | | | | | | |
| I | Et | $D_{44}$ | 680<br>(≥520w) | 540up<br>585<br>650vw | i ≤ 620<br>ac | | | | | | |

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[a] ac, Almost continuous; c, continuous, fi, fairly intense, i, intense, il, isolated, lc, loosely connected, m, moderate; mc, moderately continuous, mi, moderately intense, up, unpronounced, vw, very weak, vwt, very weak trace, w, weak

some interesting observations. The electron-donating β-p-dimethylaminophenyl substituent has, in all cases, extended absorption over the analogous dyes containing the electron-attracting β-p-nitrophenyl or just the β-phenyl substituents.

As far as the hetero-6-substituted dyes are concerned, the absorption values of β-phenyl and β-p-nitrophenyl are almost the same, but when the substituent is β-p-dimethylaminophenyl a noticeable bathochromic shift of about 5 mμ is observed. The overall contribution of the 6-substituents in the heterocyclic system, though small, is regular and systematic Thus progressive weighting has caused progressive bathochromic shifts in the series already reported,[7 8] the sequence being

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

and also

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

and the present results conform with the earlier observations.[17-20]

The absorption data of the dyes having the condensed β-naphthaquinaldine system are anomalous, but a weighting effect is clearly discernible, in that these dyes absorbed at longer wavelengths than the analogous β-unsubstituted dyes [11 14]

That the weighting of the dye molecule causes bathochromic shift is also observed in ethoquaternised dyes ($D_{41}$–$D_{44}$) when compared with their methoquaternised analogues ($D_{33}$–$D_{36}$).

## 2.2. Photosensitisation

It has been found that β-p-dimethylaminophenyl substituted metho- and etho-quaternised hemicyanines (series 1) are superior sensitisers with respect to maximum extension and intensity of extrasensitisation among all the dyes studied (series 2 and 3) by the authors.[7-9] In most cases ($D_{34}$, $D_{38}$, $D_{39}$, $D_{40}$ and $D_{42}$) two peaks are observed and in 6-Br and 6-I dyes ($D_{35}$, $D_{36}$, $D_{43}$ and $D_{44}$) even three are discernible. Among the dyes under report bathochromic shifts are in several cases as large as 1600 Å Since the methoquaternised dyes ($D_{33}$–$D_{40}$) of the present communication were found to be fairly good sensitisers, four ethoquaternised dyes ($D_{41}$–$D_{44}$) were prepared with a view to examine whether weighting improved sensitisation In fact, etho dyes were found to be greater sensitisers than their metho analogues.

A further examination of the sensitisation data of the dyes studied in this work and also of the authors' earlier reported dyes[7,8] reveals that the extension of optical sensitisation of the dyes caused by 6-substituents in the heterocyclic moiety, follows the sequence:

$$\mathrm{I} > \mathrm{Br} > \mathrm{Cl} > \mathrm{H}$$

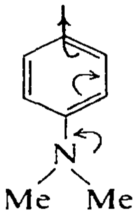
and

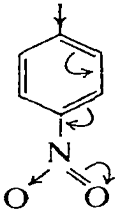
$$\mathrm{EtO} \geqslant \mathrm{MeO} \geqslant \mathrm{Me} > \mathrm{H} > \beta\text{-naphthyl}$$

These dyes are slightly better sensitisers probably because of the presence of the effective electron-donating auxochrome (—$NMe_2$) in the chain *β*-substituent

### 2.3. General comparative conclusion

It is evident that with identical hetero substituents, the *β*-*p*-dimethylaminophenyl substituted dyes have uniformly absorbed at longer wavelengths and are better sensitisers.





The obvious conclusion that electron accession to the conjugated system aids the bathochromic absorption shift and sensitisation is untenable, because the *β*-*p*-nitrophenyl substituted dyes are almost equally effective sensitisers and absorb in almost the same range when there is electron recession to the conjugated system. It seems, therefore, that the electron transporting character of *β*-substituted groups does not materially affect the optical property of the dyes

## 3. EXPERIMENTAL

### 3.1. Chain substituted hemicyanines

The quinaldinium salt, obtained by the procedure reported earlier.[7] and 4,4'-bis(dimethylamino)benzophenone (1:1 molar) were dissolved in a minimum volume of absolute ethanol, a few drops of piperidine were added and the mixture was refluxed gently under a moisture trap for about 2 h. The resulting solution on cooling afforded the dye, which was recrystallised from methanol

### 3.2. Recording of optical properties

The absorption maxima of the dyes were recorded on a Beckmann Spectrophotometer, Model DU, in 1/1000 solutions in absolute ethanol. The sensitisation spectrographs were recorded on an Adam Hilger Wedge Spectrograph, on Ilford N40 process plates bathed in dilute ethanolic solutions (1/50 000) of the dyes. After bathing for 4 min, the plates were dried and exposed for 4 min to light from a 150 cp point-o-lite AC lamp source The spectrograph of an unbathed process plate was also recorded for comparison

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