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 activity1-8. Though some of the acysyanine colorants are reported 9,10 but less work is discernible in synthesing the acyscyanine colorants having benzothiazolium salts. For this fifteen butadienyl chain substituted benzothiazole acyscyanine colorants were synthesized by catalytic condensation of 4-dimethyl aminostyrylphenyl ketone, 4-dimethyl aminostyryl -3'-bromophenyl ketone 4-dimethyl aminostyryl-3'-methoxyphenyl ketone with 2-methyl-3-(1-methylethyl) Benzothiazolium iodide and 2-methyl-6-substituted-3-(1-methyl ethyl)benzothiazolium iodide 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 decrease of absorption maxima when collated with analogues having longer chain such as hexatriene chain.

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

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 quaternised by earlier method² with some procedural alteration³. 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 decrease in absorption maxima when conjugated chain is longer and shorter.

Synthesis of complex auxochromic ketones

4-Dimethylaminostyrylphenyl ketone (reported) and 4-dimethylaminostyryl-3-substituted
(bromo, methoxylphenyl ketones were synthesized by usual process using N-dimethylbenzaldehyde, acetophenone and 3-substituted (bromo, methoxy) acetophenone.

4-Dimethylaminostyrylphenyl 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; H, 4.85; N, 4.22%
IR spectra: KBr (cm⁻¹) 1625 (CH=CH), 1685 (C=O), 1615 (C=N), 560 (Br₂).

4-Dimethylaminostyryl-3'-methoxyphenyl ketone
The crude product was recrystallised from ethanol as mustard yellow crystals
Yield: 62% m.p. 78°C
Found: C, 76.85; H, 6.77; N, 4.97%
IR Spectra KBr (cm⁻¹): 1613 (CH=CH), 1675(C≡O), 1617(C≡N), 1070(C—O—C).

Synthesis of butadienyl chain substituted benzothiazole asycyannine colorants
The condensation to obtain the colorants were carried out by earlier method with some modification. 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 temperature. The afforded colorant was recrystallised from methanol. The analytical and UV Spectral data of the colorants are given in table 1.

\[ \text{(Y= H, Br, OMe) 4-Dimethylaminostyrylphenyl ketones} \]

\[ \text{(X= H,Cl, I, Me, OMe) 2- Methyl- 3-(1-methylethyl)benzothiazolium iodide} \]

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 described previously and hexatrienyl chain permits the following generalization to be made.

The chain \( \beta \)-aryl substituents causes general increase in absorption maxima in comparison with unsubstituted analogues. Irrespective of the nature of any additional group at \( \beta \)-position of aromatic ring whether electron donating i.e.-OMe or electron 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 (electron donating or electron 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>
<thead>
<tr>
<th></th>
<th>colorants</th>
<th>Yield %</th>
<th>m.p. ( ^\circ )C</th>
<th>( \lambda_{\text{max}} ) (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Series I (X =H,Cl., I,Me,OMe; Y=OMe)</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C1</td>
<td>26</td>
<td>204</td>
<td>frl</td>
<td>412</td>
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<td>C2</td>
<td>27</td>
<td>211</td>
<td>grn</td>
<td>415</td>
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<td>205</td>
<td>grc</td>
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</tr>
<tr>
<td>C5</td>
<td>22</td>
<td>210</td>
<td>y'sc</td>
<td>414</td>
</tr>
<tr>
<td><strong>Series II (X =H,Cl., I,Me,OMe; Y=Br)</strong></td>
<td></td>
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<td>23</td>
<td>203</td>
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<td>C9</td>
<td>26</td>
<td>205</td>
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<td>424</td>
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<tr>
<td>C_{10}</td>
<td>28</td>
<td>207</td>
<td>d'bs''''</td>
<td>428</td>
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<tr>
<td><strong>Series III(X =H,Cl., I,Me,OMe; Y=H)</strong></td>
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<td>414</td>
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<tr>
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<td>230</td>
<td>r'n</td>
<td>417</td>
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<tr>
<td>C_{14}</td>
<td>21</td>
<td>210</td>
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<td>412</td>
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<tr>
<td>C_{15}</td>
<td>22</td>
<td>214</td>
<td>br''</td>
<td>413</td>
</tr>
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</table>

\( ^a \)The structure of the product was identified by IR,NMR and elemental analysis.

\( ^b \)Abreviation abbreviations: 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 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 (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 (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).

REFERENCES

1. Zollinger, H; Colour chemistry, Xvi,VCH,V6940, weinheim,Germany 1991; Nakarsujui, S;