

## Synthesis and solvatochromic behaviour of new asymmetrical mono-(tri)-methine cyanine dyes

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**Abstract.** 6-Amino-5-cyano-3-methyl-1,4-diarylpyrano[2,3-*c*]pyrazole derivatives were prepared via the interaction of  $\alpha,\beta$ -unsaturated nitriles with 3-methyl-1-phenylpyrazol-5-one as starting materials in the synthesis of new asymmetrical mono-(tri)-methine cyanine dyes. The new cyanines were characterised by elemental analysis, IR and  $^1\text{H-NMR}$  spectral data. The visible absorption spectra of some selected dyes were investigated in pure and mixed solvents as well as in aqueous buffer solutions.

**Keywords.** Monomethine cyanines; charge transfer; electronic absorption spectra.

### 1. Introduction

A variety of methine cyanine dyes incorporating pyrazoline moiety were reported<sup>1–6</sup>. Monomethine cyanines are used as photosensitisers in blue green<sup>7</sup> and they are also useful as analytical reagents over a wide *pH* range<sup>8</sup>. Trimethine cyanines can be used as laser dyes<sup>9</sup> in light<sup>10</sup> and as superphotographic sensitisers for silver halide emulsion<sup>11</sup>.

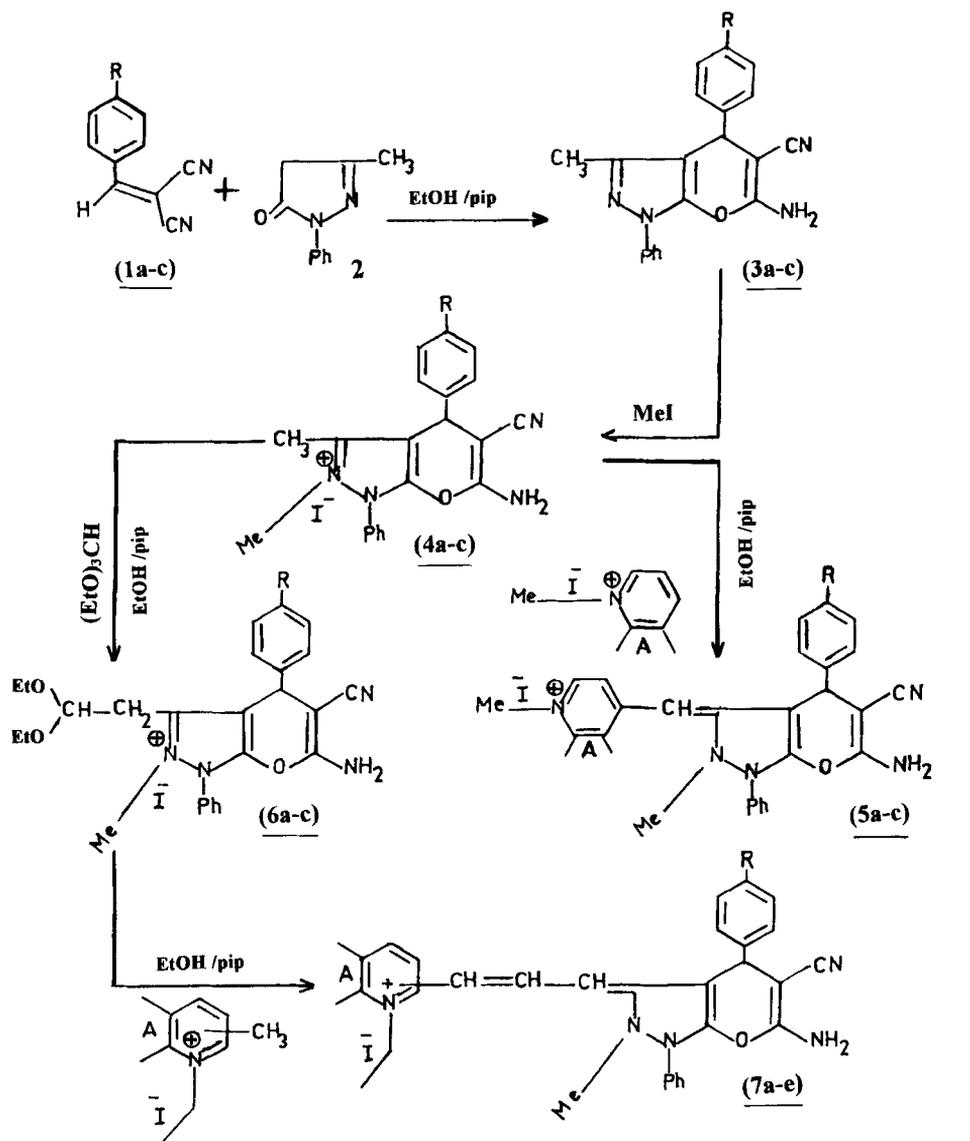
In this work, we report here the synthesis of some new asymmetrical mono-(tri)-methine cyanine dyes incorporating pyrano[2,3-*c*] pyrazole moieties viz. compounds (5a-e) and (7a-e) on the basis that such dyes might exhibit a photosensitisation effect.

### 2. Results and discussion

Arylidene malononitrile (1a-d) react with 3-methyl-1-phenylpyrazol-5-one (2) in ethanol and piperidine as a basic catalyst to give the corresponding biheterocyclic system of 6-amino-5-cyano-1,4-diarylpyrano[2,3-*c*]pyrazole derivatives<sup>12</sup> (3a-c). The structure of compounds (3a-c) were corroborated by the synthesis of these compounds via the interaction of 4-arylidene-3-methyl-1-phenylpyrazol-5-one derivatives with malononitrile.

Quaternisation of (3a-c) using iodomethane gave the corresponding pyrano-[2,3-*c*]pyrazolium-2-yl iodide (4a-c). Interaction of (4a-c) with equimolar amounts the 1-methyl-(pyridinium-quinolinium and/or iso-quinolinium) iodide in the presence of piperidine as a basic catalyst afforded the desired asymmetric 6-amino-5-cyano-1,4-diarylpyrano[2,3-*c*]pyrazolo-3-yl[4(1)]-monomethine cyanine dyes (5a-e). Meanwhile, interaction of (4a-c) with an equimolar amounts of triethoxymethane in the presence of piperidine achieved the corresponding intermediate compounds (6a-c). Further reaction of (6a-c) with 2(4)-methyl-substituted heterocyclic quaternary salts  $\alpha,\gamma$ -picoline and/or quinaldine ethyl iodide] under piperidine catalysis gave the asymmetric pyrano[2,3-*c*]pyrazole-3-yl[2(4)]-trimethine cyanine dyes (7a-e) (scheme 1).

\* For correspondence



1,3,4,6	a	b	c		
R	H	-OCH <sub>3</sub>	-NO <sub>2</sub>		
5	a	b	c	d	e
R	H	H	H	-OCH <sub>3</sub>	-NO <sub>2</sub>
A	H-4-yl	C <sub>6</sub> H <sub>4</sub> -4-yl	C <sub>6</sub> H <sub>4</sub> -1-yl	C <sub>6</sub> H <sub>4</sub> -4-yl	C <sub>6</sub> H <sub>4</sub> -4-yl
7	a	b	c	d	e
R	H	H	H	-OCH <sub>3</sub>	-NO <sub>2</sub>
A	H-2-yl	C <sub>6</sub> H <sub>4</sub> -2-yl	C <sub>6</sub> H <sub>4</sub> -4-yl	C <sub>6</sub> H <sub>4</sub> -2-yl	C <sub>6</sub> H <sub>4</sub> -2-yl

Scheme 1.

The structure of compounds (*4a-c*, *5a-e*, *6a-c* and *7a-e*) were confirmed by elemental analysis (table 1, parts I, II and III), IR and  $^1\text{H-NMR}$  spectral data are shown in table II.

The asymmetric monomethine cyanines (*5a-e*) possess red to violet colour while, trimethine cyanines (*7a-e*) are reddish-violet to intense violet colour in solutions. Both mono- and tri-methine cyanine dyes are fairly soluble in polar organic solvents and in conc.  $\text{H}_2\text{SO}_4$  liberate iodine vapour on gentle heating. They have permanent colours in alkaline medium which are discharged on acidification.

### 2.1 Relation between molecular structure and spectral behaviour of the cyanines

The  $\lambda_{\text{max}}$  and  $\epsilon_{\text{max}}$  values of compounds (*5a-e*) in 95% ethanol are collated in (table 3, part I). Substituting A = H-2-yl salt in compound *5a* by A =  $\text{C}_6\text{H}_4$ -2-yl salt moiety in compound *5b* resulted in red shifts of 5 and 35 nm in the bands at 515 and 425 nm, respectively, accompanied by the appearance of one new shoulder at 570 nm. This could be attributed to the more extensive  $\pi$ -delocalisation in compound *5b*. The visible absorption spectra of (*5b-e*) depend on the nature of the substituent R. Thus, the shoulder within the range 545–580 nm is influenced by the type of substituent R, this being attributable to an electronic transition involving the whole molecule associated with intramolecular charge transfer. Substituting R = p –  $\text{OCH}_3$  in compound *5d* by

**Table 1.** Characterisation data for 6-amino-5-cyano-3-methyl-1,4-diaryl pyrano[2,3-c]-pyrazolium-2-yl-iodide (*4a-c*), asymmetric-3-yl[4(1)] mono-methine cyanines dyes (*5a-e*), intermediate compounds of trimethine (*6a-c*) and asymmetric-3-yl[2(4)] trimethine cyanine dyes (*7a-e*).

Compd no.	M.p. $^{\circ}\text{C}$	Yield %	Mol. Formula (Mol. wt.)	Elemental analysis % Calculated (Found)		
				C	N	N
<i>I Compounds 4a-c</i>						
4a	155–3	65	$\text{C}_{21}\text{H}_{19}\text{N}_4\text{O I}$ (470·31)	53·58(53·69)	4·04(3·95)	11·91(12·01)
4d	110–2	75	$\text{C}_{22}\text{H}_{21}\text{N}_4\text{O}_2\text{ I}$ (500·34)	52·76(53·83)	4·20(4·11)	11·19(11·25)
4c	160–3	56	$\text{C}_{21}\text{H}_{18}\text{N}_5\text{O}_3\text{ I}$ (515·31)	48·90(48·99)	3·49(3·39)	13·58(13·62)
<i>II Compounds 5a-e</i>						
5a	115–7	69	$\text{C}_{27}\text{H}_{24}\text{N}_5\text{O I}$ (561·42)	57·71(57·83)	4·28(4·17)	12·47(12·53)
5b	168–6	76	$\text{C}_{31}\text{H}_{26}\text{N}_5\text{O I}$ (611·48)	60·84(61·01)	4·25(4·12)	11·45(11·33)
5c	130–2	65	$\text{C}_{31}\text{H}_{26}\text{N}_5\text{O I}$ (611·48)	60·84(60·96)	4·25(4·08)	11·45(11·39)
5d	180–2	65	$\text{C}_{32}\text{H}_{28}\text{N}_5\text{O}_2\text{ I}$ (641·51)	59·86(59·97)	4·37(4·29)	10·91(10·95)
5e	210–2	71	$\text{C}_{31}\text{H}_{25}\text{N}_6\text{O}_3\text{ I}$ (656·49)	56·67(56·59)	3·81(3·71)	12·80(12·75)
<i>III Compounds 6a-c</i>						
6a	153–5	72	$\text{C}_{26}\text{H}_{29}\text{N}_4\text{O}_3\text{ I}$ (572·37)	54·51(54·39)	5·07(4·95)	9·78(9·86)
6b	178–6	83	$\text{C}_{27}\text{H}_{31}\text{N}_4\text{O}_4\text{ I}$ (602·40)	53·79(53·63)	5·15(5·09)	9·30(9·44)
6c	135–3	68	$\text{C}_{26}\text{H}_{28}\text{N}_5\text{O}_5\text{ I}$ (617·37)	50·54(50·66)	4·54(4·39)	11·34(11·21)
<i>III Compounds 7a-e</i>						
7a	130–2	68	$\text{C}_{30}\text{H}_{28}\text{N}_5\text{O I}$ (601·49)	59·85(59·97)	4·66(4·49)	11·64(11·73)
7b	155–3	75	$\text{C}_{34}\text{H}_{30}\text{N}_5\text{O I}$ (651·55)	62·62(62·75)	4·60(4·55)	10·74(10·84)
7c	105–7	69	$\text{C}_{30}\text{H}_{27}\text{N}_5\text{O I}$ (601·49)	59·85(60·01)	4·66(4·59)	11·64(11·68)
7d	125–3	89	$\text{C}_{35}\text{H}_{32}\text{N}_5\text{O}_2\text{ I}$ (681·57)	61·62(61·49)	4·70(4·78)	10·27(10·33)
7e	185–2	69	$\text{C}_{34}\text{H}_{29}\text{N}_6\text{O}_3\text{ I}$ (696·55)	58·57(58·67)	4·16(3·98)	12·06(12·14)

**Table 2.** IR and <sup>1</sup>H-NMR spectral data for some selected products.

Compd. no.	IR( $\nu_{\text{Cm}^{-1}}^{\text{KBr}}$ ) <sup>a</sup>	<sup>1</sup> H-NMR(CDCl <sub>3</sub> ), (ppm) <sup>b</sup>
4a	2980–2940( $\nu$ CH <sub>3</sub> I)	6.6–7.2(m, 11 H, Ar – H + heter – H) 4.5(s, 2H, NH <sub>2</sub> ) 2.8(s, 3H, CH <sub>3</sub> -joined to ammonium center)
4b	2960–2930( $\nu$ CH <sub>3</sub> I)	1.4(s, 3H, CH <sub>3</sub> -of pyrazole) 6.6–7.2(m, 13 H, Ar – H + heter – H) 4.3(s, 2H, NH <sub>2</sub> ) 2.8(s, 3H, CH <sub>3</sub> -joined to ammonium center)
4c	2970–2920( $\nu$ MeI)	1.4(s, 3H, CH <sub>3</sub> -of pyrazole) 6.7–7.4(m, 10 H, Ar – H + heter – H) 4.6(s, 2H, NH <sub>2</sub> ) 2.8(s, 3H, CH <sub>3</sub> -joined to ammonium center)
5a	2980–2940( $\nu$ MeI) 1610–1600( $\nu$ C=C)	1.4(s, 3H, CH <sub>3</sub> -of pyrazole) 6.5–7.3(m, 16 H, Ar – H + heter – H + – CH =) 4.5(s, 2H, NH <sub>2</sub> ) 2.3(s, 3H, CH <sub>3</sub> -joined to immonium centre)
5d	2970–2930( $\nu$ CH <sub>3</sub> I) 1610–1600( $\nu$ C=C)	1.9(s, 3H, CH <sub>3</sub> -N-pyrazole) 6.4–7.2(m, 17 H, Ar – H + heter – H + – CH =) 4.5(s, 2H, NH <sub>2</sub> ) 2.3(s, 3H, CH <sub>3</sub> -joined to immonium centre)
6a	2960–2940( $\nu$ CH <sub>3</sub> I) 1620–1600( $\nu$ C=C) 1580–1540( $\nu$ C=N)	1.9(s, 3H, CH <sub>3</sub> -N-pyrazole) 6.4–7.1(m, 11 H, Ar – H + heter – H) 4.5(s, 2H, NH <sub>2</sub> ) 2.8(s, 3H, CH <sub>3</sub> -joined to immonium centre) 2.1(t, 6H, two CH <sub>3</sub> -groups) 3.8(q, 4H, two CH <sub>2</sub> -groups) 4.0(t, 1H, CH –) 1.95(d, 2H, CH <sub>2</sub> -pyrazole)
6c	2970–2930( $\nu$ C <sub>2</sub> H <sub>5</sub> I) 1610–1600( $\nu$ C=C) 1580–1550( $\nu$ C=N)	6.2–7.0(m, 10 H, Ar – H + heter – H) 4.5(s, 2H, NH <sub>2</sub> -) 2.8(s, 3H, CH <sub>3</sub> -joined to immonium centre) 2.2(t, 6H, two CH <sub>3</sub> -groups) 3.9(q, 4H, two CH <sub>2</sub> -groups) 4.0(t, 1H, CH-) 1.95(d, 2H, CH <sub>2</sub> -pyrazole)
7a	2980–2940( $\nu$ CH <sub>3</sub> I) 1620–1600( $\nu$ C=C) 1580–1540( $\nu$ C=N)	6.4–7.1(m, 18 H, Ar – H + heter – H + – CH = CH = CH) 4.5(s, 2H, NH <sub>2</sub> ) 2.8(q, 2H, CH <sub>2</sub> -joined to immonium centre) 2.1(t, 3H-CH <sub>3</sub> -of EtI) 1.9(s, 3H, CH <sub>3</sub> -pyrazole)
7d	2975–2940( $\nu$ C <sub>2</sub> H <sub>5</sub> I) 1610–1600( $\nu$ C=C) 1580–1550( $\nu$ C=N)	6.6–7.2(m, 17H, Ar – H + heter – H + CH = CH – CH =) 4.5(s, 2H, NH <sub>2</sub> ) 2.8(q, 2H, CH <sub>2</sub> -joined to immonium centre) 2.1(t, 3H-CH <sub>3</sub> -of EtI) 1.9(s, 3H, CH <sub>3</sub> -purazole)

R = p – NO<sub>2</sub> in compound **5g** causes strong hypsochromic shift by 35 nm. This is due to the presence of the nitro group (negative inductive effect)<sup>13</sup>.

The UV/VIS absorption spectra of biheterocyclic trimethine cyanines (**7a-e**) in ethanol showed that the absorption bands, the position and molar extinction coefficient

**Table 3.** Characterisation data of the electronic absorption spectra of symmetric monomethine (*5a-e*) and trimethine cyanine dyes (*7a-e*)

<i>I Cyanine dyes 5a-e</i>				
5a	5b	5c	5d	5e
$\lambda_{\max}/\text{nm} [10^{-3}\epsilon_{\max}(\text{l.mol}^{-1}\text{cm}^{-1})]$				
400(17.80)	sh 405(10.08)	— —	— —	— —
425(6.70)	— —	425(0.88)	440(3.92)	sh 425(5.60)
— —	470(8.80)	— —	470(4.44)	— —
515(3.36)	sh 520(3.11)	— —	sh 530(1.19)	545(1.60)
— —	sh 570(1.21)	— —	sh 580(0.93)	— —
<i>II Cyanine dyes 7a-e</i>				
7a	7b	7c	7d	7e
$\lambda_{\max}/\text{nm} [10^{-3}\epsilon_{\max}(\text{l.mol}^{-1}\text{cm}^{-1})]$				
— —	— —	— —	— —	370(7.22)
— —	sh 400(5.50)	— —	400(3.92)	— —
— —	— —	sh 440(2.45)	440(4.10)	430(2.11)
— —	sh 470(3.91)	— —	485(4.44)	470(5.22)
500(1.96)	505(6.68)	510(3.98)	500(5.24)	500(5.87)
— —	550(5.68)	— —	sh 530(1.19)	555(0.44)
— —	sh 610(2.42)	— —	sh 580(0.93)	— —
— —	— —	— —	660(0.44)	— —

which were influenced by the nature of heterocyclic residue A and the substituent R attached to the biheterocyclic system, i.e., pyrano[2,3-c] pyrazole moiety (table 3, part II). Thus, the visible bands of trimethine *7b*, incorporating A = C<sub>6</sub>H<sub>4</sub>-2-yl salt, show larger red shifts (50–110 nm) accompanied by the appearance of two new shoulders at 400 and 470 nm than those of the analogues where A = H-2-yl salt in compound *7a*. This can be attributed to the more extensive  $\pi$ -delocalisation within the quaternary heterocyclic moiety *7b*. The visible bands of (*7b-e*) undergo bathochromic or hypsochromic shifts, depending on the nature of the substituent R, (table 3, part II). Substituting R = p-NO<sub>2</sub> in compound *7e* by R = p-OCH<sub>3</sub> in compound *7d* resulted in strong red shift of 45 to 105 nm. This can be attributed to increasing the conjugation due to the presence of donating character of -OCH<sub>3</sub> group (positive inductive effect)<sup>13</sup>.

## 2.2 Solvatochromic behaviour of pyrano[2,3-c]-pyrazole-3-yl(4)-mono-methine cyanines *5a,b* and 3-yl[2(4)]-trimethine cyanine dyes *7b,c* in pure organic solvents at 27°C.

The  $\lambda_{\max}$  and  $\epsilon_{\max}$  values of the absorption bands due to different electronic transition, within the solute molecules (*5a-b*) and (*7b-c*) were obtained in pure solvents of different dielectric constant<sup>14</sup> (viz. H<sub>2</sub>O, DMF, EtOH, CHCl<sub>3</sub>, CCl<sub>4</sub> and dioxane), which are represented in table 4.

The spectra of compounds *5a* and *5b* in ethanol consists of three and four essential absorption bands, respectively. Meanwhile, the spectra of compounds *7b* and *7c* in ethanol consists of three and five essential absorption bands, respectively. The UV bands, located at up at 342 nm, can be assigned to  $\pi$ - $\pi^*$  transitions of the benzeneoid

**Table 4.** Characterisation data of the electronic absorption spectra<sup>a</sup> of some selected asymmetric monomethine **5a**, **5b** and trimethine cyanine dyes **7b**, **7c** in pure organic solvents at 27°C.

Compd. no.	Water	DMF	EtOH	CHCl <sub>3</sub>	CCl <sub>4</sub>	Dioxan
$\lambda_{\max}$ (nm) with $\epsilon_{\max} \times 10^{-3} (\text{mol}^{-1} \text{cm}^2)$						
5a	390(16.32)	410(16.48)	400(17.80)	407(15.72)	405(12.00)	404(10.60)
	495(8.40)	435(8.65)	425(6.70)	428(10.71)	— —	— —
5b	— —	520(12.40)	515(2.36)	510(9.20)	515(8.92)	515(5.48)
	— —	sh 400(10.40)	sh 405(5.80)	sh 400(10.80)	sh 405(10.72)	sh 405(11.20)
	430(11.160)	480(8.44)	470(8.80)	455(8.36)	— —	— —
	sh 505(7.20)	500(8.32)	— —	500(8.20)	500(8.08)	485(8.16)
	— —	530(4.42)	sh 520(3.11)	sh 520(7.14)	— —	— —
7b	— —	sh 570(5.20)	sh 570(4.28)	sh 570(5.08)	— —	— —
	— —	400(0.73)	400(5.80)	400(7.64)	405(4.12)	405(6.50)
	465(3.20)	475(6.68)	470(6.24)	473(5.56)	— —	— —
	495(3.06)	510(7.20)	505(5.56)	510(6.72)	510(3.26)	510(5.25)
	560(1.76)	560(6.50)	550(5.56)	550(6.00)	550(2.73)	— —
7c	— —	sh 610(2.80)	sh 610(3.18)	sh 610(3.18)	— —	— —
	340(8.62)	345(17.56)	342(13.76)	345(15.76)	347(8.22)	345(7.78)
	— —	445(2.24)	440(2.40)	398(7.20)	395(3.58)	395(3.60)
	500(1.60)	515(4.00)	510(3.98)	512(3.12)	510(0.76)	510(1.64)

and biheterocyclic system. These bands are slightly influenced by the change in the solvent polarity. The other absorption bands at longer wavelengths can be attributed to  $n-\pi^*$  transitions and to the intermolecular charge transfer (CT) interaction<sup>15</sup> originating from both oxygen atoms of the pyran ring and/or N-methyl of the pyrazole ring as a source to the positively charged heterocyclic quaternary (N) atom as a sink.

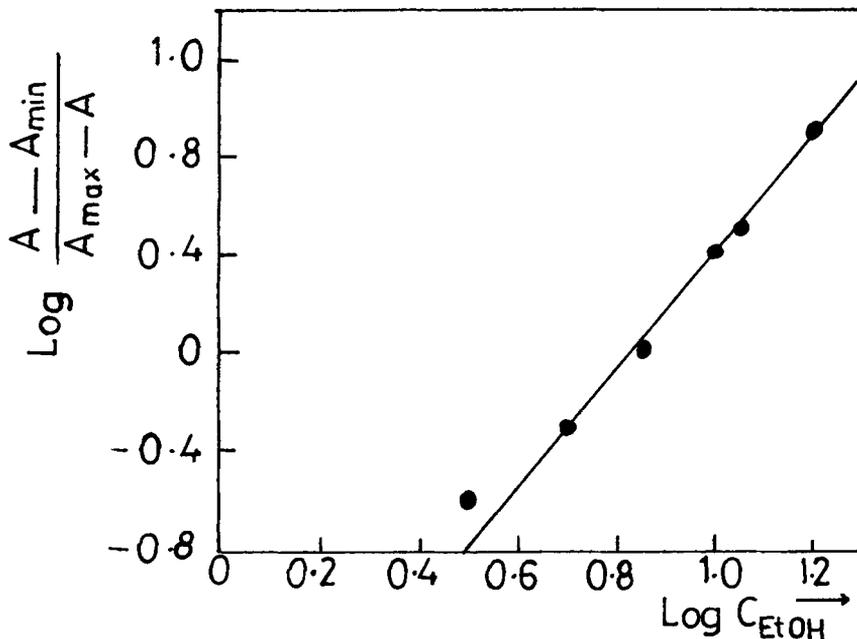
Examination of the results reported in table 4 reveals that the bands corresponding to  $n-\pi^*$  and CT transitions show a slight red shift on changing the solvent from EtOH to DMF, CHCl<sub>3</sub>, CCl<sub>4</sub> and dioxane. The small blue shift observed in ethanol can be explained as a result of hydrogen bonding between the ethanol and the lone pair of electrons of the pyrano oxygen atom and/or N-methylpyrazole ring. These result in a slight decrease in the electron density of the oxygen atom and/or nitrogen atom and consequently decreases, to some extent, the mobility of the attached  $\pi$ -electrons to the conjugated pathway. The slight blue shift observed in the  $\lambda_{\max}$  of the CT band in water (for all compounds) relative to ethanol, as well as the lower extinction coefficient, can be mainly ascribed to the stronger interaction of H<sub>2</sub>O molecules with the lone pair of electrons of pyrano-oxygen atom and/or N-methylpyrazole through hydrogen bonding.

### 2.3 Solvatochromic behaviour of 6-amino-5-cyano-1,4-diaryl-pyrano[2,3-c]-pyrazole-3-yl(4)-monomethine cyanine dye **5b** in DMF/EtOH mixed solvent at 27°C

The visible spectra of compound **5b** was measured in DMF-EtOH mixture. This was done in order to study the possibility of H-bonding between the solute molecules and a H-bond acceptor solvent. The visible spectrum of compound **5b** in pure EtOH displayed a band with  $\lambda_{\max} = 470$  nm. On addition of DMF, a new band at  $\sim 500$  nm appeared, its absorbance increasing as the molarity of DMF was increased. The

**Table 5.** Data obtained for the cyanine dye 5b in mixed solvent at 27°C.

System	Excitation energy (KJ mol <sup>-1</sup> )		Orientation energy (KJ mol <sup>-1</sup> )	H-bond energy (KJ mol <sup>-1</sup> )	n	K <sub>f</sub>	ΔG (KJ mol <sup>-1</sup> )
	pure Solvent	pure EtOH					
DMF-EtOH (DMF)	57.2 ± 0.11	60.85 ± 0.09	0.65 ± 0.05	1.85 ± 0.07	1 ± 0.01	10 ± 0.03	1.25 ± 0.011
		(EtOH)					


**Figure 1.** Log  $(A - A_{\min}/A_{\max} - A)$  versus log  $C_{\text{EtOH}}$  for compound 5b in DMF — EtOH mixture at 27°C.

stability constant ( $K_f$ ) of the complex can be determined from a consideration of the behaviour<sup>16-19</sup> in the mixed solvents applied using the previously applied relationship (1)<sup>18,19</sup>.

$$\text{Log } K_f = \text{Log} \frac{A - A_{\min}}{A_{\max} - A} - n \text{ log } C_{\text{EtOH}} \quad (1)$$

(where  $A$  is the absorbance,  $A_{\min}$  and  $A_{\max}$  are the low and high absorbance and  $C$  is the concentration of the solute and ethanol).

The value of  $K_f$  the H-bonded molecular complex liable to form in solution between the molecules of compound 5b and EtOH is equal to  $k_f = 10$  (table 5). The values of  $K_f$  and  $n$  (the number of EtOH molecules which are complexed with the solute molecule) indicate that a 1:1 complex is formed in solution between solute and ethanol molecules, figure 1.

The plot of  $\Delta\bar{\nu}$  of the longer wavelength band as a function of  $(D-1)/(D+1)^{20}$  for compound **5b** is nonlinear. Therefore, the CT band shift is governed by other factors in addition to the dielectric constant of the medium<sup>21</sup>. These factors include solute-solvent interaction (figure 2).

On drawing the excitation energy  $E$  of the CT band in the mixed solvent versus the ethanol mole fraction for compound **5b**, a broken line with three segments is obtained. The first segment indicates the orientation of the molecules around the solute molecules. The second one represents molecular complex formation while, the third segment represents the steady state of the energy attained after the complete formation of the molecular complex, figure 3. Evidence for hydrogen-bond formation between the solute molecules and ethanol can be obtained from data on the free energy change of formation ( $\Delta G$ ) molecular complex, calculated using the relationship (2).

$$\Delta G = -RT \ln K_f \quad (2)$$

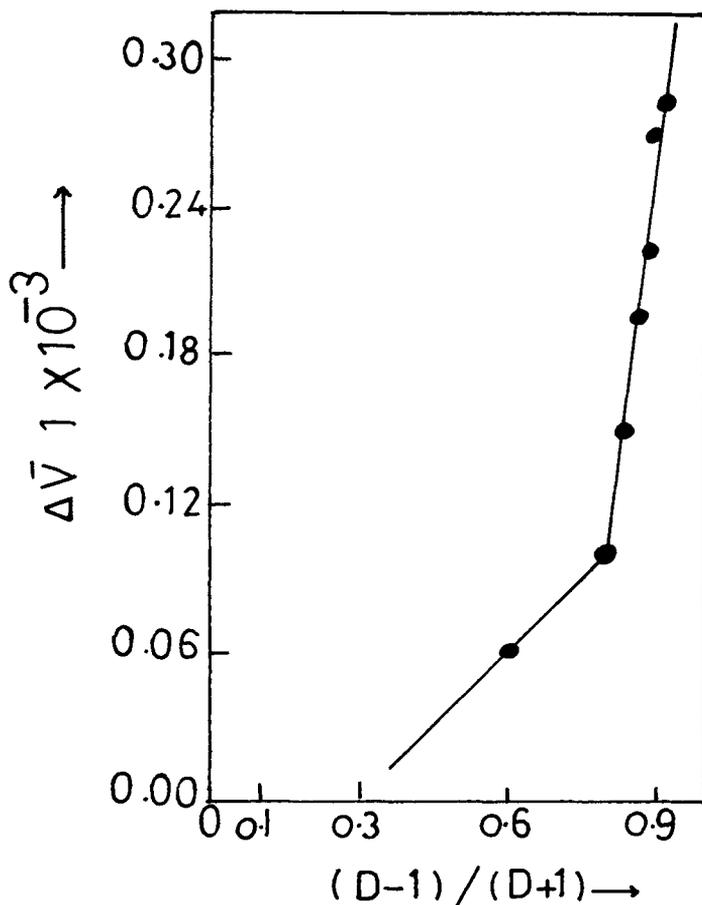
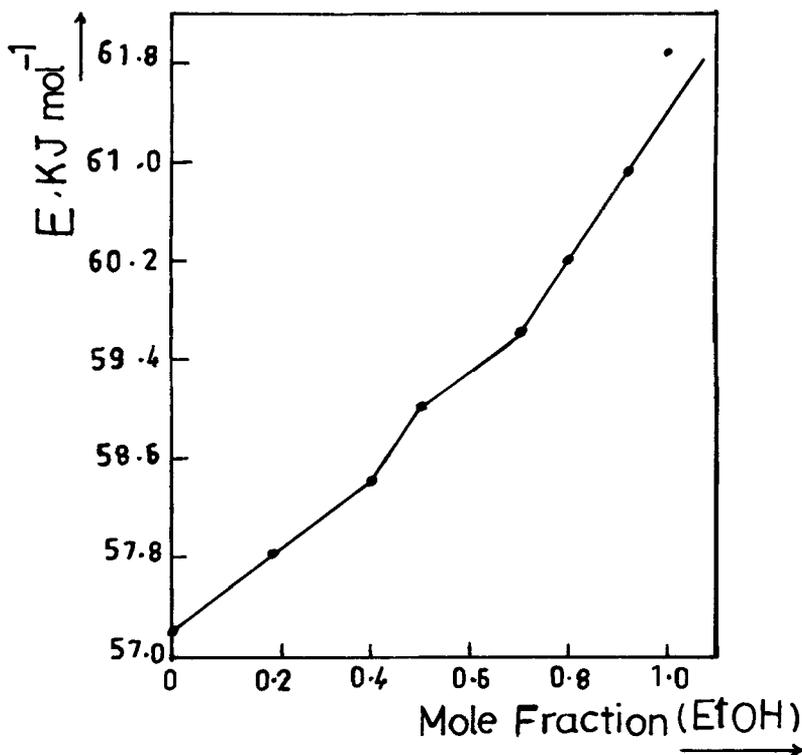


Figure 2. CT band shifts ( $\Delta\bar{\nu}$ ) versus  $(D-1)/(D+1)$  for compound **5b** in DMF—EtOH mixture at 27°C.

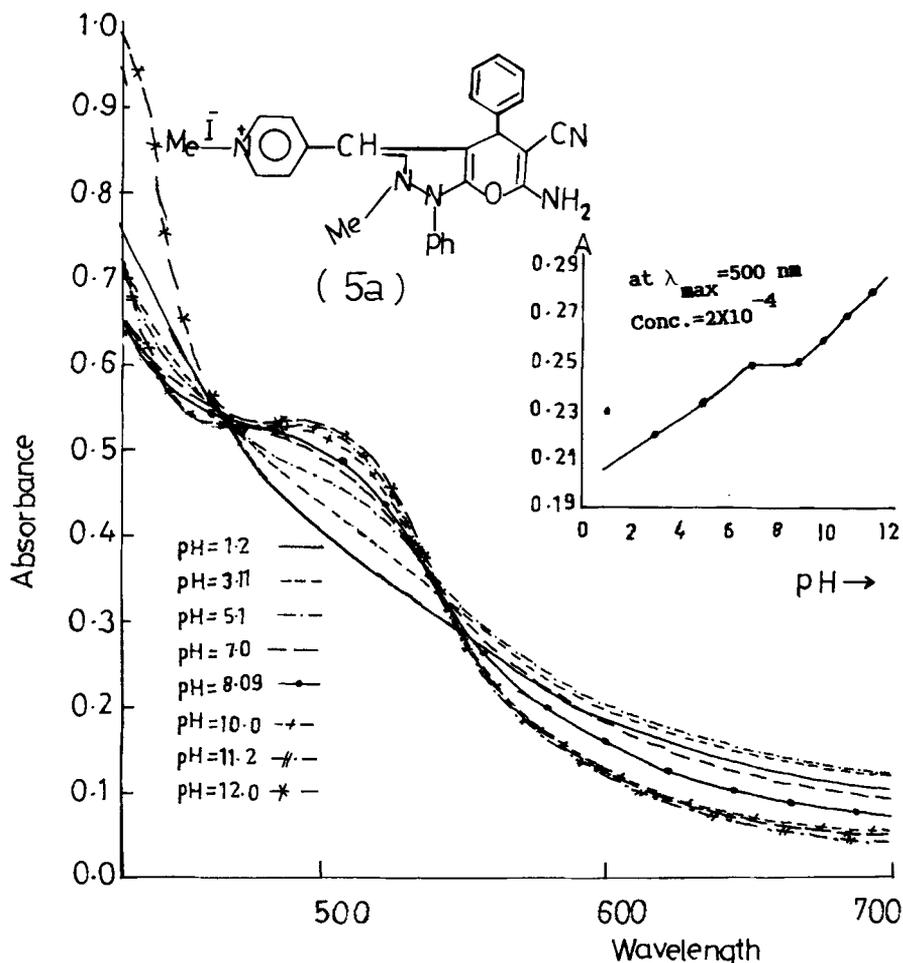


**Figure 3.** CT band excitation energy ( $E$ ) versus EtOH mole fraction for compound **5b** in DMF — EtOH mixture at 27°C.

#### 2.4 Acid base properties of some selected new asymmetrical mono- (tri)-methine cyanine dyes **5a**, **5b** and **7b** in aqueous universal buffer solutions

The solution of some selected mono-(tri)-methine cyanine dyes give a permanent colour in the basic medium which discharged on acidification. This prompted us to study the spectral behaviour of these three compounds in aqueous universal buffer solution in order to ensure the optimal  $pH$  in the application of these dyes as photosensitisers. The effectiveness of the compounds as photosensitisers increases when they are present in the ionic form, which has a higher planarity.

The electronic absorption spectra of cyanine dyes (**5a**, **5b**) and **7b** in aqueous buffer solutions of varying  $pH$ s (1.3–12.0) show regular changes with the increasing  $pH$  of the medium, especially the CT bands. Increasing the  $pH$  of the medium results in increased absorbance of the CT bands. As the  $pH$  of the medium decreases, the extinction of the bands becomes lower for the two compounds **5b** and **7b** at  $pH = 1.3$ . This behaviour can be interpreted on the principle of acidic character for the two compounds **5b** and **7b** which leads to the pyrano-oxygen and/or N-methylpyrazole resistance to the protonation in solution at low  $pH$  values i.e., the CT bands slightly affected by lower  $pH$  values. Meanwhile, for compound **5a**, the extinction band disappears at  $pH < 3.01$ . This behaviour can be attributed to the fact that the pyrano-oxygen and/or



**Figure 4.** Absorption spectra of monomethine cyanine dye 5b in aqueous universal buffer solutions of various pH values at 27°C.

N-methyl pyrazole becomes protonated and therefore, the CT interaction within the protonated form is to be difficult, i.e., the protonated form does not absorb energy in the visible region. On the other hand, as the pH of the medium increases, the pyrano-oxygen and/or N-methyl pyrazole becomes deprotonated and, therefore, its mesomeric interaction with the rest of the molecule is intensified. Consequently, the CT interaction within the free base is facilitated, i.e. the free base absorbs energy in the visible region (figure 4). The recorded visible absorption spectra of compounds 5a,b and 7b in aqueous buffer solutions of varying pHs were applied to the spectrophotometric determination of the  $pK_a$  value. The absorbance pH curve is a typical dissociation constant and ( $pK_a$ ) was determined from the variation of absorbance with pH using the spectrophotometric half-height, limiting absorbance and Colleter methods<sup>22-24</sup>.

### 3. Experimental

#### 3.1 General

All melting points are uncorrected. IR spectra (KBr) were determined on a Perkin-Elmer infrared 127B spectrophotometer. The electronic absorption spectra were recorded on a Shimadzu UV/VIS recording spectrophotometer UV-240; and the  $^1\text{H-NMR}$  on an EM-390 90 MHz NMR spectrometer.

3.2 *6-Amino-5-cyano-3-methyl-1,4-diarylpyrano[2,3-c]pyrazole derivatives (3a-c) were prepared in a way similar to that described earlier<sup>12</sup>.*

Stock solutions of the dyes ( $1.0 \times 10^{-3}$  M) were prepared. The solutions used in spectral measurements were obtained by appropriate dilution. For mixed-solvent studies, an accurate volume of  $1.0 \times 10^{-3}$  M ethanolic solution of the dye was added to the required volume of ethanol and the solution made up to 10 ml with the other solvent (DMF). For pH studies, an accurate volume of  $1.0 \times 10^{-3}$  M-ethanolic solution in a 10 ml measuring flask and a modified buffer series derived from that Britton<sup>25</sup> were used.

3.3 *Synthesis of 6-amino-5-cyano-3-methyl-1,4-diarylpyrano[2,3-c]pyrazolium-2-yl-salt (4a-c)*

Excess iodomethane was added to compounds (3a-c). The reaction mixture was refluxed for 3–5 h on a water bath and the precipitate which formed was filtered, washed by ether, triturated with ethanol by refluxing, filtered hot, concentrated and cooled. The products which precipitated after dilution with water collected and crystallised from ethanol. Characterisation data for them are given in table 1, part I.

3.4 *Synthesis of 6-amino-5-cyano-1,4-diarylpyrano[2,3-c]-N-methyl-pyrazolo-3-yl[4(1)]-monomethine cyanine dyes (5a-e)*

Equimolar amounts of compounds (4a-c) and 1-methyl pyridinium, (-quinolinium and/or-isoquinolinium) iodide (0.01 mol) were dissolved in ethanol (30 ml), and piperidine (3–5 drops) was added. The reaction mixture was refluxed for 10–12 h, filtered hot, concentrated and cooled. The products were precipitated on dilution with water and were crystallised from ethanol to give (5a-e). Relevant data for them are given in table 1, part II.

3.5 *Synthesis of asymmetrical 6-amino-5-cyano-1,4-diarylpyrano[2,3-c]N-methyl-pyrazole-3-yl[2(4)]-trimethine cyanine dyes (7a-e)*

#### *Method A*

A mixture of (4a-c) (0.01 mol) and equimolar ratios of triethoxymethane (0.01 mol) in ethanol (25 ml) and piperidine (3–5 drops) were refluxed for 4–6 h. The reaction mixture was filtered hot, concentrated and cooled. The products were precipitated with water, filtered, washed with water and crystallised from ethanol to give the compounds (6a-c). Characterisation data are shown in table 1, part III.

#### *Method B*

A mixture of (6a-c) (0.01 mol) and the appropriate 2(4)-methylsubstituted heterocyclic quaternary salts  $\alpha, \gamma$ -picoline and/or quinaldine ethyl iodide (0.01 mol) in ethanol

(30 ml) and piperidine (4–6 drops) were refluxed for 8–10 h. The products were then separated in a similar manner as that described for earlier experiments. Relevant data for the compounds thus obtained are given in table 1, part III.

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