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Synthesis and Spectra of Some Asymmetric Trimethine Cyanine Dyes

A. I. M. Koraiem, Z. H. Khalil & R. M. Abu El-Hamd

Chemistry Department, Aswan Faculty of Science, Aswan, Egypt

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ABSTRACT

New asymmetric trimethine cyanine dyes were prepared by condensation of 3-β-acetanilidovinyl derivatives, with 2-methylpyridinium(quinolinium)-2-yl salts. Cyclo-condensation reaction of the dyes with urea gave new asymmetric biheterocyclic trimethine cyanines. The electronic absorption spectra of the dyes in the visible region is reported.

1 INTRODUCTION

Trimethine cyanine dyes have been described as being suitable as light-,[1] and super-photographic,[2] sensitisers for silver halide emulsions, as laser dyes,[3] and as the sensitising panchromatic layers of motion pictures.[4] They can also be used for producing offset printing plates.[5]

The new asymmetric trimethine cyanines (**3a–3e**, **5a–5d**, **7** and **9**) were prepared and a study of their spectral behaviour was made.

2 RESULTS AND DISCUSSION

A selected 4-benzylideno-2-ethyl-3-methyl-1-phenylpyrazolium salt (**1a–1d**) was reacted with diphenyl formamidine in equimolar amounts in the presence of acetic anhydride to give the corresponding 3-β-acetanilidovinyl derivatives (**2a–2d**). Further reaction of **2a–2d** with heterocyclic quaternary salts containing an active methyl group, e.g. 1-ethylpyridinium

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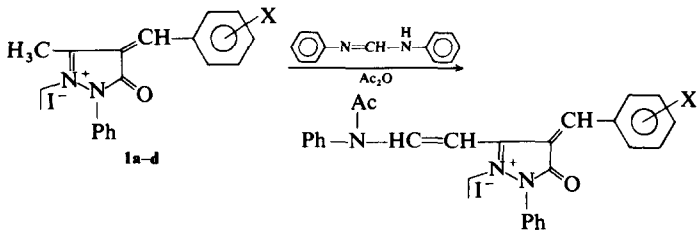
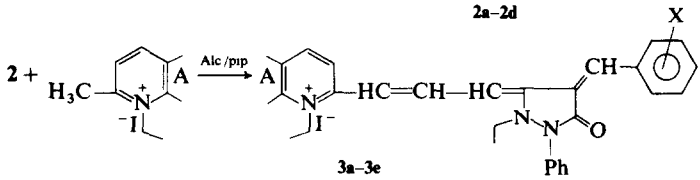
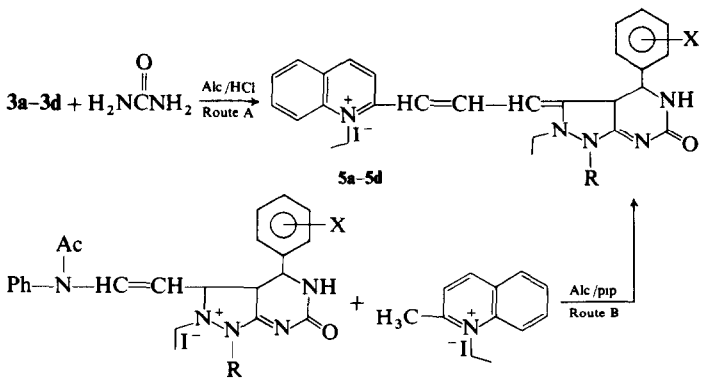
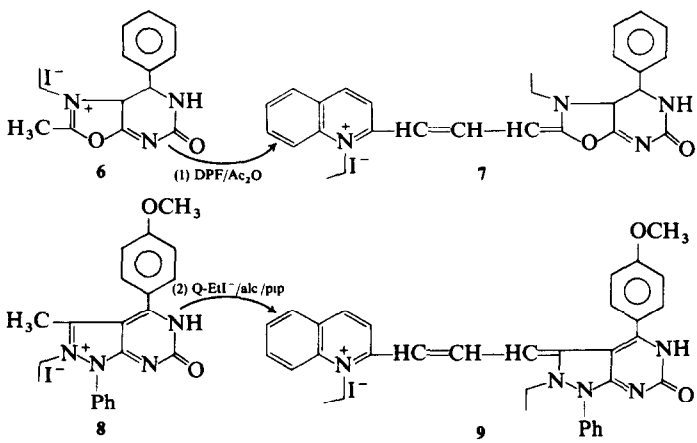




2a–2d: X = H (**a**), *p* – OCH_3 (**b**), *p* – OH (**c**), *o* – OH (**d**)
3a–3e: X = H, A = C_6H_4 – 2-yl salt (**a**)
X = *p*-OCH_3, A = C_6H_4 – 2-yl salt (**b**)
X = *p*-OH, A = C_6H_4 – 2-yl salt (**c**)
X = *o*-OH, A = C_6H_4 – 2-yl salt (**d**)
X = *o*-OH, A = H – 2-yl-salt (**e**)



4a–4d, **5a–5d**: R = H; X = H (**a**), *p* – OCH_3 (**b**), *p*-NO_2 (**c**)
R = Ph; X = *p*-OCH_3 (**d**)



Scheme 1

(quinolinium)-2-yl salts, gave the corresponding asymmetric trimethine cyanines **3a–3e**. The reaction proceeds smoothly due to the high reactivity of 4-benzylideno-2-ethyl-3-methyl-1-phenylpyrazoline (Scheme 1).

The asymmetric trimethine cyanines **3a–3e** were then cyclo-condensed with urea in the presence of ethanol containing concentrated hydrochloric acid to yield the corresponding asymmetric pyrazolo[4,5-*d*]pyrimidine trimethine cyanine dyes (**5a–5d**). These were also synthesised via 3-*β*-acetanilidovinylpyrazolo[4,5-*d*]pyrimidine-6(5*H*)-one (**4a–4d**) followed by further reaction with an 1-ethyl-2-methylquinolinium-2-yl salt.

In the same manner, 2-methyl-3-ethyloxazolo[4,5-*d*]pyrimidinium salt (**6**) and/or 2-ethyl-3-methylpyrazolo[4,5-*d*]pyrimidine (**8**) were used in the synthesis of other asymmetric bis-heterocyclic trimethine cyanine dyes, **7** and **9** (Scheme 1).

The structures of the compounds were established by elemental analyses, IR and ^{1}H-NMR spectral data; relevant data are shown in Tables 1–6. The dyes were readily soluble in non-polar solvents giving orange to intense violet solutions with green or intense blue fluorescence, depending upon the solvent used. In polar solvents, they gave orange or violet solutions with a green fluorescence. Their ethanolic solutions give a yellow colour in acidic medium, turning violet on basification with strong alkali.

The electronic absorption spectra of the asymmetric trimethine cyanines **3a–3e** in 95% ethanol showed hypsochromic or bathochromic shifts depending upon the nature of the heterocyclic quaternary salt A and of the benzylidene substituents X. Thus, the trimethine cyanine **3d** (A = C_6H_4–2-yl salt) showed a significant red shift compared with **3e** (A = H–2-yl salt), both

TABLE 1

Characterisation of 3*β*-Acetanilidovinyl-4-arylidino-2-ethiodide-1-phenylpyrazol-5-one (**2a–2d**)

Compound	*M.p.* (°C)	*Yield* (%)	*Molecular formula* (*Mol. wt.*)	*Colour of crystalline products*	*Analysis (%):* *Calcd* (*Found*)		
					C	*H*	*N*
2a	122	35	$C_{28}H_{26}N_3O_2I$ (563)	Brown	59·7 (59·3)	4·6 (4·2)	7·5 (7·4)
2b	185	29	$C_{29}H_{28}N_3O_3I$ (593)	Deep brown	58·7 (58·3)	4·7 (4·4)	7·1 (7·1)
2c	145	31	$C_{28}H_{26}N_3O_3I$ (579)	Brown–red	58·0 (57·9)	4·5 (4·7)	7·25 (7·2)
2d	107	33	$C_{28}H_{26}N_3O_3I$ (579)	Brown	58·0 (58·15)	4·5 (4·65)	7·25 (7·3)

TABLE 2
Characterisation of Asymmetric Trimethine Cyanine Dyes (**3a–3e**)

Compound	*M.p.* (°C)	*Yield* (%)	*Molecular formula* (*Mol. wt*)	*Colour of crystalline product*	*Analysis (%): Calcd (Found)*			*Absorption spectra*	
					C	*H*	*N*	λ_{max} (*nm*)	$\varepsilon_{max} \times 10^3$ ($m^{-1}\,cm^2$)
3a	158	53	$C_{32}H_{30}N_3OI$ (599)	Intense violet	64·1 (64·1)	5·0 (5·05)	7·0 (7·0)	480	12 480
								512	13 920
								558	14 280
								585sh	12 160
								695	3 120
3b	205	73	$C_{33}H_{32}N_3O_2I$ (629)	Bluish violet	63·0 (62·9)	5·1 (5·1)	6·7 (6·7)	520	9 960
								560	13 120
								695	1 400
3c	210	68	$C_{32}H_{30}N_3O_2I$ (615)	Violet	62·4 (62·5)	4·9 (4·9)	6·8 (6·8)	478sh	15 520
								506	16 800
								553	11 680
								690	1 920
3d	180	62	$C_{32}H_{30}N_3O_2I$ (615)	Violet	62·4 (62·4)	4·9 (4·9)	6·8 (6·85)	412sh	12 720
								439	13 480
								480	12 800
								510	14 040
								555	13 280
								690	1 840
3e	162	43	$C_{28}H_{28}N_3O_2I$ (565)	Brown	59·5 (59·45)	5·0 (5·0)	7·4 (7·4)	455	11 720

TABLE 3
Characterisation of 3β-Acetanilidovinyl Pyrazolopyrimidine Moieties (**4a–4d**)

Compound	*M.p.* (°C)	*Yield* (%)	*Molecular formula* (*Mol. wt*)	*Colour of crystalline product*	*Analysis* (%): *Calcd* (*Found*)		
					C	*H*	*N*
4a	110	28	$C_{23}H_{24}N_5O_2I$ (529)	Brown	52·2 (52·2)	4·5 (4·5)	13·2 (13·05)
4b	120	33	$C_{24}H_{26}N_5O_3I$ (559)	Red–brown	51·5 (51·6)	4·65 (4·5)	12·5 (12·55)
4c	135	25	$C_{23}H_{23}N_6O_4I$ (574)	Deep brown	48·1 (48·2)	4·0 (3·9)	14·6 (14·6)
4d	105	35	$C_{30}H_{30}N_5O_3I$ (635)	Deep brown	56·7 (56·8)	4·7 (4·7)	11·0 (11·1)

dyes having the same benzylidene substituent (X = *o*-OH). Where X = *p*-OCH_3 (compound **3b**) a small red shift of 2–8 nm occurs relative to the unsubstituted analogue where X = H (**3a**).

Similarly, the absorption bands of the bis-heterocyclic trimethine cyanines (**5a–5d**, **7**, **9**) showed hypsochromic or bathochromic shifts depending on the nature of the substituent X, and on the nature of the bis-heterocyclic system (Tables **4** and **6**). Compound **9**, which combines the unsaturated pyrimidine ring with the *N*-phenylpyrazole ring, shows an increase in the number of absorption bands relative to the saturated pyrimidine **5d** (Tables 4 and 6). On the other hand, replacing the parent pyrazoline by the oxazole moiety in the oxazolopyrimidine trimethine cyanine **7** gives an increase in the number of absorption bands accompanied by red shifts of 2–134 nm with increase in band intensity. This may be attributed to the presence of the oxazole nucleus, which facilitates the CT interaction between the *N*-ethyloxazole residue and the nitrogen atom of the quinolinium salt (Table 6).

Compound **9**, in aqueous universal buffers showed bathochromic or hypsochromic shifts respectively in alkaline or acidic medium. The bathochromic shift in alkali is mainly due to the relatively increased negative charge density of the *N*-ethylpyrazolo[4,5-*d*]pyrimidine nucleus. The hypsochromic shift in acidic media is due to protonation of the pyrazolo[4,5-d]pyrimidine residue, thus decreasing CT interaction. As the pH of the medium increases, the pyrazolo[4,5-*d*]pyrimidine reactive becomes deprotonated, facilitating the CT interaction from the free base (Fig. 1). From a plot of the absorbance of compound **9** at λ_{max} 572 nm against pH (Fig. 2), pK_a values of 3·8 and 6·7 were derived.

TABLE 4

Characterization of Asymmetric Bis-heterocyclic Trimethine Cyanines (**5a–5d**)

Compound	*M.p.* (°C)	*Yield* (%)	*Molecular formula* (*mol. wt*)	*Colour of crystalline product*	*Analysis* (%): *Calcd* / (*Found*)			*Absorption spectra*	
					C	*H*	*N*	λ_{max} (*nm*)	$\varepsilon_{max} \times 10^3$ ($m^{-1}\,cm^2$)
5a	210	31	$C_{27}H_{28}N_5OI$ (565)	Violet	57·35 (57·6)	5·0 (4·9)	12·4 (12·3)	475sh 513 556	6 800 7 200 7 520
5b	218	51	$C_{28}H_{30}N_5O_2I$ (595)	Violet	56·5 (56·6)	5·0 (5·0)	9·4 (9·4)	475sh 517 558	6 840 8 720 9 960
5c	208	74	$C_{27}H_{27}N_6O_3I$ (610)	Violet	53·1 (53·2)	4·4 (4·6)	13·8 (13·6)	475sh 513 560 590sh	6 800 8 000 8 120 1 280
5d	180	70	$C_{34}H_{34}N_5O_2I$ (671)	Violet	60·8 (61·0)	5·1 (4·8)	10·4 (10·4)	480 504 607 690	13 600 14 400 4 400 2 000

TABLE 5
Characterisation of Quaternary Salts (**6a–6e**)

Compound	*M.p.* (°C)	*Yield* (%)	*Molecular formula* (*Mol. wt*)	*Colour of crystalline products*	*Analysis* (%): *Calcd* (*Found*)		
					C	*H*	*N*
6a	165	53	$C_{14}H_{17}N_4OI$ (384)	Brown	43·75 (43·7)	4·4 (4·6)	14·6 (14·3)
6b	170	45	$C_{15}H_{19}N_4O_2I$ (414)	Brown	43·5 (43·4)	4·6 (4·4)	13·5 (13·5)
6c	180	34	$C_{14}H_{16}N_5O_3I$ (429)	Brown	39·2 (39·0)	3·7 (3·8)	16·3 (16·3)
6d	155	37	$C_{21}H_{23}N_4O_2I$ (490)	Orange-brown	51·4 (51·3)	4·7 (4·8)	11·4 (11·4)
6e	203	61	$C_{14}H_{16}N_3O_2I$ (385)	Yellowish-green	43·6 (43·6)	4·2 (4·0)	10·9 (11·0)

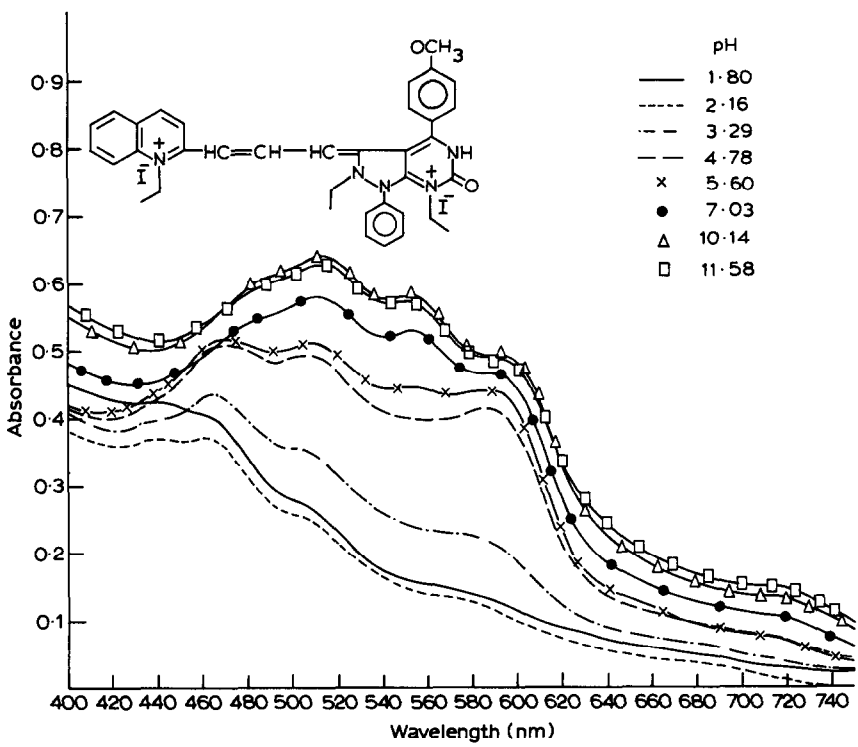


Fig. 1. Electronic absorption spectra of compound **9**, 1×10^{-4} g/mole in aqueous universal buffers.

TABLE 6
Characterisation of Asymmetric Bis-heterocyclic Trimethine Cyanines (7, 9)

Compound	*M.p.* (°C)	*Yield* (%)	*Molecular formula* (*Mol. wt*)	*Colour of crystalline product*	*Analysis* (%): *Calcd* / (*Found*)			*Absorption spectra*	
					C	*H*	*H*	λ_{max} (*nm*)	$\varepsilon_{max} \times 10^3$ ($m^{-1}\,cm^2$)
7	168	60	$C_{27}H_{27}N_4O_2I$	Bluish-violet	57·2	4·8	9·9	477	9 400
								519	12 400
			(566)		(57·4)	(4·6)	(9·9)	560	16 640
								600sh	13 600
								660	4 280
								690	3 240
9	157	55	$C_{34}H_{32}N_5O_2I$	Intense violet	61·0	4·8	10·5	480	10 000
								510	11 120
			(669)		(60·85)	(4·7)	(10·4)	557	9 520
								590	2 280
								658sh	2 480
								690	2 160

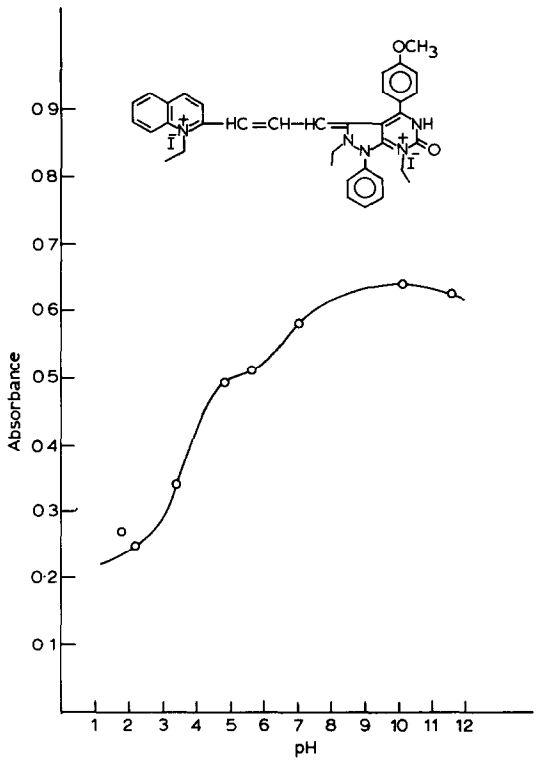


Fig. 2. The variation of absorbance with pH values in λ_{max} 512 nm for compound **9**, 1×10^{-4} g/mole.

3 EXPERIMENTAL

3.1 General

All melting points are uncorrected. The IR spectra were determined with a Perkin–Elmer infrared 127B spectrophotometer. The visible absorption spectra were recorded on a Shimadzu UV-Vis recording spectrophotometer UV-240. The ^{1}H-NMR spectra were recorded on an EM-390 90 MHz NMR spectrometer.

4-Benzylideno-3-methyl-1-phenylpyrazolinium-2-yl salts[7] (**1a–1d**) and 3(2)-methylpyrazolo/oxazolo[4,5-*d*]pyramidine-6(5*H*)-one-2-(3)-ethiodides (**6, 8**) were prepared on the basis of known methods.[8]

For spectra at different pH, an accurate volume of 10^{-3} M ethanol solution of the dye **9** was added to 5 ml of buffer solution, the modified buffer series being prepared as described previously.[9]

3.2 Synthesis of 3β-acetanilidovinyl-4-arylidino-2-ethiodide-1-phenylpyrazol-5-one (2a–2d)

A mixture of the appropriate 4-benzylideno-1-phenyl-3-methyl-pyrazolone-2-ethiodide (**1a–1d**, 0·01 mol) and diphenylformamidine (0·01 mol) was refluxed in Ac_2O (30 ml) for 1·5 h. The reaction liquor was concentrated, cooled and the precipitated products were collected, washed with methanol and crystallised from acetic acid to give **2a–2d**. Relevant data are given in Table 1.

3.3 Synthesis of 4-benzylideno-2-ethyl-1-phenylpyrazol-5-one-3(2)-trimethine cyanines (3a–3e)

Equimolar ratios (0·01 mol) of **2a–2d** and the appropriate methyl quaternary salts (α-picoline and quinaldine ethiodides) were dissolved in ethanol to which piperidine (2–5 drops) was added. The reaction was refluxed for 2 h, filtered hot, concentrated, the filtrate acidified with acetic acid, diluted with water and the precipitated products collected, washed with aqueous ethanol and crystallised from chloroform to give **3a–3e**. The results are summarised in Table 2. ^{1}H-NMR ($CDCl_3$) for **3a** (δ, ppm) 7·2–6·3 (m, 18H, arom. + heter. + α,γ-H of polymethine), 3·8 (q, 2H, CH_2 joined to immonium centre), 2·6 (t, 3H, CH_3I), 2·3 (q, 2H, CH_2 joined to nitrogen), 1·6 (s, 1H, =CH benzylidene), 1·3 (t, 3H, CH_3 joined to CH_2N) and 6·2 (t, 1H, B—H of polymethine).

3.4 Synthesis of 3-β-acetanilidovinylpyrazolopyrimidine derivatives (4a–4d)

These compounds were prepared in a similar manner to that described above using the 3-methyl-1-ethyliodide-pyrazolo[4,5-*d*]pyrimidine derivative **6** instead of **1a–1d**. The results are listed in Table 3.

3.5 Synthesis of asymmetric bis-heterocyclic trimethine cyanine dyes (5a–5d)

These compounds were prepared via two routes.

Method A

An alcoholic solution (10 ml) of **3a–3e** (0·02 mol) was refluxed with 2 g of urea and concentrated hydrochloric acid (20 ml) for 8–10 h. The reaction mixture was filtered hot and allowed to cool. The products which precipitated after neutralising with 5M NaOH were filtered, washed several times with water and crystallised from methanol. The results are listed in Table 4.

Method

Equimolar ratios (0·01 mol) of **4a–4d** and the appropriate 1-ethyl-2-methylquinolinium-2-yl salts were dissolved in ethanol to which piperidine (2–5 drops) was added. The reaction mixture was refluxed for 2 h, filtered hot and concentrated. The filtrate was acidified with acetic acid, diluted with water and the precipitated products were collected, washed with aqueous ethanol and crystallised from methanol to give the same products as Method A,

IR (ν_{max}^{KBr}, cm^{-1}) for (**5a**): 3000–2900 cm^{-1} (ν EtI), 3500 cm^{-1} (ν NH), 1600 cm^{-1} (ν C=C), 1380 cm^{-1} (ν CH_3) and 1700 cm^{-1} (ν C=O of pyrimidinone).

3.6 Synthesis of bis-heterocyclic trimethine cyanines of types 7 and 9

In a similar manner, the oxazolo[4,5-*d*]pyrimidine trimethine cyanine **7** and the unsaturated pyrazolo[4,5-*d*]pyrimidine trimethine cyanine **9** were prepared. The results are listed in Table 6.

^{1}H-NMR ($CDCl_3$) for **9** (δ, ppm) 7·0–6·3 (m, 16H, arom. + heter. + αH), 1·1 (t, 3H, CH_3), 5·8 (s, 1H, B—H), 6·2 (d, 1H, γ—H), 2·0 (s, 3H, *p*-OCH_3), 2·3 (q, 2H, CH_2), 2·5 (t, 3H, CH_3), 3·5 (q, 2H, , CH_2I), 5·9 (s, 1H, OH enolic), and 8·4 (s, 1H, NH exchangeable with D_2O).

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