Dyes and Pigments **12** (1990) 77–96

Synthesis of some New Solvatochromic β(γ)-Substituted Cyanine Dyes

Ahmed I. M. Koraiem

Chemistry Department, Aswan Faculty of Science, Aswan, Egypt

(Received 30 September 1988; accepted 18 November 1988)

ABSTRACT

New asymmetrical β-substituted dimethine cyanines, β-substituted bis(styryl) cyanines, γ-ketostyryl cyanines and β-substituted aza bis(styryl) cyanines are prepared. The new cyanines were identified by spectral determination and the solvatochromic behaviour of selected cyanines was investigated and their ionization constants determined.

1 INTRODUCTION

Styryl cyanine dyes find extensive application as photosensitizers for silver halide emulsions,[1] textile dyes[2] and as bactericidal agents.[3] Some of these dyes are growth inhibitors to bacteria[4] and to the mitosis of fertilized sea urchin eggs.[5] They possess hormonal effects on plant growth.[6] The mutagenic and developmental effects of styryl and aza analogues of cyanine dyes have been investigated[7] and also the effect of both analogues on breaking the period of dormancy in cloves of garlic CVS.[7] The compounds are potent mitodepressive and mutagenic agents and the aza analogues are more effective than the styryl types.[7,8] The dyes were found to display a structure–activity relationship with regard to cytological effects.

In this present work, some new asymmetrical β-substituted dimethine cyanines, β-substituted bis(styryl), γ-ketostyryl and β-substituted aza bis(styryl) cyanines were prepared, in order to study their spectral and solvatochromic behaviour with respect to their exhibiting possible photosensitization behaviour. The absorption spectra in buffer solution

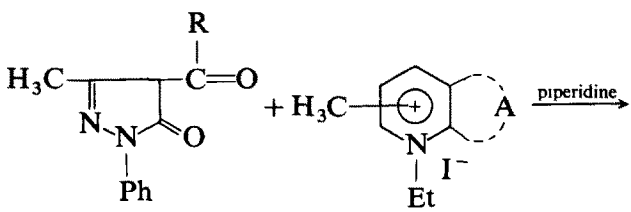
Dyes and Pigments 0143-7208/89/$03·50

have been utilized for the determination of the acid dissociation constants for some of the compounds in order to permit selection of a suitable pH for the compounds to be applied as photosensitizers.

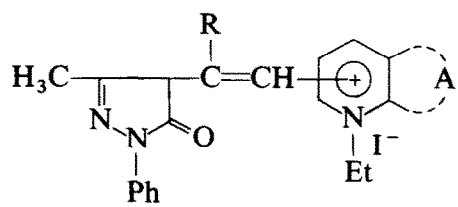
2 RESULTS AND DISCUSSION

4-Acetyl-, 4-trifluoroacetyl and 4-benzoyl-3-methyl-1-phenyl-2-pyrazolin-5-one (**2a–2c**), starting materials for the synthesis of the desired cyanine dyes, were prepared by fusion of pyrazolone with acetamide,[9] trifluoroacetamide or benzamide, respectively, followed by hydrolysis. The interaction of equimolar amounts of **2a–2c** with 2(4)-methyl quaternary salts, such as the 1-ethyl-2-methylpyridinium-2-yl salt, the 1-ethyl-2-methyl quinolinium-2-yl salt and the 1-ethyl 4-methyl pyridinium-4-yl salt in the presence of piperidine as catalyst, afforded the corresponding asymmetrical β-substituted dimethine cyanines **3a–3e** (Scheme 1). The structure of these compounds was established by microanalyses and by IR and ^{1}H-NMR data.

The asymmetrical β-substituted dimethine cyanines **3a–3e** were reddish-violet to intense violet and were soluble in polar organic solvents and in conc. sulphuric acid, from which iodine was liberated on heating. They exhibited a strong green fluorescence in solution, depending on the substituents, and their ethanolic solutions were yellow in acidic medium,



2a–2c



3a–3e

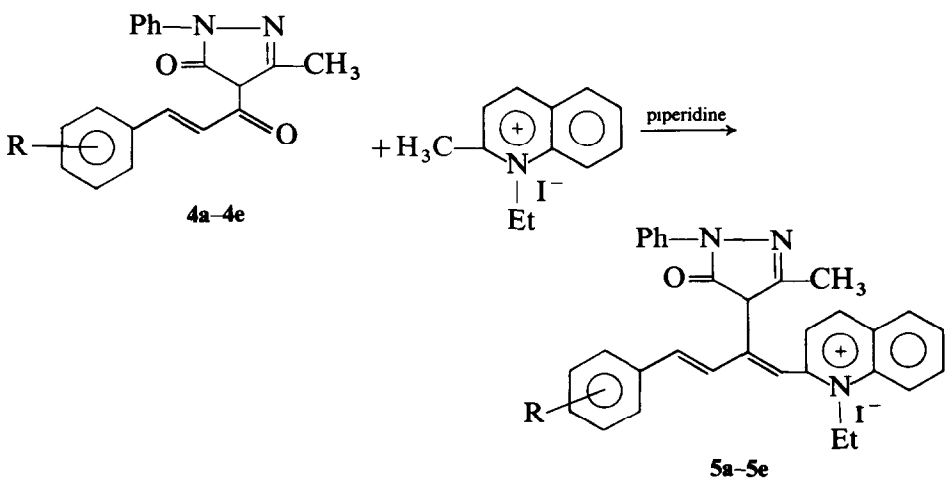
a R = CH_3, A = 1-ethylpyridinium-2-yl salt;
b R = CH_3, A = 1-ethylquinolinium-2-yl salt;
c R = CH_3, A = 1-ethylpyridinium-4-yl salt;
d R = CF_3, A = 1-ethylquinolinium-2-yl salt;
e R = C_6H_5, A = 1-ethylquinolinium-2-yl salt.

Scheme 1

turning violet on making alkaline. This reversible colour change indicates their possible use as acid–base indicators in protometric titrations.

The visible absorption spectra of **3a–3e** in 95% ethanol showed several bands, the position and molar extinction coefficients of which were influenced by the nature of the heterocyclic quaternary residue (A). Thus, compound **3a** (R = CH_3, A = 1-ethylpyridinium-2-yl salt) had λ_{max} at 485 and 590 nm (ε_{max} 2120, 860 mol^{-1} cm^2), whilst replacing the 1-ethylquinolinium-2-yl salt moiety for A (**2b**) resulted in an increase in the number and intensity of the absorption bands (λ_{max} 480, 508 and 555 nm; ε_{max} 6360, 7200, 5340 mol^{-1} cm^2). Absorption maxima, λ_{max}, were also influenced by changes in the β-substituents (R). Thus, where R = CF_3 (compound **3d**) a blue shift of 33–80 nm in the CT band occurred (R = CF_3, A = 1-ethylquinolinium-2-yl salt, λ_{max} 365 and 475 nm, ε_{max} 9120 and 16 000 mol^{-1} cm^2), this shift being attributable to the electron-accepting character of the fluorine atoms. Where R = C_6H_5 a slight blue shift of 28–55 nm (**3e** R = C_6H_5, A = 1-ethylquinolinium-2-yl salt), λ_{max} 480 and 500 nm, ε_{max} 26 700 and 26 580 mol^{-1} cm^2) compared with **3b** (Table 1).

In previous investigations, interaction of **2a** with equimolar amounts of benzaldehyde derivatives afforded the corresponding 4-cinnamoyl-3-methyl-1-phenyl-2-pyrazolin-5-one derivatives (**4a–4e**).[9] Interaction of equimolar amounts of **4a–4e** with the 1-ethylquinolinium-2-yl salt in the presence of piperidine as catalyst afforded the corresponding asymmetrical β-substituted bis(styryl) cyanines **5a–5e** (Scheme 2). The structures of compounds **5a–5e** were assigned on the basis of microanalyses and spectral data.



R = H(**a**), *p*-OCH_3(**b**), *p*-$N(CH_3)_2$(**c**), *p*-NO_2(**d**), *p*-OH(**e**).

Scheme 2

TABLE 1

Characterization Data for β-Substituted Dimethine Cyanine Dyes (**3a–3d**) and Their β-Bis(styryl) Derivatives (**5a–5e**)

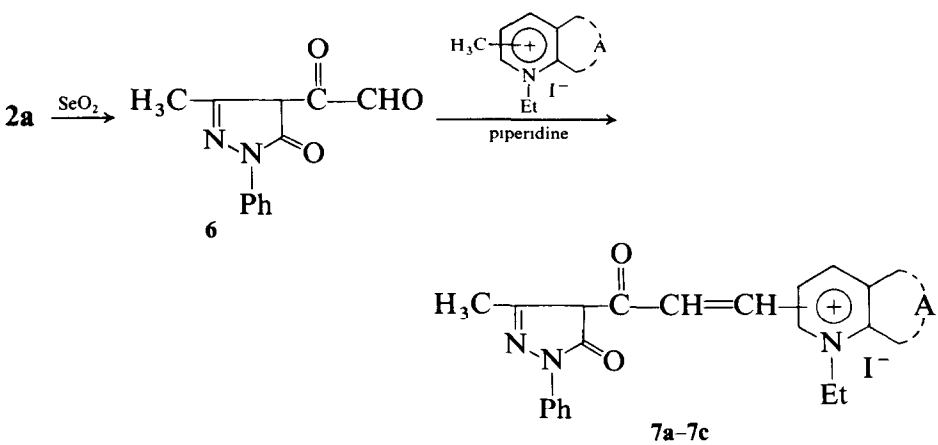
Compd. no.	*M.p.* (°C)	*Yield* (%)	*R*	*Molecular formula* (*M. wt*)	*Nature of products*	*Analysis (%) Calcd (Found)*			*Absorption spectra*	
						C	*H*	*N*	λ_{max} (*nm*)	ε_{max} ($mol^{-1}\,cm^2$)
3a	135	45	CH_3	$C_{20}H_{22}N_3OI$ (447)	Reddish-violet crystals	53·7	4·9	9·4	485	(2 120)
						(53·75)	(5·0)	(9·5)	590	(860)
3b	125	67	CH_3	$C_{24}H_{24}N_3OI$ (497)	Intense violet crystals	57·95	4·8	8·45	480	(6 360)
						(58·0)	(5·0)	(8·7)	508	(7 200)
									555	(5 340)
3c	165	48	CH_3	$C_{20}H_{22}N_3OI$ (447)	Brownish-violet crystals	53·7	4·9	9·4	390	(6 040)
						(53·8)	(5·1)	(9·6)	470	(6 800)
3d	112	70	CF_3	$C_{24}H_{21}N_3OIF_3$ (589·8)	Intense violet crystals	52·4	3·8	7·6	365	(9 120)
						(52·5)	(3·9)	(7·8)	475	(16 000)
3e	100	65	C_6H_5	$C_{29}H_{26}N_3OI$ (559)	Intense violet crystals	62·25	4·65	7·5	480	(26 700)
						(62·4)	(4·8)	(7·75)	500	(26 580)
5a	115	55	H	$C_{31}H_{28}N_3OI$ (585)	Intense violet crystals	63·6	4·8	7·2	390	(3 000)
						(63·7)	(4·9)	(7·2)		
5b	152	63	*p*-OCH_3	$C_{32}H_{30}N_3O_2I$ (615)	Intense violet crystals	62·4	4·9	6·8	415	(5 200)
						(62·6)	(4·95)	(6·9)	438	(5 800)
									485	(3 820)
									545	(2 100)
5c	145	45	*p*-$N(CH_3)_2$	$C_{33}H_{33}N_4OI$ (628)	Intense violet crystals	63·1	5·25	8·9	515	(2 960)
						(63·1)	(5·4)	(9·1)	555	(3 800)
5d	175	68	*p*-NO_2	$C_{31}H_{27}N_4O_3I$ (630)	Intense violet crystals	59·05	4·3	8·9	515	(11 760)
						(59·3)	(4·4)	(9·0)	580	(9 600)
5e	154	70	*p*-OH	$C_{31}H_{28}N_3O_2I$ (601)	Intense violet crystals	61·9	4·7	7·0	380	(3 240)
						(62·0)	(4·75)	(7·0)	500	(4 600)

These asymmetrical β-substituted bis(styryl) cyanines had a characteristic intense violet colour and were soluble in polar organic solvents and in conc. sulphuric acid, from which iodine was liberated on heating. They exhibited strong green fluorescence in solution. An unusual feature of the bis(styryl) cyanines substituted by a methoxy or hydroxy group was the formation of a red colour in alkali and an orange colour in acid, these colours being interchangeable, with discharge at pH 3·2.

The position and molar estimation coefficients of the λ_{max} of **5a–5e** in 95% ethanol were influenced by the nature of the aryl substituent (R). Thus **5a** (R = H) had λ_{max} at 390 nm (ε_{max} 3000 mol^{-1} cm^2). Substitution by the electron-donating substituent, e.g. *p*-OCH_3, *p*-$N(CH_3)_2$ and *p*-OH components (**5b**, **5c**, and **5e**) for R increased the number and intensity of the bands (Table 1). Introduction of the electron-withdrawing *p*-NO_2 group caused a slight blue shift of 10 nm relative to that of **5a**.

Selective oxidation of **2a** with SeO_2 in ethanol[10] gave the corresponding 3-methyl-1-phenyl-2-pyrazolin-5-one-4-glycosal (**6**) which on condensation with a 2(4)-methyl quaternary salt gave the γ-ketostyryl cyanines **7a–7c** (Scheme 3). The structures of these compounds was confirmed by microanalysis and by IR and ^{1}H-NMR data.

The asymmetrical γ-ketostyryl cyanines **7a–7c** had colours ranging from reddish-violet to intense violet and were soluble in polar organic solvents, exhibiting an intense green fluorescence. They were soluble in conc. sulphuric acid from which iodine was liberated on heating. Their ethanolic solution gave a yellow colour in acidic medium which turned violet on basification.



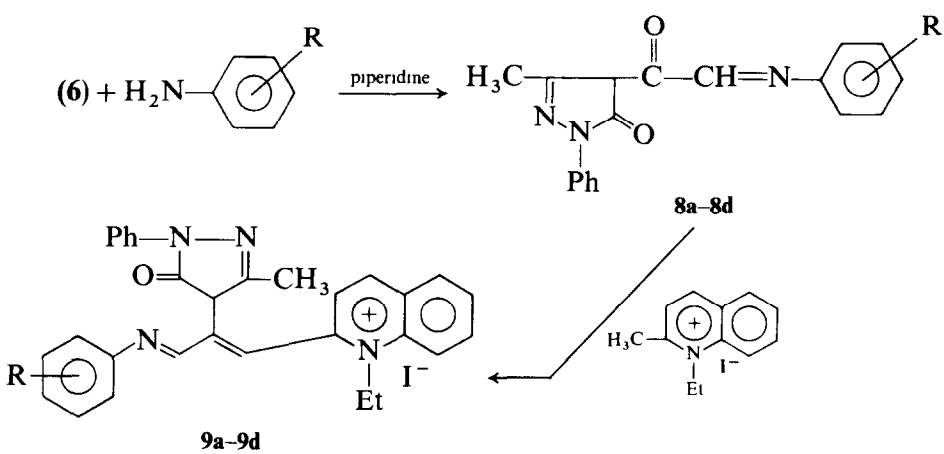
A = 1-ethylpyridinium-2-yl salt(**a**), 1-ethylquinolinium-2-yl salt(**b**), 1-ethylpyridinium-4-yl salt(**c**)

Scheme 3

The absorption bands in the electronic spectra of **7a–7c** in 95% ethanol also underwent bathochromic or hypsochromic shifts depending on the nature of the heterocyclic quaternary residue (A), the bands becoming more intense and showing a strong red shift with increase in the conjugation of A. Thus, **7a** (A = 1-ethylpyridinium-2-yl salt) had λ_{max} at 370 and 475 nm (ε_{max} 8800 and 7760 mol^{-1} cm^2). Replacing the pyridyl nucleus by quinoline (compound **7b**) caused a strong red shift of 33 nm (λ_{max} 375 and 508 nm; ε_{max} 4600 and 9800 mol^{-1} cm^2). A similar behaviour was also shown by **7c** (A = 1-ethylpyridinium-4-yl salt), λ_{max} 365 and 490 nm (ε_{max} 5000 and 6400 mol^{-1} cm^2) (Table 2).

Compound 6 reacted with primary aromatic amines to give the corresponding 4-glycosylidene arylamine derivatives (**8a–8d**). The interaction of equimolar amounts of **8a–8d** with a 1-ethylquinolinium-2-yl salt in the presence of piperidine as catalyst afforded the corresponding asymmetrical β-substituted aza bis(styryl) cyanines **9a–9d** (Scheme 4) which had similar colour to the bis(styryl) cyanines **5a–5e.** Their ethanolic solutions were violet with a blue fluorescence in alkali, changing to yellow with a green fluorescence on acidification.

As with **5a–5e**, the λ_{max} of **9a–9e** in 95% ethanol also underwent a bathochromic or hypsochromic shift depending on the nature of the substituent R, e.g. λ_{max} at 510, 550 and 580 (sh) nm (ε_{max} 10 000, 8320 and 6000 mol^{-1} cm^2) for **9a** (R = H); λ_{max} 465, 500, 530 and 640 nm (ε_{max} 13 360, 11 520, 9200 and 550 mol^{-1} cm^2) for **9b** (R = *p*-OCH_3); λ_{max} 365, 515, 550, 570 and 690 nm (ε_{max} 8200, 7320, 6840, 5500 and 1320 mol^{-1} cm^2) for **9c** (R = *p*-NO_2); and λ_{max} 440, 523 (sh) and 565 nm (ε_{max} 6800, 9120 and



R = H(**a**), *p*-OCH_3(**b**), *p*-NO_2(**c**), *p*-OH(**d**)

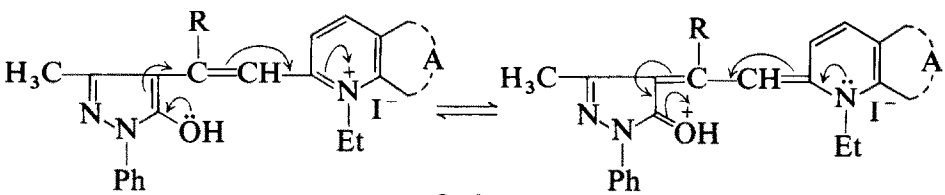
Scheme 4

16 600 mol^{-1} cm^2) for **9d** (R = *p*-OH) (Table 2). Comparison of the spectra of **5a–5e** and **9a–9d** shows that the aza bis(styryl) cyanines **9a–9d** show red shifts with more intense absorption compared with **5a–5e**.

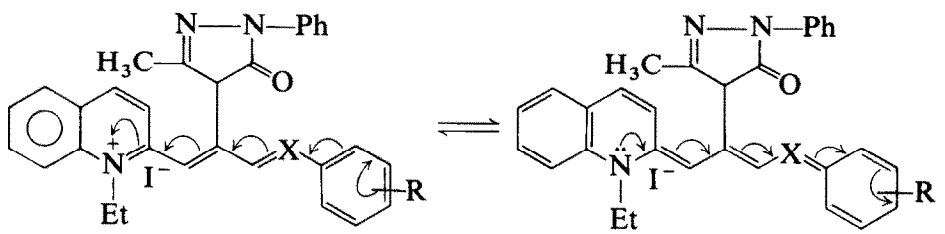
The charge transfer band exhibits lower excitation energy in protic solvents such as ethanol, isobutanol and $CHCl_3$ relative to aprotic solvents such as DMF (Table 3). This is relatable to the differences in stabilization of both the ground and excited states by hydrogen bonding interaction with the protic solvents, since there is no difference in the polarity of the ground and excited states of the compounds.

The visible bands observed in the spectra of selected dyes (**3a–3c**, **5b–5e**, **7b**, **9a–9d**) in ethanol (Table 3) can be interpreted as evidence of the possible existence of these compounds in a mesomeric equilibrium. Thus, the shorter- and longer-wavelength bands can be ascribed to an intramolecular CT transition occurring within the two mesomeric structures. This is confirmed by solvent effects on the visible spectra of the compounds. Generally, it is observed that increase in solvent polarity in the sequence $CHCl_3 \rightarrow$ ethanol $\rightarrow$ isobutanol $\rightarrow$ DMF results in an increase in the extinction of the longer-wavelength band. Such mesomeric structures can be represented as shown in Scheme 5. Evidence for the existence of these compounds in mesomeric equilibrium is provided by the well-defined isobestic point observed on studying the dependence of the visible spectra of the compounds in ethanol with changes in the water content (Fig. 1).

However, the unexpected blue shift observed in the λ_{max} at the longer-wavelength visible band, as well as the lower extinction on increasing the water content in ethanol, can be mainly ascribed to the possible interaction of water molecules with the lone pair of electrons of the OH group resulting



3a–3e



5a–5e, X = C; **9a–9e**, X = N

Scheme 5

TABLE 2

Characterization Data for γ-Ketostryryl Cyanines (**7a–7c**), 4-Glycosylidene Derivatives (**8a–8d**) and β-Substituted Aza Bis(styryl) Cyanines (**9a–9d**)

Compd. no.	*M.p.* (°C)	*Yield* (%)	*R*	*Molecular formula* (*M. wt*)	*Nature of products*	*Analysis (%) Calcd (Found)*			*Absorption spectra*	
						C	*H*	*N*	λ_{max} (*nm*)	ε_{max} ($mol^{-1}\,cm^2$)
7a	157	72	—	$C_{20}H_{22}N_3O_2I$ (463)	Reddish-violet crystals	51·8	4·75	9·1	370	(8 800)
						(52·0)	(4·9)	(9·2)	475	(7 760)
7b	178	75	—	$C_{24}H_{24}N_3O_2I$ (513)	Intense violet crystals	56·1	4·7	8·2	375	(4 600)
						(56·3)	(4·8)	(8·3)	508	(9 800)
7c	160	65	—	$C_{20}H_{22}N_3O_2I$ (463)	Brownish-violet crystals	51·8	4·75	9·1	365	(5 000)
						(51·9)	(4·85)	(9·15)	490	(6 400)
8a	150–152	45	H	$C_{18}H_{15}N_3O_2$ (305)	Deep brown needles	70·8	4·9	13·8	—	
						(70·95)	(5·1)	(13·9)	—	
8b	145	48	p-OCH_3	$C_{19}H_{17}N_3O_3$ (335)	Pale violet crystals	68·1	5·1	12·5	—	
						(68·2)	(5·2)	(12·7)	—	

8c	195–197	57	*p*-NO_2	$C_{18}H_{14}N_4O_4$ (350)	Brownish violet crystals	61·7	4·0	16·0	—	
						(61·9)	(4·1)	(16·1)	—	
8d	180	52	*p*-OH	$C_{18}H_{15}N_3O_3$ (321)	Intense violet needles	67·3	4·7	13·1	—	
						(67·4)	(4·8)	(13·3)	—	
9a	166	40	H	$C_{30}H_{27}N_4OI$ (586)	Reddish-violet needles	61·4	4·6	9·6	510	(10 000)
						(61·5)	(4·8)	(9·7)	550	(8 320)
									580 sh	(6 000)
9b	190	45	*p*-OCH_3	$C_{31}H_{29}N_4O_2I$ (616)	Intense violet crystals	60·4	4·7	11·4	465	(13 360)
						(60·55)	(4·9)	(11·45)	500	(11 520)
									530	(9 200)
									640	(550)
9c	172	52	*p*-NO_2	$C_{30}H_{26}N_5O_3I$ (531)	Brownish-violet needles	57·05	4·1	11·1	365	(8 200)
						(57·2)	(4·2)	(11·2)	515	(7 320)
									550	(6 840)
									570	(5 500)
									690	(1 320)
9d	148–149	50	*p*-OH	$C_{30}H_{27}N_4O_2I$ (602)	Intense violet crystals	59·8	4·5	9·3	440	(6 800)
						(59·95)	(4·6)	(9·45)	523	(9 120)
									565	(16 600)

TABLE 3
Absorption Spectra of $\beta(\gamma)$-Substituted Cyanines in Different Solvents[a]

Compd no.	*Ethanol* $\lambda(\varepsilon)$	*Isobutanol* $\lambda(\varepsilon)$	*$CHCl_3$* $\lambda(\varepsilon)$	*DMF* $\lambda(\varepsilon)$
3a	480 (6 300)	480 (5 800)	480 (3 460)	—
	505 (7 180)	510 (6 960)	508 (3 840)	505 (5 800)
	555 (6 320)	555 (4 740)	559 (2 000)	557 (3 900)
3b	475 (1 600)	375 (6 800)	405 (6 820)	385 (5 440)
	—	488 (9 020)	475 (4 520)	—
	—	—	507 (4 300)	505 (9 040)
3c	—	393 (5 960)	400 (9 520)	390 (5 750)
	480 (26 700)	475 (6 720)	485 (12 280)	475 (7 600)
	500 (26 580)	505 (9 000)	510 (12 760)	505 (9 000)
5b	415 (4 200)	440 (3 200)	425 (8 760)	415 (9 120)
	435 (5 780)	455 (3 000)	452 (9 600)	440 (9 520)
	485 (3 840)	488 (3 100)	482 (9 840)	510 (2 560)
	545 (2 100)	555 (740)	560 (1 880)	550 (2 000)
5c	515 (2 960)	518 (9 540)	520 (13 200)	522 (16 200)
	555 (3 780)	562 (11 940)	560 (18 000)	564 (22 260)
5d	505 (11 520)	485 (14 960)	493 (15 040)	497 (19 600)
	—	520 (15 040)	526 (15 600)	520 (19 040)
	580 (9 600)	585 (14 000)	583 (10 720)	560 (16 080)
	—	—	—	604 (14 320)
5e	380 (3 240)	395 (3 900)	420 (4 040)	395 (7 800)
	500 (4 620)	505 (4 700)	500 (3 760)	508 (8 880)
7b	375 (4 600)	380 (2 520)	410 (7 520)	390 (7 440)
	—	—	490 (6 000)	—
	505 (9 780)	510 (5 480)	515 (5 480)	510 (13 920)
	—	—	593 (2 400)	—
9a	510 (9 960)	518 (13 320)	510 (6 600)	515 (15 420)
	550 (8 320)	560 (11 200)	550 (6 180)	555 (13 920)
	580 (6 000)	—	590 (4 600)	590 (96 000)
9b	465 (13 400)	—	—	400 (11 940)
	500 (11 520)	520 (13 520)	515 (12 200)	515 (19 920)
	530 (9 200)	560 (11 160)	555 (12 400)	553 (18 660)
	—	—	588 (10 680)	590 (14 280)
	640 (2 240)	680 (1 640)	690 (1 920)	695 (3 300)
9c	525 (7 300)	523 (8 000)	480 (8 600)	380 (11 680)
	550 (6 840)	560 (7 360)	522 (10 000)	520 (10 400)
	583 (5 400)	—	558 (10 280)	590 (8 000)
	690 (1 340)	—	590 (8 520)	—
9d	440 (6 800)	445 (7 600)	—	—
	523 (9 120)	570 (19 600)	570 (12 200)	570 (2 000)
	565 (16 600)	670 (2 680)	—	620 (1 400)

[a] Units: λ, nm; ε, $mol^{-1}\ cm^2$.

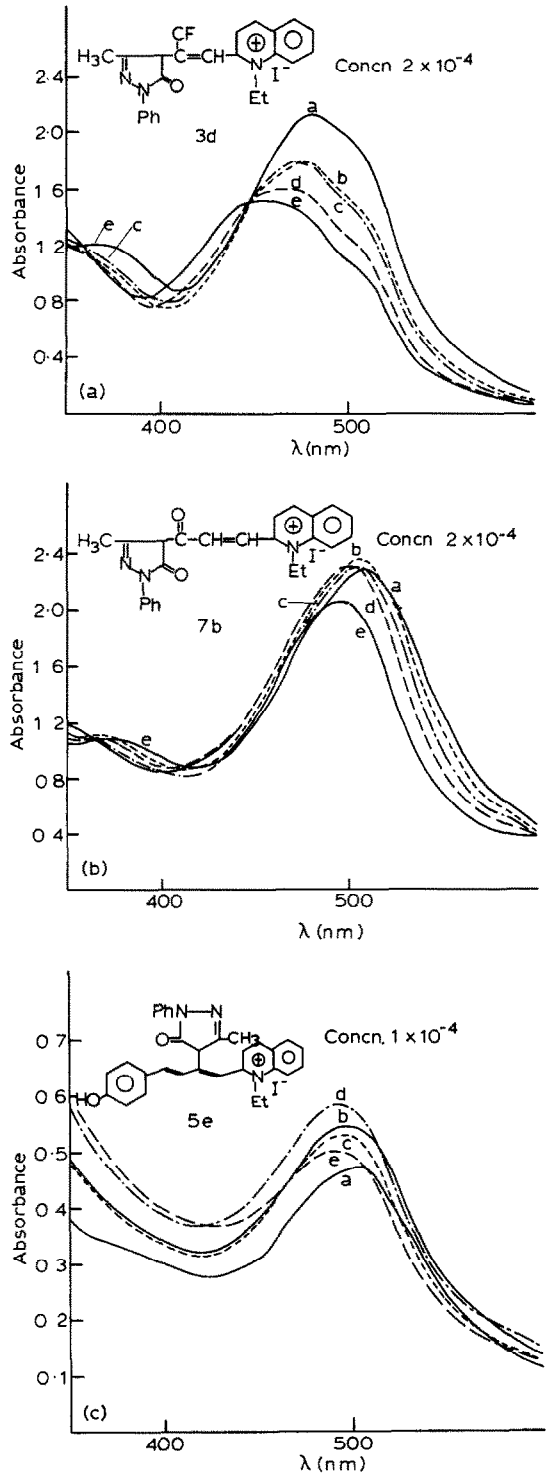


Fig. 1. Electronic absorption spectra of **3d**, **5e** and **7b** in ethanol–water mixtures: a, 0% water; b, 20% water; c, 40% water; d, 60% water; e, 80% water.

from enolization through hydrogen bonding. This results in a more difficult electron transfer from the enolic OH to the heterocyclic quaternary nitrogen as the water content in the medium is increased.

Other evidence for the existence of the compounds in a mesomeric equilibrium is provided by the well-defined isobestic point observed in the spectra in mixed solvents. This is carried out in order to study the hydrogen-bonding solvated complex liable to be formed between the solute molecules and hydrogen bond acceptor solvents. Thus, the visible spectra of compound **3d** in $CHCl_3$ displays two bands (Fig. 2). On adding DMF, the absorbance of the longer-wavelength band (510 nm) is increased as the molarity of DMF is increased, and at the same time the absorbance of the shorter-wavelength band (400 nm) decreases, with a slight blue shift. A fine isobestic point is obtained, indicating the existence of an equilibrium between the solvated complex and the free solute molecules (Fig. 2).

With compound **7b** in $CHCl_3$–EtOH, the absorbance of the longer-wavelength band (515 nm) increases as the molarity of EtOH is increased. At the same time, the absorbance of the shorter-wavelength band (400 nm) decreases with a slight blue shift, and a fine isobestic point is obtained. This behaviour indicates that DMF and EtOH have a greater tendency to form a solvated complex with the solute molecules relative to $CHCl_3$. This is due to the low ionization potential of DMF and EtOH and to the high hydrogen bond accepting character of **7b**.

The charge transfer nature of the transition leading to the band at longer wavelength can be supported by considering the spectral behaviour of the compounds in solutions of varying hydrogen ion concentrations (Fig. 3). It was found that for compounds **3b**, **5e** and **7b**, the band showed largely red shifts in alkaline media. These shifts are mainly due to a relatively increased negative charge density on the enolate OH group in these compounds. On the other hand, the longer-wavelength absorption band of compound **3d** ($R = CF_3$) showed a blue shift in alkali. This shift is due to the high electron accepting character of the CF_3 group, which inhibits charge transfer from the enolate OH group to the positively charged heterocyclic quaternary nitrogen.

Similarly, it was found that in compound **5c** ($R = N(CH_3)_2$) the band showed a red shift in alkaline media, this shift being due to the relatively increased negative charge density on the alkylamino group. This behaviour can be interpreted on the basis that the dialkylamino group becomes protonated in solutions of low pH and CT interaction within the protonated form is difficult. On the other hand, as the pH of the medium increases, the dialkylamino group becomes deprotonated and therefore its mesomeric interaction with the rest of the molecule increases, and consequently, the CT interaction in the free base is facilitated.

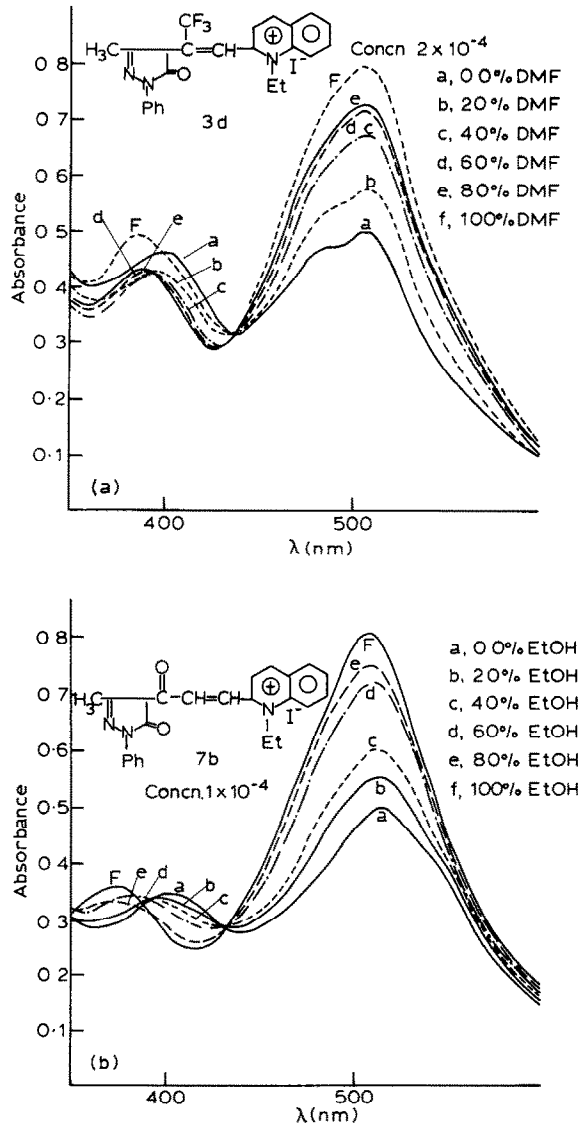


Fig. 2. (a) Electronic absorption spectra of **3d** in $CHCl_3$–DMF mixtures. (b) Electronic absorption spectra of **7b** in $CHCl_3$–ethanol mixtures.

The acid dissociation or protonation constants of selected cyanines (**3b**, **3d**, **5c**, **5d** and **7b**) were determined in order to ensure the optimal pH in the application of these dyes as photosensitizers. The effectiveness of the compounds as photosensitizers increases when they are present in the ionic form, which has a higher planarity. Thus, the absorbance of the CT band in these compounds increases with increasing pH. The variation of absorbance

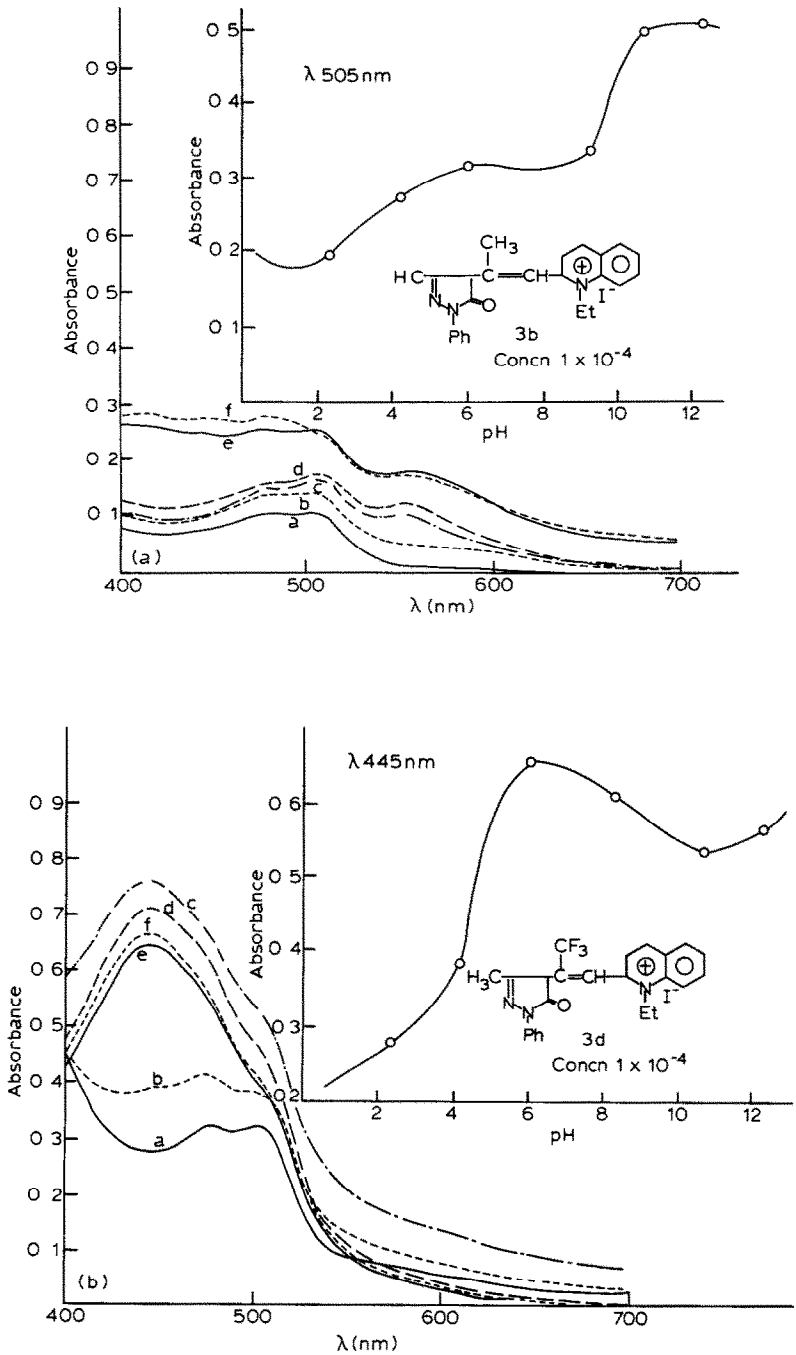
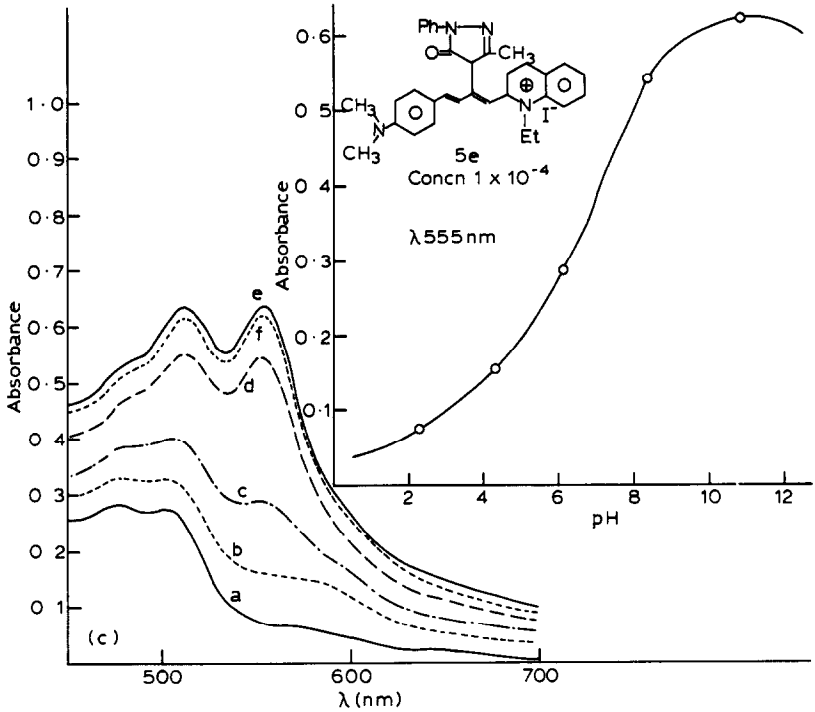


Fig. 3. Electronic absorption spectra of **3b**, **3d**, **5c**, **5e** and **7b** in universal buffers pH 2·30 (a), 4·24 (b), 5·91 (c), 8·17 (d), 10·60 (e) and 12·16 (f).


Absorbance
λ (nm)
(c)
a
b
c
d
e
f
5e
Concn 1 x 10⁻⁴
λ555nm
pH

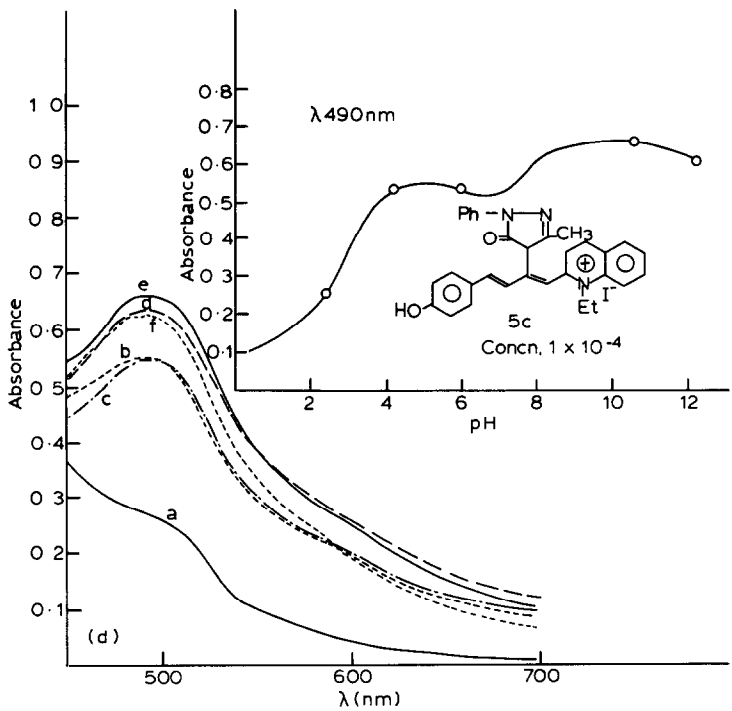

Absorbance
λ (nm)
(d)
a
b
c
d
e
f
λ490nm
5c
Concn. 1 x 10⁻⁴
pH

Fig. 3.—*contd.*

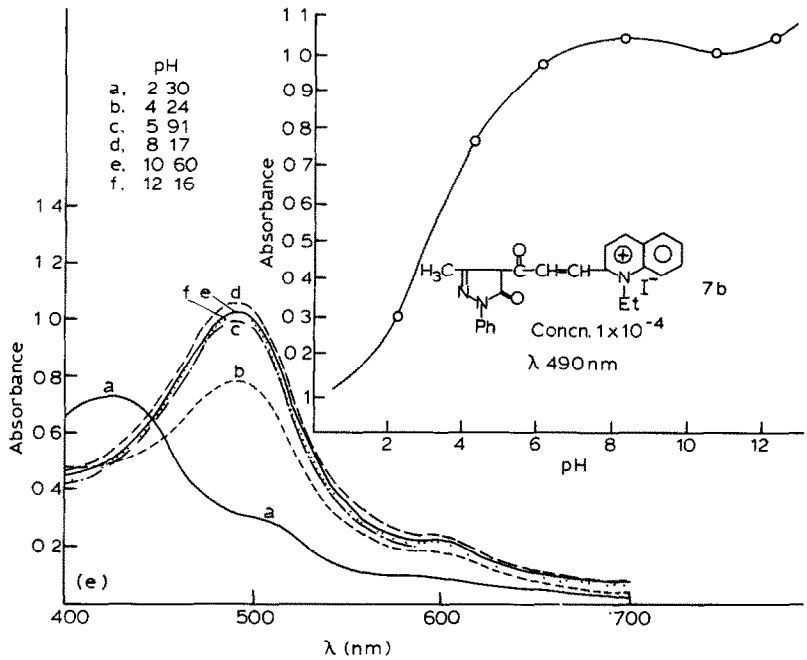


Fig. 3.—*contd.*

with pH can be utilized for the determination of the ionization constant of the organic compounds.[11] By plotting the absorbance at λ_{max} versus pH, S-shaped curves were obtained. The values are listed in Table 4. The horizontal portion of the S-curve corresponds to the acidic form of the compound, whilst the upper portion to the right corresponds to the basic form, since the pK_a is defined as the pH value for which one-half of the compound is in the

TABLE 4
Electronic Spectra[a] at Different pH for Selected $\beta(\gamma)$-Substituted Styryl Cyanines

pH	*Compound*					
	3b	**3d**	**5c**	**5e**	**7b**	**9d**
	λ_{max}					
	505 nm	*445 nm*	*555 nm*	*490 nm*	*490 nm*	*560 nm*
2·30	0·20	0·28	0·08	0·26	0·31	0·06
4·24	0·28	0·39	0·16	0·54	0·78	0·10
5·91	0·32	0·76	0·29	0·54	0·99	0·24
8·17	0·34	0·71	0·55	0·63	1·06	0·25
10·60	0·50	0·64	0·64	0·66	1·02	0·34
12·16	0·51	0·67	0·62	0·62	1·06	0·44

[a] Absorbance values at λ_{max}

basic form and the other in the acidic form. This point is determined by the intersection of the curve with a horizontal line midway between the left and right segments. From Fig. 3, the pK_a values are 3·5, 7·5 and 10·0 for **3b**; 4·5 and 9·0 for **3d**; 7 for **5c**; 3·2 and 8·2 for **5e**; and 4·2 and 9·3 for **7b**.

3 EXPERIMENTAL

3.1 General

Melting points are uncorrected. IR spectra were determined on a Unicam SP1200 spectrophotometer. Absorption spectra were recorded on a Shimadzu UV–Vis 240 recording spectrophotometer and the ^{1}H-NMR spectra on an EM-390 90 MHz NMR spectrometer. 4-Acetyl-3-methyl-1-phenyl-2-pyrazoline-5-one (**2a**) and the 4-cinnamoyl derivatives (**4a–4e**) were prepared according to Ref. 9.

The aqueous universal buffer solutions of pH 2·30–12·20 were prepared as described in Ref. 12, and the pH of the solutions checked at 25°C using an Orion pH-meter model 60/A.

3.2 Trifluoroacetyl- (and benzoyl)-3-methyl-1-phenyl-2-pyrazolin-5-one, 2b and 2c

These compounds were prepared in an analogous manner to **2a.**

*3.2.1 Compound **2b***

Yield 60%, m.p. 120°C.

$C_{12}H_9N_2O_2F_3$ Calcd.: C, 52·4; H, 3·3; N, 10·2.
Found: C, 52·45; H, 3·4; N, 10·2%.

IR(KBr): ν 1740 (C = O), 1560 cm^{-1} (C = N). ^{1}H-NMR ($CDCl_3$/TMS_{int}): δ 1·6 (s, 3H, CH_3), 7·5 (s, 5H, aromatic), 12·21 ppm (s, 1H, enolate OH).

*3.2.2 Compound **2c***

Yield 55%, m.p. 95°C.

$C_{17}H_{14}N_2O_2$ Calcd.: C, 73·4; H, 5·0; N, 10·1.
Found: C, 73·5; H, 5·1; N, 10·1%.

IR (KBr): ν 1730 (C=O), 1540 cm^{-1} (C=N). ^{1}H-NMR ($CDCl_3$/TMS_{int}): δ 1·6 (s, 3H, CH_3), 7·8 (m, 1OH, arom.), 12·20 ppm (s, 1H, enolate OH).

3.3 Asymmetrical β-substituted dimethine cyanines (3a–3e)

Equimolar ratios of **2a–2c** and the appropriate 2-methyl quaternary salts (α-picoline, quinaldine, γ-picoline; 0·01 mol), and piperidine (2 ml) in absolute

ethanol (30 ml) were refluxed for 15–20 h. The precipitated products were filtered and recrystallized from ethanol. Relevant data are given in Table 1.

3.3.1 Compound ***3b***

IR(KBr): ν 3480 (enolate OH), 2940 (heterocyclic quaternary residue), 1600 (C=C), 1520 cm^{-1} (C=N). ^{1}H-NMR ($CDCl_3$/$TMS_{int.}$): δ 7·5 (m, 11H, arom., heter.), 12·21 (enolate OH), 1·6 (s, 6H, $2CH_3$), 3·3 (s, 1H, olefinic), 2·5 (q, 2H, CH_2), 2·2 ppm (t, 3H, CH_3).

3.4 Asymmetrical β-substituted bis(styryl) cyanines (5a–5e)

These were prepared in an analogous manner to that described above for **3a–3e** using 4-cinnamoyl-3-methyl-1-phenyl-2-pyrazolin-5-one (**4a–4e**)[9] and the 1-ethyl-2-methylquinolinium-2-yl salt in place of the 4-acetyl derivatives **2a–2c**. Data on these compounds are given in Table 1.

3.4.1 Compound ***5e***

IR(KBr): ν 3450 (enolate OH), 2930 (heterocyclic quaternary residue), 1710 (C=O), 1600 (conj. C=C), 1520 cm^{-1} (C=N). ^{1}H-NMR ($CDCl_3$/$TMS_{int.}$): δ 7·5 (m, 15H atom., heter.), 12·21 (s, 1H, enolate OH), 1·6 (s, 3H, CH_3), 3·4 (d, 2H, olefinic), 2·5 (q, 2H, CH_2), 2·2 ppm (t, 3H, CH_3).

3.5 3-Methyl-1-phenyl-2-pyrazolin-5-one-4-glycosal (6)

A mixture of **2a** (2·15 g, 0·01 mol) and selenium dioxide (1·13 g, 0·01 mol) in ethanol (20 ml) was refluxed for 10 h. The mixture was filtered, concentrated and the precipitate obtained on cooling was filtered and recrystallized from ethanol (yield 1·5 g, m.p. 120°C).

$C_{12}H_{11}N_2O_3$ Calcd.: C, 62·3; H, 4·8; N, 12·1.
Found: C, 62·5; H, 4·8; N, 12·2%.

IR(KBr): ν 1635 (CHO), 1740 (C=O), 1500 cm^{-1} (C=N). ^{1}H-NMR ($CDCl_3$/$TMS_{int.}$): δ 7·5 (s, 5H, arom.), 1·6 (s, 3H, CH_3), 9·9 (s, 1H, CHO), 12·21 ppm (s, 1H, enolate OH).

3.6 Asymmetrical γ-ketostyryl cyanines (7a–7c)

A solution of **6** 2·31 g, 0·01 mol, the appropriate quaternary salt (α-picoline, quinaldine, γ-picoline; 0·01 mol) and piperidine (2 ml) was refluxed in absolute ethanol (25 ml) for 12–15 h. The products were filtered and recrystallized from ethanol. Results are given in Table 2.

3.6.1 Compound ***7b***
IR(KBr): ν 3440 (enolate OH), 2990 (heter. quaternary residue), 1730 (C=O), 1620 (conj. C=C), 1540 cm^{-1} (C=N). ^{1}H-NMR ($CDCl_3/TMS_{int.}$): δ 7·5 (m, 15H, arom., heter.), 12·20 (s, 1H, enolate OH), 1·7 (s, 3H, CH_3), 3·5 (d, 2H, olefinic), 2·5 (q, 2H, CH_2), 2·3 ppm (t, 3H, CH_3).

3.7 3-Methyl-1-phenyl-2-pyrazolin-5-one-4-glycosylidene arylamine derivatives (8a–8c)

A mixture of **6** (2·31 g, 0·01 mol), the appropriate arylamine (aniline, *p*-anisidine, *p*-nitroaniline, 0·01 mol) and piperidine (2 ml) was refluxed in absolute ethanol (20 ml) for 8–10 h. The mixture was filtered, concentrated and the products filtered and recrystallized from ethanol. Results are summarized in Table 2.

3.7.1 Compound ***8a***
IR(KBr): ν 3490 (enolate OH), 1720 (C=O), 1520 cm^{-1} (C=N). ^{1}H-NMR ($CDCl_3/TMS_{int.}$): δ 7·6 (m, 10H, arom.), 1·6 (s, 3H, CH_3), 3·4 (s, 1H, olefinic), 12·20 ppm (s, 1H, enolate OH).

3.8 Asymmetrical β-substituted aza bis(styryl) cyanines (9a–9d)

These were prepared in an analogous manner to that described for **5a–5e** using the 3-methyl-1-phenyl-2-pyrazolin-5-one-4-glycosylidene arylamine derivatives **8a–8c** and the 1-ethyl-2-methylquinolinium-2-yl salt (equimolar ratios, 0·01 mol) in place of the 4-cinnamoyl derivatives **4a–4e**. Results are given in Table 2.

3.8.1 Compound ***9a***
IR(KBr): ν 3500 (enolate OH), 2940 (heter. quaternary residue), 1710 (C=O), 1620 (conj. C=C), 1520 cm^{-1} (C=N). ^{1}H-NMR ($CDCl_3/TMS_{int.}$): δ 6·95 (m, 16H, arom., heter.), 12·25 (s, 1H, enolate OH), 1·2 (t, 3H, CH_3), 0·95 (s, 3H, CH_3), 3·4 (d, 2H, olefinic), 2·5 ppm (q, 2H, CH_2).

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