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Synthesis of Some β- and γ-Substituted Azotrimethine Cyanine Dyes

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ABSTRACT

New β-substituted azotrimethine cyanine dyes were prepared by condensation of phenyl glycosals with arylamines followed by reaction of the products with 2-methyl quaternary salts. The spectra data were recorded and the pH sensitivity of selected dyes was also determined.

1 INTRODUCTION

A property typical of tri-methine derivatives is their photochemical instability. Conformational changes, occuring after excitation along the polymethine chain, were found to precede the degradation process.[1] These structural fluctuations also account for the relatively low fluorescence yield observed for many cyanine dyes. By making the molecular structure more rigid, improved fluorescence yields and photostability may be obtained.[2]

We describe here the synthesis of some new β- and γ-substituted azotrimethine cyanines (**3a**–**3i**, **5**) with a view to assessing their photosensitization properties. The acid–base characteristics of the cyanine **3a** were also investigated with respect to the potential application of these dyes as photosensitizers.

2 RESULTS AND DISCUSSION

New β-substituted aryl azotrimethine cyanine dyes (**3a**–**3i**) were obtained by the reaction of phenylglyoxal derivatives (**1a**–**1e**) with aromatic amines in the presence of piperidine to give the corresponding intermediate compounds (**2a**–**2h**). The IR spectra of these showed characteristic bands at $1600 cm^{-1}$ ($\nu_{C=N}$) and $1670 cm^{-1}$ ($\nu_{C=O}$). Further reaction of equimolar amounts of (**2a**–**2h**) with 2-methyl quaternary ammonium salts in presence of ethanol and piperidine afforded the appropriately substituted aryl azotrimethine cyanines (**3a**–**3i**). This reaction depends on the nature of the substituents X and Y within the aryl moiety residues, being more facile with electron-donating substituent, e.g. as X = p-OCH_3 or o-OH and Y = o-OH, p-CH_3 or p-OCH_3 (Scheme 1).

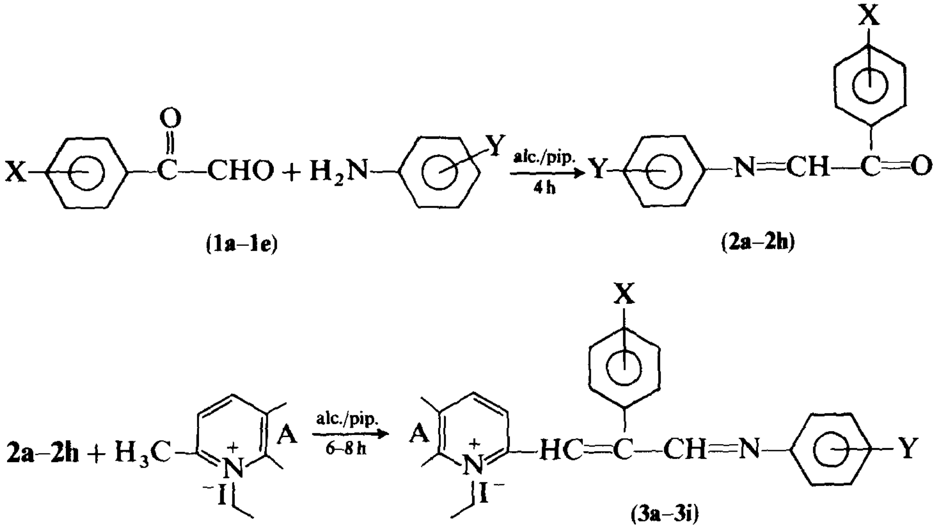
The structure of compounds **3a**–**3i** were confirmed by elemental analysis, IR and ^{1}H-NMR spectral data (Table 2). The compounds were partially soluble in non-polar solvents, in which they gave orange or violet solutions with a green or intense blue fluorescence depending upon the solvent used. They were also readily soluble in polar solvents, exhibiting violet solutions with an intense green fluorescence. Ethanolic solutions were violet in alkaline medium, the colour being discharged on acidification in a reversible colour change.

The reaction of equimolar amounts of **1e** with 2-methyl-1-ethylquinolinium-2-yl salt followed by the reaction of the product **4**[3] in presence of piperidine gave the corresponding γ-[4-chlorophenyl]-azotrimethine cyanine dye **5**.

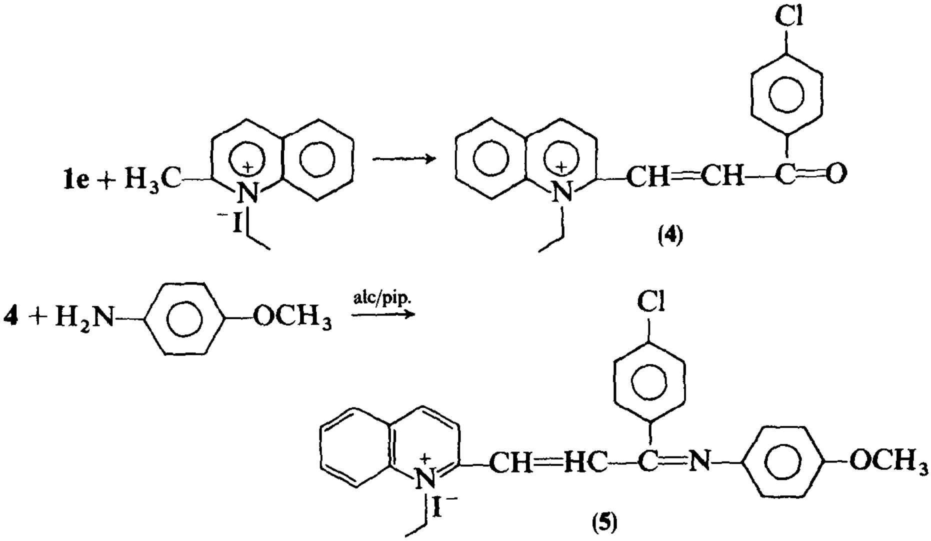
The absorption maxima of the 2[4-chlorophenyl]pyridinium (quinolinium)-2-yl salts of azotrimethine cyanines (**3a**–**3i**) in 95% ethanol depended on the nature of the heterocyclic quaternary ammonium residue A. Thus, compound **3d** (A = C_6H_4) showed a red shift with more intensive absorption compared with compound **3e** (A = H) (Table 2).

On the other hand, changes in the nature of the aryl substituents (X) had no significant effect on the absorption bands. However, the λ_{max} of **3a**–**3i** were shifted bathochromically or hypsochromically depending on the nature of the aryl substituent Y attached to the nitrogen atom of the azopolymethine chain. Thus, compound **3a** (X = p-Cl, Y = H, A = C_6H_4-2-yl salt) had λ_{max} at 555 nm (ε_{max} 15 920). Where Y was an electron-donor group (e.g. p-OCH_3 or o-OH in compounds **3b** and **3d** respectively) a slight bathochromic shift (2 nm) occurs. This may be attributed to the partial mixing of the lone pair orbitals of the oxygen atom with the π-system of azopolymethine group, leading to a modified set of energy levels and a shift of the band to longer wavelength. In the case of compound **3d** (Y = o-OH), the lowering of intensity is probably due to intramolecular hydrogen bonding between the o-OH and the azopolymethine groups. On the other hand, where Y is an electron-withdrawing group (e.g. p-NO_2, compound **3c**) a blue shift of 7 nm occurs (Table 2).

Comparison of absorption spectra of the aryl β-substituted azotrimethine



2a–2h: X = *p*-Cl; Y = H (**a**), *p*-OCH_3 (**b**), *p*-NO_2 (**c**), *o*-OH(**d**).
Y = *o*-OH; X = H (**e**), *p*-CH_3 (**f**), *p*-OCH_3 (**g**), *p*-NO_2 (**h**).
3a–3i: X = *p*-Cl; Y = H, A = C_6H_4-2-yl salt (**a**)
Y = *p*-OCH_3, A = C_6H_4-2-yl salt (**b**)
Y = *p*-NO_2, A = C_6H_4-2yl salt (**c**)
Y = *o*-OH, A = C_6H_4-2-yl salt (**d**)
Y = *o*-OH, A = H-2-yl-salt (**e**)
Y = *o*-OH; X = H, A = C_6H_4-2-yl salt (**f**)
X = *p*-CH_3, A = C_6H_4-yl salt (**g**)
X = *p*-OCH_3, A = C_6H_4-2-yl salt (**h**)
X = *p*-NO_2, A = C_6H_4-2-yl salt (**i**)



Scheme 1

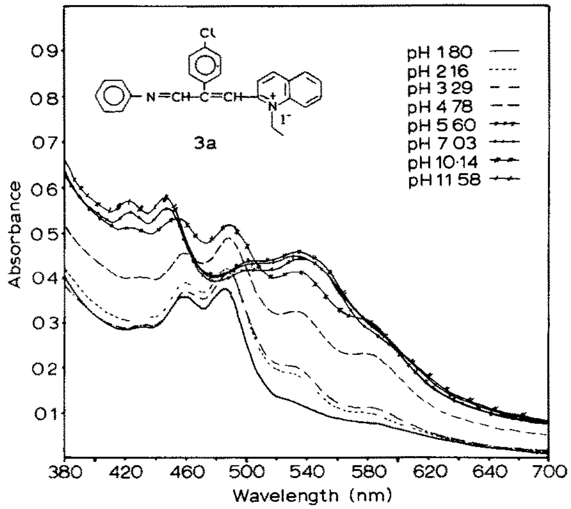


Fig. 1.

cyanine incorporating the quaternary quinolinium nucleus (**3b**) with its γ-analogue (**5**) shows that changing the 4-chlorophenyl residue from the β- to the γ-position results in a large bathochromic shift of 28 nm, this being due to the mesomeric effect of the aryl substituents attached to chromophoric N=C group.

The absorption spectra of **3a** in aqueous universal buffers showed that the compound underwent bathochromic and hypsochromic shifts in alkaline and acidic media respectively. The bathochromic shift in alkali is mainly due to the relatively increased negative charge density of the azopolymethine group. The band is hypsochromically shifted in acidic media as a result of protonation of the azopolymethine group, and consequent desorption of CT interaction in the protonated form. As the pH of the medium increases the azopolymethine group becomes deprotonated and mesomeric interaction with the rest of the molecules increases with consequent enhancement of the CT interaction in the free base (Fig. 1). Plotting the absorbance at λ_{max} against pH, an S-shaped curve is obtained, and from the intersection of the curve with a horizontal line midway between the left and right segments[4] a pK_a value of 4·5 for compound **3a** was calculated.

3 EXPERIMENTAL

3.1 General

All melting points are uncorrected. IR spectra were determined on a Perkin–Elmer Infrared 127B spectrophotometer. The visible spectra were recorded on a Shimadzu UV 240 UV-Vis recording spectrophotometer and ^{1}H-NMR spectra on an EM-390 90 MHz NMR spectrometer. A modified buffer series, derived from that of Britton, was prepared for use in the electronic spectra. An accurate volume of the stock solution was added to 5 ml of the buffer solution and then made up to 10 ml. The pH of this solution was checked before spectral measurements were made.

The β-[4-chlorobenzoyl]-quinolinium-2-yl salt dimethine cyanine derivative (**4**) was prepared by a method similar to that described in Ref. 3.

3.2 Synthesis of β-substituted azotrimethine cyanine dyes (3a–3i)

3.2.1 Synthesis of the intermediate compounds (2a–2h)

Equimolar amounts (0·01 mol) of the phenyl glycosal derivatives (**1a–1e**) and the approximate arylamine were dissolved in absolute ethanol (20 ml) containing piperidine (3–5 drops). The reaction mixture was refluxed for 4 h, filtered hot, concentrated and acidified with acetic acid. On standing, the products **2a–2h** precipitated. These were filtered, washed with ether and recrystallized from absolute ethanol to give yellow–brown crystals. Relevant data are shown in Table 1. IR 1600 cm^{-1} ($\nu_{C=N}$) and 1670 cm^{-1} ($\nu_{C=O}$) for compound **2c** and 3450 cm^{-1} (ν_{OH}) for **2d**.

TABLE 1
Characterization of Intermediate Compounds **2a–2h**

Compound no.	*M.p. (°C)*	*Yield (%)*	*Molecular formula (mol. wt)*	*Colour of products*	*Analysis (%) Calcd/(Found)*		
					C	*H*	*N*
2a	167	60	$C_{14}H_{10}NOCl$ (243·5)	Yellow	69·0 (68·5)	4·1 (4·3)	5·75 (5·7)
2b	200	58	$C_{15}H_{12}NO_2Cl$ (273·5)	Orange	65·8 (65·4)	4·4 (4·2)	5·1 (5·1)
2c	138	55	$C_{14}H_9N_2O_3Cl$ (288·5)	Orange	58·2 (58·5)	3·1 (3·3)	9·7 (9·8)
2d	100	70	$C_{14}H_{10}NO_2Cl$ (259·5)	Orange–brown	64·7 (64·9)	3·85 (3·7)	5·4 (5·4)
2e	105	52	$C_{14}H_{11}NO_2$ (225)	Pale yellow	74·7 (74·95)	4·9 (5·0)	6·2 (6·3)
2f	92	63	$C_{15}H_{13}NO_2$ (239)	Yellow	75·3 (75·1)	5·4 (5·7)	5·7 (5·8)
2g	95	68	$C_{15}H_{13}NO_3$ (255)	Orange	70·6 (70·7)	5·1 (5·5)	5·5 (5·5)
2h	120	45	$C_{14}H_{10}N_2O_4$ (270)	Pale brown	62·2 (62·8)	3·7 (3·45)	10·4 (10·5)

TABLE 2

Characterization of β-Substituted Azotrimethine Cyanine Dyes **3a–3i**

Compound no.	*M.p. (°C)*	*Yield (%)*	*Molecular formula (mol. wt)*	*Colour of products*	*Analysis (%)*			*Absorption spectra*	
					Calcd/(Found)				
					C	*H*	*N*	λ_{max} *(nm)*	$(\varepsilon_{max}) \times 10^3$ $(m^{-1}\ cm^2)$
3a	148	45	$C_{26}H_{22}N_2ClI$ (524·5)	Violet	59·5 (59·5)	4·2 (4·2)	5·3 (5·3)	437 456 486 519 555 586 (sh)	(19 530) (20 280) (25 890) (19 990) (15 920) (11 800)
3b	140	56	$C_{27}H_{24}N_2OClI$ (554·5)	Intense violet	58·4 (58·45)	4·3 (4·3)	5·05 (5·1)	490 519 557	(15 420) (18 960) (16 260)
3c	173–75	40	$C_{26}H_{21}N_3O_2ClI$ (569·5)	Violet	54·8 (54·8)	3·7 (3·7)	7·4 (7·4)	487 519 548 586 (sh)	(14 280) (13 020) (12 240) (9 300)
3d	95	51	$C_{26}H_{22}N_2OClI$ (540·5)	Violet	57·7 (57·7)	4·1 (4·1)	5·2 (5·2)	395 489 513 557 605 (sh) 650 (sh)	(12 720) (10 620) (12 840) (14 400) (7 500) (4 200)

3e	118	43	$C_{22}H_{19}N_2OClI$ (489·5)	Brown	53·9 (54·0)	3·9 (3·9)	5·7 (5·8)	366 418 437 510 (sh) 550 (sh)	(6 600) (8 000) (9 000) (1 840) (1 360)
3f	105	40	$C_{26}H_{23}N_2OI$ (506)	Violet	61·7 (61·7)	4·55 (4·5)	5·5 (5·6)	478 (sh) 512 558	(7 040) (9 160) (9 920)
3g	110	38	$C_{27}H_{25}N_2OI$ (520)	Violet	62·3 (62·35)	4·8 (4·8)	5·4 (5·4)	480 (sh) 511 557	(11 320) (14 120) (12 200)
3h	108	45	$C_{27}H_{25}N_2O_2I$ (536)	Violet	60·45 (60·4)	4·7 (4·7)	5·2 (5·2)	418 440 480 (sh) 512 558	(9 320) (10 320) (10 800) (13 720) (14 000)
3i	150	55	$C_{26}H_{22}N_3O_3I$ (551)	Intense violet	56·6 (56·6)	4·0 (4·0)	7·6 (7·6)	486 (sh) 517 558	(8 720) (9 600) (12 760)

3.2.2 Synthesis of the cyanines **3a–3i)**

Equimolar ratios (0·01 mol) of compounds **2a**–**2h** and the appropriate methyl quaternary salts (α-picoline and quinaldine ethiodide) were dissolved in 30 ml ethanol to which piperidine (3–5 drops) was added. The reaction mixture was refluxed for 6–8 h until a constant colour was obtained, and then it was filtered hot, concentrated, cooled and then acidified with acetic acid. The precipitated products were filtered and recrystallized from absolute ethanol to give **3a**–**3i**. Characterization data are given in Table 2. IR showed no C=O band at 1670 $\mathrm{cm^{-1}}$, but characteristic bands were present at 2900–2850 $\mathrm{cm^{-1}}$ (ethiodide of heterocyclic residue). The ^{1}H-NMR ($CDCl_3$) of **3d** (X = *p*-Cl, Y = *o*-OH, A = C_6H_4-2-yl salt) showed δ 7·2–6·4 ppm (m, 15H, arom. + heter. + CH=C), δ 7·6 ppm (d, 1H, OH), δ 3·2 ppm (q, 2H, CH_2), δ 1·5 ppm (t, 3H, CH_3) and δ 6·5 ppm (s, 1H, CH=N).

3.2.3 Synthesis of γ[4-chlorophenyl]azotrimethine cyanine **(5)**

Equimolar amounts (0·01 mol) of compound **4**[3] and *p*-anisidine were refluxed in ethanol (30 ml) and piperidine (3–5 drops) for 6 h. The reaction mixture was filtered hot, cooled, and the precipitated product collected, washed with water and recrystallized from absolute ethanol to give violet crystals of **5**, m.p. 90°C (yield 30%).

$C_{27}H_{24}N_2OClI$ requires: C, 58·4; H, 4·3; N, 5·05.
Found: C, 58·45; H, 4·3; N, 5·0%.

λ_{max} (ethanol): 550 and 585 nm.
IR 1600 $\mathrm{cm^{-1}}$ ($\nu_{C=O}$), 1580 $\mathrm{cm^{-1}}$ ($\nu_{C=N}$) and 2990–2900 $\mathrm{cm^{-1}}$ (ethiodide of quinolinium salt).

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