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Synthesis and spectroscopic studies of some butadienyl chain substituted benzothiazole asycyanine colorants

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ABSTRACT

Fifteen new Butadienyl chain substituted benzothiazole asycyanine colorants have been synthesized by catalytic condensation of 4-dimethyl aminostyrylphenyl ketone ,4- dimethyl aminostyryl -3'-bromophyenyl ketone 4- dimethyl aminostyryl-3'-methoxyphyenyl ketone with with 2-methyl -3-(1-methylethyl) Benzothizolium iodied and 2-methyl -6-substituted -3-(1-methyl ethyl)benzothizolium iodied using piperidine as catalyst and ethanolic D.M.F.as solvent . The butadienyl chain substituted benzothia acysyanine were found to exhibit uniform increase of absorption maxima when collated with analogues having no substitution in the β-phenyl nucleus and the analogues having vinylene chain but exhibit uniform decease of absorption maxima when collated with analogues having longer chain such as hexatriene chain .

Key words: Benzothiazole asycyanine colorants, dimethylaminostyrylphenyl ketone, benzothiazolium iodide, absorption maxima.

INTRODUCTION

Copious survey of the literature explore that numerous research have been carried out to dilate the horizon of the cynine and acycyanine colorants for example ,in key materials for optical information display media ,as energy transfer media for solar batteries in therapeutic antimaligant photodynamics, in absorptivity ,photosensitity and antimicrobial activity[1-8]. Though some of the acysyanine colorants are reported [9,10] but less work is discernible in synthesing the acysyanine colorants having benzothiazolium salts.For this fifteen butadienyl chain substituted benzothiazole acysyanine colorants were synthesized by catalytic condensation of 4-dimethyl aminostyrylphenyl ketone ,4- dimethyl aminostyryl -3'-bromophyenyl ketone with ,4- dimethyl aminostyryl -3'-methoxyphyenyl ketone 2-methyl -3-(1-methylethyl) Benzothizolium iodide and 2-methyl -6-substituted -3-(1-methylethyl)benzothizolium iodied using piperidine as catalyst and ethanolic DMF as solvent by earlier method [2] and some modification[3,4] (scheme 1).

These coloarants were synthesized with the aim, to study the effect of substituent of the 3-position in the chain β - phenyl nucleus and at 6 - position of benzothiazole moiety ,to study the effect of substituent present at the 3- position with respect to 4- position in the chain -phenyl nucleus at the 6-position of benzothiazole moiety and to study increase and decreas in absorption maxima when conjugated chain is longer and shorter.

EXPERIMENTAL

Synthesis of 2-methyl-3-(1-methylethyl) benzothiazolium iodides

2-methyl-3-(1-methylethyl) benzothiazolium iodide four 2-methyl-3-(1-methylethyl)-6-substituted (chloro, iodo, methyl, methoxy) benzothiazolium iodide were synthesized and quanternised by earlier method[2] with some procedural alteration[3].

Synthesis of complex auxochromic ketones

4-Dimethylaminostyryphenyl ketone (reported) and 4-dimethylaminostyryl-3-substituted

(bromo, methoxylphenyl ketones were synthesized by usual process[4] using N-dimethylbenzaldehyde, acetophenone and 3-substituted (bromo, methoxy) acetophenone.

4-Dimethylaminostyryphenyl ketone

The crude product was recrystallised from ethanol bright yellow leaf.

Yield 69% m.p. 110°
(Lit Yield 70% m.p. 110°

4-Dimethylaminostyryl-3'-bromophenyl ketone

The crude product was recrystallised as deep bright yellow crystal

Yield: 75% m.p. 83°C
Found: C,61.8 H4.85 N-4.22%
IR spectra: KBr (Cm^{-1}) 1625 (CH=CH), 1685 (C=O), 1615 (C=N), 560 (Br_2).

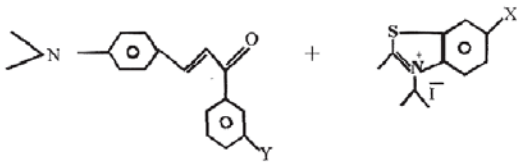
4-Dimethylaminostyryl-3'-methoxyphenyl ketone

The crude product was recrystallised from ethanol as mustard yellow crystals

Yield : 62% mp 78 °C
Found: C,76.85; H,6.77; N 4.97%
IR Spectra KBr (cm^{-1}) : 1613 (CH=CH), 1675(C=0), 1617(C=N), 1070(C—0—C)

Synthesis of butadienyl chain substituted benzothiazole asycyannine colorants

The condensation to obtain the colorants were carried out by earlier method [2] with some modification.[3,4] A solution containing the quaternised salt and complex auxochromic ketone in millimolar ratio in ethanolic DMF(25 cc) in the presence of basic catalyst piperidine (2-3 drops) was refluxed for 6-8 hrs under anhydrous conditions. The resulting mixture was concentrated ,cooled and left overnight at room tempreture . The afforded colorant was recrystallised from methanol. The analytical and UV Spectral data of the colorants are given in table 1.

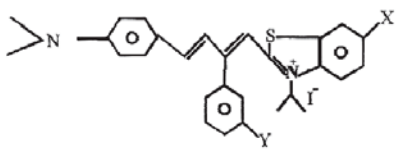


(Y= H, Br, OMe)
4-Dimethylaminostyrylphenyl ketones

(X= H,Cl, I, Me, OMe)
2- Methyl- 3-(1-methylethyl)benzothiazolium iodide

Condensation
Reflux , 6-8 hrs.

Piperidine
EtOH, DMF



Colorants.

Scheme 1

RESULTS AND DISCUSSION

A comparison of absorption maxima of the fifteen newly synthesized colorants among themselves with those vinyl chain analogues [11] described previously and hexatrienyl chain [8] permits the following generalization to be made .

The chain β- aryl substituents causes general increase in absorption maxima in comparison with unsubstituted analogues[6]. Irrespective of the nature of any additional group at β-position of aromatic ring whether electrone donating i.e.-OMe or electrone accepting i.e.-Br they showed again an increase in absorption maxima.Furthermore bromo group absorbs at longer wave length than methoxy group. The increase in absorption maxima due to presence of substituents (electrone donating or electone withdrawing) present at 3 -position is because of inductive effect of substituents which lower the ionization energy.

The functional group at the 6- position of the benzothiazole moiety showed increase in absorption maxima with respect to unsubstituted benzothiazole moiety .The 6 -additives causes increase in absorption maxima due to progressive weighting .

When the absorption maxima of these synthesized colorants having 3' -substituted phenyl system is compared with reported 4' - substituted

Table 1: Analytical and UV spectral data of the colorants.

[a] colorants	Yield %	m.p.°C	[b] crystal shape and colour.	λmax (nm) (in abs.EtOH)
		Series I (X =H,Cl., I,Me,OMe; Y=OMe)		
C_1	26	204	frl	412
C_2	27	211	grn	415
C_3	28	240	yc	419
C_4	24	205	grc	413
C_5	22	210	y'sc	414
		Series II (X =H,Cl., I,Me,OMe; Y=Br)		
C_6	23	203	s'c	423
C_7	31	212	dysc	425.2
C_8	33	242	l'bsc	433.6
C_9	26	205	yn	424
C_{10}	28	207	d'bs""	428
		Series III(X =H,Cl., I,Me,OMe; Y=H)		
C_{11}	19	205	y'bc	410
C_{12}	26	212	frl	4l4
C_{13}	29	230	r'n	417
C_{14}	21	210	r'bc	412
C_{15}	22	214	br"	413

[a.] The structure of the product was identified by IR,NMR and elemental analysis .

[b.] Abreviation bbreviations: b-brown c- crystal , , d'-dark,d-deep, f-faint, g-glazing, l-leaflets , l'-light, n-needles, r-red , **r'**-reddish , **r"**-reflux, s-sandy, S'- shining, S""-stout, y-yellow Y'- yellowish.

phenyl analogues [12,13] . than decrease in absorption maxima were observed . It may be due to the fact that in former only week inductive effect operate but in later both inductive effect and stronger resonance effect operate too .

When these colorants absorption maxima is compared with reported vinylene chain [11] (shorter chain) than it is found that synthesized colorants showed increase in absorption maxima but when these colorants absorption maxima is compared with reported hexatriene chain [8] (longer chain) then it showed decrease in absorption maxima. This happens due to greater resonance effect in hexatriene chain (longer chain) and lessor resonance effect in vinylene chain (shorter chain).

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