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Synthesis & Structural Correlation with UV Absorption Maxima of Some Novel Hexamethine Quinaldine Asycyanine Colorants

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ABSTARCT

In this study new hexamethine asy-cyanine colorants were synthesized by the reaction of N,N-dimethylaminophenylbutadienylphenyl ketone, N,N-dimethyl-aminophenylbutadienyl-4'-bromophenyl ketone and N,N-dimethylamino-phenylbutadienyl-4'-methylphenyl ketone with 2-methyl-N-propyl quinolinium iodide and 6-substituted-2-methyl-N-propyl quinolinium iodides in ethanolic DMF with piperidine catalyst. These colorants were shown to have uniform bathochromic shifts (BS) when compared to analogues with no substituent at β-phenyl nucleus or analogues having dimethine or tetramethine asy-cyanine colorants. They further showed bathochromic shifts with electron withdrawing group (NO_2 group) electron donating (CH_3 group) at 4'-position at β-phenyl nucleus.

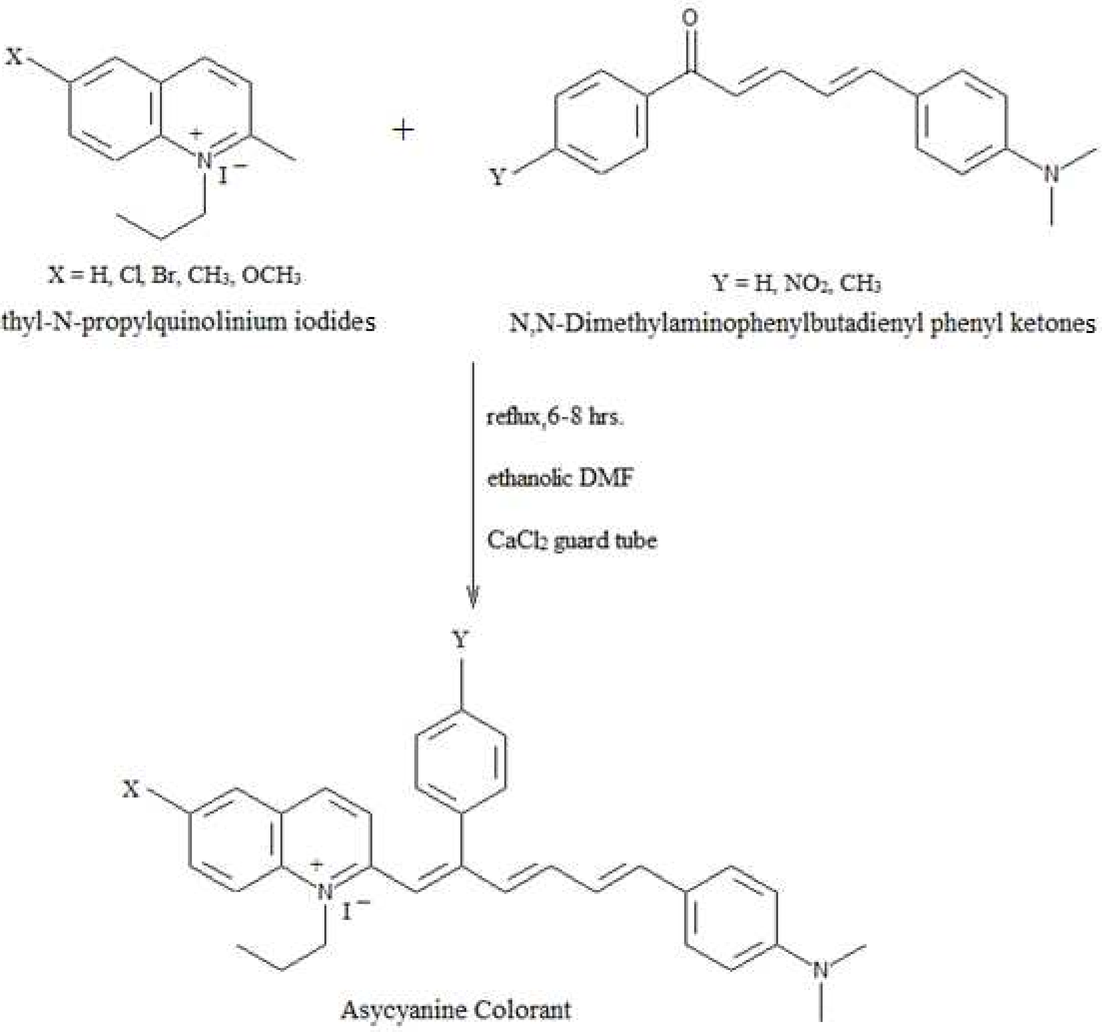
Keywords: Asy-cyanine colorants, Hexamethine, N,N-dimethylaminophenylbuta-dienyl phenyl ketone, 2-methyl-N-propylquinolinium iodide

INTRODUCTION

Several cyanine and asycyanine colorants have been extensively studied over the past century mainly as photosensitizers for photography [1]. There are greatly increasing interests in development of near-infrared absorbing colorants which were used as purpose of optical recording media and bio-fluorescent probes [2,3]. As Gallium-Arsenic (Ga/As) semiconductor lasers with wave length of (800-830)nm are now being used as a light source for optical information processing systems such as optical disc file equipments and laser beam printing [4-8]. Also, these colorants are increasingly used as fluorescent tags in DNA sequencing immunoassay [9-12]. Asycyanine colorants are used for absorptivity, photosensitivity and antimicrobial efficiency [13-22].

The asycyanine colorants in this study have been synthesized by condensation reaction between a hetrocylic base containing an activated methyl group and an unsaturated auxochromic ketone (**Scheme 1**). This paper reports the synthesis & collating of fifteen hexamethine asycyanines with ultraviolet –visible absorption maxima.

Scheme 1



MATERIALS AND METHODS

All reagents and solvents were of chemical pure grade and were used without further purification. UV-spectra were determined on a Sistonic 119 UV-spectrophotometer. All melting points are uncorrected and measured in open capillaries in an electrothermal M-21 apparatus IR-spectra (KBr) were recorded Fouries transform spectrophotometer, elemental microanalyzer (H, X) were taken on Perkin Elmer-240 Analyzer.

The auxochromic ketone: For the preparation of auxochromic ketone general methods [19] are adopted with some procedual modifications using N,N-dimethylamino-cinnamaldehyde and acetophenone 4'-nitro/methylacetophenone in pure methanol with pellets of KOH.

4-Dimethylaminophenylbutadienylphenyl ketone: The crude product was re-crystallized from ethanol as dark orange crystals.

m.p. = 136 °C (Lit. [19] yield = 74%; m.p. = 136 °C) Yield = 73%;

4-Dimethylaminophenylbutadienyl-4'-nitrophenyl ketone

The crude product was recrystallised from ethanol as dark red crystalline solid.

Yield = 78%; m.p. = 196°C (Lit. [19] yield = 82%; m.p. = 196 °C)

4-Dimethylaminophenylbutadienyl-4'-methylphenyl ketone

The crude product was recrystallised from ethanol as dark red colored needles.

Yield = 81%; m.p. = 168°C (Lit. [19] yield = 80%; m.p. = 168°C)

The quaternised 2-methyl-N-propylquinolinium iodides: Five 2-methyl-N- propylquinolinium iodide and 6-substituted-2-methyl-N- propylquinolinium iodide were synthesized and quaternised by earlier methods [13].

Synthesis of colorants: The condensation to obtain the colorants was carried out by the earlier methods with some modification.

A solution containing the quaternised salt and complex auxochromic ketone in milli molar ratio in ethanolic DMF (25 ml) in the presence of basic catalyst piperidine (2-3 drops) was refluxed for 6-8 hrs under anhydrous conditions using $CaCl_2$ guard tube. The resulting mixture was concentrated, cooled and left overnight at room temperature. The afforded colorants was recrystallised from methanol. The analytical and UV spectral data of the colorants are given in table 1.

Table 1: Physical parameters

Colorants	**Molecular Formula**	**X**	**Y**	**Color**	**Crystal**	**Yield %**	**m.p(°C)**
C_1	$C_{32}H_{33}N_2I$	H	H	Dark brown	Needles	72	201
C_2	$C_{32}H_{32}N_2ICl$	Cl	H	Brown	Needles	76	205
C_3	$C_{32}H_{32}N_2BrI$	Br	H	Reddish Brown	Needles	75	212
C_4	$C_{33}H_{35}N_2I$	CH_3	H	Dark brown	Flakes	67	218
C_5	$C_{34}H_{37}N_2OI$	OEt	H	Brown	Flakes	78	200
C_6	$C_{32}H_{32}N_3O_2I$	H	NO_2	Dark brown	Needles	72.5	190

C_7	$C_{32}H_{31}N_3O_2ICl$	Cl	NO_2	Brown	Needles	74	200
C_8	$C_{32}H_{31}N_3O_2BrI$	Br	NO_2	Violet	Needles	73	198
C_9	$C_{33}H_{34}N_3O_2I$	CH_3	NO_2	Violet	Needles	75	194
C_{10}	$C_{34}H_{36}N_3O_3I$	OEt	NO_2	Dark brown	Tiny needles	76	181
C_{11}	$C_{33}H_{35}N_2I$	H	CH_3	Violet	Needles	78	218
C_{12}	$C_{33}H_{34}N_2ICl$	Cl	CH_3	Brown	Flakes	78	213
C_{13}	$C_{33}H_{34}N_2BrI$	Br	CH_3	Violet	Needles	76	203
C_{14}	$C_{34}H_{37}N_2I$	CH_3	CH_3	Brown	Needles	72	198
C_{15}	$C_{35}H_{39}N_2OI$	OEt	CH_3	Reddish brown	Needles	74	195

Table 2: Analytical data & Spectral data (UV) of the Colorants

S.No.	**Compounds**	**%C Cal. (Found)**	**%H Cal. (Found)**	**%N Cal. (Found)**	**%Cl Cal. (Found)**	**%Br Cal. (Found)**	**% I Cal. (Found)**	**Absorption maxima λ(max) (nm)**
1.	$C_{32}H_{33}N_2I$	67.13	5.76	4.89	-	-	22.10	570

		(67.23)	(5.74)	(4.88)			(22.11)	
2.	$C_{32}H_{32}N_2ICl$	63.31 (62.80)	5.27 (5.22)	4.61 (4.58)	-	5.85 (5.81)	20.93 (20.67)	585
3.	$C_{32}H_{32}N_2BrI$	58.98 (58.86)	4.91 (4.79)	4.30 (4.28)	-	12.28 (12.22)	19.50 (19.31)	580
4.	$C_{33}H_{35}N_2I$	67.57 (67.48)	5.97 (5.96)	4.77 (4.74)	-	-	21.67 (21.43)	585
5.	$C_{34}H_{37}N_2OI$	66.23 (66.33)	6.00 (5.96)	4.54 (4.51)	-	-	20.61 (20.33)	588
6.	$C_{32}H_{32}N_3O_2I$	62.23 (62.08)	5.18 (5.16)	6.80 (6.72)	-	-	20.58 (20.33)	596
7.	$C_{32}H_{31}N_3O_2ICl$	58.94 (58.42)	4.75 (4.71)	6.44 (6.41)	5.44 (5.42)	-	19.49 (19.21)	578
8.	$C_{32}H_{31}N_3O_2BrI$	55.17 (54.88)	4.45 (4.41)	6.03 (6.01)	-	11.40 (11.38)	18.24 (18.01)	589
9.	$C_{33}H_{34}N_3O_2I$	61.20 (61.10)	5.25 (5.21)	6.49 (6.43)	-	-	19.62 (19.47)	580
10.	$C_{34}H_{36}N_3O_3I$	61.72 (61.62)	5.44 (5.41)	6.35 (6.30)	-	-	19.21 (19.06)	588
11.	$C_{33}H_{35}N_2I$	67.57 (67.48)	5.97 (5.96)	4.77 (4.74)	-	-	21.67 (21.43)	588
12.	$C_{33}H_{34}N_2ICl$	63.81 (63.44)	5.47 (5.46)	4.51 (4.49)	5.72 (5.68)	-	20.46 (20.12)	576
13.	$C_{33}H_{34}N_2BrI$	59.54	5.11	4.21	-	12.03	19.09	584

			(5.09)	(4.20)		(12.01)	(8.84)	
14.	$C_{34}H_{37}N_2I$	68.00 (67.62)	6.16 (6.11)	4.66 (6.61)	-	-	20.12 (19.91)	578
15.	$C_{35}H_{39}N_2OI$	66.66 (66.65)	6.19 (6.10)	4.44 (4.42)	-	-	20.15 (19.95)	580

Table 3: Spectral data (I.R.) of the Colorants

Compounds	Bond Range (Cm^{-1})	Assignment
$C_{1,6,11}$	2940-3050 C-H	Stretching (aromatic)
	1450-1630 C=C	Stretching (aromatic) & conjugation with C=N plane Vibration
	1040-1380 C-O	Stretching (alkoxy)
	730-910 C-H	Bending (aromatic)
	1320-1360 C-H	Stretching (aromatic)
	510-740 C-X	Stretching
	1310-1330 C-N-C	Stretching
	1630-1660 C=N	Stretching (conjugated) with aromatic Nucleus
	2410-2450 C=N	Quaternary nitrogen
$C_{4,9,14}$	2860-3030 C-H	Stretching (aromatic)
	1430-1630 C=C	Stretching (aromatic) & conjugation with C=N plane Vibration
	1055-1390 C-O	Stretching (alkoxy)
	710-950 C-H	Bending (aromatic)
	1330-1360 C-H	Stretching (aromatic)
	510-770 C-X	Stretching
$C_{5,10,15}$	2980-3030 C-H	Stretching (aromatic)
	1420-1630 C=C	Stretching (aromatic) & conjugation with C =N plane Vibration
	1040-1330 C-O	Stretching (alkoxy)
	710-920 C-H	Bending (aromatic)
	1330-1350 C-H	Stretching (aromatic)
	500-780 C-X	Stretching
	1325-1340 C-N-C	Stretching
	1610-1660 C=N	Stretching (conjugated) with aromatic nucleus
	2410-2480 C=N	Quaternary nitrogen
$C_{2,7,12}$	2910-3060 C-H	Stretching (aromatic)
	1430-1660 C=C	Stretching (aromatic) & conjugation

			with C=N plane Vibration
	1020-1380	C-O	Stretching (alkoxy)
	710-910	C-H	Bending (aromatic)
	1320-1360	C-H	Stretching (aromatic)
	520-780	C-X	Stretching
	1310-1330	C-N-C	Stretching
$C_{3,8,13}$	1630-1660	C=N	Stretching (conjugated) with aromatic nucleus
	2410-2460	C=N	Quaternary nitrogen
	2910-3030	C-H	Stretching (aromatic)
	1430-1660	C=C	Stretching (aromatic) & conjugation with C=N Plane Vibrations
	1040-1340	C-O	Stretching (alkoxy)
	710-930	C-H	Bending (aromatic)
	1330-1360	C-H	Stretching (aromatic)
	510-780	C-X	Stretching
	1320-1380	C-N-C	Stretching
	1640-1680	C=N	Stretching (conjugated) with aromatic nucleus
	2420-2455	C=N	Quaternary nitrogen

RESULTS AND DISCUSSIONS

The spectral absorption studies of absorption maxima (λ_{max}) of hexamethine asycyanine colorants lead to significant generalizations.

The β-4'-substituted hexatrienyl colorants are of same skeleton. Moreover, all the colorants are variously substituted-2-methylquinolinium at the position-6-only and are propyl quaternised, besides, β-4'-phenyl nucleus is also substituted.

The β-4'-substituted phenyl butadienyl dyes show uniform bathochromic shifts in the absorption maxima in comparison to their corresponding β-phenyl analogues irrespective of the nature of additional group attached to the β-phenyl nucleus i.e. whether they are electron attracting viz. Cl o electron donating viz. OCH_3 groups.

The bathochromic shifts are more pronounced with β-4'-chlorophenyl nucleus than β-phenyl and β-4'-methoxyphenyl nuclei. Also it has been observed that β-4'-subsituted or unsubstituted phenyl colorants show the similar bathochromic shifts as in styryl colorants [13].

The substitution in β-phenyl nucleus disturb the benzene ring both by inductive and resonance effects. The change in spectra is more influenced by resonance effect than inductive effects.

An electron donating inductive effect (+I) substituent decreases the ionization energy of the substituted benzene while an electron withdrawing inductive effect (-I) substituent increases it. The variation in ionization energy results in bathochromic shits.

It has been observed that the steric hindrance causes hypsochromic shifts as the much stretched β-phenyl and β-4'- substituted phenyl groups are in close proximity of the main butadienyl chain of the hemicyanine colorants.

In 2-methylquinolinium nucleus, the effect of 6-substituent is small but uniform and systematic for all the hemicyanine colorants. The successive increase in the molecular weight of 6-substituents brings about a successive bathochromic shifts in all the series. The result is in conformity with the 2-methylquinolinium/benzothiazolium colorants reported earlier. [13, 14-19]. The sequenced is in the order as

6-Br > 6-Cl > 6-H in halide series and

6-OCH_3 > 6-CH_3 > 6-H in alkyl and alkoxy series.

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