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Synthesis, Absorptivity and Antimicrobial Activity of Chromophoric Chain β-substituted benzothiazolo-Hemicyanine Dyes

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A number of chromophoric chain β-substituted benzothiazolo-hemicyanine (CCSBH) dyes have been synthesized by condensing 2-methyl benzothiazolo-methiodide and 2-methyl-6-substituted benzothiazolo-methiodides with dimethylaminobenzophenone derivatives using piperidine as basic catalyst and ethanolic DMF as solvent. These dyes were synthesized with a view to study the effect of the nature of the chain-β-substituents on their absorption spectra and to investigate their antimicrobial efficacy. The dyes were found to show bathochromic shifts irrespective of the functional additives whether electron donating or withdrawing but hypsochromic shifts with respect to butadienylene chain hemicyanines. Purified samples were also subjected to *in vitro* antimicrobial screening to evaluate their bactericidal activity and halo derivatives were found to be highly active against *Staphylococcus aureus* and *Escherichia coli*.

INTRODUCTION

A survey of literature reveals that many cyanine and hemicyanine dyes possess multidimensional applications, such as in electrophotography, optical recording systems, photodynamic therapy, absorptivity and antimicrobial activity[1–7]. Although the hemicyanines have been extensively studied[4–7] from different points of view, mostly the effect of diverse substitutions in the heterocyclic moiety, but very little work has been carried out to study the effect of substituents in the prime chromophoric chain of the dye molecule using benzothiazole nucleus.

The present communication deals with the synthesis of the title CCSBH dyes differently substituted with electron donating and withdrawing groups on the benzothiazole nucleus and on aromatic ring, and study the effect of substitution and unsaturation on the absorption spectra. For this purpose three auxochromic benzophenone derivatives *i.e.* (a) 4-dimethylaminobenzophenone, (b) 4-dimethylamino-4′-chlorobenzophenone, and (c) 4-dimethylamino-4′-hydroxybenzophenone were synthesized and each condensed with 2-methylbenzothiazolo-methiodide

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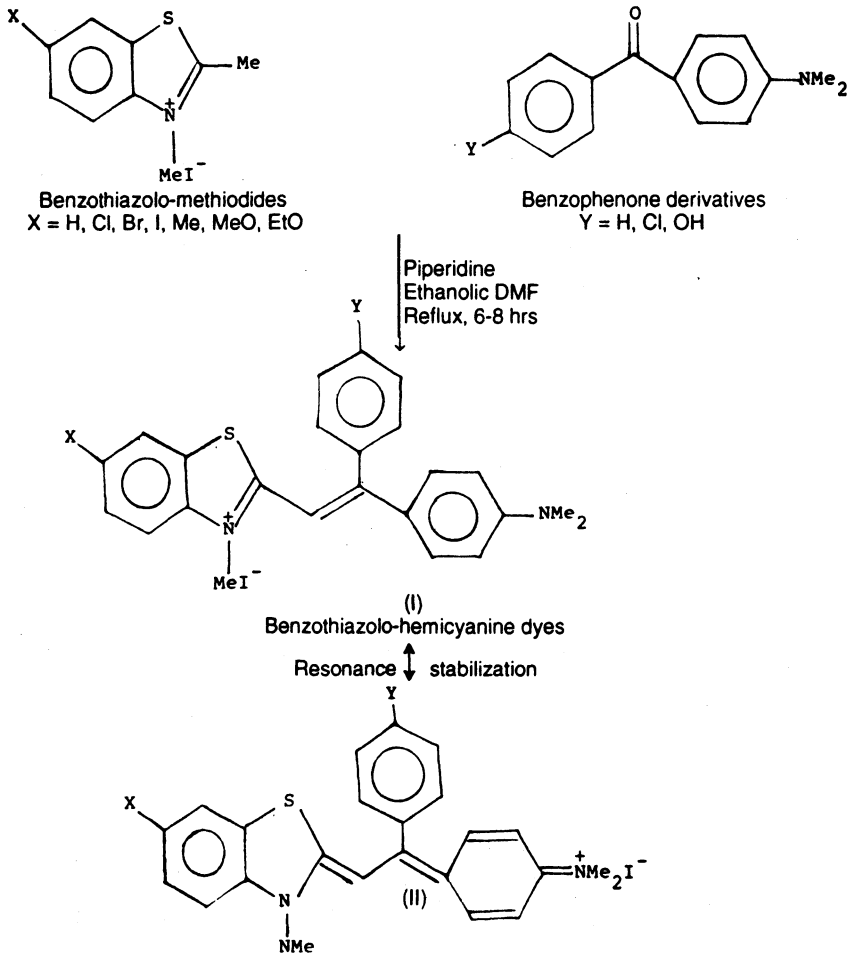
and 2-methyl-6-substituted benzothiazolo-methiodides, using ethanolic DMF as solvent and piperidine as basic catalyst (Scheme I).



The electronic spectra of the afforded dyes were collected and compared. They show bathochromic shifts when compared to their unsubstituted chain analogues. But when compared to some butadienylene chain hemicyanines either having benzothiazole nucleus[7] or quinaldine nucleus, they show hypsochromic shifts. The screened dyes were also tested *in vitro* against *S. aureus* and *E. coli* and some of them were found to be highly active against the microbes.

EXPERIMENTAL

Synthesis of benzothiazolo-methiodides

Seven 2-methylbenzothiazole and 2-methyl-6-substituted benzothiazoles were

synthesized by following the methods of Jacobson[8], Mills[9], Beilenson and Hammer[10] and their quaternization was carried out by adopting the method of Johnson and Adams[11] with some modifications[7].

Synthesis of 4-dimethylaminobenzophenones

4-Dimethylaminobenzophenone, 4-dimethylamino-4′-chlorobenzophenone and 4-dimethylamino-4′-hydroxybenzophenone were synthesized by using the method of Shah *et al.*[12] with some procedural modifications.

Synthesis of benzothiazolo-hemicyanine dyes

The condensation of these dyes was carried out as follows:

The quaternized bases (1 M) and the benzophenone derivatives (1 M) were dissolved in ethanolic DMF (20 mL) with few drops of piperidine, and refluxed for 6–8 h connected with the moisture trap. The resulting solution was concentrated and left overnight at room temperature. The separated crude dyes were recrystallised from wood spirit (Scheme I).

The UV absorption spectra were recorded by Shimadzu UV-Vis Recording Spectrophotometer UV-160. The IR spectra of the afforded dyes were recorded on Fourier Transform Spectrophotometer using solvent KBr.

Purified and screened CCSBH dyes were subjected to *in vitro* antimicrobial activity by "Disc Sensitivity Technique"[13] to evaluate their bactericidal activity on the basis of inhibitory zone data (DZi) collected at different concentrations in ethanolic medium against *S. aureus* and *E. coli* in nutrient agar medium at optimum temperature (35–37°C) (Table-1).

RESULTS AND DISCUSSION

Analytical data and bactericidal potentiality are givne in Table-1.

Absorptivity

Scrutiny of the UV absorption data of the CCSBH dyes of the present investigation together with those of the author's previous work[7] and of the β-unsubstituted dyes[4–6] quoted from the literature leads to the following generalization.

The chromophoric chain β-substitution has uniformly resulted in bathochromic shifts over their β-unsubstituted analogues. But when compared to chain β-substituted butadienylenehemicyanines they show hypsochromic shifts. It may be due to chain shortening and steric inhibition of resonance due to bulky aryl group at the β-position of vinylene chain (Scheme I).

The bathochromism among the dyes under investigation in comparison with the β-unsubstituted ones is due to the fact that whether they are electron donor or acceptor, they cause variation of ionisation energy by electron donating or withdrawing inductive effect and resonance effect, thus causing bathochromic shifts, which is in accordance with the reported data[4–7]. Further chloro group absorbs at longer wavelength than hydroxy group.

The functionalities at the 6-position of the benzothiazole ring show regular

TABLE-1
ANALYTICAL DATA AND ANTIMICROBIAL ACTIVITY OF CCSBH DYES

Dyes	X	Y	Yield (%)	m.p. (°C)	% Analysis obs. (calcd.) %		Crystal shape and color	ν_{max} (cm^{-1})	λ_{max} (nm)	Bactericidal potentiality			
					N	Hal.				*S. aureus* P.S.	*S. aureus P.R.*	*E. coli* P.S.	*E. coli* P.R.
Series I:													
$^{I}D_1$	H	H	42	161	5.57 (5.63)	25.51 (25.55)	bgsp	2950–3040 (C—H) aromatic	349, 309	+	+	–	–
$^{I}D_2$	Cl	H	47	172	5.23 (5.27)	30.51 (30.57)	dbc	1590–1640 (C=C) aromatic under conjugation with C=N	351, 312	++	+	++	++
$^{I}D_3$	Br	H	63	184	4.81 (4.86)	35.89 (35.94)	dd'bc		354, 312	++	+	++	+
$^{I}D_4$	I	H	46	210	4.43 (4.49)	40.72 (40.77)	dlc	550–740 (C—X)	356, 313	+++	++	++	+++
$^{I}D_5$	Me	H	58	164	5.43 (5.48)	24.79 (24.85)	rbs'l	2420–2450 quaternary nitrogen and sulphur atom	350, 311	+	+	+	+
$^{I}D_6$	MeO	H	55	192	5.23 (5.31)	24.04 (24.10)	dgl's''c		352, 311	+	+	–	+
$^{I}D_7$	EtO	H	53	210	5.11 (5.17)	23.40 (23.47)	bsl		353, —	+	+	+	+

Dyes	X	Y	Yield (%)	m.p. (°C)	% Analysis obs. (calcd.) %		Crystal shape and color	ν_{max} (cm^{-1})	λ_{max} (nm)	Bactericidal potentiality			
					N	Hal.				*S. aureus* P.S.	*S, aureus P.R.*	*E. coli* P.S.	*E. coli* P.R.
Series II:													
$^2D_1$	H	Cl	45	183	5.21 (5.27)	30.49 (30.57)	I″gs‴mc	3000–3060 (C—H) aromatic	359, 320	++	+	+	+
$^2D_2$	Cl	Cl	47	188	4.91 (4.95)	34.93 (34.98)	d″bfn	1622–1670 (C═C) aromatic under conjugation with (C═N)	362, 342	++++	++++	++	+++
$^2D_3$	Br	Cl	51	181	4.54 (4.58)	39.67 (39.72)	dvss″c	570–780 (C—X)	365, 343	++	++	+	++
$^2D_4$	I	Cl	50	220	4.20 (4.26)	43.98 (44.03)	rbfc	2420–2460 may be due to quaternary nitrogen and sulphur atoms	368, 348	++++	+++	+++	+
$^2D_5$	Me	Cl	43	184	5.07 (5.13)	29.74 (29.79)	dbc		360, 311	++	++	–	–
$^2D_6$	MeO	Cl	45	186	4.97 (4.98)	28.93 (28.94)	dtc		361, 311	++	++	–	+
$^2D_7$	EtO	Cl	41	216	4.81 (4.86)	28.17 (28.23)	d″bc		363, 312	+++	+++	–	–

Dyes	X	Y	Yield (%)	m.p. (°C)	% Analysis obs. (calcd.) % N	% Analysis obs. (calcd.) % Hal.	Crystal shape and color	ν_{max} (cm^{-1})	λ_{max} (nm)	Bactericidal potentiality *S. aureus* P.S.	*S. aureus* P.R.	*E. coli* P.S.	*E. coli* P.R.
Series III:													
$^3D_1$	H	OH	51	182	7.68 (7.75)	23.35 (23.43)	bgsl	3090–3000 (C—H) aromatic	355, 312	+	+	++	–
$^3D_2$	Cl	OH	51	202	7.22 (7.28)	28.10 (28.18)	rbsl	1690–1640 (C=C) aromatic under	357, 332	++	+	+	+
$^3D_3$	Br	OH	56	208	6.70 (6.76)	33.26 (33.33)	os'c	conjugation with (C=N)	359, 338	++	+	+++	++
$^3D_4$	I	OH	58	238	6.23 (6.29)	37.94 (38.02)	bc'g'l	1070–1040 (C—O) alkoxy	361, 340	+++	+	+++	+
$^3D_5$	Me	OH	48	209	7.50 (7.55)	22.78 (22.84)	i"bsl	790–560 (C—X)	356, 328	++	++	++	+++
$^3D_6$	MeO	OH	56	202	7.27 (7.34)	22.12 (22.20)	fg'l	2450–2420 may be due to quaternary	358, 335	++	+	+	+
$^3D_7$	EtO	OH	52	208	7.12 (7.17)	21.60 (21.67)	bgsfc	nitrogen and sulphur atoms	360, 336	++	++	++	++

Abbv—b, brown; bg, bottle green; c, crystals; c', coloured; d, dark; d', dense; d", dirty; f, fine; g, green; g', glazing; l, leaflets; f', lustrous; l", light; m, minute; n, needles; p, platelets; r, reddish; s, shining; s', scintillating; s", sandy; s"', soft; t, tan; v, violet; P.R., Pen. res; P.S., Pen. sen; DZi, Very high, ++++; high, +++; moderate, ++; poor, +; no effect, –.

increase of absorption maxima in comparison with the unsubstituted ones in the following order:

$$-I > -Br > -Cl > -H \quad \text{and} \quad -OEt > OMe$$

These may be due to electron contribution, polarization ability and progressive weighting of the species.

Antimicrobial activity

The microbial activity of the dyes under discussion are given in the Table-1. They are tested against *S. aureus* and *E. coli.* β-haloaryl derivatives, particularly the chloro derivatives, were found to be more active when compared to the other substituted derivatives.

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REFERENCES

1. F.H. Moser and A.L. Thomas, The Phthalocyanine, CRC Press, USA, p. 59 (1983).
2. S. Yasui, *Shikizai Kyokai-Shi*, **60**, 212 (1987).
3. H. Ali, R. Langlois and J.E. Van Lier, *Photochem. & Photobiol.*, **47**, 705 (1988).
4. B.N. Jha and J.C. Banerji, *Dyes & Pigments (England)*, **1**, 161 (1980).
5. J.C. Banerji, A.K. Mandal and B.K. Banerji, *Dyes & Pigments*, **3**, 273 (1982).
6. B.N. Jha, D. Kumari Jha, R.K. Jha and A. Jha, Chemistry of Functional Dyes, Mita Pub. Corp., Japan (1989).
7. A.S. Ansari, D. Kumari Jha and B.N. Jha, *J. Indian Council Chem.* (in press).
8. P. Jacobson, *Ber.*, **19**, 1067 (1886).
9. W.H. Mills, *J. Chem. Soc.*, 455 (1922).
10. B. Beilenson and F.M. Hammer, *J. Chem. Soc.*, 1225 (1936).
11. J.R. Johnson and R. Adams, *J. Am. Chem. Soc.*, **43**, 2237 (1921).
12. R.C. Shah, R.K. Deshpande and J.S. Chaubal, *J. Chem. Soc.*, 645 (1932).
13. C.M. Nolan and H.N. Beaty, *Am. J. Med.*, **60**, 495 (1976).

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