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SYNTHESIS, ABSORPTION, STRUCTURE RELATIONSHIP & SOLVATOCHROMIC STUDY OF SOME NEW ETHENYL ASYCYANINE COLORANTS

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ABSTRACT

Fifteen new Ethenyl asycyanine colorants (EAC) have been synthesized by catalytic condensation of five propoquaternised quinaldinium salt and three 4-X-4'-N, N-dimethylaminobenzophenone (where X=H, Cl, Me). These colorants were synthesized to study their absorption behavior among themselves and with previously prepared colorants along with their solvatochromic properties. The absorption maxima of asycyanine colorants are found to be dependent on the nature of its structure, extended conjugation and changes made in substituent. Also the value of λ-max is influenced by solvent and Hydrogen bond as in water which shows negative solvatochromism as transfer from non-polar to polar solvent.

Keywords: Asycyanine colorants, ethenyl, propoquaternised quinolinium salt, N,N-dimethyl aminobenzophenones, solvatochromism.

INTRODUCTION

Conjugated asycyanine colorants are the class of compounds that have captured the interest of scientific community as in space photography [1-3], photosensitization [4-8] protein labeling [3] antimicrobial character [5-9] etc.

Extending our previous work [10-15] fifteen new β–substituted ethenyl asycyanine colorants (BSEAC) were synthesized (Scheme I) with the objective to study their electronic absorption spectra in ethanolic DMF solution and solvatochromic behavior.

MATERIALS AND METHODS

Melting points are uncorrected. Elemental analysis was carried out by elemental analysis Euro-E-300. IR spectra (KBr) were performed by Perkin Elmer FT-IR spectrum. The visible absorption spectra were recorded on Sistonic 119 UV-visible spectrophotometer. H^1 NMR spectra were recorded with Em 390 90 MHz NMR spectrophotometer.

The colorants 6-X-2-(4-Y-Phenyl)-2-(4-N, N-dimethylamino) phenyl)ethenyl)-1-propylquinolin-1-ium iodide were synthesised by earlier methods [7-10] with some procedural changes.

Synthesis of Auxochromic Ketone 2(a-e)

4-N, N-dimethylaminobenzophenone 2(a-e) were synthesized by usual process [7, 10] using benzanilide 1(a-e), dimethyl aniline and phosphorous oxychloride. The crude product was recrystallized from ethanol.

2a: Molecular formula: $C_{15}H_{15}NO$; m.p.: 89 °C; yield: 69%

(Lit. m.p. 90 °C, yield 65%)

Found %= C (79.95), H (6.70), N (6.21), O (7.09)

Calculated % = C (79.97), H (6.71), N (6.22), O (7.10). Crystals Color: Pale yellow.

2b: Molecular formula: $C_{16}H_{17}NO$

m.p. 135 °C, yield = 68% (Lit. m.p. =135 °C, yield = 66.4%)

Found % = C (69.34), H (5.42), Cl (13.63), N (5.38), O (6.15)

Calculated % = C (69.36), H (15.43), Cl (13.65), N (5.39), O (6.16). Crystals Color: greenish leaflets.

2c: Molecular formula: $C_{15}H_{14}ClNO$

m.p=104 °C, yield=64% (Lit. m.p=104.1°C, yield=62%)

Found %= C(80.28), H(7.16), N(5.84), O(6.67)

Calculated % = C(80.30), H(7.16), N(5.85), O(6.69)

IR for **2a,c** 1610(CH=CH), 1695(C=O), 1617(C=N) and

for **2b** 1610(CH=CH), 1680(C=O), 1617(C=N). Crystals Color: Pale blue.

^{1}HNMR ($CDCl_3$)

2a 7.69(d, 2H), 7.48(d, 2H), 7.52 (t, H), 7.49(t, 2H), 6.87(d, 2H), 2.91(s, 6H)

2b 7.74(d, 2H), 7.89(d, 2H), 7.53(d, 2H), 6.87(d, 2H), 2.89(s, 6H)

2c 7.69(d, 2H), 7.48(d, 2H), 7.49(d, 2H), 6.87(d, 2H), 2.89(s, 6H), 3.01(s, 3H)

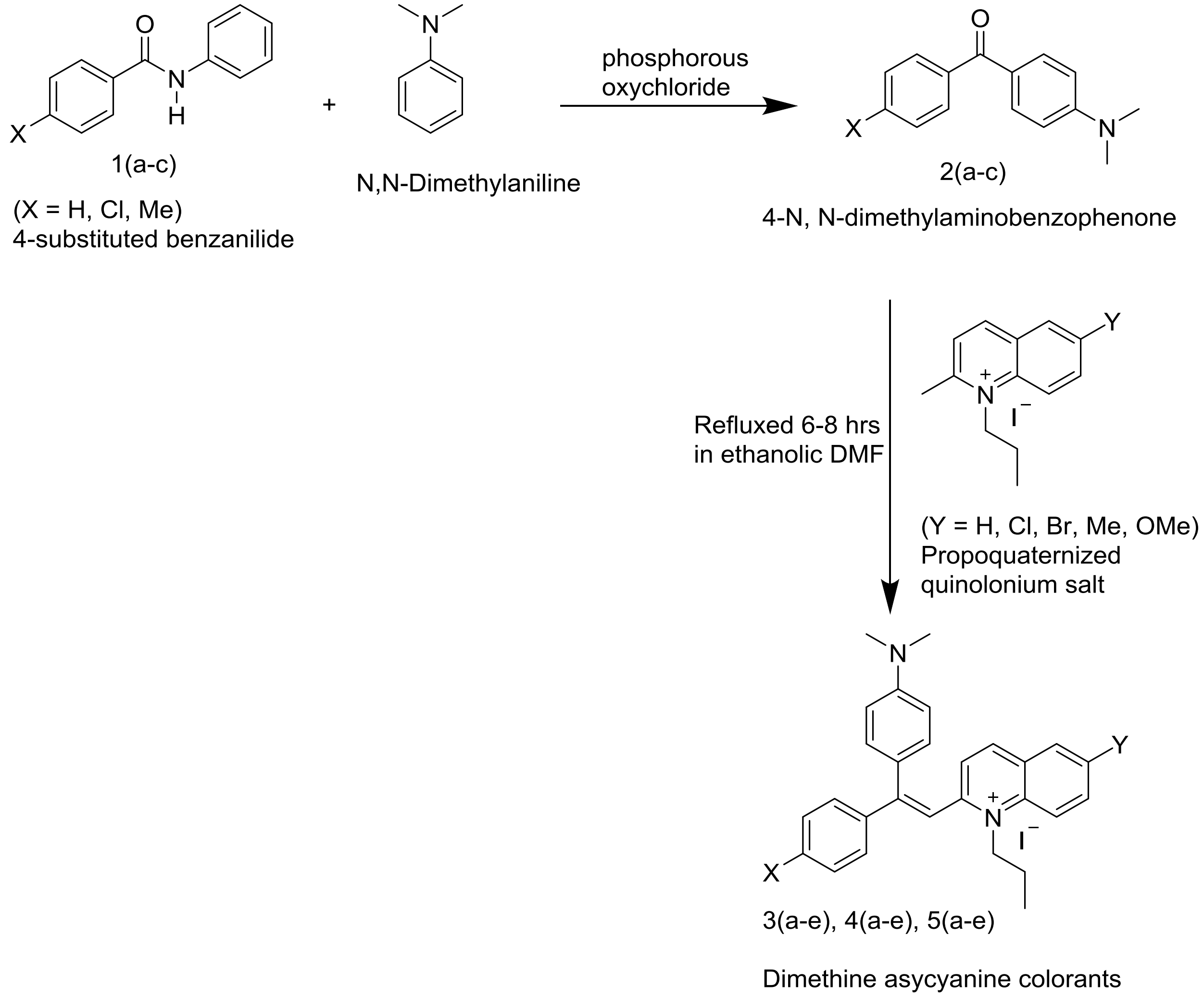
Synthesis of 6-Y-2(2-(4-X-phenyl)-2-(4-N, N-dimethylamino)phenyl)ethenyl)-1-propylquinoline-1-ium iodide asycyanine colorants 3(a-e), 4(a-e) and 5(a-e)

The condensation to obtain the foresaid colorants was carried out by earlier methods [7-13] with some modifications. Equimolar amount of 2(a-e) with various quaternized quinolium salts were dissolved in ethanolic DMF in the presence of basic catalyst piperidine (2-3 drops) and were refluxed for 6-8 hours under anhydrous condition using $CaCl_2$ guard tube. The resulting mixture was concentrated, cooled and left overnight at room temperature. The afforded colorants were recrystallized from methanol. Relevant data of all the colorants are described in corresponding Table (1 and 2).

SOLVATOCHROMIC STUDY

The solvent used was of spectroscopic grade and used without any further purification. A stoke solution (10^{-3}M) of these colorants were further diluted to appropriate volume in order to obtained required concentrations.

Scheme I



The structure of all newly prepared colorants 3(a-e), 4(a-e) and 5(a-e) were confirmed by elemental analysis, IR and H^1NMR spectral data (Table 1)

Table 1: Analytical data of the colorants

Compound No	Molecular formula	Calculated % Found %						
		C	H	N	O	Cl	Br	I
3a (X=H, Y=H)	$C_{28}H_{29}IN_2$	64.62 64.60	5.62 5.61	5.38 5.37	-	-	-	24.38 24.36
3b (X=H, Y=Cl)	$C_{28}H_{28}ClIN_2$	60.61 60.59	5.09 5.08	5.05 5.04	-	6.39 6.38	-	22.87 22.85
3c (X=H, Y=Br)	$C_{28}H_{28}BrIN_2$	56.11 56.09	4.71 4.70	4.67 4.66	-	-	13.33 13.32	21.17 21.16
3d (X=H, Y=Me)	$C_{29}H_{31}IN_2$	65.17 65.15	5.85 5.84	5.24 5.23	-	-	-	23.74 23.72
3e (X=H, Y=OMe)	$C_{30}H_{33}IN_2O$	63.27 63.25	5.68 5.67	5.09 5.08	2.91 2.90	-	-	23.05 23.03
4a (X=Cl, Y=H)	$C_{28}H_{28}ClIN_2$	60.61 60.59	5.09 5.08	5.05 5.04	-	6.39 6.38	-	22.87 22.86
4b (X=Cl, Y=Cl)	$C_{28}H_{27}Cl_2IN_2$	57.06 57.04	4.62 4.61	4.75 4.74	-	12.03 12.02	-	21.53 21.52
4c (X=Cl, Y=Br)	$C_{28}H_{27}BrClIN_2$	53.06 53.04	4.29 4.28	4.42 4.41	-	5.59 5.58	12.61 12.60	20.02 20.01
4d (X=Cl, Y=Me)	$C_{29}H_{30}ClIN_2$	61.22 61.20	5.32 5.31	4.92 4.91	-	6.23 6.22	-	22.31 22.30
4e (X=Cl, Y=OMe)	$C_{29}H_{30}ClIN_2O$	59.55 59.53	5.17 5.16	4.79 4.78	2.74 2.73	6.06 6.05		21.70 21.69
5a (X=Me, Y=H)	$C_{29}H_{31}IN_2$	65.17 65.15	5.85 5.84	5.24 5.23	-	-	-	23.74 23.73
5b (X=Me, Y=Cl)	$C_{29}H_{30}ClIN_2$	61.22 61.20	5.32 5.31	4.92 4.91	-	6.23 6.22	-	22.31 22.29
5c (X=Me, Y=Br)	$C_{29}H_{30}BrIN_2$	56.79 56.77	4.93 4.92	4.57 4.56	-	-	13.03 13.02	20.69 20.67
5d (X=Me, Y=Me)	$C_{30}H_{33}IN_2$	65.69 65.67	6.06 6.05	5.11 5.10	-	-	-	23.14 23.12
5e (X=Me, Y=OMe)	$C_{30}H_{33}IN_2O$	63.83 63.81	5.89 5.88	4.96 4.95	2.83 2.82	-	-	22.48 22.46

Table 2

Compound No	Crystals	Yield %	m.p. (°C)
3a	Needles	72	130 °C
3b	Flakes	76	163 °C
3c	Shining Crystals	74	173 °C
3d	Scintillating Crystals	74	165 °C
3e	Glazing crystals	67	165 °C
4a	Crystals	78	125 °C
4b	Needles	77	176 °C
4c	Shining crystals	74	167 °C
4d	Shining crystals	72	182 °C
4e	Crystals	74	159 °C
5a	Platelets	72	116 °C
5b	Shining crystals	74	125 °C
5c	Sandy crystals	73	95 °C
5d	Shining crystals	73	137 °C
5e	Crystals	75	132 °C

Table 3. Spectral data of the colorants

Compound No	Band range (cm^{-1})		Assignments
3(a-e)	2950-3055	C-H	Stretching (aromatic)
	1460-1630	C=C	Stretching (aromatic) and conjugation with C=N plane vibration
	1040-1380	C-O	Stretching (alkoxy)
	720-900	C-H	Bending (aromatic)
	1320-1360	C-H	Bending (alkane)
	510-690	C-X	Stretching
	1310-1330	C-N-C	Stretching
	1640-1660	C=N	Stretching (conjugation with aromatic nucleus)
	2410-2450	C=N	Quaternary nitrogen
4(a-e)	2865-2970	C-H	Stretching (aromatic)

	1440-1630	C=C	Stretching (aromatic) and conjugation with C=N plane vibration
	1050-1390	C-O	Stretching (alkoxy)
	720-950	C-H	Bending (aromatic)
	1330-1365	C-H	Bending (alkane)
	510-760	C-X	Stretching
	1310-1340	C-N-C	Stretching
	1640-1670	C=N	Stretching (conjugation with aromatic nucleus)
	2420-2475	C=N	Quaternary nitrogen
5(a-e)	2920-3060	C-H	Stretching (aromatic)
	1440-1660	C=C	Stretching (aromatic) and conjugation with C=N plane vibration
	1030-1380	C-O	Stretching (alkoxy)
	720-910	C-H	Bending (aromatic)
	1325-1360	C-H	Bending (alkane)
	520-790	C-X	Stretching
	1310-1340	C-N-C	Stretching
	1630-1650	C=N	Stretching (conjugation with aromatic nucleus)
	2410-2460	C=N	Quaternary nitrogen

Table 4: Electronic absorption spectra of ethenyl asycyanine colorants in 95% ethanol

1. Ethenyl asycyanine colorants 3(a-e)

λ-max (nm)				
3a	**3b**	**3c**	**3d**	**3e**
472	502	507	465	459
417	412	415	417	414

2. Ethenyl asycyanine colorants 4(a-e)

λ-max (nm)				
4a	**4b**	**4c**	**4d**	**4e**
509	517	518	493	492
416	412	432	412	413

3. Ethenyl asycyanine colorants 5(a-e)

λ-max (nm)				
5a	**5b**	**5c**	**5d**	**5e**
532	537	535	534	512
422	423	417	418	420

Table 5. Characteristic data of some selected ethenyl asycyanine colorants on pure organic solvents

Compound No.	Water λ-max (nm)	Ethanol λ-max (nm)	DMG λ-max (nm)	$CHCl_3$ λ-max (nm)	CCl_4 λ-max (nm)	Δλ (DMS-CCl_4)
3a	442 345	477 418	477 418	477 417	450 410	32 8
3b	475 375	502 412	507 424	507 424	475 412	32 12
4a	467 393	509 416	513 426	513 426	485 410	28 16
4b	487 381	519 412	522 424	522 424	495 415	27 9
5a	501 385	532 422	536 432	536 432	510 428	26 14
5b	505 393	537 423	542 430	542 432	515 418	27 12

RESULTS AND DISCUSSIONS

Reaction of various benzanilide 1(a-c), dimethyl aniline and phosphorous oxychloride afforded the corresponding compounds 2(a-c). Equimolar ratio of 2(a-c) and various 6-substituted-2-methyl-N-propyl quinolinium iodide in presence of piperidine as basic catalyst and ethanolic DMF as solvent afforded the corresponding 6-Y-2-(4-X-phenyl)-2-(4-N,N-dimethylamino)phenyl)ethenyl)-1-propylquinoline-1-ium iodide ethenyl ayscyanine colorants.

Effect of molecular structure on electronic spectra of synthesized asycyanine colorants

The spectral properties of these asycyanine colorants were determined by studying their electronic visible absorption spectra in 95% ethanolic solution which were depicted in (Table 4). The collation of electronic absorption spectra of these newly synthesized ethenyl asycyanine colorants (Scheme I) among themselves, with unsubstituted analogues, with ethenyl colorants and finally with 3-methyl substituted instead of 3-(1-methylethyl) substitution reveals fascinating observations.

The β-4-substituted phenylethenyl asycyanine colorants 3(a-e), 4(a-e) and 5(a-e) showed conform bathochromic shifts in the absorption maxima in comparison to their corresponding β-phenyl analogues irrespective of the nature of additional groups attached to phenyl nucleus [14-23] i.e. whether they are electron attracting Cl group or electron donating Me group. Substituting Y = H in compound 3(a-e) with Y = CH_3 in compound 4(a-e), brought about red shift, this may be attributed to increment of hyperconjugative of the methyl group. It is also observed that substituting Y = Cl in compound 5(a-e) brought about strong bathochromic shift than β-4-methyl analogous 4(a-e), this may be due to increment of strong electron withdrawing inductive effect of Cl group. Therefore, β-4-substituted phenyl group or β-4-phenyl group itself attached with methine chain of the ethenologues both result in very similar bathochromic shift corresponding to the previous findings.

Additionally on comparison of absorption spectra of previously prepared β-4'-substituted butadienyl analogues and hexatrienyl analogues with these synthesized analogues results remarkable variations. The absorption maxima of hexatrienyl analogues and butadienyl analogues colorants were fairly higher than the synthesized ethenyl analogues. This was due to more resonance in former with decrease in conjugation chain in later.

Again the electronic characterization of these colorants having 4-substituted phenyl system were collated with reported 3'-substituted phenyl analogues strong bathochromic shifts were observed (18). It may be due to the fact that inductive effect and resonance effect were applicable, where as in later only inductive effect was effective.

Solvatochromic behavior of conjugated ethenyl asycyanine colorants 3(a-e), 4(a-e) and 5(a-e) in pure solvent at 27 °C

The electronic absorption spectra of the total colorants in the wavelength range 350-700 nm have been also studied in different organic solvents (H_2O, EtOH, DMF, CCl_4 and $CHCl_3$), and the results are presented in Table 5. This is constructed with intention of illustrating the solvatochromic behavior of these colorants. It is clear from these data that λ-max of intramolecular charge transfer band exhibit a marked red shift on transfer from non-polar to polar solvent. This behavior indicate that the polar excited state of these asycyanine colorants are stabilized by polarization interaction force as the polarisibility of solvent is increased. In case of water as solvent absorption maxima exhibit blue shift. This may be due to the strong interaction of solvent (H-bond) which gave hypsochromic shift. The afforded colorants were recrystalized from methanol. Relevant data of all the colorants are described in Table (1, 2 and 3).

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