

## Syntheses and absorption–structure relationships of some new photosensitizer cyanine dyes

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**Abstract.** New biheterocyclic compound was synthesized as starting material to prepare new photosensitizers mono-, tri-, substituted tri-, azadimethine and mixed cyanine dyes. Absorption–structure relationship of the synthesized cyanine dyes were determined by studying their electronic spectral behaviour in ethanol. The structure of the compounds were identified by elemental analysis, IR and <sup>1</sup>HNMR spectral data.

**Keywords.** Cyanine dyes; absorption–structure relationship; photosensitizer dyes; biheterocyclic compounds.

### 1. Introduction

Cyanine dyes find extensive application as photosensitizers in blue green light<sup>1</sup>. Some of these dyes are growth inhibitors to bacteria<sup>2</sup> and to the mitosis of fertilized sea urchin eggs<sup>3</sup>. They possess hormonal effects on plant growth<sup>4</sup> and can be used for the determination of the sensitivity of micro-organism to antibiotics<sup>5</sup>. They can also be used as laser dyes<sup>6,7</sup> and producing offset printing plates<sup>8,9</sup>.

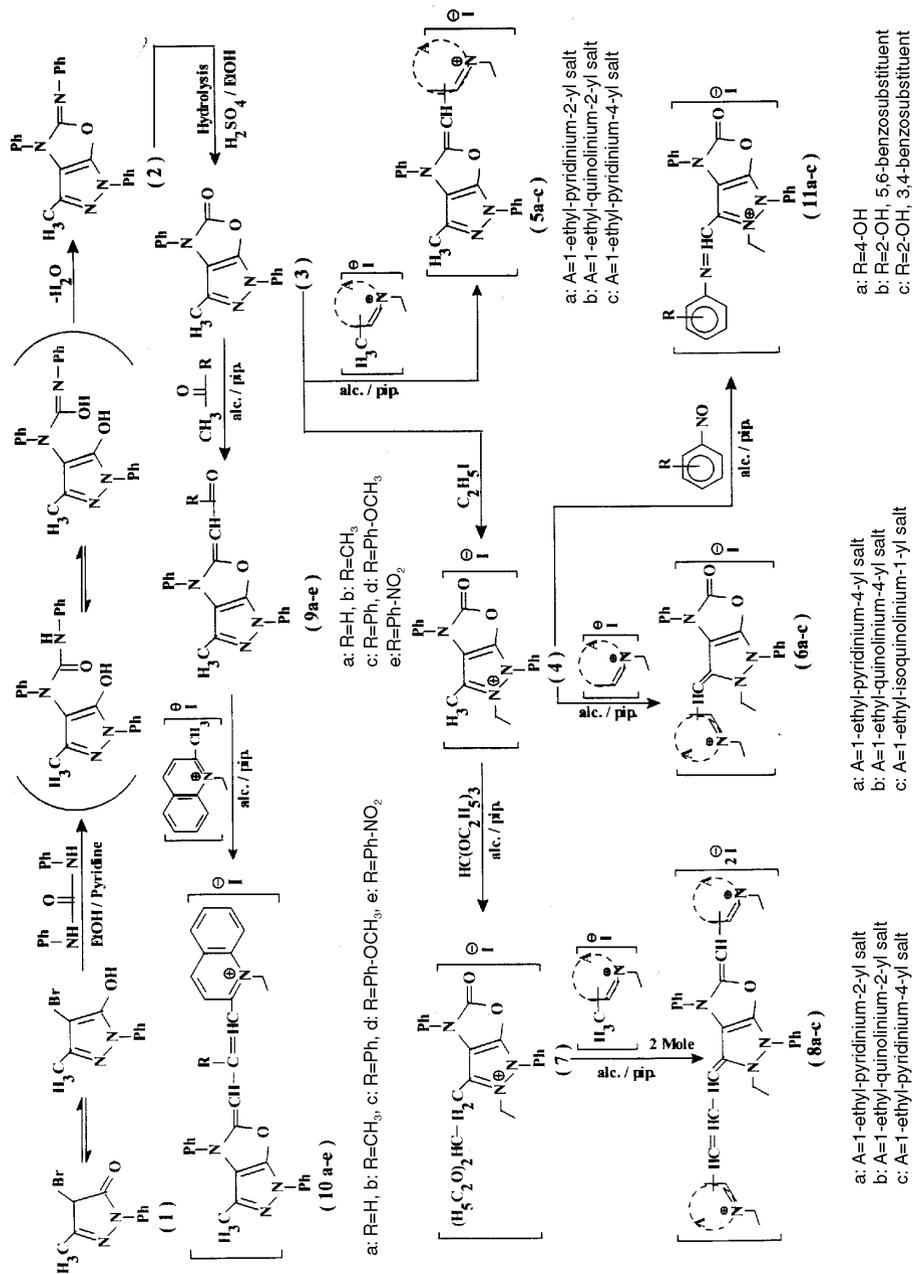
### 2. Results and discussion

#### 2.1 Synthesis

As an extension to our previous publications<sup>10,11</sup>, 4-bromo-3-methyl-1-phenyl-pyrazole-5-one (**1**) was reacted with diphenyl urea in equimolar ratios and in ethanol/pyridine to achieve 3-methyl-1,4-diphenyl-1H-pyrazolo[4,5-*d*][1,3]oxazole-5-phenyl azomethine (**2**). Hydrolysis of **2** in H<sub>2</sub>SO<sub>4</sub>/EtOH furnished 3-methyl-1,4-diphenyl-1H-pyrazolo[4,5-*d*][1,3]oxazole-5-one (**3**). Quaternization of (**3**) using iodoethane resulted in its 2-ethyl iodide salt (**4**) (scheme 1, table 1).

Interaction of equimolar ratios of (**3**) and 2(4)-methyl quaternary salts such as 1-ethyl-2-methyl-pyridinium iodide, 1-ethyl-2-methyl-quinolinium iodide and 1-ethyl-4-methyl-pyridinium iodide in ethanol as organic solvent and piperidine as basic catalyst produced the 5[2(4)]-monomethine cyanine dyes (**5a–c**) (scheme 1, table 2). Otherwise, interaction of the quaternized compound (**4**) with equimolar amounts of iodoethane quaternary salts of pyridine, quinoline and isoquinoline in ethanol under piperidine catalysis afforded the 3[4(1)]-monomethine cyanine dyes (**6a–c**) (scheme 1, table 2).

On the other hand, interaction of the quaternized compound (**4**) with equimolar amounts of triethyl orthoformate in ethanol under piperidine catalysis furnished the intermediate compound (**7**). Further reaction of **7** with the N-iodoethane quaternary salt



**Table 1.** Characterization of 3-methyl-1,4-diphenyl-1H-pyrazolo[4,5-*d*][1,3]oxazole-5-phenyl azomethine (**2**), 3-methyl-1,4-diphenyl-1H-pyrazolo [4,5-*d*][1,3]oxazole-5-one (**3**) and its 2-ethyl iodide salt (**4**).

Compd. no.	m.p. (°C)	Yield (%)	Mol. formula (mol. wt.)	Colour of crystals	Analysis (%)		
					Calcd. (Found)		
					C	H	N
<b>2</b>	185	43	C <sub>23</sub> H <sub>18</sub> N <sub>4</sub> O (366)	Red/brown	75.40 (75.42)	4.91 (4.95)	15.30 (15.33)
<b>3</b>	130	84	C <sub>17</sub> H <sub>13</sub> N <sub>3</sub> O <sub>2</sub> (291)	Pale brown	70.10 (70.15)	4.46 (4.49)	14.43 (14.45)
<b>4</b>	150	98	C <sub>19</sub> H <sub>18</sub> N <sub>3</sub> O <sub>2</sub> I (447)	Brown	51.00 (51.04)	4.02 (4.05)	9.39 (9.43)

of **a**picoline, quinaldine and **g**picoline in 1:2 molar ratios in ethanol and in presence of piperidine as catalyst gave the 3[2(4)]-tri-5[2(4)]-mono-methine mixed cyanine dyes (**8a-c**) (scheme 1, table 3).

Additionally, interaction of equimolar ratios of (**2**) and methyl carbonyl compounds such as acetaldehyde, acetone, acetophenone, *p*-methoxy acetophenone and *p*-nitro acetophenone in ethanol under piperidine catalysis resulted in 5-acylmethylideno derivatives (**9a-e**) as intermediate compounds. Further reaction of (**9a-e**) with 1-ethyl-2-methylquinolinium iodide in equimolar ratios, in ethanol as solvent and piperidine as catalyst furnished 5(2)-tri-(substituted tri-) methine cyanine dyes (**10a-e**) (scheme 1, table 4).

3(1)-Azadimethine cyanine dyes (**11a-c**) were also prepared via interaction of equimolar ratios of the quaternized compound (**4**) and nitroso compounds such as *p*-nitroso phenol, **a**nitroso-**b**naphthol and **b**nitroso-**a**naphthol in ethanol and presence of piperidine (scheme 1, table 5).

The structures of the synthesized compounds were characterized by elemental analysis, IR<sup>12</sup> and <sup>1</sup>H NMR<sup>13</sup> spectral data.

## 2.2 Characterization

The synthesized cyanine dyes are highly coloured compounds, partially soluble in non-polar organic solvents and easily soluble in polar organic solvents giving coloured solutions, accompanied by pale to intense fluorescence. The intensity and colour of the fluorescence depends upon the type of dye and solvent used. The dyes are soluble in concentrated H<sub>2</sub>SO<sub>4</sub>, liberating iodine vapour on warming. They are also *pH*-sensitive dyes, and hence their ethanolic solutions give changeable colours in acid/base media being yellow or colourless on acidification and getting back their intense colour on basification. The intensity of their colour is due to the two suggested mesomeric structures (A and B) having delocalized positive charges over the conjugated system (scheme 2).

## 2.3 Absorption-structure relationship

Absorption-structure relationships of the prepared cyanine dyes were determined by studying their electronic absorption spectral behaviour in 95% ethanol. Thus, the

**Table 2.** Characterization of 3-methyl-1,4-diphenyl-1H-pyrazolo[4,5-d][1,3]oxazole-5[2(4)]-monomethine cyanine dyes (**5a-c**) and 2-ethyl-1,4-diphenyl-1H-pyrazolo[4,5-d][1,3]oxazole 5-one-3[4(1)]-monomethine cyanine dyes (**6a-c**).

Compd. no.	m.p. (°C)	Yield (%)	Mol. formula (mol. wt.)	Colour of crystals	Analysis (%) – Calcd. (Found)			Vis. Abs. max. in 95% EtOH		
					C	H	N	$\lambda_{\text{max}}$ (nm)	$\epsilon_{\text{max}}$ (mol <sup>-1</sup> cm <sup>2</sup> )	
<b>5a</b>	160	38	C <sub>23</sub> H <sub>23</sub> N <sub>4</sub> OI (522)	Brown	57.47 (57.50)	4.40 (4.44)	10.72 (10.80)	395	1200	
<b>5b</b>	180	46	C <sub>29</sub> H <sub>25</sub> N <sub>4</sub> OI (572)	Violet	60.83 (60.91)	4.37 (4.45)	9.79 (9.85)	655, 600, 555, 520, 460	1200, 1700, 1900, 1900, 2800	
<b>5c</b>	165	39	C <sub>23</sub> H <sub>23</sub> N <sub>4</sub> OI (522)	Brown	57.47 (57.52)	4.40 (4.46)	10.72 (10.82)	400	1400	
<b>6a</b>	170	95	C <sub>26</sub> H <sub>25</sub> N <sub>4</sub> O <sub>2</sub> I (552)	Red	56.52 (56.59)	4.52 (4.57)	10.14 (10.20)	418	1900	
<b>6b</b>	175	98	C <sub>30</sub> H <sub>27</sub> N <sub>4</sub> O <sub>2</sub> I (602)	Deep red	59.80 (59.85)	4.48 (4.55)	9.30 (9.36)	565, 462	1200, 2200	
<b>6c</b>	185	98	C <sub>30</sub> H <sub>27</sub> N <sub>4</sub> O <sub>2</sub> I (602)	Red	59.80 (59.88)	4.48 (4.58)	9.30 (9.40)	420	1200	

**Table 3.** Characterization of the intermediate compound **7** and its 2-ethyl-1,4-diphenyl-1H-pyrazolo[4,5-d][1,3]oxazole-5[2(4)]-mono-3[2(4)]-tri-methine mixed cyanine dyes (**8a-c**).

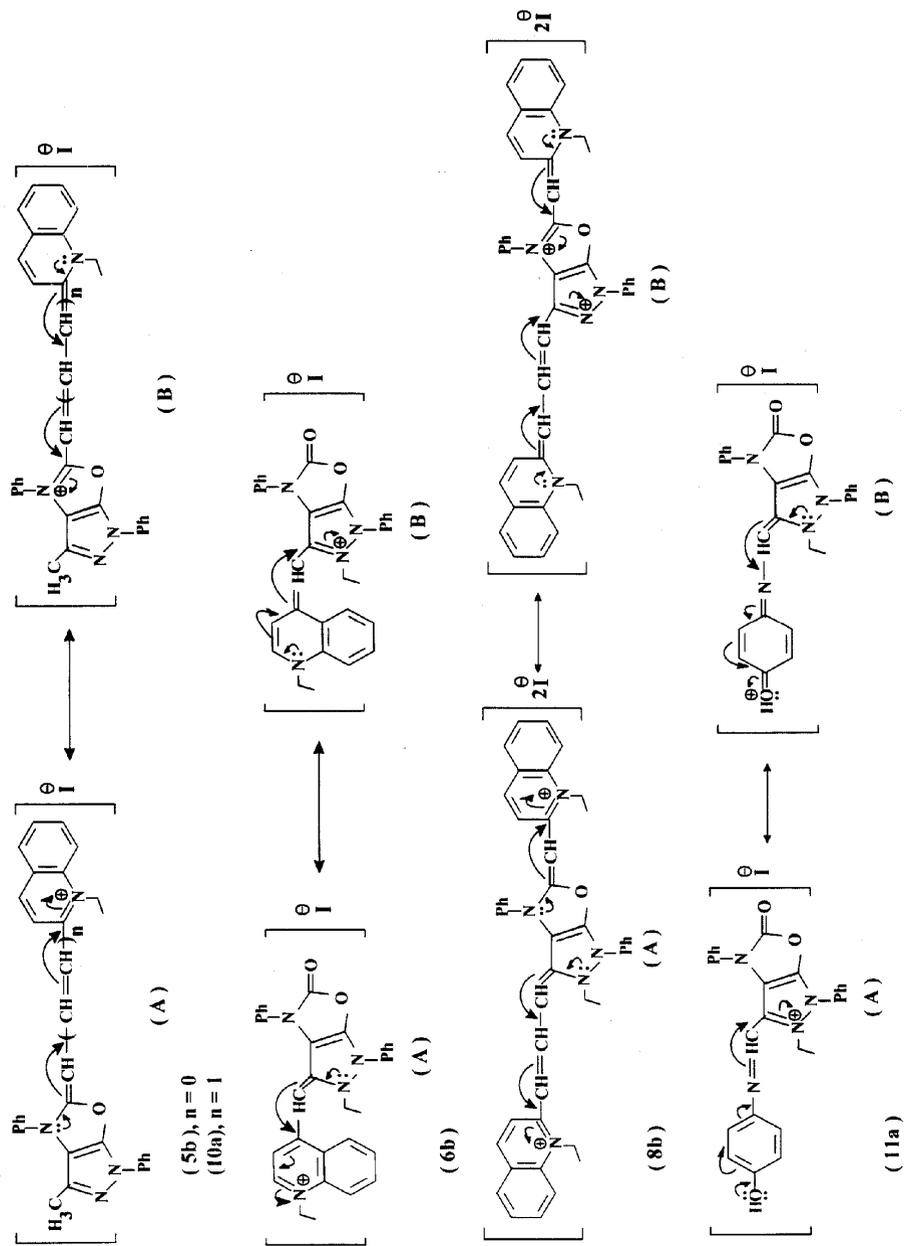
Compd. no.	m.p. (°C)	Yield (%)	Mol. formula (mol. wt.)	Colour of crystals	Analysis (%) – Calcd. (Found)			Vis. Abs. max. in 95% EtOH		
					C	H	N	$\lambda_{\text{max}}$ (nm)	$\epsilon_{\text{max}}$ (mol <sup>-1</sup> cm <sup>2</sup> )	
<b>7</b>	190	73	C <sub>24</sub> H <sub>28</sub> N <sub>5</sub> O <sub>4</sub> I (549)	Brown	52.45 (52.50)	5.10 (5.20)	7.65 (7.72)	–	–	
<b>8a</b>	215	57	C <sub>36</sub> H <sub>37</sub> N <sub>5</sub> OI <sub>2</sub> (809)	Deep brown	53.39 (53.46)	4.57 (4.62)	8.65 (8.69)	420	1600	
<b>8b</b>	230	92	C <sub>44</sub> H <sub>41</sub> N <sub>5</sub> OI <sub>2</sub> (909)	Deep violet	58.08 (58.15)	4.51 (4.61)	7.70 (7.78)	660, 605, 560, 465	0800, 1500, 1800, 2900	
<b>8c</b>	220	61	C <sub>36</sub> H <sub>37</sub> N <sub>5</sub> OI <sub>2</sub> (809)	Violet	53.39 (53.49)	4.57 (4.66)	8.65 (8.75)	510, 400	1400, 2800	

**Table 4.** Characterization of 5-acylmethylideno derivatives as intermediate compounds (**9a–e**) and their 3-methyl-1,4-diphenyl-1H-pyrazolo[4,5-*d*][1,3]oxazole-5(2)-tri- and meso-substituted tri-methine cyanine dyes (**10a–e**).

Compd. no.	m.p. (°C)	Yield (%)	Mol. formula (mol. wt.)	Colour of crystals	Analysis (%) – Calcd. (Found)			Vis. Abs. max. in 95% EtOH		
					C	H	N	$\lambda_{\max}$ (nm)	$\epsilon_{\max}$ (mol <sup>-1</sup> cm <sup>2</sup> )	
<b>9a</b>	140	58	C <sub>19</sub> H <sub>15</sub> N <sub>3</sub> O <sub>2</sub> (317)	Deep brown	71.92 (71.99)	4.73 (4.81)	13.24 (13.30)	–	–	–
<b>9b</b>	145	48	C <sub>20</sub> H <sub>17</sub> N <sub>3</sub> O <sub>2</sub> (331)	Deep brown	52.51 (52.55)	5.14 (5.18)	12.69 (12.73)	–	–	–
<b>9c</b>	155	53	C <sub>25</sub> H <sub>19</sub> N <sub>3</sub> O <sub>2</sub> (393)	Deep brown	76.33 (76.41)	4.83 (4.92)	10.68 (10.75)	–	–	–
<b>9d</b>	160	60	C <sub>26</sub> H <sub>21</sub> N <sub>3</sub> O <sub>3</sub> (423)	Deep brown	73.75 (73.83)	4.96 (5.00)	9.92 (9.99)	–	–	–
<b>9e</b>	170	79	C <sub>25</sub> H <sub>18</sub> N <sub>4</sub> O <sub>4</sub> (438)	Deep brown	68.49 (68.55)	4.10 (4.20)	12.78 (12.85)	–	–	–
<b>10a</b>	200	57	C <sub>31</sub> H <sub>27</sub> N <sub>4</sub> OI (598)	Deep violet	62.20 (62.31)	4.51 (4.65)	9.36 (9.45)	650, 595, 550, 500, 450	1100, 2000, 2400, 2600, 3400	–
<b>10b</b>	210	46	C <sub>32</sub> H <sub>29</sub> N <sub>4</sub> OI (612)	Deep violet	62.74 (62.81)	4.73 (4.76)	9.15 (9.25)	660, 605, 560, 510, 460	1200, 2200, 2600, 2800, 3600	–
<b>10c</b>	240	64	C <sub>37</sub> H <sub>31</sub> N <sub>4</sub> OI (674)	Deep violet	65.87 (65.95)	4.59 (4.70)	8.30 (8.50)	640, 585, 540, 490, 440	1600, 2400, 3000, 3600, 4200	–
<b>10d</b>	255	59	C <sub>38</sub> H <sub>33</sub> N <sub>4</sub> O <sub>2</sub> I (704)	Deep violet	64.77 (64.85)	4.68 (4.79)	7.95 (8.00)	645, 590, 545, 495, 445	0800, 1200, 1600, 1800, 2600	–
<b>10e</b>	260	58	C <sub>37</sub> H <sub>30</sub> N <sub>5</sub> O <sub>3</sub> I (719)	Deep violet	61.75 (61.86)	4.17 (4.30)	9.73 (9.88)	635, 580, 435, 485, 435	1000, 1600, 2000, 2600, 3400	–

**Table 5.** Characterization of 2-ethyliodide-1,4-diphenyl-1H-pyrazolium[4,5-d][1,3]oxazole-5-one-3(1)-azadimethine cyanine dyes (**11a–c**).

Compd. no.	m.p. (°C)	Yield (%)	Mol. formula (mol. wt.)	Colour of crystals	Analysis (%) – Calcd. (Found)			Vis. Abs. max. in 95% EtOH	
					C	H	N	$\lambda_{\text{max}}$ (nm)	$\epsilon_{\text{max}}$ (mol <sup>-1</sup> cm <sup>2</sup> )
<b>11a</b>	167	68	C <sub>25</sub> H <sub>21</sub> N <sub>4</sub> O <sub>3</sub> I (552)	Deep brown	54.34 (54.40)	3.80 (3.95)	10.14 (10.21)	300, 440	1400, 1000
<b>11b</b>	182	81	C <sub>29</sub> H <sub>23</sub> N <sub>4</sub> O <sub>3</sub> I (602)	Deep brown	57.80 (57.88)	3.82 (3.90)	9.30 (9.40)	320, 460	1600, 0500
<b>11c</b>	179	50	C <sub>29</sub> H <sub>23</sub> N <sub>4</sub> O <sub>3</sub> I (602)	Violet	57.80 (57.86)	3.82 (3.92)	9.30 (9.41)	415, 540	2800, 1200



Scheme 2.

electronic absorption spectra of the monomethine cyanines **5a–c** (**6a–c**) showed absorption bands that underwent bathochromic or hypsochromic shifts depending upon the nature of the heterocyclic quaternary moieties and their linkage position. Therefore, the absorption spectra of the monomethine cyanine dyes **5a** (**6a**), A = 1-ethyl-pyridinium-2-yl salt (1-ethyl-pyridinium-4-yl salt) showed absorption bands hypsochromically shifted if compared with the dyes **5b** (**6b**), A = 1-ethyl-quinolinium-2-yl salt (1-ethyl-quinolinium-4-yl salt), with increasing number and intensity of the absorption bands for the latter dyes (table 2, scheme 1). This is due to the extra conjugation in quinoline. Additionally, changing the linkage position of the pyridinium (quinolinium) residue from the 2-yl salt (4-yl salt) in dyes **5a** (**6b**) to the 4-yl salt (1-yl salt) in dyes **5c** (**6c**), A = 1-ethyl-pyridinium-4-yl salt (1-ethyl isoquinolinium 1-yl salt), resulted in bathochromic (hypsochromic) shifts of absorption bands with increasing (decreasing) intensity of the absorption bands (table 2, scheme 1). This is due to increasing (decreasing) conjugation in the substituted heterocyclic quaternary residue in **5c** (**6c**) than its analogous **5a** (**6b**) (table 2, scheme 1).

Also the electronic absorption spectra of the 5[2(4)]-mono-3[2(4)]-tri-methine mixed cyanine dyes (**8a–c**) showed absorption spectra bands, their positions and intensity depending upon the nature of the heterocyclic quaternary residue A. Thus, substituting A = 1-ethylpyridinium-2-yl salt in the 5(2)-mono-3(2)-tri-methine mixed cyanine dye (**8a**) by A = 1-ethyl-quinolinium-2-yl-salt to give the 5(2)-mono-3(2)-tri-methine mixed cyanine dye (**8b**) causes a bathochromic shift accompanied by increasing number and intensity of the absorption bands (table 3, scheme 1). This is due to increasing conjugation in the quinolinium salt residue compared that in the pyridinium salt residue. Otherwise, substituting A = 1-ethyl-pyridinium-2-yl salt by A = 1-ethyl-pyridinium-4-yl salt transferring from 5(2)-mono-3(2)-tri-methine mixed dye (**8a**) to 5(4)-mono-3(4)-tri-methine mixed dye (**8c**) resulted in a bathochromic shift and increasing number of absorption bands (table 3, scheme 1). This is due to increasing conjugation in pyridinium-4-yl salt compared to its analogous pyridinium-2-yl salt.

On the other hand, the position and molar extinction coefficients of the absorption bands in the electronic absorption spectra of 5(2)-tri- and meso-substituted tri-methine cyanine dyes (**10a–e**) were influenced by the meso-substituted R in the diene side chain. Thus, substituted R=H in dye (**10a**) by R = CH<sub>3</sub> to give dye (**10b**) causes a bathochromic shift owing to the donating nature of the CH<sub>3</sub> group. Reversibly substituting R = H by R = C<sub>6</sub>H<sub>5</sub> passing from dye (**10a**) to dye (**10c**) causes a hypsochromic shifts for the absorption bands (table 4, scheme 1). This is due to the electron-attracting character of the benzene ring. It is also interesting to note that the position of the absorption spectra bands of the dye (**10c**), R = C<sub>6</sub>H<sub>5</sub> is hypsochromically shifted if compared with the dye (**10d**), R = C<sub>6</sub>H<sub>5</sub>-OCH<sub>3</sub> and bathochromically shifted if compared with the dye (**10e**), R = C<sub>6</sub>H<sub>5</sub>-NO<sub>2</sub> (table 4, scheme 1). This is due to the electron-donating nature of the OCH<sub>3</sub> group and the electron-attracting nature of the NO<sub>2</sub> group in the dyes (**10d**) and (**10e**) respectively.

3(1)-Azadimethine cyanine dyes (**11a–c**) showed electronic absorption spectra bands, their positions underwent bathochromic or hypsochromic shifts depending upon the type of substituent R in the benzene ring attached to the azomethine (–N=CH) group. Thus, the dyes **11b** (**11c**), R = 2-OH, 5,6-benzosubstituent (2-OH-3,4-benzosubstituent) showed absorption bands bathochromically shifted if compared with the dye (**11a**), R = 4-OH (table 5, scheme 1). This is due to the increasing conjugation in the naphthyl rings in dyes (**11b**), (**11c**) compared with the phenyl ring in dye (**11a**). Also the dye **11c**, R = 2-OH-

3,4-benzosubstituent showed absorption spectra bands bathochromically shifted with intensification if compared with the dye (**11b**), R = 2-OH-5,6-benzosubstituent (table 5, scheme 1). This may be attributed to the higher planarity of the dye (**11c**).

### 3. Experimental

#### 3.1 General

All melting points are uncorrected. Elemental analysis were carried out at the Micro-analytical Center of Cairo University. IR spectra were determined on a Perkin-Elmer Infrared 127 spectrophotometer (Cairo University), and the  $^1\text{H}$ NMR spectra were obtained using an Em-390 spectrophotometer (Cairo University). Electronic Visible Absorption spectra were carried out on a Shimadzu UV-VIS 240 spectrophotometer (Faculty of Science, Aswan).

#### 3.2 Synthesis

Synthesis of individual dyes are detailed below.

3.2a *3-Methyl-1,4-diphenyl-1H-pyrazolo[4,5-d][1,3]oxazole-5-phenyl azomethine (2)*: Equimolar ratios of 4-bromo-5-pyrazolone **1** (2.53 gm, 0.01 mole) and diphenyl urea (2.12 gm, 0.01 mole) were dissolved in a mixture of ethanol (50 ml) and pyridine (20 ml). The reaction mixture was refluxed for 8–10 h, filtered while hot, and acidified with concentrated hydrochloric acid. The product which precipitated out on addition of ice-cold water was filtered off, washed several times with water, dried and recrystallized from ethanol to give (**2**) as red/brown crystals. Relevant data are given in table 1.

IR spectrum (KBr) ( $\text{cm}^{-1}$ ) for **2**: 696, 754 (benzene mono-substituted); 1052, 1155 (C–O–C cyclic); 1312 (C–N); 1596 (C=N), 1649 (C=C).

$^1\text{H}$  NMR spectrum ( $\text{CDCl}_3$ ) (**d**) for **2**: 0.85 (s, 3H,  $\text{CH}_3$  H-atoms); 6.6–8.8 (m, 15H, aromatic H-atoms).

3.2b *Synthesis of 3-methyl-1,4-diphenyl-1H-pyrazolo[4,5-d][1,3]oxazole-5-one (3)*: 40% sulphuric acid (50 ml) was added to a suspension of **2** (1 gm, 0.003 mole) in ethanol (50 ml). The mixture was refluxed for 2h, until **2** dissolved, and then heated for an additional 1h, cooled and diluted with an equal volume of water whereupon the unchanged **2** that precipitated was filtered off, and the filtrate extracted with chloroform. The extract was concentrated to near dryness, yielding pale brown product, which was recrystallized from excess ethanol to give pale brown crystals of **3**. The results are listed in table 1.

IR spectrum (KBr) ( $\text{cm}^{-1}$ ) for **3**: 694, 752 (benzene mono-substituted); 1073, 1176 (C–O–C cyclic); 1312 (C–N); 1597 (C=N), 1651 (C=C); 1700 (C=O).

$^1\text{H}$  NMR spectrum ( $\text{CDCl}_3$ ) (**d**) for **3**: 0.9 (s, 3H,  $\text{CH}_3$  H-atoms); 6.7–8.0 (m, 10H, aromatic H-atoms).

3.2c *2-Ethylidide-3-methyl-1,4-diphenyl-1H-pyrazolum[4,5-d][1,3]-oxazole-5-one (4)*: A pure sample of **3** (2.91 gm, 0.01 mole) was suspended in excess iodoethane and heated in a sealed tube in an electric oven at  $140^\circ\text{C}$  for 3 h<sup>14,15</sup>. The sealed tube was first cooled,

then opened and the product (**4**) collected, washed with ether and recrystallized from ethanol to give brown crystals. The results are summarized in table 1.

IR spectrum (KBr) ( $\text{cm}^{-1}$ ) for **4**: 693, 753 (benzene mono-substituted); 1072, 1175 (C–O–C cyclic); 1310 (C–N); 1547 (C=N), 1597 (C=C); 1703 (C=O); 2922 (quaternary salt).

$^1\text{H}$  NMR spectrum ( $\text{CDCl}_3$ ) (**d**) for (**4**): 1.0 (*s*, 3H,  $\text{CH}_3$  H-atoms at position 3); 1.35 (*t*, 3H,  $\text{CH}_3$  H-atoms of  $\text{CH}_3\text{CH}_2\text{N}^+$ -pyrazolum); 2.25 (*q*, 2H,  $\text{CH}_2$  H-atoms of  $\text{CH}_3\text{CH}_2\text{N}^+$ -pyrazolum); 6.7–8.5 (*m*, 10H, aromatic H-atoms).

3.2d *3-Methyl-1,4-diphenyl-1H-pyrazolo[4,5-d][1,3]oxazole-5[2(4)]-monomethine cyanine dyes (5a–c)*: Piperidine (5–7 drops) was added to a mixture of equimolar ratios (2.91 gm, 0.01 mole) of **3** and the iodoethane quaternary salt of **a**picoline (2.49 gm, 0.01 mole), quinaldine (2.99 gm, 0.01 mole), **g**picoline (2.49 gm, 0.01 mole) in ethanol (50 ml). The reaction mixture was refluxed for 3–5 h, filtered while hot, concentrated, cooled, acidified with acetic acid and precipitated by addition of cold water. The precipitate was filtered, washed with water, and recrystallized from ethanol. The results are given in table 2.

IR spectrum (KBr) ( $\text{cm}^{-1}$ ) for **5b**: 694, 753 (benzene mono-substituted); 833, 896 (benzene disubstituted); 1048, 1187 (C–O–C cyclic); 1310 (C–N); 1543 (C=N), 1597 (C=C); 2925 (quaternary salt).

$^1\text{H}$  NMR spectrum ( $\text{CDCl}_3$ ) (**d**) for **5b**: 0.95 (*s*, 3H,  $\text{CH}_3$  H-atoms at position 3); 1.5 (*t*, 3H,  $\text{CH}_3$  H-atoms of  $\text{CH}_3\text{CH}_2\text{N}^+$ -quinolinium); 2.4 (*q*, 2H,  $\text{CH}_2$  H-atoms of  $\text{CH}_3\text{CH}_2\text{N}^+$ -quinolinium); 6.7–9.3 (*m*, 17H, aromatic + heterocyclic + =CH–H-atoms).

3.2e *2-Ethyl-1,4-diphenyl-1H-pyrazolo[4,5-d][1,3]oxazole-5-one-3[4(1)]-monomethine cyanine dyes (6a–c)*: A mixture of equimolar amounts of **4** (4.47 gm, 0.01 mole) and iodoethane quaternary salt of pyridine (2.35 gm, 0.01 mole), quinoline (2.85 gm, 0.01 mole), and isoquinoline (2.85 gm, 0.01 mole) in ethanol (50 ml) was refluxed for 7–9 h in presence of piperidine (5–7 drops). The mixture was filtered while hot, concentrated, cooled and acidified with acetic acid. The precipitated product which appeared on dilution with water was filtered, washed with water several times, dried and recrystallized from ethanol. The data are shown in table 2.

IR spectrum (KBr) ( $\text{cm}^{-1}$ ) for **6b**: 694, 753 (benzene mono-substituted); 829, 896 (benzene disubstituted); 1078, 1199 (C–O–C cyclic); 1308 (C–N); 1539 (C=N), 1596 (C=C); 1702 (C=O); 2925 (quaternary salt).

$^1\text{H}$  NMR spectrum ( $\text{CDCl}_3$ ) (**d**) for **6b**: 1.2 (*t*, 3H,  $\text{CH}_3$  H-atoms of  $\text{CH}_3\text{CH}_2\text{N}$ -pyrazole); 2.1 (*q*, 2H,  $\text{CH}_2$  H-atoms of  $\text{CH}_3\text{CH}_2\text{N}$ -pyrazole); 1.4 (*t*, 3H,  $\text{CH}_3$  H-atoms of  $\text{CH}_3\text{CH}_2\text{N}^+$ -quinolinium); 2.3 (*q*, 2H,  $\text{CH}_2$  H-atoms of  $\text{CH}_3\text{CH}_2\text{N}^+$ -quinolinium); 6.6–9.2 (*m*, 17H, aromatic + heterocyclic + =CH–H-atoms).

3.2f *Intermediate compound (7)*: Equimolar amounts of **4** (4.47 gm, 0.01 mole) and triethyl orthoformate (1.48 gm, 0.01 mole) were dissolved in ethanol (30 ml), and piperidine (5–7 drops) was then added. The reaction mixture was heated under reflux for 5–7 h, filtered while hot, concentrated, cooled, acidified with acetic acid and diluted with water. The precipitated products were filtered and recrystallized from ethanol to give the intermediate compound **7** (see table 3).

IR spectrum (KBr) ( $\text{cm}^{-1}$ ) for **7**: 694, 753 (benzene mono-substituted); 1072, 1175 (C–O–C cyclic); 1232 (acetal); 1309 (C–N); 1597 (C=N), 1648 (C=C); 1705 (C=O); 2925 (quaternary salt).

$^1\text{H}$  NMR spectrum ( $\text{CDCl}_3$ ) (**d**) for **7**: 1.45 (*t*, 3H,  $\text{CH}_3$  H-atoms of  $\text{CH}_3\text{CH}_2\text{N}^+$ -pyrazolium); 2.35 (*q*, 2H,  $\text{CH}_2$  H-atoms of  $\text{CH}_3\text{CH}_2\text{N}^+$ -pyrazolium); 0.95 (*t*, 6H,  $2\text{CH}_3$  H-atoms of 2  $\text{OC}_2\text{H}_5$ ); 1.65 (*q*, 4H,  $2\text{CH}_2$  H-atoms of 2  $\text{OC}_2\text{H}_5$ ); 3.40 (*d*, 2H,  $\text{CH}_2$  H-atoms of  $\text{CH}_2\text{CH}(\text{OEt})_2$ ); 1.6 (*t*, 1H, CH H-atom of  $\text{CH}_2\text{CH}(\text{OEt})_2$ ); 6.7–8.5 (*m*, 10H, aromatic H-atoms).

3.2g *2-Ethyl-1,4-diphenyl-1H-pyrazolo[4, 5-d][1, 3]oxazole-5[2(4)]-mono-3[2(4)]-tri-methine mixed cyanine dyes (8a–c)*: Molar ratios (1:2) of **7** (5.49 gm, 0.01 mole) and iodoethane quaternary salt of 2(4)-methylpyridine (4.98 gm, 0.02 mole) or quinoline (5.98 gm, 0.02 mole) were refluxed for 3–5 h in ethanol (30 ml) containing a few drops of piperidine. The precipitated compounds after cooling and acidified with acetic acid were filtered and recrystallized from aqueous ethanol (see table 3).

IR spectrum (KBr) ( $\text{cm}^{-1}$ ) for **8b**: 694, 753 (benzene mono-substituted); 830, 873 (benzene disubstituted); 1080, 1183 (C–O–C cyclic); 1308 (C–N); 1543 (C=N), 1597 (C=C); 2924 (quaternary salt).

$^1\text{H}$  NMR spectrum ( $\text{CDCl}_3$ ) (**d**) for **8b**: 1.3 (*t*, 3H,  $\text{CH}_3$  H-atoms of  $\text{CH}_3\text{CH}_2\text{N}$ -pyrazole); 2.2 (*q*, 2H,  $\text{CH}_2$  H-atoms of  $\text{CH}_3\text{CH}_2\text{N}$ -pyrazole); 1.5 (*t*, 3H,  $\text{CH}_3$  H-atoms of  $\text{CH}_3\text{CH}_2\text{N}^+$ -quinolinium at position 5); 2.4 (*q*, 2H,  $\text{CH}_2$  H-atoms of  $\text{CH}_3\text{CH}_2\text{N}^+$ -quinolinium at position 5); 1.6 (*t*, 3H,  $\text{CH}_3$  H-atoms of  $\text{CH}_3\text{CH}_2\text{N}^+$ -quinolinium at position 3); 2.5 (*q*, 2H,  $\text{CH}_2$  H-atoms of  $\text{CH}_3\text{CH}_2\text{N}^+$ -quinolinium at position 3); 6.7–9.8 (*m*, 26H, aromatic + heterocyclic + =CH–H-atoms).

3.2h *5-Acylmethylideno derivatives as intermediate compounds (9a–e)*: Equimolar amounts of **3** (2.91 gm, 0.01 mole) and the carbonyl compound (acetaldehyde) (0.44 gm, 0.01 mole), acetone (0.58 gm, 0.01 mole), acetophenone (1.2 gm, 0.01 mole), 4-methoxy acetophenone (1.5 gm, 0.01 mole), 4-nitroacetophenone (1.65 gm, 0.01 mole) were heated under reflux in ethanol (30 ml) with piperidine (5–7 drops) catalysis for 5–7 h. The reaction mixture was filtered while hot, concentrated and the isolated resinous material was triturated with ether followed by water where the precipitated products were filtered and recrystallized from aqueous ethanol (table 4).

IR spectrum (KBr) ( $\text{cm}^{-1}$ ) for **9a**: 693, 756 (benzene mono-substituted); 1012, 1115 (C–O–C cyclic); 1310 (C–N); 1556 (C=N); 1597 (C=C); 1707 (CHO).

$^1\text{H}$  NMR spectrum ( $\text{CDCl}_3$ ) (**d**) for **9a**: 0.85 (*s*, 3H,  $\text{CH}_3$  H-atoms); 6.7–8.0 (*m*, 11H, aromatic + =CH–H-atoms); 9.75 (*d*, 1H, CHO H-atom).

3.2i *3-Methyl-1,4-diphenyl-1H-pyrazolo[4,5d][1,3]oxazole-5(2)-tri-and meso substituted tri-methine cyanine dyes (10a–e)*: Equimolar amounts of **9a–e** (3.17 gm, 0.01 mole; 3.31 gm, 0.01 mole; 3.93 gm, 0.01 mole; 4.23 gm, 0.01 mole; 4.38 gm, 0.01 mole) and iodoethane quaternary salt of 2-methylquinoline (2.99 gm, 0.01 mole) were dissolved in ethanol (30 ml), to which piperidine (5–7) drops was added. The reaction mixture was refluxed for 3–5 h. until it attained a permanent colour, filtered while hot, concentrated, cooled and acidified with acetic acid. The precipitated products were filtered and recrystallized from ethanol, characterization data are shown in table 4.

IR spectrum (KBr) ( $\text{cm}^{-1}$ ) for **10a**: 694, 753 (benzene mono-substituted); 834, 873 (benzene disubstituted); 1085, 1123 (C–O–C cyclic); 1310 (C–N); 1496 (C=N); 1597 (C=C); 2925 (quaternary salt).

$^1\text{H}$  NMR spectrum ( $\text{CDCl}_3$ ) (**d**) for **10a**: 0.98 (s, 3H,  $\text{CH}_3$  H-atoms); 1.55 (t, 3H,  $\text{CH}_3$  H-atoms of  $\text{CH}_3\text{CH}_2\text{N}^+$ -quinolinium); 2.45 (q, 2H,  $\text{CH}_2$  H-atoms of  $\text{CH}_3\text{CH}_2\text{N}^+$ -quinolinium); 6.7–9.5 (m, 19H, aromatic + heterocyclic + =CH–H-atoms).

3.2j *2-Ethyl iodide-1,4-diphenyl-1H-pyrazolum[4,5d][1,3]oxazole-5-one-3(1)-azadimethine cyanine dyes (11a–c)*: A mixture of equimolar ratios (0.01 mole) of **4** (4.47 gm, 0.01 mole) and the nitroso compounds (*p*-nitrosophenol (1.23 gm, 0.01 mole), **a**nitroso-**b**naphthol (1.73 gm, 0.01 mole), **b**nitroso-**a**naphthol (1.73 gm, 0.01 mole)) was refluxed in presence of piperidine (5–7 drops) as basic catalyst and ethanol (30 ml) as organic solvent for 9–13 h. The reaction mixture attained a permanent deep brown/violet colour. It was filtered off while hot, cooled and acidified with acetic acid. The precipitated product after dilution with cold water was filtered off, washed with water, and crystallized from ethanol, relevant data are given in table 5.

IR spectrum (KBr) ( $\text{cm}^{-1}$ ) for **11c**: 695, 753 (benzene mono-substituted); 831, 894 (benzene disubstituted); 1072, 1110 (C–O–C cyclic); 1310 (C–N); 1596 (C=N); 1648 (C=C); 1704 (C=O); 2924 (quaternary salt); 3290 (OH).

$^1\text{H}$  NMR spectrum ( $\text{CDCl}_3$ ) (**d**) for **11c**: 1.4 (t, 3H,  $\text{CH}_3$  H-atoms of  $\text{CH}_3\text{CH}_2\text{N}^+$ -pyrazolum); 2.3 (q, 2H,  $\text{CH}_2$  H-atoms of  $\text{CH}_3\text{CH}_2\text{N}^+$ -pyrazolum); 6.7–9.4 (m, 18H, aromatic + naphthyl + =CH– + OH H-atoms).

### 3.3 Spectral behaviour

Spectral behaviour of all the synthesized cyanine dyes in 95% ethanol were recorded using 1 cm cells. A stock solution ( $10^{-3}$  M) of the dyes was diluted to appropriate volume in order to obtain the required concentrations.

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