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Synthesis and Electronic Spectra of Some Bis-heterocyclic Methine Cyanine Dyes

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ABSTRACT

*New asymmetric and symmetric pyrazolo[3,4-*d*]pyrazole (and isoxazole) methine cyanines of the monomethine, azomethine and trimethine type were prepared. The new new dyes were characterised by IR and ^{1}H-NMR spectral data. The electronic spectra data of the dyes are discussed.*

1 INTRODUCTION

Monomethine cyanines are used as photosensitisers in blue green[1–6] and they are also useful as analytical reagents over a wide pH range.[7] Their biological activity is also of interest and they have been described as inhibitors of cell growth and division[8] and as anticancer agents.[9]

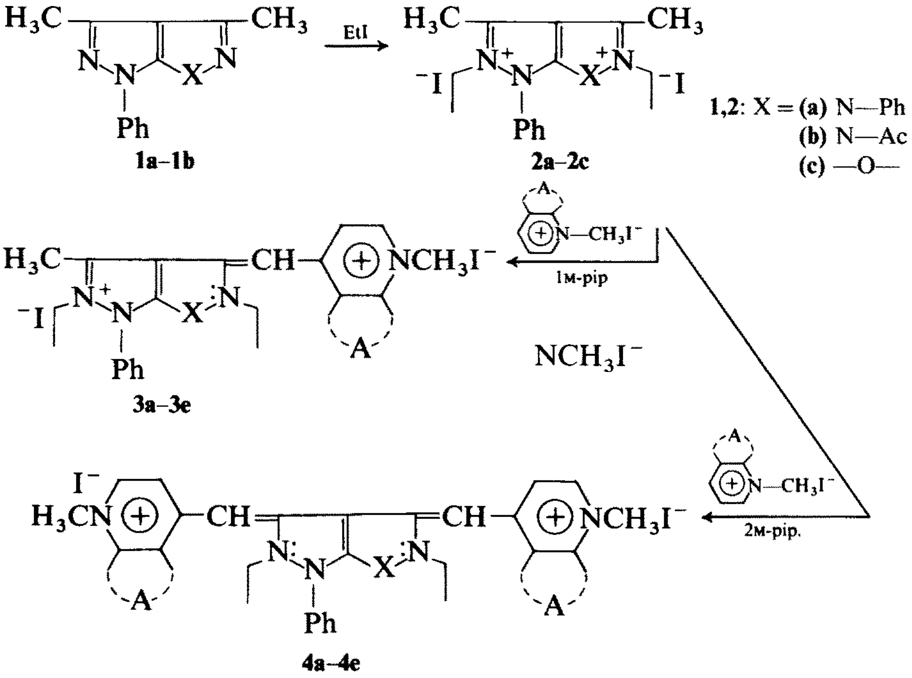
Trimethine cyanines can be used as laser dyes[10] and in light[11] and super photographic[12] sensitisers for silver halide emulsions, and also for producing offset printing plates.[13]

We report here the synthesis of some new asymmetric and symmetric monomethine and trimethine cyanines incorporating pyrazolo[3,4-*d*]-pyrazole (or isoxazole) moieties (viz. compounds **3a**–**3e**, **4a**–**4e**, **5a**–**5e**, **6a**–**6e**, **9a**–**9f** and **10a**–**10f**) on the basis that such dyes might exhibit a photosensitisation effect.

2 RESULTS AND DISCUSSION

Starting materials for the synthesis of the title compounds were the 3,4-dimethylpyrazolo[3,4-*d*]pyrazole (or isoxazole)-2,5-bis(ethyl iodides) **2a**–**2c**.

These were obtained by quaternisation of the corresponding 3,4-dimethylpyrazolo[3,4-*d*]pyrazole (or isoxazole) derivatives (**7a**–**7c**)[14] using excess ethyl iodide. Interaction of **2a**–**2c** with equimolar or bimolar ratios of 1-methylpyridinium (quinolinium or isoquinolinium) iodide under piperidine catalysis afforded the corresponding asymmetric (and symmetric) monomethine cyanine (**3a**–**3e**, **4a**–**4e**). These reactions are outlined in Scheme 1.



(**a**) X = N—Ph, A = H-4-yl salt
(**b**) X = N—Ph, A = C_4H_4-4-yl salt
(**c**) X = N—Ph, A = C_4H_4-1-yl salt
(**d**) X = N—Ac, A = C_4H_4-4-yl salt
(**e**) X = —O—, A = C_4H_4-4-yl salt

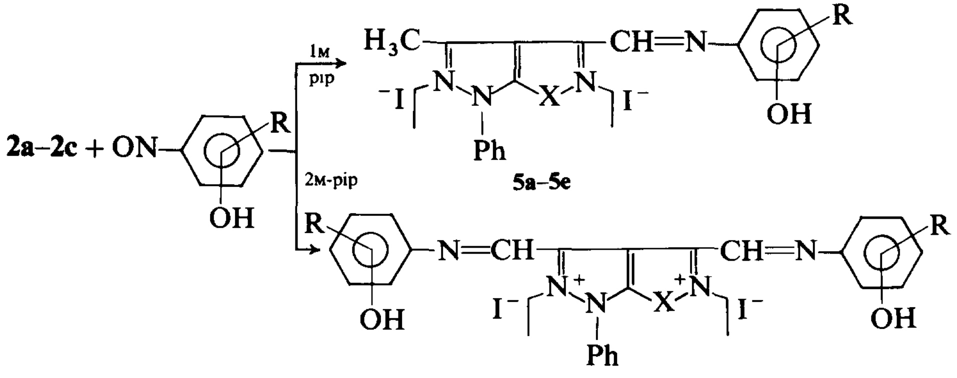
Scheme 1

The structures of the compounds synthesised as shown in Scheme 1 were confirmed by elemental analyses and by IR and ^{1}H-NMR spectra data (Tables 1 and 4). The cyanine dyes **3a**–**3e** and **4a**–**4e** were highly coloured compounds ranging from reddish-violet to intense violet and they were soluble in polar solvents, in which they exhibited a green fluorescence. They underwent a reversible colour change (violet⇌yellow) in basic and acidic media.

Absorption bands in the electronic spectra of **3a**–**3e** and of **4a**–**4e** in 95%

ethanol were dependent on the nature of both the heterocyclic quaternary salts (A) and the bis-heterocyclic system and also on the type of cyanine molecule, i.e. whether asymmetric or symmetric. For example, monomethine cyanines containing quinolinium or isoquinolinium iodide (**3b**–**3e**, **4b**–**4e**) moieties were bathochromic with respect to the pyridinium iodide analogues **3a** and **4a**. The cyanine derivatives of pyrazolo[3,4-*d*]isoxazole (**3e**, **4e**) were bathochromic by 20 nm compared with the pyrazolo[3,4-*d*]-*N*-acetyl (or phenyl)pyrazoles (**3b**, **3d**; **4b**, **4d**); see Table 1. The symmetric cyanine **4b** showed a red shift relative to the asymmetric cyanines **3b** due to the increase in conjugation.

The reaction of compounds **2a**–**2c** with equimolar bimolar ratios of nitroso compounds such as *p*-nitrosophenol and α- or β-nitroso-β(or α)-naphthol in the presence of piperidine as basic catalyst and ethanol as solvent afforded the corresponding asymmetric (and symmetric) 3-azomethine or 3,4-bis(azomethine) cyanines (**5a**–**5e**, **6a**–**6e**) respectively. The reactions are outlined in Scheme 2.



6a–6e

5,6: (**a**) X = N—Ph, 4-OH, R = H
(**b**) X = N—Ph, 2-OH, R = 5,6-benzo
(**c**) X = N—Ph, 2-OH, R = 3,4-benzo
(**d**) X = N—Ac, 2-OH, R = 5,6-benzo
(**e**) X = —O—, 2-OH, R = 5,6-benzo

Scheme 2

The structures of these compounds (**5a**–**5e**, **6a**–**6e**) were confirmed by elemental analysis and by IR and ^{1}H-NMR spectra data (Tables 2 and 4). They were reddish-violet to intense violet in colour and their solutions in polar solvents had an intense green fluorescence. The reversible colour change between acid and basic media was colourless to red respectively.

Electronic absorption maxima, in 95% ethanol, were as single broad

TABLE 1
Characterisation Data for Pyrazolo[3,4-*d*]pyrazole (and Isoxazole) 2,4-yl Salt Moieties (**2a–2c**) and their 4-Asymmetric or Bis-3,4-symmetric Monomethine Cyanine Dyes (**3a–3e**, **4a–4e**)

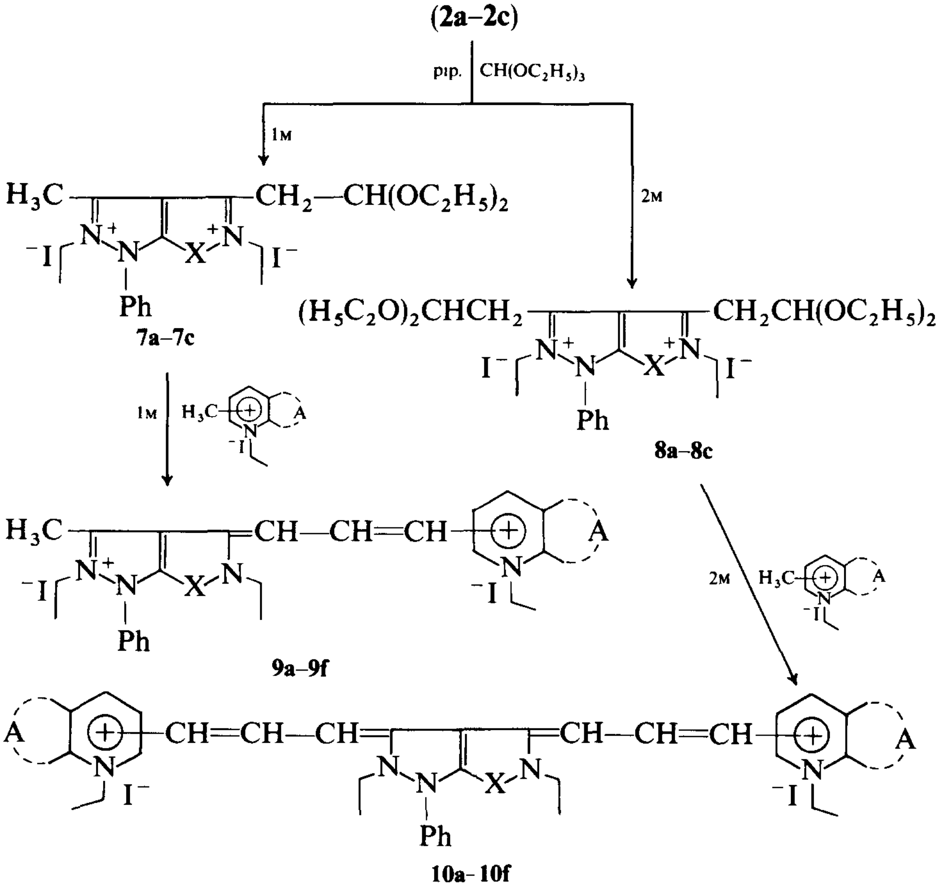
Compd	*M.p. (°C)*	*Yield (%)*	*Mol. formula (mol. wt)*	*Analysis (%): Calcd/Found*			*Absorption spectra in 95% ethanol*	
				C	*H*	*N*	λ_{max} *(nm)*	ε_{max} $(m^{-1}\,cm^{-1})$
2a	210–212	59	$C_{22}H_{26}N_4I_2$ (609)	44·0 (43·6)	4·3 (4·7)	9·3 (8·9)	—	—
2b	185–187	67	$C_{18}H_{24}N_4O_2I_2$ (591)	37·1 (37·4)	4·1 (4·0)	9·6 (9·1)	—	—
2c	196–198	81	$C_{16}H_{21}N_3OI_2$ (525)	36·6 (37·0)	4·0 (4·25)	8·0 (7·8)	—	—
3a	114–116	29	$C_{28}H_{31}N_5I_2$ (691)	48·6 (49·1)	4·5 (4·1)	10·1 (9·8)	525	2 800
3b	120–122	49	$C_{32}H_{33}N_5I_2$ (741)	51·8 (52·2)	4·45 (4·9)	9·45 (9·9)	460	8 000
3c	135–137	35	$C_{32}H_{33}N_5I_2$ (741)	51·8 (52·1)	4·45 (4·6)	9·45 (10·0)	455	2 880
3d	205	29	$C_{28}H_{31}N_5O_2I_2$ (723)	46·5 (45·8)	4·3 (4·5)	9·7 (9·3)	445	7 320
3e	180	32	$C_{26}H_{28}N_4OI_2$ (666)	46·9 (47·2)	4·2 (4·5)	8·4 (8·8)	480	7 260
4a	150	33	$C_{34}H_{36}N_6I_2$ (782)	52·2 (53·0)	4·6 (5·1)	10·7 (10·3)	530	560
4b	140	45	$C_{42}H_{40}N_6I_2$ (882)	57·1 (58·0)	4·5 (5·1)	9·5 (10·0)	470	7 600
4c	110–112	35	$C_{42}H_{40}N_6I_2$ (882)	57·1 (57·0)	4·5 (4·7)	9·5 (9·8)	465	976
4d	190–192	43	$C_{38}H_{38}N_6O_2I_2$ (864)	52·8 (52·7)	4·4 (4·95)	9·7 (10·0)	450, 520	11 200, 5 240
4e	215	32	$C_{36}H_{35}N_5OI_2$ (807)	53·5 (54·0)	4·3 (4·8)	8·7 (9·1)	460	20 040

TABLE 2

Characterisation Data for 4-Asymmetric and Bis-3,4-symmetric Pyrazolium[3,4-*d*]pyrazolium (and Isoxazolium) Azomethine Cyanine Dyes (**5a–5e**, **6a–6e**)

Compd	*M.p. (°C)*	*Yield (%)*	*Mol. formula (mol. wt)*	*Analysis (%): Calcd (Found)*			*Absorption spectra in 95% ethanol*	
				C	*H*	*N*	λ_{max} *(nm)*	ε_{max} *(m^{-1} cm^{-1})*
5a	220–222	33	$C_{28}H_{29}N_5OI_2$ (705)	47·7 (48·1)	4·1 (3·9)	9·9 (10·3)	490	8 120
5b	170–172	46	$C_{32}H_{31}N_5OI_2$ (755)	50·9 (49·45)	4·1 (4·3)	9·3 (9·1)	510 570sh	8 400 5 200
5c	184–182	43	$C_{32}H_{31}N_5OI_2$ (755)	50·9 (49·55)	4·1 (4·3)	9·3 (9·55)	520	6 880
5d	110–112	39	$C_{28}H_{29}N_5O_3I_2$ (737)	45·6 (46·1)	3·9 (4·4)	9·5 (9·9)	530	3 000
5e	175–177	37	$C_{26}H_{26}N_4O_2I_2$ (680)	45·9 (46·3)	3·8 (3·75)	8·2 (8·65)	395 418	3 860 3 840
6a	145	53	$C_{34}H_{32}N_6O_2I_2$ (810)	50·4 (50·1)	3·95 (4·45)	10·4 (9·9)	520	3 440
6b	112–114	61	$C_{42}H_{36}N_6O_2I_2$ (910)	55·4 (55·0)	3·5 (4·0)	9·2 (9·5)	395, 419 520	4 600, 4 200 3 420
6c	115–117	67	$C_{42}H_{36}N_6O_2I_2$ (910)	55·4 (54·7)	3·5 (3·75)	9·2 (9·55)	465	1 276
6d	118–120	59	$C_{38}H_{34}N_6O_4I_2$ (892)	51·1 (51·4)	3·8 (3·9)	9·4 (9·7)	505	3 900
6e	160–162	51	$C_{36}H_{31}N_5O_3I_2$ (835)	51·7 (52·1)	3·7 (4·1)	8·3 (8·7)	420 525	4 176 2 012

bands, which became more intense and showed a strong red in the dyes containing a naphthoyl residue (Table 2). The nature of the bis-heterocyclic system also influenced λ_{max}. Thus, the dye with an *N*-phenylpyrazole residue attached to another *N*-phenylpyrazole residue showed a blue shift of 20 nm compared with the 6-acetylpyrazole or isoxazole analogues (Table 2). Comparison of the absorption spectra of the asymmetric 3-azomethine cyanine (**5b**) and the symmetric 3,4-bis(azomethine)cyanine (**6b**) showed that **6b** was the more bathochromic. This is due to the presence of two



9,10: (**a**) X = N—Ph, A = H-2-yl salt
(**b**) X = N—Ph, A = C_4H_4-2-yl salt
(**c**) X = N—Ph, A = H-4-yl salt
(**d**) X = N—Ph, A = C_4H_4-4-yl salt
(**e**) X = N—Ac, A = C_4H_4-2-yl salt
(**f**) X = —O—, A = C_4H_4-2-yl salt

Scheme 3

electronic charge pathways in the symmetric type (**6b**) and to an increase in the overall conjugation.

Interaction of compounds **2a**–**2c** with equimolar bimolar amounts of diphenylformamidine in the presence of acetic anhydride or with ethyl orthoformate in the presence of piperidine afforded compounds **7a**–**7c** and **8a**–**8c** respectively. These compounds are the key intermediates for the synthesis of the asymmetric or symmetric trimethine cyanines **9a**–**9f** and **10a**–**10f** through their condensation with equimolar bimolar ratios of 2- or 4-methyl quaternary salts under piperidine catalysis. The reactions are shown in Scheme 3.

Characterisation data for these compounds (**7a**, **9b**, **10b**) is shown in Tables 3 and 4. The dyes were reddish-violet to intense violet in colour and were soluble in polar solvents, in which they exhibited a green fluorescence. A reversible colour change (violet$\rightleftharpoons$yellow) occurred in basic and acidic media.

Absorption bands in 95% ethanol were intense and strong red shifts were observed for the dyes involving quinolinium-2 (or 4)-yl salts. The nature of the bis-heterocyclic system also influenced λ_{max} (Table 3). The symmetric trimethine (**10a**–**10f**) cyanines were more bathochromic than their asymmetric analogues **9a**–**9f**.

Comparison of the absorption spectra of the asymmetric and symmetric trimethine cyanines (**9b** and **10b**) with those of asymmetric and symmetric monomethine cyanines (**3b** and **4b**) showed that the trimethine cyanines were red-shifted relative to the monomethine types. This is due to the increase in the number of methine groups between the *N*-ethyl group and the positively nitrogen heterocyclic quaternary salts, thus enhancing charge transfer.

3 EXPERIMENTAL

3.1 General

Melting points are uncorrected. IR spectra were determined on a Unicam SP 1200 spectrophotometer (KBr). Absorption spectra were recorded on a Shimadzu UV–VIS 240 recording spectrophotometer and ^{1}H-NMR spectra on an EM-390 90-MHz NMR spectrometer.

3,4-Dimethyl-1,6-diphenylpyrazolo[3,4-*d*]pyrazole and their derivatives (**1a**–**1c**) were prepared as previously described.[14]

3.2 Synthesis of 3,6-dimethylpyrazolium[3,4-*d*]pyrazolium and (isoxazolium)bis(2,4-yl) salt moieties (2a–2c)

Excess ethyl iodide was added to compounds **1a**–**1c**. The reaction mixture was refluxed for 3–5 h on a water bath and the precipitate which formed was

TABLE 3

Characterisation Data for the Intermediate Compounds (**7a**–**7c**, **8a**–**8c**) and their 3-Asymmetric or Bis-3,4-symmetric Pyrazolo[3,4-*d*]pyrazolium (or Isoxazolium) 2-(and 4)-Trimethine Cyanides (**9a**–**9f**, **10a**–**10f**)

Compd	*M.p.* (°*C*)	*Yield* (%)	*Mol. formula* (*mol. wt*)	*Analysis* (%) *Calcd* (*Found*)			*Absorption spectra in 95% ethanol*	
				C	*H*	*N*	λ_{max} (*nm*)	ε_{max} (m^{-1} cm^{-1})
7a	139–140	45	$C_{27}H_{36}N_4O_2I_2$ (702)	46·15 (46·0)	5·1 (5·2)	9·8 (10·3)	—	—
7b	118–120	57	$C_{23}H_{34}N_4O_4I_2$ (684)	40·35 (40·6)	4·8 (5·1)	8·0 (8·3)	—	—
7c	140–142	53	$C_{21}H_{31}N_3O_3I_2$ (627)	40·2 (40·3)	4·95 (5·1)	6·7 (7·1)	—	—
8a	116–118	41	$C_{32}H_{46}N_4O_4I_2$ (804)	47·8 (47·2)	5·7 (5·2)	7·0 (7·15)	—	—
8b	143–145	65	$C_{28}H_{44}N_4O_6I_2$ (786)	42·75 (43·0)	5·6 (5·1)	7·1 (7·0)	—	—
8c	167–169	71	$C_{26}H_{41}N_3O_5I_2$ (729)	42·8 (43·1)	5·6 (5·4)	5·8 (6·1)	—	—
9a	120–122	21	$C_{31}H_{35}N_5I_2$ (731)	50·9 (51·23)	4·8 (5·3)	9·6 (10·0)	475	1 004

9b	125–127	65	$C_{35}H_{37}N_5I_2$ (781)	53·8 (53·4)	4·7 (4·25)	9·0 (9·3)	510, 554, 660sh 696	5 030, 4 198, 2 800 1 460
9c	135	24	$C_{31}H_{35}N_5I_2$ (731)	50·9 (51·1)	4·8 (5·2)	9·6 (10·0)	495 555sh	966 600
9d	129–131	59	$C_{35}H_{37}N_5I_2$ (781)	53·8 (53·8)	4·7 (4·7)	9·0 (9·0)	590, 670 708	2 596, 4 460 2 560
9e	150–152	55	$C_{31}H_{35}N_5O_2I_2$ (49·13)	47·75 (49·1)	4·6 (5·1)	9·2 (9·3)	518, 559 565	9 000, 11 520 2 640
9f	186–188	44	$C_{29}H_{32}N_4OI_2$ (706)	49·3 (48·1)	4·5 (4·7)	7·9 (8·05)	517	11 640
10a	108–110	28	$C_{40}H_{44}N_6I_2$ (862)	55·6 (56·1)	5·1 (5·45)	9·7 (10·0)	480	976
10b	168–170	56	$C_{48}H_{48}N_6I_2$ (962)	59·9 (59·1)	5·0 (4·8)	8·7 (9·1)	520, 557 698	12 040, 18 800 1 260
10c	100–102	30	$C_{40}H_{44}N_6I_2$ (862)	55·6 (55·9)	5·1 (5·25)	9·7 (10·2)	485 640sh	1 096 240
10d	148	59	$C_{48}H_{48}N_6I_2$ (962)	59·9 (59·7)	5·0 (4·65)	8·7 (9·2)	595, 673 709·8	3 600, 6 300 5 248
10e	178	54	$C_{44}H_{46}N_6O_2I_2$ (944)	55·9 (56·35)	4·8 (5·1)	8·9 (9·1)	512, 555, 585 640sh	11 160, 10 860, 9 600 1 480
10f	189–191	51	$C_{42}H_{43}N_5OI_2$ (887)	56·8 (57·1)	4·85 (5·1)	7·9 (9·0)	511	18 400

TABLE 4
IR and ^{1}H-NMR Spectra Data of Selected Dyes

Compd	*IR* (ν_{max}^{KBr} (*cm*$^{-1}$))[a]	^{1}*H-NMR* (*DMSO*), δ (*ppm*)[b]
2a	1 610–1 600 (C=C)	6·4–6·8 (m, 10H, arom. rings)
	2 980–2 940 (ethiodide)	1·8–2·4 (m, 10H, ethiodide)
		1·2 (s, 6H, CH_3)
2b	1 620–1 600 (C=C)	7·2–7·9 (m, 5H, arom. ring)
		1·6–1·8 (m, 10H, ethiodide)
3d	1 620–1 600 (C=C)	6·4–6·8 (m, 10H, arom. + hetero)
	2 980–2 940 (ethiodide)	2·5–2·6 (s, 3H, CH_3I)
		1·9–2·5 (t, q, 5H, CH_3CH_2I)
		1·7 (s, 7H, CH=)
		1·05–1·5 (t, q, 5H, CH_3CH_2)
		0·7 (s, 3H, CH_3)
4b	1 640–1 610 (C=C)	7·0–7·8 (m, 11H, arom. + hetero)
	2 980–2 940 (ethiodide)	2·1–2·5 (m, 6H, CH_3I)
		1·9 (s, 2H, CH=)
		1·3–1·8 (t, q, 10H, CH_3CH_2)
5e	1 640–1 600 (C=C)	7·5–8·2 (m, 11H, arom. rings)
	1 725–1 700 (C=N)	2·01–3·1 (t, q, 10H, ethiodide)
	2 980–2 940 (ethiodide)	1·3–1·4 (s, 3H, CH_3)
		1·6–1·8 (s, 7H, CH=N)
6e	1 630–1 600 (C=C)	7·2–8·2 (m, 17H, arom. rings)
	1 720–1 700 (C=N)	2·01–3·1 (t, q, 10H, ethiodide)
	2 980–2 940 (ethiodide)	1·57 (s, 2H, CH=N)
8a	1 600 (C=C)	7·4–7·9 (m, 10H, arom. rings)
	1 725–1 700 (C=N)	2·4 (d, 4H, CH=CH)
	2 980–2 940 (ethiodide)	2·1–2·3 (t, q, 10H, CH_3, CH_2I)
		0·9–1·4 (m, 10H, CH_3CH_2)
9b	1 620–1 600 (C=C)	7·2–7·9 (m, 16H, arom. + hetero)
	1 725–1 700 (C=N)	2·0–2·6 (t, q, 5H, CH_3CH_2I)
	2 980–2 940 (ethiodide)	1·5–1·7 (t, 3H, =CH—CH=CH)
		1·3 (s, 3H, CH_3)
		0·7–1·1 (m, 5H, CH_3CH_2)
10b	1 620–1 600 (C=C)	7·3–8·1 (m, 22H, arom. + hetero)
	1 725–1 700 (C=N)	1·7–2·4 (t, q, 5H, CH_3CH_2I)
	2 975–2 940 (ethiodide)	1·4–1·6 (t, 3H, =CH—CH=CH)
		0·9–1·3 (m, 5H, CH_3CH_2)

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[a] Ref. 15.

[b] Ref. 16.

filtered, washed by ether, triturated with ethanol by refluxing, filtered hot, concentrated and cooled. The product which precipitated after dilution with water were collected and recrystallised from ethanol. Characterisation data for them are given in Table 1.

3.3 Synthesis of asymmetric (and symmetric) pyrazolium[3,4-*d*]pyrazolium (and isoxazolium) 2(and 4)-yl salt 4(and bis-3,4)-monomethine cyanine moieties (3a–3e, 4a–4a)

A mixture of **2a**–**2c** (0·01 mol) and equimolar or bimolar ratios of the appropriate methyl quaternary salt (pyridinium, quinolinium and/or isoquinolinium iodide) (0·01 or 0·02 mol) were dissolved in ethanol (40 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 recrystallised from ethanol to give **3a**–**3e** and **4a**–**4e** respectively. Relevant data for them are given in Table 1.

3.4 Synthesis of asymmetric (and symmetric) pyrazolium[3,4-*d*]pyrazolium (and isoxazolium) 2(and 4)-yl salt 4(and bis-3,4)-azomethine cyanine moieties (5a–5e, 6a–6e)

A mixture of **2a**–**2c** (0·01 mol) and equimolar or bimolar ratios of *p*-nitrosophenol or α(or β)-nitroso-β(or α)-naphthol (0·01 or 0·02 mol) in ethanol (25 ml), was treated with piperidine (3–5 drops). The reaction mixture was refluxed for 6–8 h. The separation of the products was carried out in a way similar to that described above. Characterisation data for the products are given in Table 2.

3.5 Synthesis of asymmetric (and symmetric) pyrazolium[3,4-*d*]pyrazolium (and isoxazolium) 4(and bis-3,4)-trimethine 2(and 4)-cyanine moieties (9a–9f, 10a–10f)

Method A

A mixture of **2a**–**2c** (0·01 mol) and equimolar or bimolar ratios of ethyl orthoformate (0·01 mol or 0·02 mol) in ethanol (25 ml) and piperidine (3–5 drops) was 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 recrystallised from aqueous ethanol to give **7a**–**7c** and **8a**–**8c**. Characterisation data are shown in Table 3.

Method B

A mixture of **7a**–**7c**, or **8a**–**8c** (0·01 mol) and the appropriate 2- (or 4-)methyl quaternary salts [α(γ)-picoline, quinaldine and/or lipidine ethyl iodide, 0·01 or 0·02 mol] in ethanol (40 ml) and piperidine (4–6 drops) was refluxed for 8–10 h. The products were separated in similar manner to that described for earlier experiments. Relevant data for the compounds thus obtained are given in Table 3.

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