Electronic spectra of some new synthesised methine cyanine dyes

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Abstract. New methine cyanine dyes such as monomethine (3a-e), azamethine (4a-c) and trimethine (6a-i) and (8a-c) incorporating a fused pyrazolo [3,4-*d*] oxazole nucleus were prepared. The new synthesised cyanines were identified by elemental and spectral analyses. The visible absorption spectra of some selected dyes were investigated in pure and mixed solvents as well as in aqueous buffer solutions. Molecular complex formation with ethanol was verified by mixed solvent studies. The variation of absorbance with pH was utilized for the determination of the *pKa* values for selected compounds.

Keywords. Cyanine dyes; synthesis; solvatochromism; acid-base properties.

1. Introduction

Methine cyanine dyes have found various applications as photosensitisers in blue-green light (Kozlov *et al* 1972) as laser dyes (Dgdyusha *et al* 1978) and as analytical reagents over a wide pH range (Koraïem *et al* 1986). They are also considered as being suitable for super- and light photographic sensitizers for silver halide emulsion (Konishiroko 1976, 1978).

In the present work, new mono-, aza- and tri-methine cyanine dyes incorporating fused pyrazolo [3,4-*d*] oxazole nucleus 3a-e, 4a-c, 6a-i and 8a-c were prepared to study their spectral behaviours, solvatochromic and acid-base properties anticipating the potential application of such dyes as photosensitizers.

2. Results and discussion

Our approach to the synthesis of mono-, aza- and tri-methine cyanines started with the preparation of 5-aryl-3-methyl-1-phenyl pyrazolo [3,4-*d*] oxazole-2,4-bis ethiodide 2a-e via quaternization of 5-aryl-3-methyl-1-phenyl pyrazolo [3,4-*d*] oxazole derivatives 1a-e (Koraïem *et al* 1990) using excess amount of ethyl iodide under controlled conditions. Interaction of 2a-e (table 1) and 1-methyl quinolinium iodide in equimolar ratios under piperidine catalysis gave the corresponding asymmetrical pyrazolo [3,4-*d*] oxazole-(4)-monomethine cyanine dyes 3a-e (scheme 1).

The structures of synthesised compounds were confirmed by elemental analysis, IR and ¹H NMR (Schimann 1970) spectral data (tables 2-4). The asymmetrical monomethine dyes 3a-e were coloured compounds and were partially soluble in non-polar solvents, in which they gave orange solutions with a green fluorescence. They were readily soluble in most polar solvents, giving reddish-brown solutions with intense green fluorescence. They were soluble in conc. H₂SO₄ liberating iodine vapour on

1, 2, 3, 5, : **a**, $\text{R} = \text{H}$; **b**, $\text{R} = p\text{-OCH}_3$; **c**, $\text{R} = p\text{-NO}_2$; **d**, $\text{R} = p\text{-OH}$; **e**, $\text{R} = p\text{-Cl}$

4a-c : **a**, $\text{R} = p\text{-NO}_2$, 4OH , $\text{Y} = \text{H}$; **b**, $\text{R} = p\text{-NO}_2$, 2OH , $\text{Y} = 5,6\text{-benzo}$;

c, $\text{R} = p\text{-NO}_2$, 2OH , $\text{Y} = 3,4\text{-benzo}$.

6a-i : **a**, $\text{R} = \text{H}$, $\text{A} = \text{C}_4\text{H}_4\text{-2-yl salt}$; **b**, $\text{R} = \text{H}$, $\text{A} = \text{C}_4\text{H}_4\text{-4-yl salt}$; **c**, $\text{R} = p\text{-OCH}_3$, $\text{A} = \text{C}_4\text{H}_4\text{-2-yl salt}$; **d**, $\text{R} = p\text{-OCH}_3$, $\text{A} = \text{C}_4\text{H}_4\text{-4-yl salt}$; **e**, $\text{R} = p\text{-NO}_2$, $\text{A} = \text{C}_4\text{H}_4\text{-2-yl salt}$;

f, $\text{R} = p\text{-OH}$, $\text{A} = \text{C}_4\text{H}_4\text{-2-yl salt}$; **g**, $\text{R} = p\text{-OH}$, $\text{A} = \text{C}_4\text{H}_4\text{-4-yl salt}$; **h**, $\text{R} = p\text{-Cl}$, $\text{A} = \text{C}_4\text{H}_4\text{-2-yl salt}$; **i**, $\text{R} = p\text{-Cl}$, $\text{A} = \text{C}_4\text{H}_4\text{-4-yl salt}$.

7, 8 : **a**, $\text{R} = \text{H}$; **b**, $\text{R} = p\text{-NO}_2$; **c**, $\text{R} = p\text{-OH}$.

DPF^a : diphenylformamidine.

TEMb : Triethoxymethane.

Scheme 1

Table 2. The characterization of asymmetrical pyrazolo [3,4-*d*] oxazolo-3-monomethine/azamethine cyanine moieties **3a-c** and **4a-c**.

Compound	m.p. (°C)	Yield (%)	Mol formula (Mol. wt.)	Nature of product	Analysis (%): Calcd. found				Absorption spectra in 95% ethanol	
					C	H	N	$\lambda_{\max}$ (nm)	$\epsilon_{\max}$ (m ⁻¹ cm ²)	
3a	172	59	C ₃₁ H ₃₀ N ₄ OI ₂ (728)	Red powder	51.10 (51.61)	4.12 (4.66)	7.69 (7.51)	467	3912	
3b	165	63	C ₃₂ H ₃₂ N ₄ O ₂ I ₂ (758)	Red powder	50.66 (51.90)	4.22 (4.39)	7.39 (7.30)	510	5600	
3c	168	48	C ₃₁ H ₂₉ N ₅ O ₃ I ₂ (773)	Brownish red crystals	48.12 (48.61)	3.75 (4.17)	9.06 (8.89)	457	3568	
3d	180	65	C ₃₁ H ₃₀ N ₄ O ₂ I ₂ (744)	Red crystals	50.00 (50.12)	4.03 (4.52)	7.53 (7.32)	350, 445, 530	9040, 2076, 12148	
3e	144	53	C ₃₁ H ₂₉ N ₄ OI ₂ Cl (762.5)	Brownish red crystals	48.79 (49.19)	3.80 (4.29)	7.34 (7.59)	460	2768	
4a	218	76	C ₂₇ H ₂₅ N ₅ O ₄ I ₂ (737)	Brown crystals	43.96 (44.51)	3.39 (4.13)	9.50 (10.11)	370	13800	
4b	136	78	C ₃₁ H ₂₇ N ₅ O ₄ I ₂ (787)	Shiny brownish crystals	47.27 (48.12)	3.43 (3.99)	8.89 (9.14)	550	3960	
4c	145	73	C ₃₁ H ₂₇ N ₅ O ₄ I ₂ (787)	Brownish red crystal	47.27 (48.16)	3.43 (4.10)	8.89 (9.17)	350, 445	9980, 2800	

Table 3. Characterisation data for asymmetrical/symmetrical pyrazolo-[3, 4-*d*] oxazole-3[2(4)/3] trimethine cyanine dyes 6a-i and 8a-c.

Compound	m.p. (°C)	Yield (%)	Mol. formula (Mol. wt.)	Colour of crystals	Analysis (%): Calcd. (found)			Absorption spectra in 95% ethanol	
					C	H	N	$\lambda_{\max}$ (nm)	$\epsilon_{\max}$ (m ⁻¹ cm ²)
<u>6a</u>	133	67	C ₃₄ H ₃₄ H ₄ OI ₂ (768)	Violet	53.13 (53.39)	4.43 (4.90)	7.29 (6.85)	515, 555	5640, 5260
<u>6b</u>	108	76	C ₃₄ H ₃₄ N ₄ OI ₂ (768)	Blue	53.13 (53.25)	4.43 (4.70)	7.29 (7.10)	670, 708	1000, 640
<u>6c</u>	135	70	C ₃₅ H ₃₀ N ₄ O ₂ I ₂ (798)	Violet	52.63 (53.13)	4.51 (4.75)	7.02 (7.13)	518, 560, 699	6800, 9070, 2050
<u>6d</u>	139	77	C ₃₅ H ₃₆ N ₄ O ₂ I ₂ (798)	Blue	52.63 (53.05)	4.51 (4.55)	7.02 (7.43)	580, 668	1642, 978
<u>6e</u>	158	71	C ₃₄ H ₃₃ N ₅ O ₃ I ₂ (813)	Violet	50.18 (50.56)	4.06 (4.81)	8.61 (8.53)	520, 565, 666	3850, 4080, 890
<u>6f</u>	145	74	C ₃₄ H ₃₄ N ₄ O ₂ I ₂ (783)	Violet	52.04 (52.31)	4.34 (4.84)	7.14 (7.63)	512, 557, 582	6660, 7080, 6800
<u>6g</u>	164	78	C ₃₄ H ₃₄ N ₄ O ₂ I ₂ (783)	Blue	52.04 (52.16)	4.34 (4.74)	7.14 (7.53)	585, 595, 667	2724, 2700, 1260
<u>6h</u>	118	68	C ₃₄ H ₃₃ N ₄ OI ₂ Cl (802.5)	Violet	50.84 (51.15)	4.11 (4.53)	6.98 (7.27)	510, 559, 588	4996, 4790, 4280
<u>6i</u>	128	79	C ₃₄ H ₃₃ N ₄ OI ₂ Cl (802.5)	Blue	50.84 (51.10)	4.11 (4.41)	6.98 (7.10)	590, 670	1060, 1292
<u>8a</u>	102	39	C ₄₃ H ₄₃ N ₆ O ₂ I ₂ (1056)	Brown	48.86 (49.19)	4.07 (4.57)	7.95 (8.16)	447, 539sh	18800, 8080
<u>8b</u>	126	30	C ₄₃ H ₄₁ N ₆ O ₆ I ₃ (1146)	Brown	45.03 (45.41)	3.58 (3.82)	9.77 (10.14)	438	3480
<u>8c</u>	118	35	C ₄₃ H ₄₃ N ₆ O ₄ I ₃ (1088)	Red	47.43 (47.10)	3.95 (4.15)	7.72 (8.10)	445, 525	29640, 14040

Table 4. IR and ^1H NMR spectral data of some selected starting compounds like monomethine, azamethine and asymmetrical/symmetrical trimethine cyanine dyes.

Com- pound	IR spectrum, $\nu_{\text{max}}^{\text{KBr}}(\text{cm}^{-1})$	^1H NMR (CDCl_3) spectrum, δ (ppm) ^a
<u>2a</u>	2980–2940 (ν ethiodide) 1620–1600 (ν C=C) 1590–1580 (ν C=N) 1180–1210 (ν oxazole C–O–C)	6.5–6.9 [<i>m</i> , 10H, Ar] 3.3–3.8 [<i>m</i> , 10H, ethiodide] 2.4 [<i>s</i> , 3H, CH_3 –]
<u>3a</u>	3000–2940 (ν ethyl and methyl iodide) 1620–1600 (ν C=C) 1580 (ν C=C) 1180–1210 (ν oxazole C–O–C)	6.8–7.8 [<i>m</i> , 17H, Ar, (het.)–H and =CH] 2.1–2.6 [<i>m</i> , 8H, ethyl and methyl iodide] 1.3–1.5 [<i>q</i> , 2H, CH_2^*CH_3] 1.1–1.2 (<i>t</i> , 3H, CH_2CH_3^*)
<u>4a</u>	3260–3230 (ν OH) 2980–2940 (ν ethiodide) 1725–1700 (ν –CH=N) 1530–1350 (ν conjugated NO_2) 1180–1210 (ν oxazole C–O–C)	7.8–8.4 [<i>m</i> , 15H, Ar, CH=N, & OH] 1.9–2.9 [<i>m</i> , 10H, ethiodide]
<u>6a</u>	2980–2940 (ν ethiodide) 1680–1660 (ν CH=CH–CH=) 1180–1210 (ν oxazole C–O–C) 840–820 (ν mono-sub.Ar.)	6.5–6.9 [<i>m</i> , 16H, Ar(het.)–H] 1.7–2.4 [<i>m</i> , 10H, ethiodide] 1.4–1.6 [<i>t</i> , 3H, =CH–CH=CH–] 0.9–1.3 [<i>m</i> , 5H, CH_3CH_2]
<u>8a</u>	2980–2940 (ν ethiodide) 1680–1660 (ν CH=CH–CH=) 1610–1600 (ν C=C) 1180–1210 (ν oxazole C–O–C) 840–820 (ν mono-sub.Ar.)	7.1–8.2 [<i>m</i> , 20H, Ar.] 2.3–2.5 [<i>t</i> , 3H, CH=CH–CH=] 1.6–1.9 [<i>m</i> , 15H, ethiodide] 1.1–1.4 [<i>m</i> , 5H, CH_3CH_2 –]

^aAbbreviations; *s*, singlet; *d*, doublet, *t*, triplet; *m*, multiplet

replacement of the acetanilido group by 1-ethyl quinolinium salt with interchange of the quaternary centres on the molecules. See scheme 1.

The structures of the synthesised asymmetrical 3[2(4)] trimethine cyanines 6a–i were established by elemental analysis, IR and ^1H NMR (Schimann 1970) spectral data (tables 3, 4). They are partially soluble in non-polar solvents exhibiting reddish-violet solutions with slight green fluorescence. They are soluble in polar solvents giving deep violet solutions with intense green fluorescence. They liberate iodine in warm conc. H_2SO_4 . The colour of their ethanolic solutions is discharged on acidification.

The visible absorption spectra of 6a–i in 95% ethanol exhibit absorption bands intensified and more bathochromic for quinolinium-4-yl salts than 2-yl analogues. Such absorption bands undergo bathochromic or hypsochromic shifts on substitution of aryl oxazole either with electron donating (e.g. *p*- OCH_3 , *p*-OH) or withdrawing (e.g. *p*- NO_2) groups respectively (table 3). This is due to the same reasons as suggested for compounds 3a–e.

Attention was thus turned to novel Knoevenagel-type reactions (Vogel 1956) at the 3-methyl group of 5-aryl-1-phenyl-3-methyl pyrazolo [3,4-*d*] oxazole-2,4-*bis* ethyl iodide 2a–e. These salts 2a, 2c and 2d when heated under reflux in pyridine with triethoxymethane (TEM) yielded orange crystalline products identified as symmetrical trimethine cyanine dyes 8a–c. (See scheme 1).

The structures of symmetrical trimethine cyanines **8a–c** were established by elemental analysis, IR and ^1H NMR (Schimann 1970) spectral data (tables 3, 4). They are orange coloured compounds, fairly soluble in polar and non-polar organic solvents. They are soluble in conc. H_2SO_4 liberating iodine vapour on heating.

As was observed in the electronic absorption spectra of either asymmetrical mono- and trimethine, the visible absorption spectra of symmetrical trimethine cyanine dyes **8a–c** in 95% ethanol exhibit single broad absorption band. Either its position or molar extinction coefficient is influenced by the aryl substituents attached to the pyrazolo-[3,4-*d*] oxazole moieties. (See table 3).

2.1 Solvatochromic behaviour of asymmetrical pyrazolo [3,4-*d*] oxazolium-3(4)- monomethine cyanine dye **3d** and/or 3(2)-trimethine cyanine **6f** in pure solvents

The λ_{max} and ϵ_{max} values of the absorption bands due to different electronic transitions with the solute molecules **3d** and **6f** obtained in pure solvents of different dielectric constants (Weast and Astle 1980) (viz. H_2O , DMF, EtOH, CHCl_3 , acetone, dioxane and benzene), are represented in table 5.

The spectra of compounds **3d** and **6f** in ethanol consist of three essential absorption bands located at longer wavelengths in the visible region attributed to $n-\pi^*$ transitions and intramolecular charge transfer (CT) transitions (Mahmoud *et al* 1975).

Careful examination of the results reported in table 5 reveals that the bands corresponding to CT transitions show a red shift on changing the organic solvent from EtOH to dioxane, benzene, acetone, DMF and CHCl_3 (Koraiem *et al* 1990). The unexpected blue shift observed in the λ_{max} of CT bands in ethanol can be mainly explained as a result of intermolecular H-bond formation between ethanol and the lone pair electrons of the oxazole oxygen atom. Thus, the mobility of the π -electrons to the conjugated pathway is decreased and consequently the observed high excitation energy

Table 5. Electronic absorption spectral* characteristics of the monomethine cyanine **3d** and the trimethine cyanine **6f** in single solvents at 25°C.

Compound	H_2O	DMF	EtOH	CHCl_3	Acetone	Dioxane	C_6H_6
3d	340	347	350	335	335	345 <i>sh</i>	335
	(7300)	(8000)	(9040)	(6810)	(7100)	(7000)	(8000)
	—	405	—	414	410	413	414
	—	(5500)	—	(5800)	(6800)	(5800)	(5810)
	—	—	445	458	445	—	465
	—	—	(2076)	(7100)	(7500)	—	(7400)
6f	512	550	530	555	548	545	552
	(9600)	(14100)	(14148)	(12600)	(13300)	(12100)	(12200)
	515	515	512	520	519	515 <i>sh</i>	520
	(5600)	(6200)	(6660)	(6010)	(6010)	(4910)	(6000)
	555	563	557	562	561	—	—
	(6018)	(6730)	7030	7100	(6820)	—	—
	580	585	582	—	590	588	585
	(6020)	(6800)	(6800)	—	(6910)	(6400)	(7200)
	—	615	—	608	—	622	630
	—	(6400)	—	(6820)	—	(6510)	(5800)

* Data shown are λ_{max} (nm) with ϵ_{max} ($\text{mol}^{-1}\text{cm}^2$) in parentheses; *sh* = shoulder

Figure 1. The absorption spectra of two selected cyanines (**3d**, **4f**) recorded in ethanol-water mixtures.

needed in ethanolic medium relative to the other organic solvents used. The blue shift observed in $\lambda_{\max}$ of the CT bands of compounds **3d** and **6f** in water (dielectric constant = 78.54) (Weast *et al* 1980) relative to ethanol (24.3), as well as the lower extinction, can be ascribed to the stronger interaction of water molecule with the lone pair of the electrons on the oxygen of oxazolo nucleus through H-bonding (Koraïem *et al* 1990, 1991).

2.2 Spectral behaviour of pyrazolo-[3,4-d]-oxazolium-3(4)-monomethine and/or 3(2)-trimethine cyanine dyes **3d** and **6f** in mixed solvents

Spectra in mixed solvents were recorded in order to evaluate the possibility of the formation of a hydrogen-bonded solvated complex between the solute molecules and ethanol or water. The visible spectra of compounds **3d** and **6f** in EtOH containing progressively increasing quantities of H₂O, showed (figure 1), a decrease in the absorbance of the CT band with increasing proportion of H₂O and the disappearance of the absorption band located at $\lambda_{\max}$ 445 nm for **3d**.

Evidence for hydrogen-bond formation between the solute molecules and ethanol or water can be obtained from data on the free energy change of formation (ΔG) of the molecular complex, calculated using the relationship (1).

$$\Delta G = -RT \ln K_f. \quad (1)$$

The stability constant (K_f) of the complex can be determined from a consideration of the behaviour in mixed solvents (Koraïem *et al* 1990, 1991) using the relationship (2), figure 2.

$$\log K_f = \log \frac{A - A_{\min}}{A_{\max} - A} - n \log C_{\text{EtOH}} \quad (2)$$

The values of K_f and ΔG of the hydrogen-bonded molecular complex liable to be formed in solution between the molecules of compound **3d** and EtOH or H₂O are as follows.

Figure 2. $\log(A - A_{\min})/(A_{\max} - A)$ vs $\log C_{\text{EtOH}}$ for compound **3d** in H₂O-EtOH mixtures at 25°C.

System	Excitation energy (kJ mol ⁻¹)		Orientation energy (kJ mol ⁻¹)	H-bond energy (kJ mol ⁻¹)	<i>n</i>	<i>K_f</i>	ΔG (kJ mol ⁻¹)
	Pure H ₂ O	Pure EtOH					
H ₂ O–EtOH	64.27	75.26	1.93	5.23	1	10	1.25

The values of K_f , ΔG and n (the number of EtOH or H₂O molecules which are complexed with the solute molecule) indicate that a 1:1 complex is formed.

On plotting the excitation energy (E) of the CT band in the mixed solvent versus the ethanol mole fractions (figure 3), a broken line (Chemla *et al* 1987) with three segments is obtained. The first segment indicates the orientation of the solvent molecules around the solute molecule. The second segment represents the molecular complex formation, while the third segment represents the steady state of the energy attained after the complete formation of the molecular complex. The values of orientation and H-bond energies are given above.

2.3 Acid–base properties

The ethanolic solutions of new synthesised cyanine dyes **3d**, **6f** and **8b** give a permanent colour in basic medium which was discharged on acidification. This prompted us to study their spectral behaviour in different buffer solutions in order to choose suitable pH media when used as photosensitizers.

The electronic absorption spectra of cyanine dyes **3d**, **6f** and **8b** in universal buffer solutions of varying pH (2.53–12.08) undergo hypsochromic shifts in the absorption band in acidic medium (low pH) and bathochromic shift in alkaline medium (high pH) (figure 4).

The bathochromic shift in alkaline medium is due to a relatively increased negative charge density on the pyrazolo-[3,4-*d*] oxazole system. The bands are hypsochromically shifted in acidic medium due to protonation of the nitrogen/oxygen heteroatoms

Figure 3. CT band excitation energy (E) vs EtOH mole fraction for compound **3d** in H₂O–EtOH mixtures at 25°C.

Figure 4. The variation of absorption spectra of selected cyanines (**3d**, **4f** and **8c**) with changes in pH of the medium.

of the nuclei or of the mono- and trimethine systems at low pH. CT interaction within the protonated form is thus difficult. On the other hand, as the pH of the medium increases, deprotonation occurs and the CT interaction within the free base is facilitated (figure 4).

The acid dissociation or protonation constants of cyanine compounds under study 3d, 6f and 8b have been determined in order to ensure the optimal pH in the application as photosensitizer. Such determination was measured on plotting the variation of absorbance with pH using the spectrophotometric half-height limiting absorbance and Colleter methods (Colleter 1960). The effectiveness of the compounds as photosensitizers increases when they are present in the ionic form which have higher planarity (Mahmoud *et al* 1975). The results of the *pK_a* values of the cyanines 3d (8.8) is higher than those of (6f, (7.1) & 8b, (8.2) respectively. This behaviour refers to the higher planarity and greater stability of monomethine cyanine type 3d which favour the intramolecular charge transfer. This leaves a lower negative charge density on the nucleus resulting in weaker bonding of the proton. Such dyes might be suggested to be more sensitive as photosensitizers than their analogues 6f, 8d.

3. Experimental

3.1 General

All melting points are uncorrected. Elemental analysis were carried out at the Micro-analytical Centre (Cairo University). IR spectra determined with Perkin Elemer Infrared 127 β spectrophotometer (Cairo University). Visible, solvatochromic and acid-base behaviours were recorded on Shimadzu-UV-Vis-240 recording spectrophotometer using 1 cm cells (Faculty of Science, Aswan) while ¹HNMR spectra were recorded with EM-390 90 MHz NMR spectrometer (Cairo University).

Stock solutions (10⁻³ M) of selected cyanines were prepared by dissolving the recrystallised dyes in ethanol. Solutions of lower molarities used in spectral measurements were obtained by appropriate dilution. The aqueous universal buffer solutions of pH 2.53–12.08 were prepared and checked at 25°C using an Orion pH-meter model 60/A accurate to ± 0.005 pH units.

5-Aryl-3-methyl-1-phenylpyrazolo [3,4-*d*] oxazole derivatives 1a–e were prepared according to Koraïem *et al* (1990).

3.2 Synthesis of 5-aryl-3-methyl-1-phenyl pyrazolium [3,4-*d*]-oxazolium-2,4-bis ethyl iodide 2a–e

Pure samples of compounds 1a–e were suspended in excess ethyl iodide and heated in sealed tubes at 140°C for 3 h. The tubes were then cooled, opened and the products 2a–e collected, washed with ether and crystallized from ethyl alcohol to give orange-to-brown crystals (table 1).

3.3 Synthesis of asymmetrical pyrazolo [3,4-*d*] oxazolo-3(4)-mono-methine cyanine dyes 3a–e

Equimolar amounts (0.01 mol) of 2a–e and quinoline methyl iodide were dissolved in ethanol (35 ml), then piperidine (3–5 drops) was added. The reaction mixture was refluxed for 6–8 h. The mixture was filtered hot, evaporated to half its volume and cooled. The products were precipitated after dilution with water, collected and

crystallized from aqueous ethanol to give the corresponding monocyanine dyes 3a–e. The results are listed in table 2.

3.4 Synthesis of asymmetrical pyrazolo [3,4-*d*] oxazole-3-azamethine cyanines 4a–c

Equimolar ratios of 2b and *p*-nitroso phenol, $\alpha(\beta)$ -nitroso- $\beta(\alpha)$ -naphthol compounds (0.01 mole) were dissolved in ethanol (40 ml) then piperidine (3–5 drops) was added. The reaction mixture was refluxed for 10–12 h, filtered hot, and concentrated to dryness. The precipitated products were washed and crystallized from ethanol. The results are listed in table 2.

3.5 Synthesis of asymmetrical pyrazolo [3,4-*d*] oxazolium-3-[2(4)]-trimethine cyanine moieties 6a–i

3.5a Equimolar ratios of 2a–e and diphenylformamidine (DPF, 0.01 mole) were dissolved in Ac_2O . The reaction mixture was refluxed for 4–6 h, filtered hot, evaporated and cooled. The products were precipitated with water, filtered off, washed with H_2O and crystallized from aqueous ethanol to give the intermediate compounds 5a–e.

3.5b A mixture of compounds 5a–e and 2(4)-methyl quaternary salts (quinaldine and lipidine ethyl iodide), (0.01 mole) were dissolved in ethanol (40 ml), then piperidine (2–3 drops) was added. The reaction mixture was refluxed for 6–8 h, filtered hot, concentrated and cooled. The product precipitated with water and crystallized from ethanol to give compounds 6a–i. The results are listed in table 3.

3.6 Synthesis of symmetrical pyrazolo [3,4-*d*] oxazolium-3(3)-trimethine cyanine moieties 8a–c

3.6a Bimolar ratios of 2a, 2c and 2d and triethoxymethane (TEM, 0.01 mole) were dissolved in pyridine. The reaction mixture was refluxed for 3–5 h, filtered hot and evaporated to give the non-isolated intermediate compounds 7a–c.

3.6b Triturated the non-isolated intermediate compounds 7a–c with ether and stirred. The stirred mixture was evaporated to give a coloured precipitate, filtered off and crystallized from ethanol to give the corresponding symmetrical trimethine cyanines 8a–c. The results are listed in table 3.

4. Conclusions

Spectral attention has been focused on the spectra, solvatochromic and acid-base properties of some selected cyanine dyes under investigation as a criterion of their photosensitization effects. Such effects are influenced by the nature of biheterocyclic aryl substituents, linkage position, solvent used and acid-base environment. Thus, cyanine dyes having electron donating substituents are more sensitive as photosensitizer than those having electron deactivating one. In view of linkage position, the asymmetrical 3(4)-trimethine cyanines are more sensitive as photosensitizers when compared with 3(2)-analogues. Also, within trimethine cyanines, asymmetrical trimethine cyanines are more sensitive when compared with their symmetrical analogues. On the other hand, with respect to phenolic azamethine cyanines 4a–c, the

sensitization effect as criterion from their spectral behaviour is of the following order (2-naphthol > 1-naphthol > phenol) (table 2).

These dyes are solvent dependent and pH sensitive, they exhibit general solute-solvent interaction depending on the dielectric constants of the solvent used as well as specific solute-solvent interaction. This includes hydrogen-bonding and molecular complex.

Asymmetrical monomethine dye **3d** is more pH-sensitive than asymmetrical (symmetrical)-trimethine cyanine dyes **6b** and **8b** respectively and might be used as an analytical reagent in protometric titration.

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