

Novel quinone cyanine dyes: synthesis and spectral studies

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Received 24 July 2000; received in revised form 29 August 2001; accepted 21 October 2001

Abstract

Novel dimethine, bis dimethine and tetramethine cyanine dyes derived from benzo [4,5-b; 4',5'-b'] bis furo, thieno and pyrrolo-4,8-dione were prepared. The electronic visible absorption spectra of the dyes were examined in 95% ethanol. Structural confirmation is carried out by elemental analysis, IR and ^1H NMR spectral data. © 2002 Elsevier Science Ltd. All rights reserved.

Keywords: Cyanine dyes; Synthesis; Spectral behaviour

1. Introduction

Cyanine dyes have been known as sensitizers in the photographic process [1]. Recent attempts to use these dyes as probes for the physical state and the membrane potential of liposomes and interfacial mono-layers [2–4] and as chromophores in organic solar cells [5]. polymethine cyanine dyes play an important role as laser dyes [6], as saturable absorbers in modelocked laser systems [7,8].

2. Results and discussion

2.1. Synthesis

In the light of the above introduction, and extended to our previous researches on the synthesis and studies of cyanine dyes [9–15], 1:2 molar ratios of *p*-chloranil (**1**) and ethyl acetoacetate, mercapto ethyl acetoacetate and imino ethyl acetoacetate

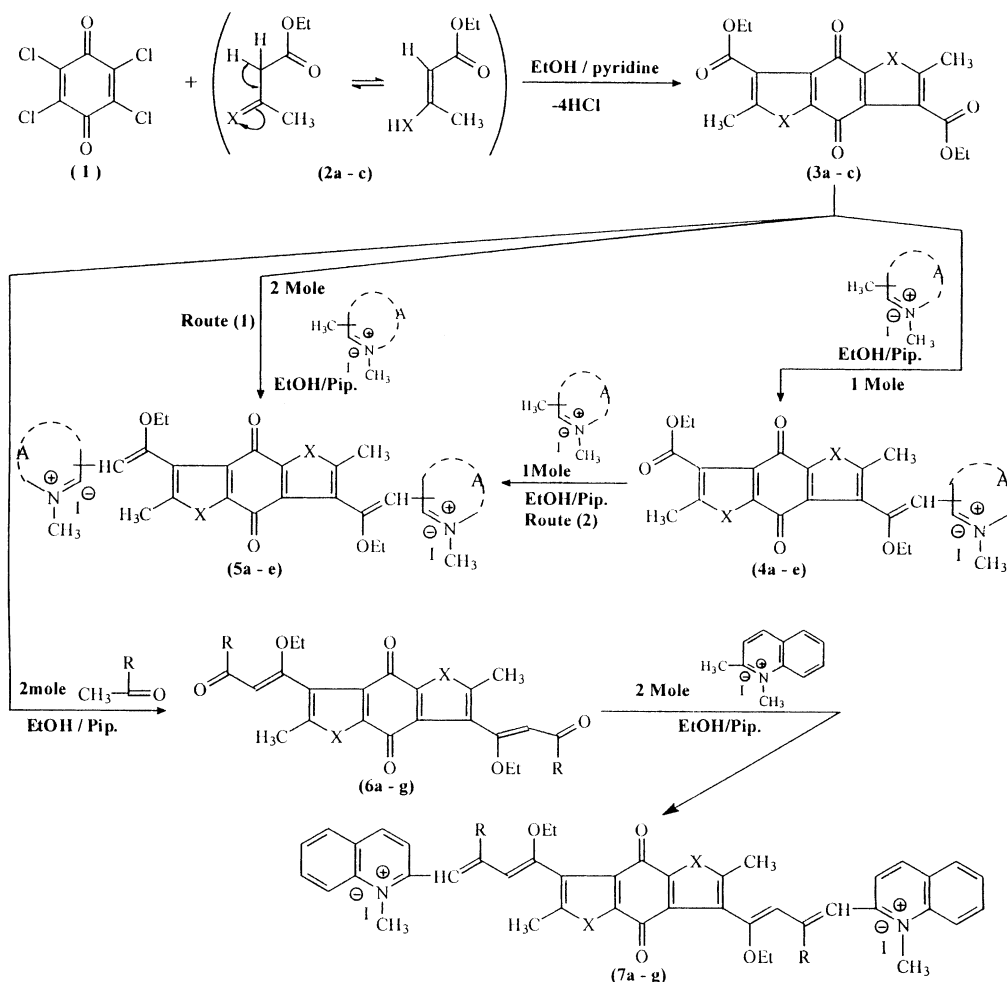
(**2a–c**) were reacted in ethanol containing pyridine and achieved 3,7-diethoxycarbonyl-2,6-dimethyl benzo [4,5-b; 4',5'-b'] bis furo, thieno and pyrrolo-4,8-dione (**3a–c**) (Scheme 1).

Interaction of equimolar ratios of (**3a–c**) and methyl iodide quaternary salts of α -picoline, quinaldine, γ -picoline in ethanol and presence of piperidine resulted the 3[2(4)]-dimethine cyanine dyes (**4a–e**), (Scheme 1).

Furthermore, ethanolic solution of unimolar ratios of (**3a–c**) reacted in presence of few drops of piperidine with bimolar ratios of *N*-methyl (α -picolinium, quinaldinium, γ -picolinium) iodide salts and yielded the 3,7[2(4)]-bis dimethine cyanine dyes (**5a–e**) (Route 1, Scheme 1). Chemical confirmation takes place via Route 2 by interaction of equimolar ratios of (**4a–e**) and iodomethane quaternary salts of α -picoline, quinaldine, γ -picoline in ethanol containing few drops of piperidine to gave the same compounds (**5a–e**) obtained by Route 1, characterized by melting points, mixed melting points, same IR and ^1H NMR spectra data (Scheme 1).

Additionally, unimolar ratios of (**3a–c**) and bimolar ratios of acyl and substituted acyl compounds

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Scheme 1. Substituents: (2a-c); (3a-c): X=O (a); S (b); NH (c). (4a-e); (5a-e): X=O, A=1-methyl pyridinium-2-yl salt (a); X=O, A=1-methyl quinolinium-2-yl salt (b); X=O, A=1-methyl pyridinium-4-yl salt (c); X=S, A=1-methyl quinolinium-2-yl salt (d); X=NH, A=1-methyl quinolinium-2-yl salt (e). (6a-g); (7a-g): X=O, R=H (a); X=O, R=CH₃ (b); X=O, R=C₆H₅ (c); X=O, R=C₆H₄-p-OCH₃ (d); X=O, R=C₆H₄-p-NO₂ (e); X=S, R=CH₃ (f); X=NH, R=CH₃ (g).

(acetaldehyde, acetone, acetophenone, *p*-methoxy acetophenone, *p*-nitro acetophenone) were reacted in ethanol as organic solvent and piperidine as basic catalyst to give (6a-g) as intermediate compounds. Subsequent reaction of the intermediate (6a-g) with *N*-iodomethane quaternary salts of quinaldine in 1:2 molar ratios, in ethanol and in presence of piperidine achieved the 3,7(2)-bis tetramethine cyanine dyes (7a-g) (Scheme 1).

The structure of the prepared compounds were identified by elemental analysis (Tables 1 and 2),

IR [16] (Table 3) and ¹H NMR [17] (Table 3) spectral data.

2.2. Characterization

The 3[2(4)] dimethine cyanine dyes (4a-e) possess different colours ranging from brown to violet and easily soluble in polar solvents and concentrated H₂SO₄ from which iodine was liberated in heating. Their ethanolic solutions gave yellow colours in acidic media turned violet on basification with

Table 1

Characterization of 3,7-diethoxycarbonyl-2,6-dimethyl-benzo [4,5-b; 4',5'-b']-bis furo, thieno and pyrrolo-4,8-dione (**3a–c**); 7-ethoxycarbonyl-2,6-dimethyl-benzo [4,5-b; 4',5'-b']-bis furo, thieno and pyrrolo-4,8-dione-3[2(4)]-dimethine cyanine dyes (**4a–e**) and 2,6-dimethyl-benzo [4,5-b; 4',5'-b']-bis furo, thieno and pyrrolo-4,8-dione-3,7[2(4)]-bis dimethine cyanine dyes (**5a–e**)

Compound	Nature of products			Molecular formula (M. Wt.)	Analysis (%)						Absorption spectra in 95% ethanol	
	Colour	Yield (%)	Mp (°C)		Calculated			Found				
					C	H	N	C	H	N	λ_{max} (nm)	ϵ_{max} (mol ⁻¹ cm ²)
3a	Brown crystals	38	145	C ₁₈ H ₁₆ O ₈ (360)	60.0	4.44	—	60.09	4.43	—	—	—
3b	Dark brown crystals	63	149	C ₁₈ H ₁₆ O ₆ S ₂ (358)	55.1	4.08	—	55.10	4.15	—	—	—
3c	Dark brown crystals	41	140	C ₁₈ H ₁₈ O ₆ N ₂ (392)	60.34	5.03	7.82	60.29	5.07	7.82	—	—
4a	Brown crystals	47	152	C ₂₅ H ₂₄ O ₇ NI (577)	51.99	4.16	2.43	51.95	4.11	2.54	510, 454	8630, 11,490
4b	Dark brown crystals	33	161	C ₂₉ H ₂₆ O ₇ NI (627)	55.5	4.15	2.23	55.40	4.22	2.26	515, 456	11,680, 13,050
4c	Brown crystals	37	155	C ₂₅ H ₂₄ O ₇ NI (577)	51.99	4.16	2.43	51.90	4.15	2.51	512, 455	11,410, 15,210
4d	Dark brown crystals	61	170	C ₂₉ H ₂₆ O ₅ S ₂ NI (659)	52.81	3.94	2.12	52.76	4.00	2.20	516, 458	11,160, 19,990
4e	Brown crystals	42	165	C ₂₉ H ₂₈ O ₅ N ₃ I (625)	55.68	4.48	6.72	55.65	4.39	6.81	590, 518	4530, 19,290
5a	Brown crystals	31	162	C ₃₂ H ₃₂ O ₆ N ₂ I ₂ (794)	48.36	4.03	3.53	48.31	3.99	3.61	517, 455	16,130, 20,540
5b	Dark brown crystals	37	167	C ₄₀ H ₃₆ O ₆ N ₂ I ₂ (894)	53.69	4.03	3.13	53.66	4.01	3.09	548, 457	12,200, 21,190
5c	Dark violet crystals	33	163	C ₃₂ H ₃₂ O ₆ N ₂ I ₂ (794)	48.36	4.03	3.53	48.29	4.01	3.61	518, 456	15,850, 20,150
5d	Dark brown crystals	51	176	C ₄₀ H ₃₆ O ₄ N ₂ S ₂ I ₂ (926)	51.83	3.88	3.03	51.78	3.91	3.06	552, 514	9550, 10,490
5e	Dark brown crystals	58	181	C ₄₀ H ₃₈ O ₄ N ₄ I ₂ (892)	53.81	4.26	6.28	53.78	4.21	6.32	595, 560	3850, 18,800

Table 2

Characterization of 2,6-dimethyl-3,7-(3-*R*-1-ethoxy-1-propene-3-one)-benzo [4,5-*b*; 4',5'-*b'*]-bis furo, thieno and pyrrolo-4,8-dione (**6a–g**) and 2,6-dimethyl-benzo [4,5-*b*; 4',5'-*b'*]-bis furo, thieno and pyrrolo-4,8-dione-3,7(2)-bis tetramethine cyanine dyes (**7a–g**)

Compound	Nature of products			Molecular formula (M. Wt.)	Analysis (%)						Absorption spectra in 95% ethanol	
	Colour	Yield (%)	Mp (°C)		Calculated			Found				
					C	H	N	C	H	N	λ_{max} (nm)	ϵ_{max} (mol ⁻¹ cm ²)
6a	Brown crystals	60	169	C ₂₂ H ₂₀ O ₈ (412)	64.70	4.85	–	64.77	4.90	–	–	–
6b	Brown crystals	68	174	C ₂₄ H ₂₄ O ₈ (440)	65.45	5.45	–	65.41	5.49	–	–	–
6c	Brown crystals	51	171	C ₃₄ H ₂₈ O ₈ (564)	72.34	4.96	–	72.36	4.94	–	–	–
6d	Dark brown crystals	38	168	C ₃₆ H ₃₂ O ₁₀ (624)	69.23	5.13	–	69.25	5.11	–	–	–
6e	Reddish brown crystals	68	159	C ₃₄ H ₂₆ O ₁₂ N ₂ (654)	62.38	3.98	4.28	62.35	3.97	4.25	–	–
6f	Dark brown crystals	46	185	C ₂₄ H ₂₄ O ₆ S ₂ (472)	61.02	5.08	–	61.00	5.12	–	–	–
6g	Brown crystals	33	172	C ₂₄ H ₂₆ O ₆ N ₂ (438)	65.75	5.93	6.39	65.81	5.90	6.37	–	–
7a	Violet crystals	53	170	C ₄₄ H ₄₀ O ₆ N ₂ I ₂ (946)	55.81	4.23	2.96	55.80	4.27	2.91	648, 556	4870, 10,540
7b	Dark violet crystals	44	172	C ₄₆ H ₄₄ O ₆ N ₂ I ₂ (974)	56.67	4.52	2.87	56.65	4.58	2.83	655, 563	4910, 13,940
7c	Intense violet crystals	49	167	C ₅₆ H ₄₈ O ₆ N ₂ I ₂ (1098)	61.20	4.37	2.55	61.18	4.39	2.59	693, 564	5110, 17,010
7d	Blue violet crystals	36	161	C ₅₈ H ₅₂ O ₈ N ₂ I ₂ (1158)	60.10	4.49	2.42	60.12	4.46	2.39	699, 574	5710, 21,870
7e	Violet crystals	31	169	C ₅₆ H ₄₆ O ₁₀ N ₄ I ₂ (1188)	56.56	3.87	4.71	56.6	3.84	4.68	665, 560	4410, 14,320
7f	Intense violet crystals	47	191	C ₄₆ H ₄₄ O ₄ N ₂ S ₂ I ₂ (1006)	54.87	4.37	2.78	54.82	4.41	2.76	661, 570	5190, 14,050
7g	Violet crystals	41	187	C ₄₆ H ₄₄ O ₄ N ₄ I ₂ (972)	56.79	4.73	5.76	56.73	4.76	5.71	687, 577	6150, 15,930

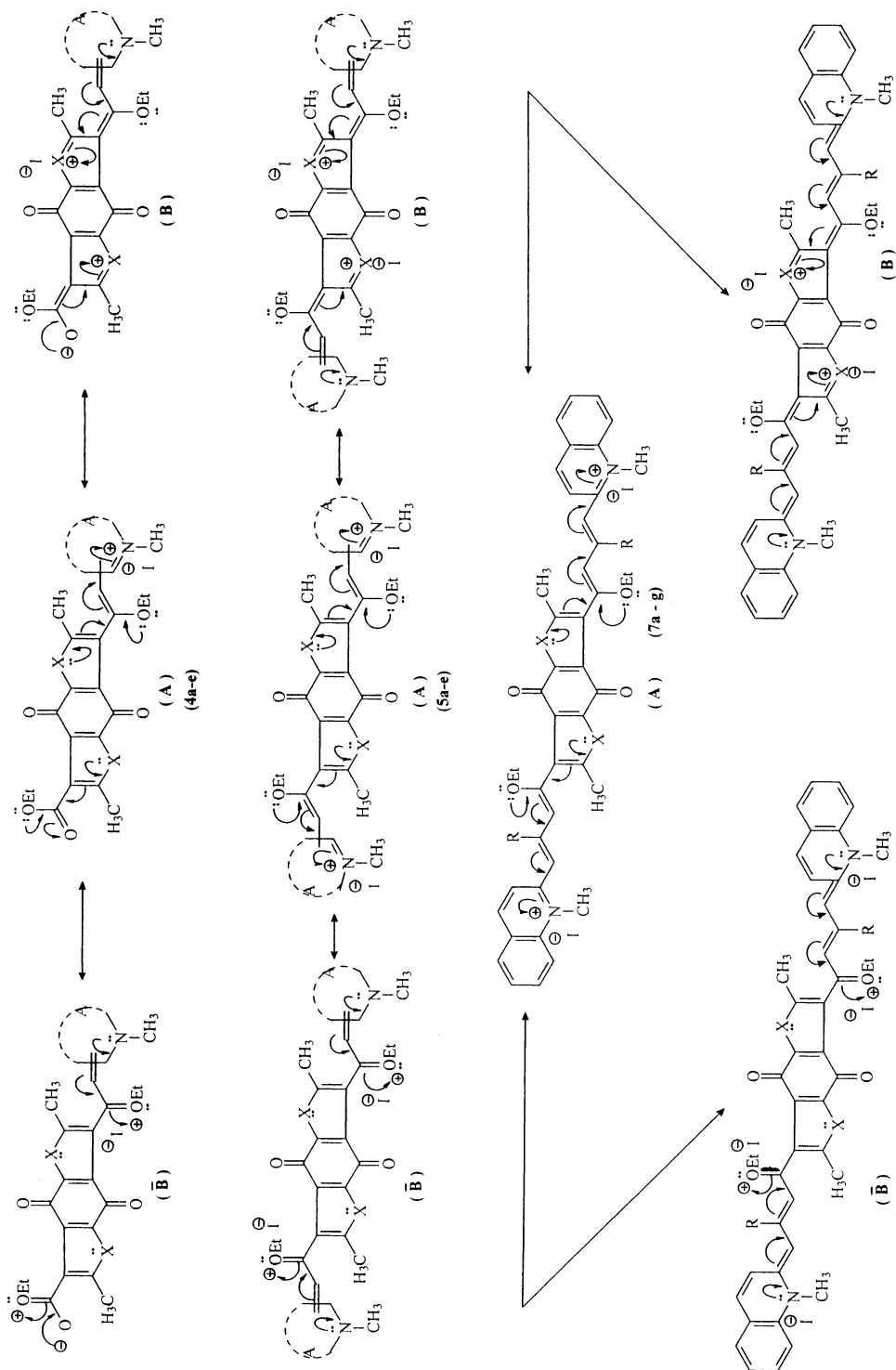
Table 3
IR and ^1H NMR spectral data of the prepared compounds

Compd	IR spectrum (KBr) (cm^{-1})	^1H NMR spectrum (DMSO) (δ)
3a	1100, 1179 (C–O–C cyclic) 1681 (C=O quinone) 1630 (C=C) 1715 (C=O)	1.30 (<i>t</i> , 6H, 2CH_3 of ethoxy) 3.35 (<i>s</i> , 6H, 2CH_3 of C_2 and C_6) 4.20 (<i>q</i> , 4H, 2CH_2 of ethoxy)
3b	427, 569 (thiophene ring) 1022, 1105, 1178 (C–S–C cyclic) 1630 (C=C) 1684 (C=O quinone) 1723 (C=O)	1.35 (<i>t</i> , 6H, 2CH_3 of ethoxy) 3.41 (<i>s</i> , 6H, 2CH_3 of C_2 and C_6) 4.35 (<i>q</i> , 4H, 2CH_2 of ethoxy)
3c	1025, 1100, 1176 (C–N–C cyclic) 1312, 1381 (pyrrole ring) 1632 (C=C) 1681 (C=O quinone) 1719 (C=O) 3373 (NH)	1.40 (<i>t</i> , 6H, 2CH_3 of ethoxy) 3.43 (<i>s</i> , 6H, 2CH_3 of C_2 and C_6) 4.45 (<i>q</i> , 4H, 2CH_2 of ethoxy) 6.10 (<i>s</i> , 2H, of 2NH)
4b	820, 860 (o. di substituted benzene) 1098, 1163 (C–O–C cyclic) 1500 (C=N) 1629 (C=C) 1677 (C=O quinone) 1723 (C=O) 2922 (quaternary salt)	1.42 (<i>t</i> , 3H, CH_3 of C_7 ethoxy) 3.00 (<i>s</i> , 3H, CH_3 of quinolinium) 3.20 (<i>s</i> , 3H, CH_3 of C_6) 4.40 (<i>q</i> , 2H, CH_2 of C_7 ethoxy) 6.72–7.89 (m, 7H, heterocyclic + $-\text{CH}=\text{}$)
5b	821, 857 (o. di substituted benzene) 1074, 1106 (C–O–C cyclic) 1461 (C=N) 1600 (C=C) 1684 (C=O quinone) 2957 (quaternary salt)	1.38 (<i>t</i> , 6H, 2CH_3 of ethoxy) 3.00 (<i>s</i> , 6H, 2CH_3 of quinolinium) 3.35 (<i>s</i> , 6H, 2CH_3 of C_2 and C_6) 4.32 (<i>q</i> , 4H, 2CH_2 of ethoxy) 6.69–8.23 (m, 14H, heterocyclic + $-\text{CH}=\text{}$)
6a	1025, 1102, 1182 (C–O–C cyclic) 1634 (C=C) 1681 (C=O quinone) 1723 (C=O)	1.41 (<i>t</i> , 6H, 2CH_3 of ethoxy) 3.40 (<i>s</i> , 6H, 2CH_3 of C_2 and C_6) 4.30 (<i>q</i> , 4H, 2CH_2 of ethoxy) 6.75 (<i>d</i> , 2H, of $2=\text{CH}-$) 9.40 (<i>d</i> , 2H, of 2 CHO)
7a	748, 853 (o. di substituted benzene) 1033, 1104, 1178 (C–O–C cyclic) 1507 (C=N) 1628 (C=C) 1681 (C=O quinone) 2924 (quaternary salt)	1.37 (<i>t</i> , 6H, 2CH_3 of ethoxy) 3.00 (<i>s</i> , 6H, 2CH_3 of quinolinium) 3.35 (<i>s</i> , 6H, 2CH_3 of C_2 and C_6) 4.30 (<i>q</i> , 4H, 2CH_2 of ethoxy) 6.65–8.54 (m, 18H, heterocyclic + $-\text{CH}=\text{}$)

alkaline hydroxides. The intensity of colour of these dyes were illustrated according to the mesomeric structures $\text{A}[\text{B}(\text{B}')]$ producing a delocalized positively charged orbital over the conjugated system (Scheme 2).

The 3,7[2(4)]-bis dimethine cyanine dyes (**5a–e**) possess colours from brown to deep violet, and

easily soluble in polar organic solvents. They are also easily soluble in concentrated sulphuric acid from which iodine vapour was liberated in heating. The intensity of the colours of these dyes were demonstrated according to the mesomeric structures $\text{A}[\text{B}(\text{B}')]$, producing delocalized positively charged orbital over the conjugated system (Scheme 2).



Scheme 2.

The 3,7(2)-bis tetramethine cyanine dyes (**7a–g**) are readily soluble in polar organic solvents exhibiting highly coloured solutions (violet to intense violet). They are fairly soluble in concentrated H_2SO_4 from which iodine was evolved on heating. Their ethanolic solutions gave a pale yellow colours in acidic media turned to dark violet on basification with alkaline hydroxides. The intensity of the colours (brown–violet) of these dyes were explained according to the mesomeric structures $\text{A}[\text{B}(\text{B}')]$ producing a delocalized positively charged orbital over the conjugated system (Scheme 2).

2.3. Spectral behaviour studies

The electronic visible absorption spectra of the dimethine (bis dimethine) cyanine dyes **4a–e** (**5a–e**) in 95% ethanol showed absorption bands in the visible region 454–590 nm (455–595 nm) which underwent bathochromic shifts or hypsochromic shifts depending on the extent of conjugation of the quaternary heterocyclic residue (A) as well as the nature of the benzbiheterocyclic system present (Table 1). So, substituting A = 1-methyl pyridinium-2-yl salt in the dimethine (bis dimethine) cyanines **4a** (**5a**) by A = 1-methyl-quinolinium-2-yl salt to give dyes **4b** (**5b**) causes a strong bathochromic shift accompanied by increasing (decreasing) the intensities of the absorption bands, this is due to increasing conjugation in quinoline thane its analogous pyridine. Otherwise, changing the linkage position from 2-yl salt to 4-yl salt passing from dyes **4a** (**5a**) to dyes **4c** (**5c**) resulted in a slight bathochromic shift with increasing (decreasing) the intensity of the absorption bands. This is due to increasing π -delocalization conjugation in the latter dyes **4c**, **5c** (Table 1).

On the other hand, changing the benzbiheterocyclic system from bis furo in dyes **4b** (**5b**) to bis thieno and bis pyrrolo to give dyes **4d**, **4e** (**5d**, **5e**) causes a bathochromic shift for the absorption bands. This is due to increasing the electronegativity of oxygen atom in dyes **4b** (**5b**) compared with sulfur and nitrogen atoms in dyes **4b**, **4e** (**5d**, **5e**). Also changing the benzbiheterocyclic system from bis thieno in dyes **4d** (**5d**) to bis pyrrolo in dyes **4e** (**5e**) resulted in bathochromic shifts for the absorption bands. This is due to increasing the

electronegativity of sulfur atom compared with nitrogen atom (Table 1).

Similarly, the electronic absorption spectra of 3,7(2)-tetramethine cyanine dyes (**7a–g**) in 95% ethanol showed electronic absorption bands in the visible region (556–699 nm) which underwent bathochromic and hypsochromic shifts depending on the nature of the substituent (R) and the type of the benzbiheterocyclic system. So substituting R = H in dye **7a** by R = CH_3 , ph to give dyes **7b**, **7c** causes bathochromic shifts with increasing number and intensities of the absorption bands (Table 2). This is due to the hyperconjugative electron donating character of the methyl group in dye **7b**, and increasing π -delocalization in dye **7c** due to the presence of phenyl ring. Additionally, the spectra of the dye **7c** showed to give hypsochromically and bathochromically shifted absorption bands if compared with dyes **7d**, **7e** respectively. This can be attributed to the electron releasing character of the *p*-methoxyl group in dye **7d** and electron attracting character of the *p*-nitro group in dye **7e**.

On the other side, the dyes that contain bis thieno and bis pyrrolo nuclei in the benzbiheterocyclic system (**7f**) and (**7g**), showed bathochromic shifts for the absorption bands if compared with dye (**7b**) which contains bis furo nuclei in the benzbiheterocyclic system. This is can be attributed to the more electron accepting character of oxygen atom in the latter dye (**7b**). Also, the dye **7f**, which contains bis thieno nuclei, showed hypsochromic shifts for the absorption bands if compared by its analogous (**7g**) which contains bis pyrrolo nuclei in the biheterocyclic system. This can be attributed to the increasing electron accepting character of sulfur atom in dye (**7f**) if compared by its analogous nitrogen atom in dye **7g** (Table 2).

3. Conclusion

From the previously mentioned study, we can conclude that the photosensitization of the prepared cyanine dyes is very marked dependant on the structure nature of the dyes. Photosensitization of the dyes increases (decreases) by increasing

(decreasing) conjugation in the dye molecule. Also the photosensitization of the dyes increases (decreases) by decreasing (increasing) the electro-negativity of the hetero atom in the biheterocyclic ring of the dye. Electron donating group increases the photosensitization of the dyes while electron accepting groups decreases the photosensitization. Increasing number of methine groups gives more photosensitizers dyes, and dyes which have two conjugated charge transfer pathways inside the dye molecule are more photosensitizers than those which have one conjugated charge transfer pathway.

4. Experimental

4.1. General

All melting points are uncorrected. Elemental analyses were carried out at the micro analytical center of Cairo University by an automatic analyzer (Heraeus). IR (KBr pellets) spectra were determined on a Perkin-Elmer Infrared 127 Spectrophotometer (Cairo University) and the ^1H NMR spectra were obtained using a varian Gemini NMR 400 and 300 MHz spectrometers (Assiut and Cairo Universities). Electronic visible absorption spectra were carried out on UV Spectrophotometer (South Valley University, Faculty of Science, Aswan).

4.2. Synthesis

4.2.1. Synthesis of 3,7-diethoxycarbonyl-2,6-dimethyl-benzo [4,5-*b*; 4',5'-*b'*]-bis furo, thieno and pyrrolo-4,8-dione (**3a–c**)

Unimolar ratios (0.01 mole) of *p*-chloranil (**1**) and bimolar ratio (0.02 mol) of ethyl acetoacetate, mercapto ethyl acetoacetate and imino ethyl acetoacetate (**2a–c**) were refluxed in ethanol (50 ml) containing pyridine (20 ml) for 8 h. The reaction mixture attained a brown colour changed to a deep brown colour at the end of refluxing. It was filtered off on hot to remove unreacted materials, concentrated, poured on an ice–water mixture, neutralized with concentrated hydrochloric acid and left to stand for about 5–7 h at room temperature, whereby buff precipitates separated. The separated products were filtered off, washed sev-

eral times with water, dried and crystallized from absolute ethanol. The results are listed in Table 1.

4.2.2. Synthesis of 7-ethoxycarbonyl-2,6-dimethyl-benzo [4,5-*b*; 4',5'-*b'*]-bis-furo, thieno and pyrrolo-4,8-dione-3[2(4)]-dimethine cyanine dyes (**4a–e**)

An equimolar ratios (0.01 mol) of (**3a–c**) and iodomethane quaternary salts of α -picoline, quinaldine and γ -picoline were dissolved in ethanol (30 ml) and then piperidine (1 ml) was added. The reaction mixture was refluxed for 7–9 h and changed its colour from brown to deep violet at the end of refluxing. It was filtered off while hot, concentrated, cooled and acidified with glacial acetic acid. The products (**4a–e**) which separated on dilution with water were filtered off, washed with water several times and crystallized from absolute ethanol. The results are summarized in Table 1.

4.2.3. Synthesis of 2,6-dimethyl-benzo [4,5-*b*; 4',5'-*b'*]-bis furo, thieno and pyrrolo-4,8-dione-3,7[2(4)]-bis dimethine cyanine dyes (**5a–e**)

Two different routes are used to prepare such cyanines.

- **Route 1** Molar ratios 1:2 of (**3a–c**) and iodomethane quaternary salts of α -picoline, quinaldine and γ -picoline were dissolved in ethanol (30 ml), then piperidine (1 ml) was added. The reaction mixture was heated under reflux for 7–9 h, filtered off on hot, concentrated to half its initial volume and neutralized by glacial acetic acid. The precipitated products after dilution with water and stirring were collected and crystallized from absolute ethanol. The results are given in Table 1.
- **Route 2** Equimolar ratios (0.01 mol) of the dimethine cyanines (**4a–e**) and *N*-methyl iodide quaternary salts of α -picoline, quinaldine and γ -picoline were heated under reflux for 3–5 h in ethanol (50 ml) and presence of few drops (3–5) of piperidine. The reaction mixture was filtered while hot, concentrated to half of its volume, cooled and neutralized by acetic acid. The precipitated products which appears on dilution with water were filtered off, washed with water, dried and crystallized from absolute ethanol to give the same com-

pounds (**5a–e**) obtained by Route 1, characterized by melting points, mixed melting points, same IR and ^1H NMR spectra data (Table 1).

4.2.4. Synthesis of 2,6-dimethyl-3,7-(3-*R*-1-ethoxy-1-propene-3-one)-benzo [4,5-*b*; 4',5'-*b'*]-bis furo, thieno and pyrrolo-4,8-dione (**6a–g**)

A mixture of (**3a–c**) (0.01 mole) and acetaldehyde, acetone, acetophenone, *p*-methoxy acetophenone *p*-nitro acetophenone (0.02 mole) were dissolved in ethanol (40 ml), then few mls of piperidine was added. The reaction mixture was heated under reflux for 5–7 h and changed its colour from brown to deep brown at the end of refluxing. It was filtered off while hot, concentrated, precipitated by adding an ice–water mixture and neutralized with acetic acid. The precipitated products were filtered off, washed several times with water, dried and crystallized from absolute ethanol. The results are listed in Table 2.

4.2.5. Synthesis of 2,6-dimethyl-benzo [4,5-*b*; 4',5'-*b'*]-bis furo, thieno and pyrrolo-4,8-dione-3,7(2)-bis tetramethine cyanine dyes (**7a–g**)

Piperidine (5–7 drops) was added to a mixture of (**6a–g**) (0.01 mol) and two equivalents of iodo-methane quaternary salt of 2-methyl quinoline (0.02 mol) dissolved in ethanol (30 ml). The reaction mixture was refluxed for 7–9 h and changed its colour from deep brown to deep violet at the end of refluxing. It was filtered while hot, concentrated and cooled. The precipitated products after dilution with water were filtered off and crystallized from absolute ethanol. The data are given in Table 2.

4.3. Spectral behaviour studies

The electronic visible absorption spectra of the dyes in 95% ethanol were recorded on UV

recording spectrophotometer using 1 cm quartz cells. The stock solution were about 1×10^{-3} M. lower molarities were obtained by accurate dilution. The spectra were recorded immediately to eliminate as much as possible the effect of time.

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