

Butadienochromophoric Chain Substituted Asocyanino Colourants

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In present report, certain specific chalcone derivatives and the quaternary bases of thioazoheteroaromatics, was condensed catalytically furnishing a number of butadienochromophoric chain substituted asocyanino colourants (BCCSAC). The colourants were synthesised with a view to evaluate absorptionspectroscopic potentialities and bacteriolytic susceptibilities, caused by diversifications in the nucleo additive and the chain elongative functionalities in the dye molecules.

INTRODUCTION

Although the hemicyanines have been extensively studied from different point of view^{1,2}—the effect of diverse substitution in the heterocyclic moiety being the one most studied, very little work has been carried out to study the effect of elongation of the chromophoric chain and the effect of substitution 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.

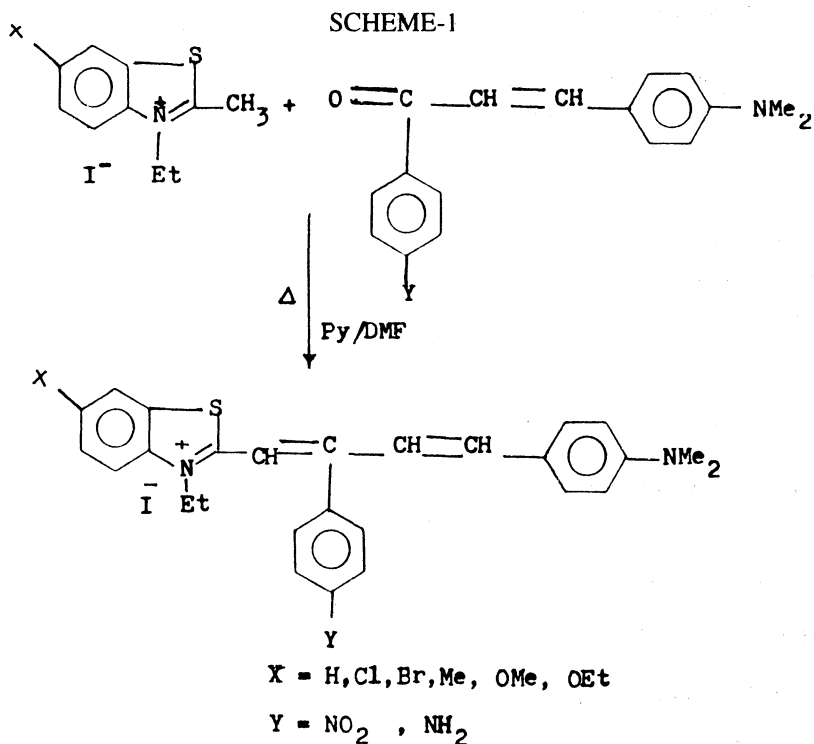
The dyes has been prepared by base catalysed condensation between 2-methyl, 6-substituted benzothiazolylum ethiodide and N-dimethylaminostyryl 4'-substituted phenyl ketone under Scheme 1.

RESULTS AND DISCUSSION

Spectral data, analytical data and some other characteristics of the dyes are given in Tables-1 and 2.

TABLE-1
ABSORPTION DATA OF THE DYES (ETHO SALT IN ABSOLUTE ETHANOL)

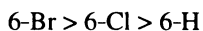
| Dye | X | Y | λ_{\max} | Dye | X | Y | λ_{\max} |
|----------------|-----|-----------------|------------------|-----------------|-----|-----------------|------------------|
| D ₁ | H | NO ₂ | 435 | D ₇ | H | NH ₂ | 440 |
| D ₂ | Cl | NO ₂ | 445 | D ₈ | Cl | NH ₂ | 451 |
| D ₃ | Br | NO ₂ | 448 | D ₉ | Br | NH ₂ | 455 |
| D ₄ | Me | NO ₂ | 438 | D ₁₀ | Me | NH ₂ | 441 |
| D ₅ | OMe | NO ₂ | 447 | D ₁₁ | OMe | NH ₂ | 455 |
| D ₆ | OEt | NO ₂ | 449 | D ₁₂ | OEt | NH ₂ | 459 |



Optical absorption: An inspection of the absorption data of the chromophoric chain β -substituted dyes of the present investigation leads to the following generalisation.

The chromophoric chain β -substitution has uniformly resulted in hypsochromic shifts in absorption maxima (λ_{max}) from chain unsubstituted dyes which corroborates the previous observation. Lengthening of the chain leads to an increment increase in λ_{max} . The study of the effect of the nature of the chain β -substitution reveals some interesting observation.

The electron donating substituents have extended absorption over the analogues dyes containing the electron attracting β -*p*-nitrophenyl substituents. The overall contribution to 6-substituents in the heterocyclic system, though small is regular and systematic. Thus the progressive weighting has caused progressive bathochromic shifts in the series sequence being



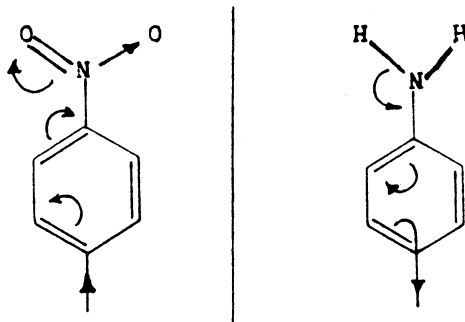
and also



General Comparative Conclusion:

It is evident that with identical hetero substituents, the β -*p*-aminophenyl substituted dyes have uniformly absorbed at longer wavelengths and are expected to be better sensitizer because of its absorption towards IR. The obvious

conclusion that electron accession to the conjugated system aids the bathochromic shift where an electron recession to the conjugated system leads to the hypsochromic shift.



EXPERIMENTAL

Chalcones:

(i) *4-Dimethylaminostyryl, 4'-nitrophenyl ketone* The general procedures for the synthesis of ketone described by Jha et al.² was adopted. Yield 78% m.p. 118-119°C (Lit. m. p. 119°C)

Analysis (%): Found C, 68.9; H, 5.4; N, 9.4 C₁₇H₁₆N₂O₃ required C, 68.9; H, 5.4; N, 9.5

IR Spectra (KBr) $\nu_{\max}(\text{cm}^{-1})$: 1165 (C—N—C); 1310 (CH=CH); 1680 (C=O); 1600 (C=N); 1465 (NO₂)

(ii) *4-Dimethylaminostyryl, 4'-aminophenyl ketone*: This compound was obtained by a method similar to that used for nitrochalcone *i.e.*, by refluxing 4-dimethylamino benzaldehyde and *p*-aminoacetophenone in presence of sodium acetate afforded the chalcone which was recrystallised from aqueous ethanol as glistening yellow leaflets; yield 70%, m. p. 178°C.

Found (%): C = 76.69; N = 10.52; H = 6.76

IR Spectra (KBr) $\nu_{\max}(\text{cm}^{-1})$: 1160 (C—N—C); 1310 (CH=CH); 1580 (C=C); 1690 (C=O)

The Quaternised Bases

The 6-substituted 2-methyl benzothiazolylum ethiodides were obtained by the method of Jacobson³ with slight modifications.

The Butadienyl Dyes

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 *ca.* 2 h. The dye, which separated on cooling was purified by recrystallisation from methanol. Analytical data, are presented in Table-2.

Antimicrobial activity: The purified and screened sample were tested for antibacterial activity against *S. aureus* and *E. coli* by the cup plate method using ethanol as a solvent (conc. 10 mg ml⁻¹). The test solution was used for 24 h study the action. The results are recorded. The halogen derivative were found more active against *S. aureus* and *E. coli*

TABLE-2
 ANALYTICAL DATA OF THE DYES

| Dye Symbol | Crystal colour & shape | Yield % | m. p. (°C) | Mol. Formula | % Found (Calcd.) | |
|-----------------|------------------------|---------|------------|--|------------------|------------------|
| | | | | | N | Hal. |
| D ₁ | vc | 61 | 164 | C ₂₇ H ₂₆ N ₃ O ₂ SI | 7.17 (7.21) | 21.60 (21.64) |
| D ₂ | Srvtn | 70 | 168 | C ₂₇ H ₂₅ N ₃ O ₂ SICl | 6.76 (6.81) | 26.10 (26.13) |
| D ₃ | vnwrl | 49 | 197 | C ₂₇ H ₂₅ N ₃ O ₂ SIBr | 6.31 (6.36) | 31.01 (31.06) |
| D ₄ | s'c'Sc | 67 | 224 | C ₂₈ H ₂₈ N ₃ O ₂ SI | 7.01 (7.04) | 21.11 (21.14) |
| D ₅ | Svtn | 42 | 161 | C ₂₈ H ₂₈ N ₃ O ₃ SI | 6.82 (6.86) | 20.52 (20.58) |
| D ₆ | dvgs"n | 61 | 179 | C ₂₉ H ₃₀ N ₃ O ₃ SI | 6.40 (6.70) | 20.08 (20.12) |
| D ₇ | dv'l'n | 51 | 195 | C ₂₇ H ₂₈ N ₃ SI | 7.55 (7.60) | 22.77 (22.82) |
| D ₈ | dvtm | 44 | 217 | C ₂₇ H ₂₇ N ₃ SICl | 7.12 (7.16) | 34.92 (34.98) |
| D ₉ | Svc | 36 | 158 | C ₂₇ H ₂₇ N ₃ SIBr | 6.63 (6.66) | 32.50 (32.53) |
| D ₁₀ | dvtm | 45 | 164 | C ₂₈ H ₃₀ N ₃ SI | 7.35 (7.42) | 22.21 (22.26) |
| D ₁₁ | dvsmn | 50 | 199 | C ₂₈ H ₃₀ N ₃ OSI | 7.16 (7.21) | 21.61 (21.64) |
| D ₁₂ | dvgs"n | 50 | 235 | C ₂₉ H ₃₂ N ₃ OSI | 7.01 (7.04) | 21.10 (21.14) |

where: v: violet, c: crystal, t: tiny, s": small, s': sky, S: shining, r: reddish, n: needles, m: minute, l: lustrous, l: lustre, g: glazing, d: dark, c': coloured, w: with.

TABLE-3

| Dye | X | Y | Diameter of inhibitory zone | | Dye | X | Y | Diameter of inhibitory zone | |
|----------------|-----|-----------------|-----------------------------|------------------------|-----------------|-----|-----------------|-----------------------------|------------------------|
| | | | <i>S. aureus</i> 24 h | <i>E. Coli</i> 24 h | | | | <i>S. aureus</i> 24 h | <i>E. Coli</i> 24 h |
| D ₁ | H | NO ₂ | 34 | 28 | D ₇ | H | NH ₂ | 30 | 24 |
| D ₂ | Cl | NO ₂ | 45 | 36 | D ₈ | Cl | NH ₂ | 40 | 34 |
| D ₃ | Br | NO ₂ | 45 | 35 | D ₉ | Br | NH ₂ | 40 | 32 |
| D ₄ | Me | NO ₂ | 30 | 22 | D ₁₀ | Me | NH ₂ | 23 | 18 |
| D ₅ | OMe | NO ₂ | 33 | 27 | D ₁₁ | OMe | NH ₂ | 28 | 23 |
| D ₆ | OEt | NO ₂ | 32 | 26 | D ₁₂ | OEt | NH ₂ | 26 | 22 |

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