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Synthesis of Some Styryl Chain Substituted Benzothiazolylium Asymmetric Cyanines: Spectral and Antimicrobial Studies

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Some styryl chain substituted benzothiazolylium asymmetric cyanines (SCCBAC) have been synthesised by the catalytic condensation of some complex auxochromic chalcones with diversely substituted 2-methyl benzothiazolylium ethiodides. The effects of electron donor and acceptor substituent on chromophoric chain and the benzothiazolylium unit were studied on their absorption maxima and their antimicrobial activity was investigated.

INTRODUCTION

Novel applications of some polyenic cyanines and infrared dyes, especially in optical information storage devices, solar energy conversion systems, chromatic sensitising, antimicrobial operations and also as tools for lasers have been described[1–4]. 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 optical absorption data and photosensitization properties[1–7]

In the present investigation tertiary amino benzophenone and 4 -substituted tertiary aminobenzophenone were catalytically condensed with 2-methyl, 6-substituted benzothiazolylium ethiodides affording a series on SCCBAC (Scheme-I). λ_{max} of the cyanines were recorded and effect of the nature of β-substituents is discussed on the basis of collected data and a comparison is made with the corresponding chain unsubstituted analogues.

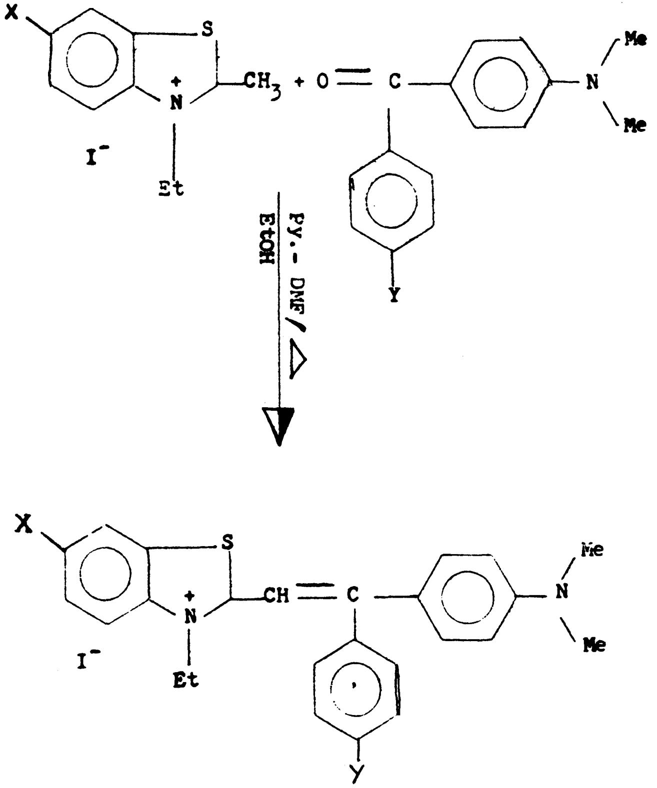
EXPERIMENTAL

Preparation of ketones: The ketones were prepared by Friedel-Crafts acylation reaction, *i.e.*, by refluxing N,N′-dimethyl aniline with benzoyl chloride or with *p*-substituted benzoyl chloride in presence of anhydrous $AlCl_3$.

p-dimethylaminobenzophenone was prepared by the method of Banerji[7] (yield 70%, m.p. 111°C).

4-Dimethylaminophenyl,4′-nitrophenyl ketone[7]: Recrystallised from petroleum ether as shining magenta crystals. Yield 65%, m.p. 120°C, m.f. $C_{15}H_{14}N_2O_3$, % Analysis, Found (Calcd.): C = 65.90 (66.60), H = 5.18 (5.18), N = 10.20 (10.37); IR bands (KBr) cm^{-1}: 1310 (CH=CH), 1680 (C=O), 1600 (C=N), 1465 (NO_2)

SCHEME-I



Series	X→	Compound's symbol						
	Y↓	—H	—Cl	—Br	—I	—Me	—OMe	—OEt
I	—H	1a	1b	1c	1d	1e	1f	1g
II	$—NO_2$	2a	2b	2c	2d	2e	2f	2g
III	—CH	3a	3b	3c	3d	3e	3f	3g

4-Dimethylaminophenyl,4'-hydroxyphenyl ketone[7]: Recrystallised from alcohol as yellow crystals. Yield 70%, m.p. 142°C, m.f. $C_{15}H_5NO_2$, % Analysis, Found (Calcd.): C = 72.68 (74.68), H = 6.00 (6.20) and N = 5.30 (5.80); IR bands ν_{man} cm^{-1} (KBr): 1315 (CH═CH), 1700 (C═O), 1620 (C═N) and 3400 (Phenolic —OH).

The quaternised bases: The ethoquaternised substituted benzothiazolium salts were prepared by the general method of preparation suggested by Jacobson with slight procedural modifications[8, 9].

Styryl cyanines: For the preparation of styryl cyanines an equimolar mixture of quaternary bases and complex chalcones dissolved in absolute ethanol was refluxed in the presence of small amount of piperidine and DMF for about 2 h.

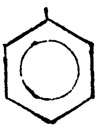
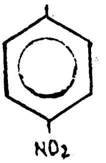
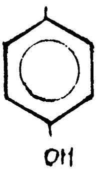
The separated crude products were recrystallised from methanol. Analytical data, yield, m.p. (uncorrected) etc. of the cyanines are recorded in Table-1.

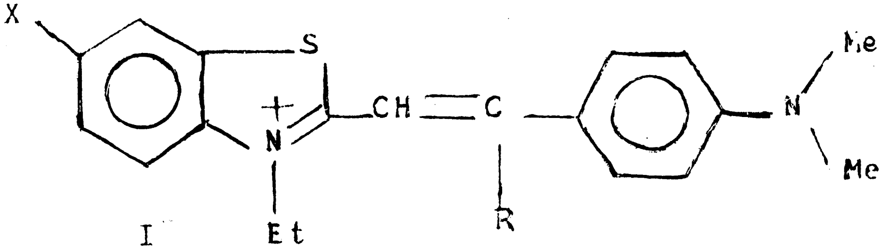
TABLE-1
PHYSICAL DATA OF COMPOUNDS

Compund No.	Molecular formula	Yield (%)	m.p. (°C)	Found (Calcd.), %			
				Halogen	N	Halogen	N
1a	$C_{25}H_{25}N_2SI$	72	205	24.1	5.0	24.7	5.1
1b	$C_{25}H_{24}N_2SIBr$	68	210	34.2	4.5	34.8	4.7
1c	$C_{25}H_{24}N_2SICl$	66	240	29.4	4.8	29.6	5.1
1d	$C_{26}H_{27}N_2SI$	75	201	23.0	4.5	24.0	5.3
1e	$C_{26}H_{27}N_2SIO$	78	190	22.8	5.0	23.4	5.1
1f	$C_{27}H_{29}N_2SIO$	65	198	22.5	4.8	22.8	5.0
1g	$C_{25}H_{24}N_2SI_2O$	70	264	38.0	4.3	38.7	4.4
2a	$C_{25}H_{24}N_3SIO_2$	55	185	21.5	7.0	22.7	7.5
2b	$C_{25}H_{23}N_3SIO_2Cl$	58	241	27.5	6.5	28.4	6.9
2c	$C_{25}H_{23}N_3SIO_2Br$	60	255	32.0	5.8	32.4	6.4
2d	$C_{26}H_{26}N_3SIO_2$	68	235	21.9	6.8	22.2	7.1
2e	$C_{26}H_{26}N_3SIO_3$	74	180	19.9	6.8	21.6	7.1
2f	$C_{27}H_{28}N_3SIO_2$	65	212	21.0	7.0	21.7	7.9
2g	$C_{25}H_{23}N_3SI_2O_3$	59	262	36.5	6.1	37.2	6.9
3a	$C_{26}H_{25}N_2SIO$	72	236	23.0	5.0	24.0	5.3
3b	$C_{25}H_{24}N_2SIOCl$	77	238	28.0	4.0	28.8	4.9
3c	$C_{25}H_{24}N_2SIOBr$	80	250	33.0	3.9	34.0	4.05
3d	$C_{26}H_{24}N_2SI_2O$	51	266	38.0	3.6	38.7	4.2
3e	$C_{26}H_{27}N_2SIO$	66	227	23.0	4.9	23.3	5.0
3f	$C_{26}H_{27}N_2SIO_2$	68	195	22.0	4.8	22.7	5.05
3g	$C_{27}H_{29}N_2SIO_2$	72	214	21.8	4.0	22.2	4.9

IR and UV absorption spectra were recorded on Perkin Elmer spectrophotometer and Schimadzu Spectrophotometer, DU, Japan (Table-2).

TABLE-2
ABSORPTION DATA OF SCCBAC DYES IN ABSOLUTE ETHANOL

R→	 Series-I		 Series-II		 Series-III	
X↓	Dye	λ_{max}, nm	Dye	λ_{max}, nm	Dye	λ_{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



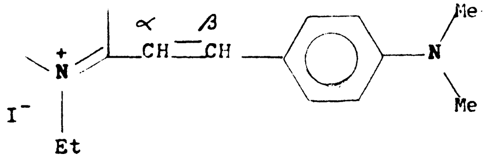
RESULTS AND DISCUSSION

A comparison was made on the λ_{max} of the SCCBAC together with chain unsubstituted reported homedrivative. The β-phenyl substituent causes in general hypsochromic shifts in absorption. Substitution at 4′-position of the β-phenyl ring leads to bathochromic shifts which was more pronounced in series with β-4′-nitrophenyl (23–40 nm) and β-4′-hydroxyphenyl (13–29 nm) substituent in chromophoric chain.

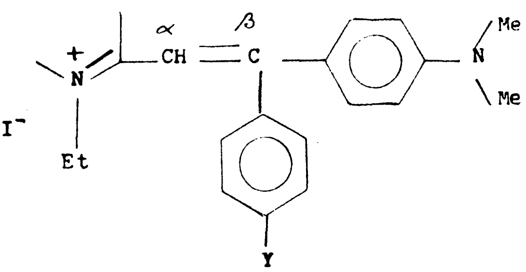
The SCCBAC absorbs within the UV region at shorter wavelength than their chain unsubstituted styryl analogues which corroborates the previous observations^{5,7}. Irrespective of the nature of the β-substituents in the methine chain, increase in mol. wt. of the 6-substituents in the heterocyclic moiety results in bathochromic shift. The β-4′-nitrophenyl and β-4′-hydroxyphenyl substituents may induce strong resonance effect but the steric effect may also be an important factor.

In β-substituted styryl dyes (ii) the two phenyl groups are directly linked to the sp^2-C atom. The dye (ii) suffers bulky group interaction and as a result the *p*-dimethylaminophenyl group suffers an out-of-plane twisting and due to such steric inhibition of resonance causes a hypsochromic shift from chain unsubstituted homologue.

(I)



(II)



In the heterocyclic benzothiazolylium system the influence of the 6-substituents on λ_{max} although is small and consistent and systematic for all the dyes (Series 1–3). 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 solvent (Conc. 10 mg mL^{-1}). The action was studied after 24 h and the results were recorded. Halogen derivatives were however found to be more effective (Table-3).

TABLE-3
ANTIMICROBIAL ACTIVITY OF SCCBAC DYES
(Test solution 0.5 mg)

Compounds	Diameter of inhibitory zone (nm) *S. aureus* 24 h	*E. coli* 24 h
Ia	32	26
Ib	42	36
Ic	42	34
Id	38	31
Ie	25	20
If	30	25
Ig	28	24

Compounds	Diameter of inhibitory zone (nm)	
	S. aureus 24 h	*E. coli* 24 h
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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