

## **SYNTHESIS OF SOME STYRYL CHAIN SUBSTITUTED BENZOTHAZOLYLIUM ASYMMETRIC CYANINES : SPECTRAL AND ANTIMICROBIAL STUDIES**

**S.A. AFSAH and JAWAID AHMAD\***

Post Graduate Department of Chemistry  
R.K. College, Madhubani – 847211 INDIA  
e-mail : ahmadjawaid@rediffmail.com

### **ABSTRACT**

Some styryl chain substituted benzothiazolylum asymmetric cyanines have been synthesized by the catalytic condensation of some complex auxochromic chalcones with diversely substituted 2-methyl benzothiazolylum ethiodides. The effects of electron donor and acceptor substituents on chromophoric chain and the benzothiazolylum unit were studied on their absorption maxima. The antimicrobial activity of these compounds was investigated.

**Key words :** Styryl chain, Benzothiazolylum asymmetric cyanines, Antimicrobial activity

### **INTRODUCTION**

Novel applications of some polyenic cyanines and infrared dyes have been described<sup>1-4</sup> especially in optical information storage devices, solar energy conversion systems, chromatic sensitising, antimicrobial operators and also as tools for lasers. The asymmetric cyanines have been the subject of several investigations and some data have been reported on the effect of substituents in the main chromophoric chain based on their optical absorption data and photosensitization properties<sup>1-7</sup>.

In the present investigations, 4-dimethyl aminobenzophenone and 4'-substituted 4-dimethyl aminobenzophenone were catalytically condensed with 2-methyl-6-substituted benzothiazolylum ethiodides to give series of SCSBAC (Scheme – I).  $\lambda_{\max}$  of these cyanines were recorded and effect of the nature of  $\beta$ -substituents has been discussed on the basis of collected data and a comparison has been made with the corresponding unsubstituted chain analogues.

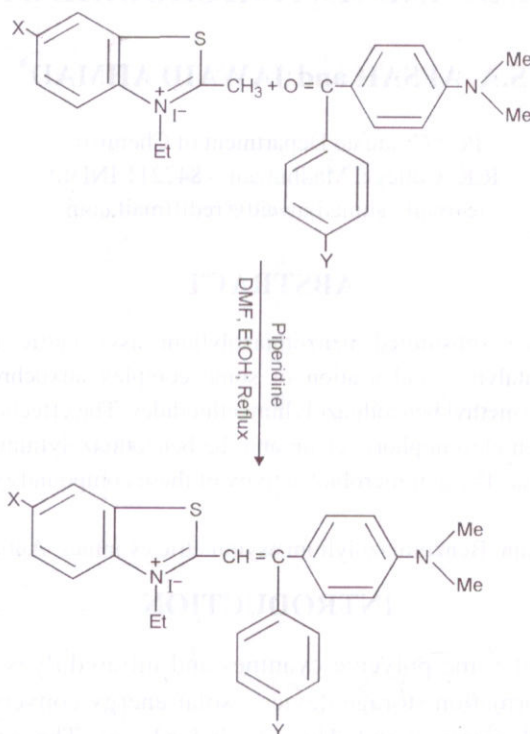
### **EXPERIMENTAL**

#### **Preparation of Ketones**

The ketones were prepared by Friedel–Crafts acylation reaction, i.e. refluxing N, N'-dimethylaniline with benzoyl chloride or p-substituted benzoyl chloride in presence of

anhydrous  $\text{AlCl}_3$ . p-dimethylaminobenzophenone was prepared by the method of Banerji and Jha<sup>7</sup> (Yield 70%, m.p. 111°C).

SCHEME 1



Series	X → Y ↓	Compound						
		-H	-Cl	-Br	-I	-Me	-OMe	-OEt
I	-H	1a	1b	1c	1d	1e	1f	1g
II	-NO <sub>2</sub>	2a	2b	2c	2d	2e	2f	2g
III	-OH	3a	3b	3c	3d	3e	3f	3g

4-dimethylaminophenyl, 4'-nitrophenyl ketone<sup>7</sup> : Recrystallised from petroleum ether as shining magenta crystals, yield 65%, m.p. 120°C, Mol. Formula:  $\text{C}_{15}\text{H}_{14}\text{N}_2\text{O}_3$ . % Analysis, Found (Calcd.) : C = 65.90 (66.60), H = 5.18 (5.18), N = 10.20 (10.37) : IR bands  $\nu_{\text{max}}$  (KBr)  $\text{cm}^{-1}$  : 1310 (CH = CH), 1680 (C = O), 1600 (C = N), 1465 ( $\text{NO}_2$ ).

4-dimethylaminophenyl, 4'-hydroxyphenyl ketone<sup>7</sup> : Recrystallised from alcohol as yellow crystals. Yield 70%, m.p. 142°C, Molecular formula.  $\text{C}_{15}\text{H}_{15}\text{NO}_2$ , % Analysis, Found (Calcd.) : C = 72.68 (74.68), H = 6.00 (6.20) and H = 5.30 (5.80) : IR bands  $\nu_{\text{max}}$   $\text{cm}^{-1}$  (KBr) : 1315 (CH = CH), 1702 (C=C), 1620 (C = N) and 3400 (Phenolic - OH).

### The quaternised bases

The ethoquaternised substituted benzothiazolylium salts were prepared by the general method of preparation suggested by Jacobson<sup>8</sup> with minors modifications.

### Preparation of styryl cyanines

An equimolar mixture of quaternary bases and complex chalcones were dissolved in absolute ethanol and then refluxed in the presence of small amount of piperidine and DMF for about 2h. The separated crude products were recrystallised from methanol. Analytical data, yield, m.p. (uncorrected) etc. of the cyanines are recorded in Table 1.




**Table 1. Physical Data of Compounds**

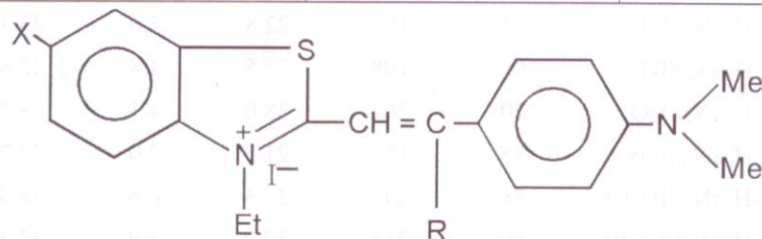
Compound No.	Molecular formula	Yield (%)	m.p. (°C)	Found		Calcd.	
				Halogen (%)	N (%)	Halogen (%)	N (%)
1a	C <sub>25</sub> H <sub>25</sub> N <sub>2</sub> SI	72	205	24.1	5.0	24.7	5.1
1b	C <sub>25</sub> H <sub>24</sub> N <sub>2</sub> SIBR	68	210	34.2	4.5	34.8	4.7
1c	C <sub>25</sub> H <sub>24</sub> N <sub>2</sub> SICl	66	240	29.4	4.8	29.6	5.1
1d	C <sub>26</sub> H <sub>27</sub> N <sub>2</sub> SI	75	201	23.0	4.5	24.0	5.3
1e	C <sub>26</sub> H <sub>27</sub> N <sub>2</sub> SIO	78	190	22.8	5.0	23.4	5.1
1f	C <sub>27</sub> H <sub>29</sub> N <sub>2</sub> SIO	65	198	22.5	4.8	22.8	5.0
1g	C <sub>25</sub> H <sub>24</sub> N <sub>2</sub> SI <sub>2</sub> O	70	264	38.0	4.3	38.7	4.4
2a	C <sub>25</sub> H <sub>24</sub> N <sub>3</sub> SIO <sub>2</sub>	55	185	21.5	7.0	22.7	7.5
2b	C <sub>25</sub> H <sub>23</sub> N <sub>3</sub> SIO <sub>2</sub> Cl	58	241	27.5	6.5	28.4	6.9
2c	C <sub>25</sub> H <sub>23</sub> N <sub>3</sub> SIO <sub>2</sub> Br	60	255	32.0	5.8	32.4	6.4
2d	C <sub>26</sub> H <sub>26</sub> N <sub>3</sub> SIO <sub>2</sub>	68	235	21.9	6.8	22.2	7.1
2e	C <sub>26</sub> H <sub>26</sub> N <sub>3</sub> SIO <sub>3</sub>	74	180	19.9	6.8	21.6	7.1
2f	C <sub>27</sub> H <sub>28</sub> N <sub>3</sub> SIO <sub>3</sub>	65	212	21.0	7.0	21.7	7.9
2g	C <sub>25</sub> H <sub>23</sub> N <sub>3</sub> SI <sub>2</sub> O <sub>2</sub>	59	262	36.5	6.1	37.2	6.9
3a	C <sub>26</sub> H <sub>25</sub> N <sub>2</sub> SIO	72	236	23.0	5.0	24.0	5.3
3b	C <sub>25</sub> H <sub>24</sub> N <sub>2</sub> SIOCl	77	238	28.0	4.0	28.8	4.9
3c	C <sub>25</sub> H <sub>24</sub> N <sub>2</sub> SIOBr	80	250	33.0	3.9	34.0	4.0
3d	C <sub>26</sub> H <sub>24</sub> N <sub>2</sub> SI <sub>2</sub> O	51	266	38.0	3.6	38.7	4.2
3e	C <sub>26</sub> H <sub>27</sub> N <sub>2</sub> SIO	66	227	23.0	4.9	23.3	5.0
3f	C <sub>26</sub> H <sub>27</sub> N <sub>2</sub> SIO <sub>2</sub>	68	195	22.0	4.8	22.7	5.0
3g	C <sub>27</sub> H <sub>29</sub> N <sub>2</sub> SIO <sub>2</sub>	72	214	21.0	4.0	22.2	4.9



IR and UV absorption spectra were recorded on Perkin–Elmer spectrophotometer and Shimadzu spectrophotometer, DU, Japan, (Table 2).

**Table 2. Absorption Data of SCSBAC Dyes in Absolute Ethanol**

X ↓ R →	 Series-I		 Series-II		 Series-III	
	Dye	$\lambda_{\max}$ (nm)	Dye	$\lambda_{\max}$ (nm)	Dye	$\lambda_{\max}$ (nm)
H	1a	412	2a	435	3a	425
Cl	1b	420	2b	445	3b	428
Br	1c	422	2c	448	3c	432
I	1d	425	2d	452	3d	441
Me	1e	413	2e	438	3e	430
OMe	1f	415	2f	447	3f	435
OEt	1g	419	2g	449	3g	438

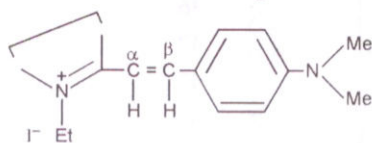
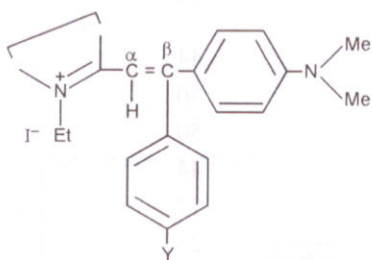


## RESULTS AND DISCUSSION

A comparison was made of the  $\lambda_{\max}$  of the SCSBAC together with chain unsubstituted homederivative reported. The  $\beta$ -phenyl substituent causes hypsochromic shifts in general. Substitution at 4'-position of the  $\beta$ -phenyl ring leads to bathochromic shifts, which was more pronounced in series with  $\beta$ -4'-nitrophenyl (23–32 nm) and  $\beta$ -4'-hydroxyphenol (8–20 nm) substituent in chromophoric chain.

The SCSBAC absorbs within the UV region at shorter wavelengths than their chain unsubstituted styryl analogues, which corroborates the previous observations<sup>5–7</sup>. An increase in molecular weight of the 6-substituent in the heterocyclic moiety results in a bathochromic shift irrespective of the nature of the  $\beta$ -substituents in the methine chain.. The  $\beta$ -4'-nitrophenyl and  $\beta$ -4'-hydroxyphenyl substituents may induce a strong resonance effect but the steric effect may also play an important role.

In  $\beta$ -substituted styryl dyes, the two phenyl groups are directly linked to the  $sp^2$  hybridized C atom and dye suffers bulky group interactions and as a result, the p-dimethylaminophenyl group is twisted out-of-plane. As a consequence of a such steric inhibition of resonance, a hypsochromic shift from chain unsubstituted homologue has been observed.

 $\beta$ -Unsubstituted $\beta$ -Substituted

Steric inhibition of resonance

In the heterocyclic benzothiazolylum system, the influence of the 6-substituents on  $\lambda_{\max}$  is although small but consistent and systematic for all the dyes (Series I–III). Progressive increase in the molecular weight of the 6-substituents causes a progressive bathochromic shift in all the three series. The sequence generally follows the order  $I > Br > Cl > H$ ;  $OEt > OMe > Me > H$ .

### Antimicrobial Activity

The purified and screened samples of cyanines were tested for their bactericidal potentiality against *Staphylococcus aureus* and *Escherichia coli* using cup-plate method in ethanol (as a solvent concn.  $10 \text{ mg mL}^{-1}$ ). The activity was studied after 24 h and the results were recorded. Halogen derivatives were found to be more effective (Table 3).

**Table 3. Antimicrobial Activity of SCSBAC Dyes (Test solution 0.5 mg)**

Compounds	Diameter of inhibitory zone (mm)	
	<i>S. aureus</i>	<i>E. coli</i>
1a	32	26
1b	42	36
1c	42	34
1d	38	31
1e	25	20

Table 1 continued...

1f	30	25
1g	28	24
2a	36	30
2b	47	38
2c	47	37
2d	32	24
2e	35	29
2f	34	28
2g	34	28
3a	44	38
3b	50	34
3c	50	38
3d	44	32
3e	27	22
3f	25	20
3g	30	26

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