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Synthesis, Electro-optical Characteristic and Antimicrobial Efficacy of Some Benzothiazolium Asycyanine Colorants

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Fourteen new benzothiazolium butadienylene chain substituted asycyanine colorants have been synthesised by catalytic condensation of two styryl phenyl ketones namely 4-dimethylaminostyryl-4′-nitrophenyl ketone and 4-dimethylaminostyryl-4′-methoxyphenyl ketone with 2-methyl benzothiazolium methiodide and 2-methyl-6-substituted benzothiazolium methiodides using piperidine as basic catalyst and ethanolic DMF as solvent. These colorants were synthesised with the object to study the effects of electron acceptor and donor substituents at the 4′-position in the chain β-phenyl nucleus, chain elongation, on visible absorption maxima and to evaluate their antimicrobial activity. The dyes were found to exhibit uniform increase of absorption maxima when collated with analogues having no substituents in the β-phenyl nucleus and the analogues having vinylene chain. Purified samples were also investigated *in vitro* against *Staphylococcus aureus* and *Escherichia coli* and some of them were found to be active.

INTRODUCTION

The literature revals that copious investigations have been carried out to dilate the horizon of cyanine and asycyanine colorants, for example, in key materials for optical information display media, as energy transfer media for solar batteries, in therapeutic antimalignant photodynamics, in absorptivity, photosensitivity and antimicrobial activity etc.[1–8] Though some of the asycyanine colorants are reported[4,6] and using quinaldine nucleus and plain/substituted styryl phenyl ketones and their absorption maxima have been analysed, but less work is discernible in synthesising the colorants using benzothiazolium salt and the above ketones.

The present piece of work incorporates the synthesis of 4-dimethylaminostyryl-4′-nitrophenyl ketone and 4-dimethylaminostyryl-4′-methoxyphenyl ketone at one hand and 2-methylbenzothiazolium methiodide and 2-methyl-6-substituted benzothiazolium methiodides at the other, and to condense them using piperidine as basic catalyst and ethanolic DMF as solvent, affording a series of

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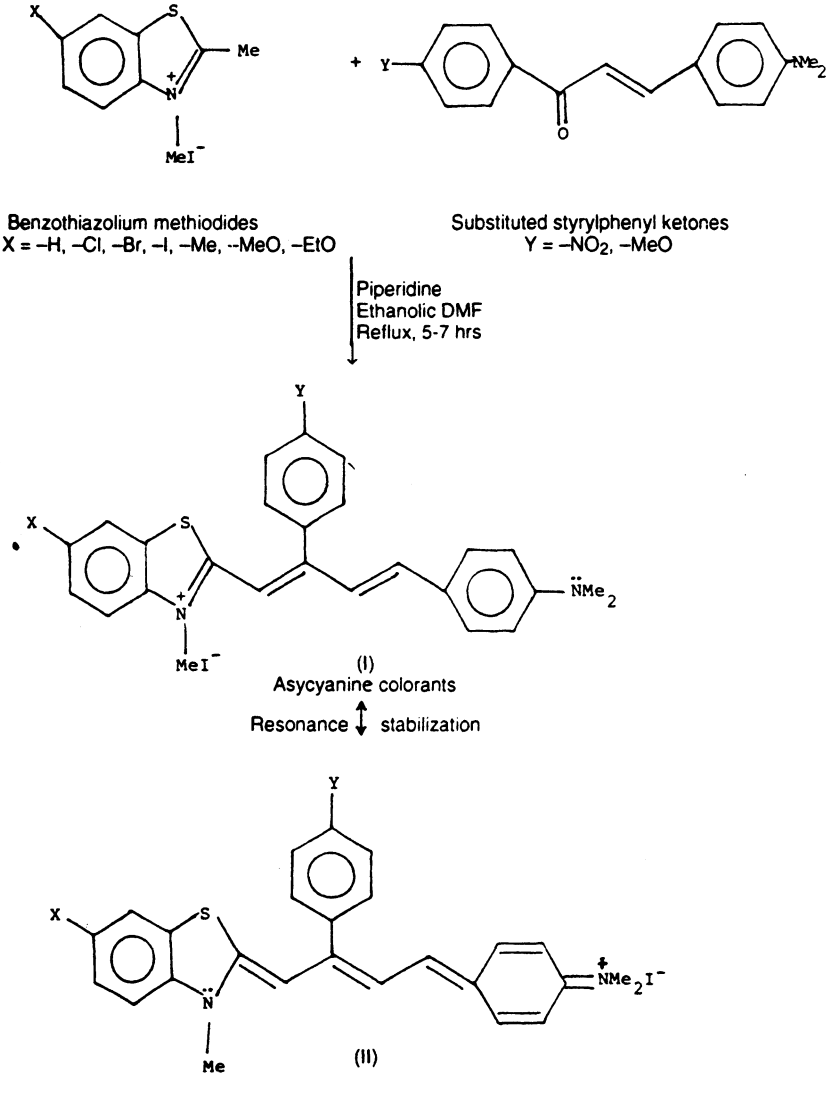
title colorants (Scheme-1). Their absorption data have been collected and collated with respect to the functional additives whether electron donor or acceptor at β-phenyl nucleus of the butadienylene chain and upon the periphery of the benzothiazolium ring. They are also compared with the reported colorants.[4-8]

The colorants show increase in λ_{max} when compared to the unsubstituted analogues[7] and other colorants having vinylene chain[8] but decrease in λ_{max} when compared with the quinaldino-asycyanine colorants.[6] The purified samples of the title colorants were tested *in vitro* against *Staphylococcus aureus* and *Escherichia coli* and some of them were found to be active against the pathogens.



Scheme-1

EXPERIMENTAL

Synthesis of benzothiazolium methiodides

2-Methyl benzothiazole and six 2-methyl-6-substituted benzothiazoles were synthesised by following the methods of Jacobson[9], Mills[10], Beilenson and Hammer[11] and their quaternisation was effected by adopting the method of Johnson and Adams[12] with some modifications.[7,8]

Synthesis of styryl phenyl ketones

4-Dimethylaminostyryl-4′-nitrophenyl ketone, 4-dimethylaminostryrl-4′-methoxyphenyl ketone were synthesised by adopting the general method.[7]

Synthesis of benzothiazolium asycyanine colorants

The colorants were synthesised by usual procedure[7,8] with some procedural alterations.

A mixture of the styrylphenyl ketone, quaternised benzothiazolium salt (equimolar proportions), absolute ethanolic DMF (10:1) and piperidine (3–4 drops) was refluxed for 4–6 h. The resultant solution after concentration and cooling in ice yielded the colorant which was recrystallised from MeOH.

Analytical data, yield and m.p. (uncorrected) are given in Table-1.

UV absorption and IR spectra: The UV absorption maxima of the colorants were recorded by Shimadzu UV-Vis Recording Spectrophotometer UV-160 and the IR spectra on Fourier Transform Spectrophotometer using solvent KBr (Table-1).

Antimicrobial efficacy: The purified and screened samples of the colorants were treated to *Staphylococcus aureus* (gram positive) and *Escherichia coli* (gram negative) *in vitro* by disc sensitivity technique[13] on the basis of inhibitory zone data (DZi) collected at different concentrations in ethanolic medium in nutrient agar at ambient temperature (35–37°C). The results were taken next day (Table-1)

RESULTS AND DISCUSSION

Analytical data and antimicrobial efficacy are given in Table-1

UV absorption maxima: Comparison of the absorption data for the fourteen benzothiazolium butadienylene chain substituted asycyanine (BBCSA) colarants (Series I and II) among themselves and with those analogues described previously[7], with β-unsubstituted dyes[4–6] and with vinylene chain analogues[8] permits the following generalisations to be made.

The chain β-aryl substituents cause general bathochromic shifts in comparison with unsubstituted analogues.[7] Further, irrespective of the nature of any additional group attached to the β-phenyl ring, whether electron transporting (—OMe) or electron accepting (—NO_2), they show again an increase in absorption maxima. Nitro group absorbs at larger wavelength than methoxy group. The electron transporting or accepting groups cause variation of ionisation energy by inductive and resonance effects thus increasing the absorption maxima which corroborate the reported data.[4] The title colorants when compared with quinaldino-asycyanine

TABLE-1
ANALYTICAL DATA AND ANTIMICROBIAL EFFICACY OF BBCSA COLORANTS

Colorants	X	Y	Yield (%)	m.p. (°C)	% Found (Calcd) N	% Found (Calcd) Hal.	Crystal shape and color	λ_{max} (nm)	ν_{max} (cm^{-1})	Antimicrobial efficacy *S.a.* P.S.	*S.a.* P.R	*E.c.* P.S.	*E.c.* P.R.
Series I:													
2-*p*-DMAP (β-4′-Np)BBzThMel	—H	—NO_2	71	210	7.34 (7.39)	22.32 (22.36)	sdrtn	441	3080–3000 C—H (str.) (Aromatic)	–	–	++	+++
2-*p*-DMAP (β-4′-Np)B-6-ClBzThMel	—Cl	—NO_2	73	216	6.90 (6.97)	26.92 (26.97)	drsmn	445, 341	1680–1630 C=C (str.) (Aromatic)	+	++	+++	+
2-*p*-DMAP (β-4′-Np)B-6-BrBzThMel	—Br	—NO_2	81	221	6.44 (6.49)	31.95 (31.99)	d′rs′n	448	under conjugation with C=N plane vibration	+	+	+++	++
2-*p*-DMAP (β-4′-Np)B-6-MeBzThMel	—I	—NO_2	74	246	5.99 (6.05)	36.55 (36.60)	drgtn	451	880–750 C—H (def.) (Aromatic nucleus)	++	+	++	+
2-*p*-DMAP (β-4′-Np)B-6-OMeBzThMel	—Me	—NO_2	72	216	7.16 (7.22)	21.74 (21.82)	cbc′mn	442, 341	790–500 C—X (str.) —Cl, Br, I	+	–	–	+
2-*p*-DMAP (β-4′-Np)B-6-OEtBzThMel	—OMt	—NO_2	74	218	6.97 (7.02)	21.19 (21.24)	d′rtln	444, 344	2480–2430 due to quaternary N and S atom	+	–	–	+
2-*p*-DMAP (β-4′-Np)B-6-OEtBzThMel	—OEt	—NO_2	75	238	6.82 (6.86)	20.70 (20.75)	drs′n	452, 268		+	+	–	+

Colorants	X	Y	Yield (%)	m.p. (°C)	% Found (Calcd) N	% Found (Calcd) Hal.	Crystal shape and color	λ_{max} (nm)	ν_{max} (cm^{-1})	Antimicrobial efficacy *S.a.* P.S.	*S.a.* P.R	*E.c.* P.S.	*E.c.* P.R.
Series II:													
2-*p*-DMAP (β-4′-Cp)BBzThMel	—H	—Cl	58	206	5.14 (5.19)	23.52 (23.56)	db′c″	419, 212	3030–2990 C—H (str.)	+	–	–	+
2-*p*-DMAP (β-4′-Cp)B-6-ClBzThMel	—Cl	—Cl	60	210	4.84 (4.88)	28.28 (28.33)	b′gmc″	423	1680–1650 C=C (str.)	+	+++	++	+
2-*p*-DMAP (β-4′-Cp)B-6-BrBZThMel	—Br	—Cl	65	216	4.47 (4.53)	33.42 (33.49)	r′b′c″	424	under conjugation with C=N plane vibration	+	++	+	++
2-*p*-DMAP (β-4′-Cp)B-6-IBzThMel	—I	—Cl	63	232	4.17 (4.21)	38.03 (38.19)	d′b′gr′r″	427		+++	+	++	+
2-*p*-DMAP (β-4′-Cp)B-6-MeBzThMel	—Me	—Cl	43	217	5.02 (5.06)	22.97 (22.96)	d′rc″	421	950–750 C—H(def.) (Ar)	++	+	–	+
2-*p*-DMAP (β-4′-Cp)B-6-OMeBzThMel	—OMe	—Cl	39	219	4.87 (4.92)	22.29 (22.32)	d′b′n	423, 219	780–500 C—X(str.) —Cl, Br, I	–	+	–	+
2-*p*-DMAP (β-4′-Cp)B-6-OEtBzThMel	—OEt	—Cl	58	222	4.76 (4.80)	21.72 (21.78)	d′rgf″	424, 260	2460–2420 due to quaternary N and S atom	+	+	–	+
									Oxytetracyclin	++++	+++	+++	++

Abbreviations: DMAP, dimethylaminophenyl; NP, nitrophenyl; B, butadienylene; BzThMel, benzothiazolium methiodide; CP, chlorophenyl; b, blood; b′, brown; c, clotted; c′, coloured; c″, crystals; d, deep; d′, dark; f, fine; g, glazing; l, lustrous; m, minute; n, needles; r, red; r′, reddish; r″, reflex; s, shining; s′, scintillating; t, tiny; *Ec, E. coli;* P.R., Penicillin resistant; P.S., Penicillin sensitive; *S.a., S. aureus;* DZi: Inhibitory zone data; very high, ++++ ; high, +++; moderate, ++; poor, +; no effect –

colorants[4,6] show hypsochromic shifts which may be due to the ring strains of the thiazole ring.

The bathochromic shifts in these colorants under investigation in comparison wth vinylene chain derivatives[8] may be attributed to chain lengthening and ease in steric effect of the β-phenyl ring (Scheme-1).

Antimicrobial Efficacy: The pure recrystallised samples of the colorants were subjected to *in vitro* antimicrobial screening against *Escherichia coli* and *Staphylococcus aureus* by disc sensitivity technique[12] and the results are given in Table-1. The halo derivatives, specially chloro derivatives, of the asycyanine colorants in general were found to be more effective in comparison with other derivatives. To our dismay none of the colorants was found more efficacious than oxytetracyclin.

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