



## **Synthesis and Spectroscopic Characterisation of Some Novel Butadienyl Asycyanine Colorants having Lepidine Moiety**

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### **Authors' contributions**

*This work was carried out in collaboration among all authors. All authors read and approved the final manuscript.*

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### **ABSTRACT**

Twenty-one novel chromophoric chain  $\beta$ -substituted butadienyl asycyanine colorants have been synthesized by catalytic condensation of (i) dimethylaminostyryl phenyl ketone, (ii) 4'-dimethylaminostyryl-4'-nitrophenyl ketone and (iii) 4'-dimethylaminostyryl-4'-methoxyphenyl ketone with seven lepidinium methyl iodide salts in ethanolic DMF medium using piperidine as basic catalyst. These colorants were synthesized with the objective to study the effect of electron acceptor and electron donor group substituent at 4'-position in the chain  $\beta$ -phenyl nucleus on visible absorption maxima. The newly prepared colorants were found to exhibit uniform increase in absorption maxima *i.e.* Red shift (RS), when collated with analogues having no substituent in the  $\beta$ -phenyl nucleus. Again the absorption maxima of the title colorants were found to be higher than the absorption maxima of previously prepared butadienyl colorants having quinoline moiety of same conjugated system.

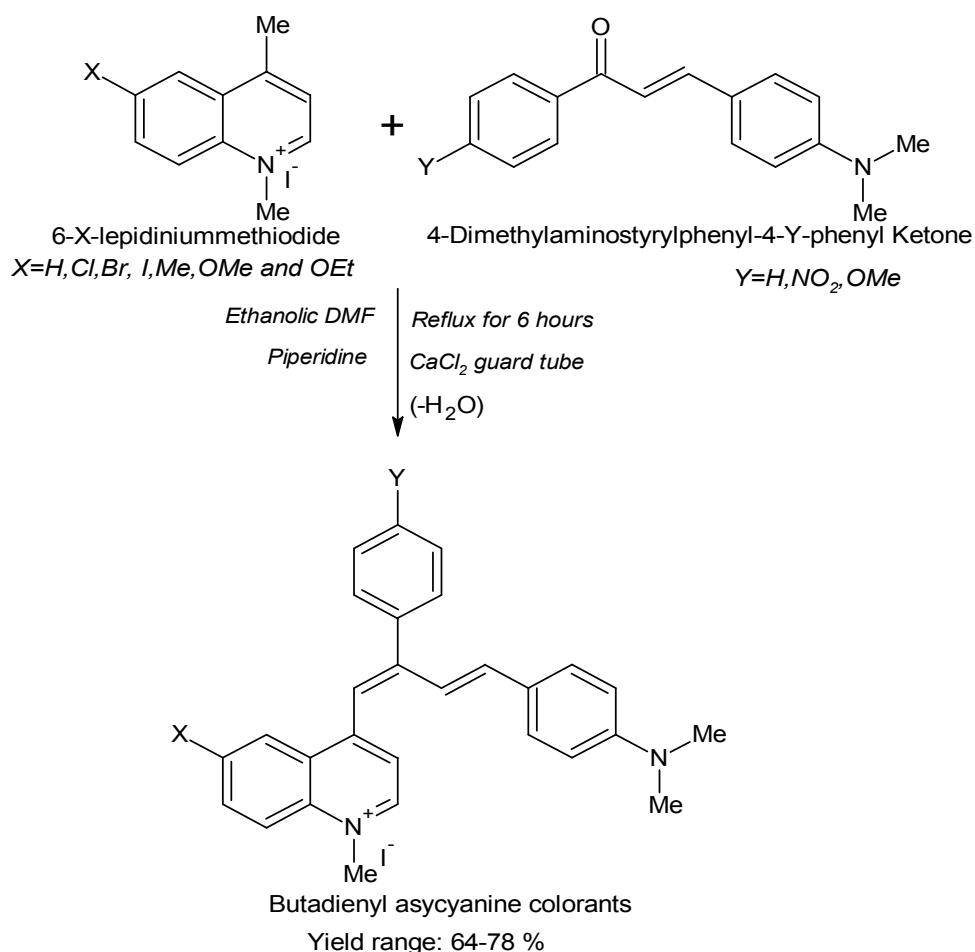
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## 1. INTRODUCTION

Of pure organic colorants, cyanine and ascyanine colorants have intense and broad absorption band in visible and near infrared region and excellent sensitizing properties in photography. Recently their multifarious applications in optical information display media, as energy transfer media for solar batteries, in therapeutic antimalignant photodynamics and antibacterial activities withdrew the attention of chemists [1-3]. Some voltage sensitive fluorescent cyanine colorants are synthesized and used in correction of motion artifact in transmembrane in heart [4-8]. Though some of ascyanine colorants are synthesized by using quinaldinium salt and benzthiazolium salts and plane/substituted styryl phenyl ketone and their absorption maxima have been analysed, but very

few literature are found about the synthesis of colorants using lepidinium salt and above ketones. The present paper would attempt to focus on the preparation of twenty-one new  $\beta$ -substituted butadienylascyanine colorants [BAC], having lepidiniumiodide salts (scheme-I) in ethanolic DMF medium using piperidine as basic catalyst and their spectroscopic analysis in suitable solvent. The absorption data of synthesised colorants have been collected and collated with respect to the functional additives whether electron donor or electron acceptor at  $\beta$ -phenyl nucleus of the butadienyl chain and upon the periphery of the lepidinium rings. The prepared colorants were also compared with reported butadienyl colorants having quinaldinium salts and showed red shift (RS) as compared to newly prepared colorants.



**Scheme-I**

## 2. MATERIALS AND METHODS

Melting points were uncorrected. Elemental analysis was carried out by elemental analyzer Euro-E-300, IR spectra (KBr) was performed by Perkin Elmer FT-IT spectrum. The visible absorption spectra were recorded on Systronic 119- U.V. Visible spectrophotometer.  $^1\text{H}$  NMR spectra were recorded with  $E_m$  390 90 MHz NMR Spectrophotometer. The colorants 6-X-2-(4-Y-phenyl)-2-(4-N,N-dimethylamino)phenyl)butadienyl)-1-methyl lepidine-1-ium iodide were synthesized by earlier methods [5-12] with some procedural change.

### 2.1 Synthesis of 4-dimethylaminostyrylphenyl Ketones

4-Dimethylaminostyrylphenyl ketone and 4-dimethylaminostyryl-4'-nitro/methoxy phenyl ketone were successfully prepared following the same facile method reported by Jha et al. [9] & Ansari et al. [10,11]. The equimolar proportions of substituted acetophenone and substituted benzaldehyde were taken in a conical flask, and dissolved in the minimum volume of extra pure methanol. Some dry pulverized caustic alkali(5-7 pellets) were added to initiate the condensation. The conical flask was tightly corked and shaken briskly by magnetic stirrer for 50 minutes and left over night at the ambient temperature for completion of reaction. The separated product was washed, dried and recrystallised from ethanol (or petroleum ether) in pure and nearly theoretical yield.

#### 4-Dimethylaminostyrylphenyl ketone:

Faint yellow crystals  
Molecular formula:  $\text{C}_{17}\text{H}_{17}\text{NO}$   
m.p.=196-198°C, yield: 77%(Lit. m.p.=197°C, yield 78%)  
Found %= C (79.95), H (6.70), N (6.21), O (7.09)  
Calculated % = C (79.97), H (6.71), N (6.22), O (7.10)  
IR 1610(CH=CH), 1695(C=O), 1615(C=N)  
 $^1\text{H}$ NMR ( $\text{CDCl}_3$ ) 7.69(d, 2H), 7.48(d, 2H), 7.52(t,H), 7.49(t,2H), 6.87(d,2H), 2.91(s, 6H)

#### 4-Dimethylaminostyrylphenyl-4'-nitrophenyl ketone:

Glazing red crystals  
Molecular formula:  $\text{C}_{17}\text{H}_{16}\text{N}_2\text{O}_3$

m.p.=118-121°C, yield=78% (Lit. m.p.=118°C, yield = 81%)  
Found %= C (68.90), H (5.40), N (9.45), O (16.21)  
Calculated % = C (68.91), H (5.42), N (9.46), O (16.22)  
IR 1610(CH=CH), 1680(C=O), 1617(C=N).  
 $^1\text{H}$ NMR ( $\text{CDCl}_3$ ) 7.74(d, 2H), 7.89(d, 2H), 7.53(d, 2H), 6.87(d, 2H), 2.89(s, 6H)

#### 4-Dimethylaminostyrylphenyl-4'-methoxyphenyl ketone:

Faint yellow crystals  
Molecular formula:  $\text{C}_{18}\text{H}_{19}\text{NO}_2$   
m.p.=196-198 °C, yield=77% (Lit. m.p.=197°C, yield=76%)  
Found %= C (76.86), H (6.76), N (4.96), O (11.38)  
Calculated % = C (76.87), H (6.78), N (4.98), O (11.39)  
IR 1610(CH=CH), 1695(C=O), 1615(C=N)  
 $^1\text{H}$ NMR ( $\text{CDCl}_3$ ) 7.69(d, 2H), 7.48(d, 2H), 7.49(d, 2H), 6.87(d, 2H), 2.89(s, 6H), 3.01(s, 3H)

### 2.2 Synthesis of Lepidinium Salts

The quaternised lepidine and their derivatives were prepared by applying the method proposed by Mikeska [12], and their metho salts were synthesised by earlier methods [7-11] by heating the base and methyl iodide for 36 hours and recrystallised using suitable solvents.

### 2.3 Synthesis of 6-X-2(2-(4-Y-phenyl)-2-(4-N,N-dimethylamino)phenyl)butadienyl)-1-Methyllepidinium Iodide Asycyanine Colorants

The target colorants have been synthesised by preparative method of Johnson and Adams [13], with some modification made by Jha et al. [9] and Ansari et al. [14,15]. A millimolar solution of quaternised lepidine and substituted lepidine base is condensed with above prepared auxochromic ketones in ethanolic DMF in the presence of basic catalyst piperidine (2-3 drops) and were refluxed for 6-8 hours under anhydrous condition using  $\text{CaCl}_2$  guard tube. The resulting mixture was concentrated cooled and left overnight at room temperature. The afforded colorants were recrystallized from methanol. Relevant data of all the colorants are described in corresponding Tables 1 and 2.

Table 1. Analytical and UV spectral data of colorants

Colorants	Molecular formula	Yield %	M.p.°C	% Found(calculated)		Appearance	$\lambda_{\max}$ in 95% EtOH
				N	I		
<b>Series I (X=H, Cl, Br, I, Me, OMe, OEt) (Y=H)</b>							
<sup>1</sup> C-1	C <sub>28</sub> H <sub>27</sub> N <sub>2</sub> I	78	179-181	5.38(5.39)	24.47(24.46)	<i>dvn,gr'</i>	440
<sup>1</sup> C-2	C <sub>28</sub> H <sub>26</sub> ClIN <sub>2</sub>	78.4	187-188	4.98(5.05)	22.94(22.93)	<i>dvn,gr'</i>	483
<sup>1</sup> C-3	C <sub>28</sub> H <sub>26</sub> BrIN <sub>2</sub>	71	199-201	4.88(4.90)	22.24(22.23)	<i>ldvn</i>	470
<sup>1</sup> C-4	C <sub>28</sub> H <sub>26</sub> I <sub>2</sub> N <sub>2</sub>	80.5	207-210	4.33(4.34)	39.37(39.37)	<i>gdvn</i>	460
<sup>1</sup> C-5	C <sub>29</sub> H <sub>29</sub> IN <sub>2</sub>	72	184-186	5.22(5.25)	23.82(23.80)	<i>dvtc</i>	443
<sup>1</sup> C-6	C <sub>29</sub> H <sub>29</sub> OIN <sub>2</sub>	76	205-208	5.08(5.10)	23.13(23.12)	<i>dvf</i>	440
<sup>1</sup> C-7	C <sub>30</sub> H <sub>31</sub> OIN <sub>2</sub>	72	184-186	4.96(4.97)	22.55(22.53)	<i>dvn</i>	437
<b>Series II (X=H, Cl, Br, I, Me, OMe, OEt) (Y=NO<sub>2</sub>)</b>							
<sup>2</sup> C-1	C <sub>28</sub> H <sub>26</sub> O <sub>2</sub> IIN <sub>3</sub>	63.8	193-195	7.42(7.44)	22.51(22.49)	<i>vrn</i>	496
<sup>2</sup> C-2	C <sub>28</sub> H <sub>25</sub> ClO <sub>2</sub> IN <sub>3</sub>	64.2	206-209	7.00(7.02)	21.21(21.20)	<i>vrn</i>	490
<sup>2</sup> C-3	C <sub>28</sub> H <sub>25</sub> BrO <sub>2</sub> IN <sub>3</sub>	65.7	223-225	6.79(6.81)	20.61(20.60)	<i>d'vr</i>	491
<sup>2</sup> C-4	C <sub>28</sub> H <sub>25</sub> O <sub>2</sub> I <sub>2</sub> N <sub>3</sub>	66	241-243	6.05(6.08)	36.81(36.79)	<i>d'vr</i>	502
<sup>2</sup> C-5	C <sub>29</sub> H <sub>28</sub> O <sub>2</sub> IN <sub>3</sub>	65.7	223-226	7.25(7.27)	2.97(21.93)	<i>vrn</i>	481
<sup>2</sup> C-6	C <sub>29</sub> H <sub>28</sub> O <sub>3</sub> IN <sub>3</sub>	69.3	227-231	7.05(7.07)	21.38(21.37)	<i>vrn</i>	495
<sup>2</sup> C-7	C <sub>30</sub> H <sub>30</sub> O <sub>3</sub> IN <sub>3</sub>	72.4	249-251	6.88(6.90)	20.88(20.87)	<i>d'rf</i>	504
<b>Series III (X=H, Cl, Br, I, Me, OMe, OEt) (Y=OMe)</b>							
<sup>3</sup> C-1	C <sub>29</sub> H <sub>29</sub> OIN <sub>2</sub>	70	173-175	5.05(5.10)	23.13(23.10)	<i>rvf</i>	448
<sup>3</sup> C-2	C <sub>29</sub> H <sub>28</sub> OClIN <sub>2</sub>	78	207-210	4.78(4.80)	21.78(21.75)	<i>lvn</i>	485
<sup>3</sup> C-3	C <sub>29</sub> H <sub>28</sub> OBrIN <sub>2</sub>	72	219-223	4.63(4.65)	21.13(21.12)	<i>r'vc</i>	475
<sup>3</sup> C-4	C <sub>29</sub> H <sub>28</sub> OI <sub>2</sub> N <sub>2</sub>	81	234-238	4.13(4.14)	37.62(37.60)	<i>r'vc</i>	466
<sup>3</sup> C-5	C <sub>30</sub> H <sub>31</sub> OIN <sub>2</sub>	73.2	197-199	4.95(4.97)	22.55(22.54)	<i>rvf</i>	445
<sup>3</sup> C-6	C <sub>30</sub> H <sub>31</sub> O <sub>2</sub> IN <sub>2</sub>	79	211-214	4.81(4.83)	21.93(21.91)	<i>Dsvn</i>	456
<sup>3</sup> C-7	C <sub>31</sub> H <sub>33</sub> O <sub>2</sub> IN <sub>2</sub>	82	231-233	4.69(4.72)	21.41(21.39)	<i>rvf</i>	440

Abbreviations: *b*-brown; *c*-crystal; *d*-dark; *f*-flakes; *g*-green; *l*-lustrous; *n*-needles; *r*-reddish; *r'*-reflux; *s*-shining; *t*-tiny; *v*-violet

Table 2. IR data of colorants

Compound no	Band range (cm <sup>-1</sup> )	Assignments
<sup>1</sup> C-1 - <sup>1</sup> C-7	2940-3050(C-H)	Stretching (aromatic)
	1450-1630(C=C)	Stretching (aromatic) and conjugation with C=N plane vibration
	510-740(C-X)	Stretching conjugated with aromatic nucleus
	1630-1660(C=N)	Quaternary Nitrogen
	2410-2450(C=N)	
<sup>2</sup> C-1 - <sup>2</sup> C-7	2910-3060(C-H)	Stretching (aromatic)
	1430-1660(C=C)	Stretching (aromatic) and conjugation with C=N plane vibration
	520-780(C-X)	Stretching conjugated with aromatic nucleus
	1630-1660(C=N)	Quaternary Nitrogen
	2410-2460(C=N)	
<sup>3</sup> C-1 - <sup>3</sup> C-7	2910-3060(C-H)	Stretching (aromatic)
	1430-1650(C=C)	Stretching (aromatic) and conjugation with C=N plane vibration
	520-780(C-X)	Stretching conjugated with aromatic nucleus
	1630-1660(C=N)	Quaternary Nitrogen
	2410-2460(C=N)	

### 3. RESULTS AND DISCUSSION

Comparison of electronic spectral data ( $\lambda_{\max}$ ) of newly synthesised butadienyl chain substituted ascyanine colorants (<sup>1</sup>C-1 - <sup>1</sup>C-7, <sup>2</sup>C-1 - <sup>2</sup>C-7 and <sup>3</sup>C-1 - <sup>3</sup>C-7) among themselves and with those analogues described

previously [16-19] with  $\beta$ -substituted colorants [20] permits the following generalisation to be made.

It was found that most of the  $\beta$ -4'-substituted phenyl butadienyl ascyanine colorants uniformly result in bathochromic shifts in absorption

maxima relative to their corresponding  $\beta$ -phenyl analogues, irrespective of the nature of any additional group attached to the  $\beta$ -phenyl ring, whether they are electron donor (-OMe) or electron acceptor (-NO<sub>2</sub>) group. Nitro group absorbs at longer wavelength than methoxy group. The electron donor or acceptor groups cause variation of ionisation energy by inductive and resonance effects, thus increasing absorption which corroborate reported data [16-21].

It was also found that the new title colorants showed more significant bathochromic shift as compared with ascyanine colorants with benzthiazole nucleus, though both having same conjugated system and functional group. It might be due to ring strain of thiazole moiety in benzthiazole nucleus.

#### 4. CONCLUSION

From the above discussions following conclusions are drawn.

- i. Twenty-one novel butadienyl ascyanine colorants were synthesized with lepidine moiety and their physico-chemical properties were studied.
- ii. All the newly prepared butadienyl ascyanine colorants result in uniform bathochromic shifts in absorption maxima irrespective of their substituents.
- iii. The order of absorption maxima is NO<sub>2</sub> > OMe > H
- iv. More significant bathochromic shifts were observed when these title colorants were compared with previously prepared colorants with benzthiazole nucleus with same substituents.

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#### COMPETING INTERESTS

Authors have declared that no competing interests exist.

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