



## Synthetic Approaches and Electronic Spectra of some New Butamethine Ascyanine Colorants

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### ABSTRACT

Fifteen new chromophoric chain  $\beta$ -substituted butamethine ascyanine (CCBSBA) colorants have been synthesized by catalytic condensation of (i) 4-Dimethylaminostyrylphenyl ketone; (ii) 4-Dimethylaminostyryl-3'-nitrophenyl ketone and (iii) 4-Dimethylaminostyryl-3'-methylphenyl ketone with 2-methyl-3-(1-methylethyl)benzothiazolium iodide and 2-methyl-6-substituted-3-(1-methylethyl)benzothiazolium iodides using piperidine as basic catalyst and ethanolic DMF as solvent.

These colorants were synthesized with the object to study the impact of various functional groups and chain enhancement and shortage of prime chain on visible electronic spectra. All the colorants showed increase in electronic spectra whether electron withdrawing or donating. These colorants led to red shifts of the electronic spectra w.r.t. the previously reported styryl chain ascyanino-colorants, and to blue shifts of electronic spectra w.r.t. previously reported ascyanine colorants having quinoline moiety.

**Key words:** Benzothiazole, Ascyanine Colorants, Dimethylaminostyrylphenyl ketone, Benzothiazolium iodides, Electronic spectra, Red shift, Blue Shift.

### INTRODUCTION

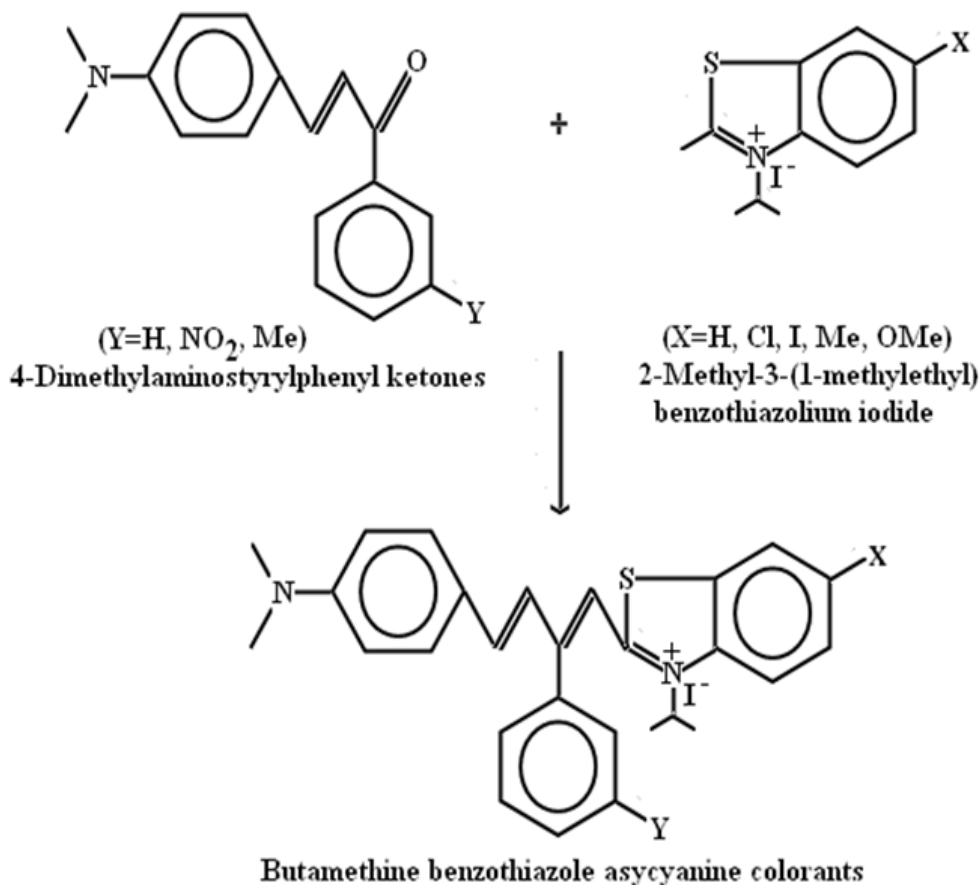
Due to multipurpose applications of cyanine, polymethinecyanine and ascyanine colorants they are being used in cosmelectronic photography, laser technology, solar energy conversion systems<sup>1-3</sup>, absorptivity and photo sensitivity<sup>4-17</sup>. Hence they became more vital in research field. For this purpose fifteen chromophoric chain  $\beta$ -aryl substituted butamethine benzothiazole ascyanine colorants were synthesized by catalytic condensation of 2-methyl-3-(1-methylethyl)

benzothiazolium iodide and 2-methyl-6-substituted-3-(1-methylethyl)benzothiazolium iodides with 4-Dimethylaminostyrylphenyl ketone, 4-Dimethylaminostyryl-3'-nitrophenyl ketone and 4-Dimethylaminostyryl-3'-methylphenyl ketone using piperidine as basic catalyst and ethanolic DMF as solvent (scheme-1).

These colorants were synthesized with the aim:

- (i) To study the effect of electron donor and electron acceptor additives at the 3- position in the chain  $\beta$ -phenyl nucleus & at the 6-

- (ii) position of heterocyclic system.  
 To study the effect of electron donor and electron acceptor additives present at the 3-position w.r.t. electron donor and electron acceptor additives present at the 4-position in the chain  $\beta$ -phenyl nucleus and at the 6-position of the heterocyclic system.
- (iii) To study the electronic spectra of synthesized colorants with reported ascyanine colorants whose length are shorter i.e. w.r.t. styryl colorants with reported ascyanine colorants whose length are longer i.e. w.r.t. hexatrienyl quinaldine system.



Scheme 1

### EXPERIMENTAL

Synthesis of 2-Methyl-3-(1-methylethyl)benzothiazolium iodide and four 2-methyl-3-(1-methylethyl)-6-substituted(chloro, iodo, methyl, methoxy)benzothiazolium iodide were synthesized by earlier methods<sup>3</sup> with some procedural alteration.

### Synthesis of complex auxochromic ketones:

4-Dimethylaminostyrylphenyl ketone (reported) and 4-Dimethylaminostyryl-3-substituted (nitro, methyl,) phenyl ketones were synthesized by usual process<sup>4-6</sup> using N,N-Dimethylamino-benzaldehyde, acetophenone, and 3-substituted (nitro, methyl)acetophenone.

**Table 1: Analytical & Spectral data of the Colorants**

Colo. rants	Yield %	m.p. (°C)	% Found (Cal)		Crystal, $\lambda_{\max}$ (nm) Shape (in abs. EtOH) & Color	PMR, p.p.m. $\Delta$ (Ar-H)	$V_{\max}$ (cm <sup>-1</sup> )	
			N	X				
<b>Series I (X=H, Cl, I, Me, OMe; Y= H)</b>								
C <sub>1</sub>	19	205	5.00 (5.07)	22.92 (23)	y'bc	410	7.01-7.02	2930-3020 C-H (Str.) (Aromatic) 2410-2450 C=N(str.)
C <sub>2</sub>	26	212	4.76 (4.77)	27.73 (27.76)	frl	414	7.20-7.28	(Quaternary N) 1390-1630 C=C(Str.)
C <sub>3</sub>	19	230	4.09 (4.12)	37.42 (37.46)	r'n	417	7.10-7.25	(Aromatic & conjugation with C=N, plane vibration)
C <sub>4</sub>	21	210	4.92 (4.94)	22.40 (22.43)	r'bc	412	6.90-7.21	(Aromatic nucleus) 730-880 C-H (Def) 500-770 C-X (Str.), -Cl, -I
C <sub>5</sub>	22	214	4.78 (4.81)	21.76 (21.82)	br''	413	6.30-7.19	3080-3110 C-H (Str.)
<b>Series II (X= H, Cl, I, Me, OMe; Y= NO<sub>2</sub>)</b>								
C <sub>6</sub>	41	210	6.99 (7.03)	21.19 (21.27)	b'psc	430	6.98-8.40	(Aromatic) 2420-2460 C=N (Str.)
C <sub>7</sub>	44	220	6.62 (6.64)	25.67 (25.69)	drs''nc	433.6	7.015-8.35	(Quaternary N) 1420-1660 C=C (Str.)
C <sub>8</sub>	48	248	5.78 (5.80)	35.10 (35.13)	grn	436.6	7.03-8.32	(Aromatic & conjugation with C=N plane vibration) 1300-1370 N=O(Str.)
C <sub>9</sub>	23	242	6.83 (6.87)	20.74 (20.78)	grc	431	6.92-8.34	745-875 C-H (Def) (Aromatic nucleus)
C <sub>10</sub>	26	220	6.67 (6.69)	20.24 (20.25)	drgl	438.8	6.28-8.30	500-770 C-X(Str.), -Cl, -I
<b>Series III (X= H, Cl, I, Me, OMe; Y= Me)</b>								
C <sub>11</sub>	27	202	4.91 (4.92)	22.39 (22.43)	tc'c	412	7.02-7.17	2990-3030 C-H (Str.) (Aromatic) 2410-2460 C=N (Str.)
C <sub>12</sub>	28	210	4.62 (4.65)	27.08 (27.12)	b'rp	415.8	7.15-7.23	(Quaternary N) 1410-1660 C=C (Str.)
C <sub>13</sub>	29	220	3.99 (4.04)	36.08 (36.70)	bs'''l	418	7.14-7.21	(Aromatic & conjugation with C=N plane vibration)
C <sub>14</sub>	25	210	4.79 (4.82)	21.88 (21.89)	l'bs'l	415	6.94-7.20	720-875 C-H (Def) (Aromatic nucleus)
C <sub>15</sub>	23	214	6.68 (4.69)	21.27 (21.30)	l'bs'l	416.8	6.25-7.19	500-780 C-X(Str.), -Cl,

Abbreviations: b- brown, b'- brick, c- crystal, c'- coloured, d- dark, f- faint, g- glazing, l- leaflets, l'- light, n- needles, p- plate, r- red, r'- reddish, r''- reflux, s- sandy, s'- shining, s''- scintillating, s'''- stout, t- tea, y'- yellowish.

**4-Dimethylaminostyrylphenyl ketone**

The crude product was recrystallised from ethanol as bright yellow leaf.

Yield 69% m.p. 110°C  
(Lit. yield 70%, m.p. 110°C)<sup>8</sup>

**4-Dimethylaminostyryl-3-nitrophenyl ketone**

The crude product was recrystallised from ethanol as deep red crystals.

Yield-80% m.p. 152-154°C  
Found : C- 68.88%; H-5.42%; N-9.44%  
IR Spectra: KBr (Cm<sup>-1</sup>) 1610 (CH=CH)  
1695 (C=O), 1615 (C=N),  
1590 (NO<sub>2</sub>)

**4-Dimethylaminostyryl -3-nitrophenyl ketone.**

The crude product was recrystallised from ethanol as turmeric yellow sandy crystals.

Yield: 60% m.p. 71°C  
Found : C- 81.45%; H- 7.20%; N- 5.25%  
IR Spectra KBr (Cm<sup>-1</sup>) 1610  
(CH=CH)  
1680 (C=O) 1617 (C=N)  
3010 (CH<sub>3</sub>)

**Synthesis of CCBSBA Colorants**

The condensation to obtain the colorants were carried out by earlier methods with some modification<sup>7-9</sup>.

A solution containing the quaternised salt and complex auxochromic ketone in milli molar ratio in ethanolic DMF (25ml) in the presence of basic catalyst piperidine (2-3 drops) was refluxed for 6-8 hrs under anhydrous conditions using CaCl<sub>2</sub> guard tube. The resulting mixture was concentrated, cooled and left overnight at room temperature. The afforded colorant was recrystallised from methanol. The analytical and UV spectral data of the colorants are given in Table 1.

**RESULTS AND DISCUSSION**

Scrutiny of the electronic spectra of fifteen newly synthesized CCBSBA ascyanine colorants (Scheme 1) among themselves, with unsubstituted

analogues<sup>10</sup>, with ethenyl colorants<sup>11</sup> and finally with 3-methyl substitution instead of 3-(1-methylethyl)substitution reveals fascinating observations.

The β -4'/3' substituted phenylbutadienyl ascyanine colorants showed uniform red shifts in the absorption maxima in comparison to their corresponding β – phenyl analogues irrespective of the nature of additional groups attached to phenyl nucleus i.e. whether they are electron attracting viz. NO<sub>2</sub> group or electron donating viz. CH<sub>3</sub> group. It is also observed that β -3'-nitro derivative show red shifts than that of β -3'-methyl analogues. Therefore β -3'-differently substituted phenyl group or β-phenyl group itself attached with the methine chain of the butalogues, both result in very similar red shifts corroborating the previous findings<sup>5-8</sup>.

Remarkable variations was discernable when the absorption maxima of the chain β-4'-substituted ethenyllogues were collated with these synthesized analogues . The absorption maxima of the ethenyllogues colorants<sup>11</sup> were fairly lower than the synthesized analogues colorants. This was due to less resonance in former with decrease in conjugated chain (i.e. shortage of chain ). The absorption maxima of hexatrienyl analogues colorants<sup>6,16</sup> were higher than synthesized β – analogues colorants. This was due to greater resonance in the former with increase in conjugated chain (i.e. chain enhancement ). When electronic characteristics of these colorants having 3'-substituted phenyl system were collated with reported 4'-substituted phenyl analogues<sup>12,15</sup> blue shifts were observed. It may be due to the fact that in former inductive effect was applicable where as in later resonance and inductive effect both were effective. In the benzothiazole nucleus the effect of 6-substituents or 3-(1-methylethyl) –substituent is small but uniform and systematic for all the colorants. The successive increase in the mol. Wt. of 6- substituent bring about successive red shifts in all the series.

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