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Cyanine dyes of new heterocyclic ring systems: Synthesis and structure-spectra studies

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Abstract

New cyanine dyes including monomethine cyanine dyes (simple cyanine dyes) and trimethine cyanine dyes (carbocyanine dyes) incorporating benzo[2,3-*b*; 2′,3′-*b*′]bispyrazolo[4,5-*b*]-1,4-(oxa-, thia-, and pyra)-zine-6,12-dione were prepared. Structure-spectra studies were carried out via measuring the electronic visible absorption spectra of these dyes in 95% ethanol. Structural confirmations were determined through elemental analysis, IR, ^{1}H NMR spectroscopy and MS spectral data at the Micro Analytical Center, Cairo University.

Keywords: Cyanines; Cyanine dyes; Synthesis; Structure-spectra studies

1. Introduction

Cyanine dyes have wide applications in various fields [1–9], such as near infra red laser dyes, fluorescent labeling agents for proteins, fluorescent tags in DNA sequencing, optical information storage devices, histological staining, antimicrobial operations, solar energy conversion systems, cosmetic ingredients, dyes for polymers, as well as sensitizers for various silver halide emulsions.

2. Results and discussion

2.1. Synthesis

1:2 molar ratios of *p*-chloranil (**1**) and 4-amino-5-(hydroxy, mercapto and imino)-3-methyl-1-phenyl-pyrazole [10] (**2a–c**) were reacted in ethanol containing pyridine to give 4,10-dimethyl-2,8-diphenyl-5,11-dihydro-benzo[2,3-*b*; 2′,3′-*b*′]bispyrazolo[4,5-*b*]-1,4-(oxa-, thia-, and pyra-)-zine-6,12-dione (**3a–c**) (Scheme 1, Table 1).

Quternization of (**3a–c**) using equimolar and/or bimolar ratios of iodoethane produced monocationic (**4a–c**) and/or dicationic (**5a–c**) derivatives. Interaction of the monocationic compounds (**4a–c**) with iodoethane quaternary salts of pyridine, quinoline and isoquinoline in equimolar ratios in ethanol containing few drops of piperidine gave 4[4(1)]-monomethine cyanine dyes (**6a–e**). Also interaction of the dicationic compounds (**5a–c**) with equimolar and/or bimolar ratios of iodoethane quaternary salts of pyridine, quinoline and isoquinoline in ethanol containing piperidine yielded 4[4(1)]-dicationic monomethine and/or 4,10[4(1)]-dicationic bismonomethine cyanine dyes (**7a–e**), (**8a–e**), respectively (Scheme 1, Table 2). Chemical confirmations for compounds (**8a–e**) were obtained through reaction of (**7a–e**) with equimolar ratios of iodoethane quaternary salts of pyridine, quinoline and isoquinoline in

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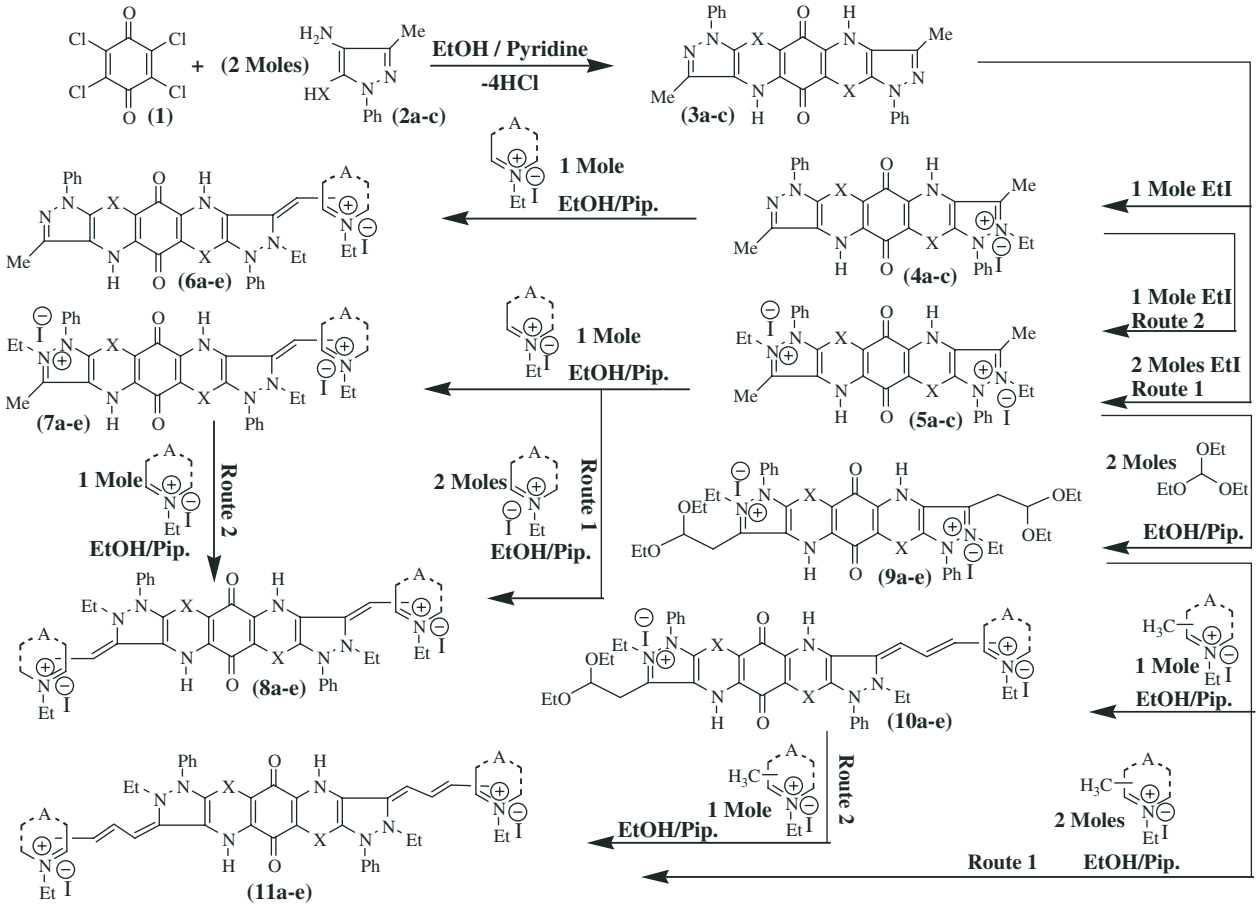

Substituents in Scheme 1:

(**1a**-**c**); (**2a**-**c**); (**3a**-**c**); (**4a**-**c**); (**5a**-**c**); & (**9a**-**c**): a, X=O; b, X=S; c, X=NH.

(**6a**-**e**); (**7a**-**e**) & (**8a**-**c**): (a) X=O, A= 1-ethyl pyridinium-4-yl salt,
(b) X=O, A= 1-ethyl quinolinium-4-yl salt,
(c) X=O, A= 2-ethyl isoquinolinium-1-yl salt,
(d) X=S, A= 1-ethyl quinolinium-4-yl salt,
(e) X=NH, A= 1-ethyl quinolinium-4-yl salt.

(**10a**-**g**) & (**11a**-**g**): (a) (a) X=O, A= 1-ethyl pyridinium-2-yl salt,
(b) X=O, A= 1-ethyl quinolinium-2-yl salt,
(c) X=O, A= 1-ethyl pyridinium-4-yl salt,
(d) X=S, A= 1-ethyl quinolinium-2-yl salt,
(e) X=NH, A= 1-ethyl quinolinium-2-yl salt.

Scheme 1.

ethanol catalyzed by piperidine to achieve the same 4, 10[4(1)]-dicationic bismonomethine cyanine dyes (**8a**–**e**), characterized by same melting points, mixed melting points, same IR and ^{1}H NMR spectra (Scheme 1 route 2, Table 2).

Additionally, ethanolic solutions of the dicationic quaternized compounds (**5a**–**c**) were reacted with bimolar ratios of triethylorthoformate in the presence of piperidine and led to the formation of the intermediate compounds (**9a**–**c**). The intermediates (**9a**–**c**) were then reacted with equimolar and/or bimolar ratios of *N*-ethyl(2-picolinium, quinaldinium, 4-picolinium) iodide salts in ethanol containing piperidine as a basic catalyst to give the 4[2(4)]-trimethine (**10a**–**e**) and/or

Table 1
Characterization of 4,10-dimethyl-2,8-diphenyl-5,11-dihydro-benzo[2,3-*b*; 2′,3′-*b*′]bispyrazolo[4,5-*b*]-1,4-(oxa-, thia-, and pyra-)-zine-6,12-dione (**3a–c**); 3-iodoethane monoquaternized salts of 4,10-dimethyl-2,8-diphenyl-5,11-dihydro-benzo[2,3-*b*; 2′,3′-*b*′]bispyrazolo[4,5-*b*]-1,4-(oxa-, thia-, and pyra-)-zine (**4a–c**); and 3,9-iodoethane diquaternized salts of 4,10-dimethyl-2,8-diphenyl-5,11-dihydro-benzo[2,3-*b*; 2′,3′-*b*′]bispyrazolo[4,5-*b*]-1,4-(oxa-, thia-, and pyra-)-zine (**5a–c**)

Comp. no.	Nature of products			Molecular formula (M.Wt.)	Analysis (%)					
	Colour	Yield (%)	M.P. (°C)		Calculated			Found		
					C	H	N	C	H	N
3a	Brown crystals	62	195	$C_{26}H_{18}N_6O_4$ (478)	65.27	3.77	15.57	65.21	3.87	15.54
3b	Reddish brown crystals	71	192	$C_{26}H_{18}N_6O_2S_2$ (510)	61.18	3.53	16.47	61.10	3.59	16.51
3c	Bright brown crystals	65	200	$C_{26}H_{20}N_8O_2$ (476)	65.55	4.20	23.53	65.50	4.12	23.49
4a	Brown crystals	60	185	$C_{28}H_{23}N_6O_{41}$ (634)	53.00	3.63	13.25	52.94	3.58	13.30
4b	Brown crystals	73	179	$C_{28}H_{23}N_6O_2S_{21}$ (666)	50.45	3.45	12.61	50.41	3.51	12.63
4c	Bright brown crystals	54	201	$C_{28}H_{25}N_8O_{21}$ (632)	53.16	3.96	17.72	53.09	3.91	17.68
5a	Reddish brown crystals	41	182	$C_{30}H_{28}N_6O_4I_2$ (790)	45.57	3.54	10.63	45.63	3.59	10.57
5b	Brown crystals	38	175	$C_{30}H_{28}N_6O_2S_2I_2$ (822)	43.80	3.41	10.22	43.75	3.39	10.31
5c	Bright brown crystals	31	191	$C_{30}H_{30}N_8O_2I_2$ (788)	45.69	3.81	14.21	45.74	3.77	14.11

4,10[2(4)]-bistrimethine (**11a–e**) cyanine dyes (Scheme 1, Table 3). A chemical confirmation for the bistrimethine cyanine dyes (**11a–e**) was obtained through reaction of the trimethine cyanine dyes (**10a–e**) with equimolar ratios of *N*-ethyl (2-picolinium, quinaldinium, 4-picolinium) iodide salts in ethanol catalyzed by piperidine to achieve the same 4,10[2(4)]bistrimethine cyanine dyes (**11a–e**), characterized by same melting points, mixed melting points, same IR and ^{1}H NMR spectra (Scheme 1 route 2, Table 3).

The structure of the prepared compounds was characterized by elemental analysis (Tables 1–3), IR [11] and ^{1}H NMR [12] spectroscopy (Table 4).

2.2. Structure-spectra studies

Structure-spectra studies of the prepared cyanine dyes were carried out by measuring their electronic visible absorption spectra in 95% ethanol (Tables 2 and 3).

The electronic absorption spectra of the monocationic monomethine (**6a–e**), dicationic monomethine (**7a–e**) and dicationic bismonomethine (**8a–e**) cyanine dyes showed absorption bands in the visible regions 493–517 nm, 501–530 nm and 517–543 nm, respectively, which undergo bathochromic and/or hypthochromic shifts depending largely upon the nature of the heterocyclic quaternary salts, its linkage position, the type of

Table 2
Characterization of 10-methyl-3-ethyl-2,8-diphenyl-5,11-dihydro-benzo[2,3-*b*; 2′,3′-*b*′]bispyrazolo[4,5-*b*]-1,4-(oxa-, thia-, and pyra-)-zine-4[4(1)]-monocationic monomethine cyanine dyes (**6a–e**); 10-methyl-3,9-diethyl-2,8-diphenyl-5,11-dihydro-benzo[2,3-*b*; 2′,3′-*b*′]bispyrazolo[4,5-*b*]-1,4-(oxa-, thia-, and pyra-)-zine-4[4(1)]dicationic monomethine cyanine dyes (**7a–e**) and 3,9-diethyl-2,8-diphenyl-5,11-dihydro-benzo[2,3-*b*; 2′,3′-*b*′]bispyrazolo[4,5-*b*]-1,4-(oxa-, thia-, and pyra-)-zine-4,10[4(1)]dicationic bismonomethine cyanine dyes (**8a–e**)

Comp. no.	Nature of products			Molecular formula (M.Wt.)	Analysis (%)						Absorption spectra in 95% ethanol	
	Colour	Yield (%)	M.P. (°C)		Calculated			Found			λ_{max} (nm)	ε_{max} ($mol^{-1}\,cm^2$)
					C	H	N	C	H	N		
6a	Brown crystals	62	196	$C_{35}H_{30}N_7O_4I$ (739)	56.83	4.06	13.26	56.80	4.01	13.23	493	10120
6b	Dark brown crystals	71	209	$C_{39}H_{32}N_7O_4I$ (789)	59.32	4.06	12.42	59.34	4.00	12.45	411, 509	16010, 12290
6c	Bright brown crystals	65	203	$C_{39}H_{32}N_7O_4I$ (789)	59.32	4.06	12.42	59.35	4.07	12.46	503	11190
6d	Brown crystals	60	207	$C_{39}H_{32}N_7O_2S_2I$ (821)	57.00	3.90	11.94	56.97	3.89	11.93	413, 517	17930, 12910
6e	Brown crystals	73	204	$C_{39}H_{34}N_9O_2I$ (787)	59.47	4.32	16.01	59.45	4.33	16.05	424, 525	18570, 13100
7a	Bright brown crystals	54	191	$C_{37}H_{35}N_7O_4I_2$ (895)	49.61	3.91	10.95	49.65	3.90	10.98	501	11280
7b	Brown crystals	41	201	$C_{41}H_{37}N_7O_4I_2$ (945)	52.06	3.92	10.37	52.01	3.97	10.34	422, 514	16910, 13370
7c	Brown crystals	38	205	$C_{41}H_{37}N_7O_4I_2$ (945)	52.06	3.92	10.37	52.10	3.94	10.39	507	12130
7d	Dark brown crystals	31	196	$C_{41}H_{37}N_7O_2S_2I_2$ (977)	50.36	3.79	10.03	50.38	3.81	10.09	421, 530	17850, 11950
7e	Bright brown crystals	61	211	$C_{41}H_{39}N_9O_2I_2$ (943)	52.17	4.14	13.36	52.15	4.13	13.31	433, 536	19150, 15100
8a	Brown crystals	54	204	$C_{44}H_{42}N_8O_4I_2$ (1000)	52.80	4.20	11.20	52.83	4.22	11.25	517	12510
8b	Violet crystals	33	216	$C_{52}H_{46}N_8O_4I_2$ (1100)	56.73	4.18	10.18	56.69	4.15	10.14	423, 534	18210, 14150
8c	Brown crystals	41	219	$C_{52}H_{46}N_8O_4I_2$ (1100)	56.73	4.18	10.18	56.72	4.17	10.12	522	13190
8d	Violet crystals	29	203	$C_{52}H_{46}N_8O_2S_2I_2$ (1132)	55.12	4.06	9.89	55.10	4.01	9.83	429, 543	16320, 13070
8e	Violet crystals	43	227	$C_{52}H_{48}N_{10}O_2I2$ (1098)	56.83	4.37	12.75	56.87	4.39	12.77	441, 546	18530, 14920

Table 3
Characterization of 4,10-di[2-diethoxyethane]-3,9-diethyl-2,8-diphenyl-5,11-dihydro-benzo[2,3-*b*; 2′,3′-*b*′]bispyrazolo[4,5-*b*]-1,4-(oxa-, thia-, and pyra-)-zine-iodide salts (**9a–c**); 10-[2-diethoxyethane]-3,9-diethyl-2,8-diphenyl-5,11-dihydro-benzo[2,3-*b*; 2′,3′-*b*′]bispyrazolo[4,5-*b*]-1,4-(oxa-, thia-, and pyra-)-zine-4[2(4)]trimethine cyanine dyes (**10a–e**) and 3,9-diethyl-2,8-diphenyl-5,11-dihydro-benzo[2,3-*b*; 2′,3′-*b*′]bispyrazolo[4,5-*b*]-1,4-(oxa-, thia-, and pyra-)-zine-4,10[2(4)]bistrimethine cyanine dyes (**11a–e**)

Comp. no.	Nature of products			Molecular formula (M.Wt.)	Analysis (%)						Absorption spectra in 95% ethanol	
	Colour	Yield (%)	M.P. (°C)		Calculated			Found			λ_{max} (nm)	ε_{max} (mol^{-1} cm^2)
					C	H	N	C	H	N		
9a	Dark brown crystals	51	183	$C_{40}H_{48}N_6O_8I_2$ (994)	48.29	4.83	8.45	48.31	4.80	8.41		
9b	Dark brown crystals	41	173	$C_{40}H_{48}N_6O_6S_2I_2$ (1026)	46.78	4.68	8.19	46.76	4.65	8.16		
9c	Bright brown crystals	68	211	$C_{40}H_{50}N_8O_6I_2$ (992)	48.39	5.04	11.29	48.43	5.02	11.33		
10a	Violet crystals	68	196	$C_{44}H_{47}N_7O_6I_2$ (1023)	51.61	4.59	9.58	51.58	4.55	9.53	551	14010
10b	Dark violet crystals	74	202	$C_{48}H_{49}N_7O_6I_2$ (1073)	53.68	4.57	9.13	53.69	4.54	9.10	451, 558	20150, 14650
10c	Violet crystals	63	199	$C_{44}H_{47}N_7O_6I_2$ (1023)	51.61	4.59	9.58	51.63	4.60	9.55	554	14220
10d	Violet crystals	57	194	$C_{48}H_{49}N_7O_4S_2I_2$ (1105)	52.13	4.43	8.87	52.15	4.40	8.82	457, 575	20910, 14980
10e	Bright violet crystals	71	215	$C_{48}H_{51}N_9O_4I_2$ (1071)	53.78	4.76	11.76	53.81	4.75	11.73	463, 584	21900, 15010
11a	Pale violet crystals	63	191	$C_{48}H_{46}N_8O_4I_2$ (1052)	54.75	4.37	10.65	54.77	4.35	10.67	564	15710
11b	Dark violet crystals	72	199	$C_{56}H_{50}N_8O_4I_2$ (1152)	58.33	4.34	9.72	58.36	4.30	9.71	461, 577	23150, 15990
11c	Violet crystals	61	189	$C_{48}H_{46}N_8O_4I_2$ (1052)	54.75	4.37	10.65	54.71	4.39	10.63	568	16010
11d	Intense violet crystals	51	187	$C_{56}H_{50}N_8O_2S_2I_2$ (1184)	56.76	4.22	9.46	56.78	4.21	9.43	463, 590	24110, 16760
11e	Intense violet crystals	74	209	$C_{56}H_{52}N_{10}O_2I_2$ (1150)	58.43	4.52	12.17	58.47	4.49	12.15	477, 602	24960, 17010

the benz-bisbiheterocyclic system present and the number of cationic centers in these dyes. For instances, the absorption spectra of the monomethine cyanine dyes **6a**, **7a**, **8a** X = O, A = 1-ethyl pyridinium-4-yl salt showed an absorption spectral band at λ_{max} 493, 501, and 517 nm, respectively. Substituting A by 1-ethyl quinolinium-4-yl salt to give dyes **6b**, **7b**, **8b** causes a bathochromic shift of 16, 13, and 17 nm, respectively, with intensification of the absorption bands, in addition to the appearance of new absorption bands at λ_{max} 411, 422, and 423 nm, respectively, owing to the extra conjugation in the quinoline moiety (Scheme 1, Table 2). On the contrary, changing the linkage position of the quinolinium residue from 4-yl, dyes **6b**, **7b**, **8b**, to 1-yl salt, dyes **6c**, **7c**, **8c**, resulted in a hypthochromic shift of 6, 7, and 12 nm, respectively, accompanied by decrease in the intensities of the absorption bands owing to decreasing conjugation in the later dyes, **6c**, **7c**, **8c** (Scheme 1, Table 2).

Additionally, the monocationic monomethine cyanine dyes **6b**, **7b**, **8b** incorporating pyrazolo-oxazine nucleus showed hypthochromically shifted bands when compared to its analogous dyes **6d**, **7d**, **8d** and **6e**, **7e**, **8e** which contain pyrazolo-thiazine and pyrazolo-pyrazine nuclei. This is due to the oxazine ring in dyes **6b**, **7b**, **8b** which has a more electron attracting character than thiazine and pyrazine rings in dyes **6d**, **7d**, **8d** and dyes **6e**, **7e**, **8e**, respectively. Also, the thiazine ring in dyes **6d**, **7d**, **8d** has a more electron attracting character than the pyrazine ring in dyes **6e**, **7e**, **8e** resulting in hypthochromic shifts.

The number of cationic centers have a prominent effect upon the spectral behaviour of the newly prepared monocationic monomethine and dicationic monomethine cyanine dyes (**6a–e** and **7a–e**) and this is illustrated by the hypthochromic shift, 5 nm, and the decrease in the intensity of the absorption bands between dyes **6b** and **7b** which is attributed to the presence of an extra cationic center that is considered as an additional charge transfer source in dye **7b**. In dyes **7b** and **8b** the nature of the charge transfer pathways has a crucial effect upon the spectral behaviour of the synthesized dicationic monomethine and dicationic bismonomethine cyanine dyes (**7a–e** and **8a–e**). This can be shown by the bathochromic shift of 20 nm as well as the decrease in the intensity of the absorption bands between dyes **8b** and **7b** which is recognized by the presence of an accumulative conjugation of the two charge transfer pathways in the dye molecule **8b** more than in its analogous dye **7b** (Scheme 1, Table 2).

Also the trimethine and bistrimethine cyanine dyes **10a–e** and **11a–e** showed electronic absorption spectra in 95% ethanol in which its band positions and molar extinction coefficients are influenced by the nature of the quaternary heterocyclic nuclei, its linkage position and the electronegativity of hetero atoms in the benz-bisbiheterocyclic system. So, substituting A = 1-ethyl pyridinium-2-yl salt in the trimethine and in the bistrimethine cyanine dyes, **10a** and **11a**, by A = 1-ethyl quinolinium-2-yl salt to give dyes **10b** and **11b** causes bathochromic shifts by 7 and 13 nm, respectively, accompanied by intensifications of the absorption bands. This is attributed to a more extensive π-delocalization that leads to an easier charge transfer in the later dyes than the former ones (Scheme 1, Table 3). Otherwise, substituting A = 1-ethyl pyridinium-2-yl salt in dyes, **10a**

Table 4
IR and ^{1}H NMR spectral data of the prepared compounds

Comp. no.	IR spectrum (KBr) (cm^{-1})	^{1}H NMR spectrum (DMSO), δ (*Ms. data*)
3a	682, 728 (monosubstituted phenyl) 1030, 1173 (C–O–C cyclic) 1342 (C–N) 1424 (C=N) 1624 (C=C) 1690 (C=O quinone) 3088 (NH cyclic)	3.05 (s, 6H, $2CH_3$ at C_4,C_{10}) 5.60 (s, 2H, 2NH) 6.90–7.7 (m, 10H, aromatic) (*m/z 478*)
3b	656, 707 (monosubstituted phenyl) 1016, 1156 (C–S–C cyclic) 1322 (C–N) 1467 (C=N) 1591 (C=C) 1664 (C=O quinone) 3182 (NH cyclic)	3.00 (s, 6H, $2CH_3$ at C_4,C_{10}) 5.85 (s, 2H, 2NH) 6.95–7.75 (m, 10H, aromatic) (*m/z 512*)
3c	641, 692 (monosubstituted phenyl) 1072, 1154 (C–N–C cyclic) 1359 (C–N) 1508 (C=N) 1631 (C=C) 1687 (C=O quinone) 3308 (NH cyclic)	3.10 (s, 6H, $2CH_3$ at C_4,C_{10}) 5.50 (s, 4H, 4NH) 7.00–7.75 (m, 10H, aromatic) (*m/z 476*)
4a	669, 724 (monosubstituted phenyl) 1097, 1172 (C–O–C cyclic) 1366 (C–N) 1441 (C=N) 1585 (C=C) 1685 (C=O quinone) 2920 (quaternary salt) 3363 (NH cyclic)	1.80–2.05 (t, 3H, CH_3 of ethyl at N^+) 3.15 (s, 6H, $2CH_3$ at C_4,C_{10}) 5.85 (s, 2H, 2NH) 6.90–7.7 (m, 10H, aromatic) (*m/z 634*)
5a	672, 763 (monosubstituted phenyl) 1041, 1163 (C–O–C cyclic) 1309 (C–N) 1481 (C=N) 1600 (C=C) 1684 (C=O quinone) 2913 (quaternary salt) 3383 (NH cyclic)	1.85–2.15 (t, 6H, $2CH_3$ of ethyl at N^+) 3.55 (s, 6H, $2CH_3$ at C_4,C_{10}) 5.95 (s, 2H, 2NH) 6.80–7.85 (m, 10H, aromatic) (*m/z 790*)
6b	673, 757 (monosubstituted phenyl) 832, 906 (*ortho*-disubstituted phenyl) 1094, 1178 (C–O–C cyclic) 1347 (C–N) 1500 (C=N) 1605 (C=C) 1693 (C=O quinone) 2941 (quaternary salt) 3332 (NH cyclic)	1.10–1.20 (t, 3H, CH_3 of ethyl at *N*-quinoline) 1.30–1.35 (t, 3H, CH_3 of ethyl at *N*-pyrazole) 3.40–3.60 (q, 2H, CH_2 of ethyl at *N*-quinoline) 3.70–3.85 (q, 2H, CH_2 of ethyl at *N*-pyrazole) 3.85 (s, 3H, CH_3 at C_{10}) 5.45 (s, 2H, 2NH) 6.90–8.00 (m, 17H, aromatic, heterocyclic and –CH=)
7b	684, 754 (monosubstituted phenyl) 843, 903 (*ortho*-disubstituted phenyl) 1092, 1166 (C–O–C cyclic) 1347 (C–N) 1494 (C=N) 1605 (C=C) 1693 (C=O quinone) 2926 (quaternary salt) 3332 (NH cyclic)	1.10–1.20 (t, 3H, CH_3 of ethyl at *N*-quinoline) 1.25–1.4 (t, 6H, $2CH_3$ of ethyl at *N*-pyrazole) 3.45–3.60 (q, 2H, CH_2 of ethyl at *N*-quinoline) 3.65–3.9 (q, 2H, CH_2 of ethyl at *N*-pyrazole) 3.95 (s, 3H, CH_3 at C_{10}) 5.40 (s, 2H, 2NH) 6.60–8.20 (m, 17H, aromatic, heterocyclic and –CH=)

(*continued on next page*)

Table 4 (*continued*)

Comp. no.	IR spectrum (KBr) (cm^{-1})	^1H NMR spectrum (DMSO), δ (*Ms. data*)
8b	658, 743 (monosubstituted phenyl) 886, 955 (*ortho*-disubstituted phenyl) 1084, 1178 (C–O–C cyclic) 1337 (C–N) 1485 (C=N) 1584 (C=C) 1683 (C=O quinone) 2921 (quaternary salt) 3277 (NH cyclic)	1.15–1.25 (t, 6H, $2CH_3$ of ethyl at *N*-quinoline) 1.30–1.45 (t, 6H, $2CH_3$ of ethyl at *N*-pyrazole) 3.45–3.65 (q, 4H, $2CH_2$ of ethyl at *N*-quinoline) 3.70–4.10 (q, 4H, $2CH_2$ of ethyl at *N*-pyrazole) 5.45 (s, 2H, 2NH) 6.60–7.95 (m, 24H, aromatic, heterocyclic and –CH=)
9a	680, 743 (monosubstituted phenyl) 1026, 1070 (C–O–C cyclic) 1134 (C–O ether) 1368 (C–N) 1485 (C=N) 1607 (C=C) 1694 (C=O quinone) 2928 (quaternary salt) 3347 (NH cyclic)	1.15–1.25 (t, 12H, $4CH_3$ of ethoxyl) 2.05–2.20 (t, 6H, $2CH_3$ of ethyl at *N*-pyrazole) 2.60–3.05 (m, 12H, $4CH_2$ of ethoxyl and $2CH_2$ at C_4, C_{10}) 3.65–4.00 (m, 6H, $2CH_2$ of ethyl at N^+ and 2CH at C_4, C_{10}) 5.95 (s, 2H, 2NH) 6.95–7.75 (m, 10H, aromatic) (*m/z 994*)
10b	693, 767 (monosubstituted phenyl) 841, 915 (*ortho*-disubstituted phenyl) 1046, 1158 (C–O–C cyclic) 1231 (C–O ether) 1359 (C–N) 1482 (C=N) 1593 (C=C) 1681 (C=O quinone) 2917 (quaternary salt) 3311 (NH cyclic)	1.10–1.90 (m, 15H, $5CH_3$ of ethyl) 3.20–4.35 (m, 13H, $5CH_2$ of ethyl and $-CH-CH_2-$) 5.45 (s, 2H, 2NH) 6.30–8.10 (m, 19H, aromatic, heterocyclic and –CH=)
11b	693, 776 (monosubstituted phenyl) 865, 915 (*ortho*-disubstituted phenyl) 1100, 1161 (C–O–C cyclic) 1363 (C–N) 1511 (C=N) 1593 (C=C) 1681 (C=O quinone) 2917 (quaternary salt) 3311 (NH cyclic)	1.05–1.20 (t, 6H, $2CH_3$ of ethyl at *N*-quinoline) 1.35–1.50 (t, 6H, $2CH_3$ of ethyl at *N*-pyrazole) 3.25–3.65 (q, 4H, $2CH_2$ of ethyl at *N*-quinoline) 3.75–4.10 (q, 4H, $2CH_2$ of ethyl at *N*-pyrazole) 5.30 (s, 2H, 2NH) 6.30–8.25 (m, 28H, aromatic, heterocyclic and –CH=)

and **11a**, by A = 1-ethyl pyridinium-4-yl salt to give dyes **10c** and **11c** causes bathochromic shifts for the absorption bands by 3 and 4 nm, respectively, this is related to the extended conjugation in the later dyes (Table 3). Additionally, substituting the oxygen atom in the benz-bisbiheterocyclic system in dyes **10b**, **11b** by sulphur and/or nitrogen atoms in dyes **10d**, **11d** and/or **10e**, **11e** causes red shifts for the absorption bands (17 nm, 13 nm and/or 26 nm, 25 nm). This is due to the electron withdrawing property of oxygen atom in dyes **10b**, **11b** in comparison with sulphur and/or nitrogen atoms in dyes **10d**, **11d** and/or **10e**, **11e**. This is the case in dyes containing sulphur atom **10d**, **11d** if compared with those containing nitrogen atom **10e**, **11e** (9 nm and 12 nm) since the higher electron seeking character of the sulphur atom in dyes **10d**, **11d** precludes the charge transfer whenever this electron seeking property would be approximately absent in case of nitrogen atom in dyes **10e**, **11e** (Table 3).

3. Conclusion

In our point of view, which is based on the current study results, the visible spectra of these cyanine dyes are highly marked depending on the nature of the dye structure. Thus, the absorption spectra of these dyes increase (decrease) by increasing (decreasing) conjugation in the dye molecule. Otherwise, increasing (decreasing) the electron attracting character of the benz-bisbiheterocyclic system leads to dyes with a hypthochromically (bathochromically) shifted spectra. It

is interesting to state that, increasing number of methine units along the methine chain gives dyes with red shifted spectra, consequently, the dyes that have two conjugated charge transfer pathways give bathochromically shifted absorption bands more than their analogous with only one charge transfer pathway.

4. Experimental

4.1. General

All the prepared compounds were *investigated and purified* using chromatographic techniques (*TLC* and *Column Chromatography*, respectively). Melting points are measured using Galenkanp melting point apparatus and are uncorrected. Elemental analyses were carried out at the Microanalytical Center of Cairo University by an automatic analyzer (Heraeus). MS spectra were recorded by mass spectrometer MS 9 (AET) EI Mode, IR (KBr pellets) spectra by 1650 FT-IR instrument, and ^{1}H NMR spectra by 300 MHz NMR Spectrometer (Cairo University). Electronic visible absorption spectra were carried out on Shimsdzu UV–Visible recording spectrometer (South Valley University, Faculty of Science at Aswan).

4.2. Synthesis

4.2.1. Synthesis of 4,10-dimethyl-2,8-diphenyl-5, 11-dihydro-benzo[2,3-b; 2′,3′-b′]bispyrazolo[4,5-b]-1,4-(oxa-, thia-, and pyra-)-zine-6,12-dione (**3a–c**)

A mixture of unimolar ratio (0.01 mol) of *p*-chloranil and bimolar ratio (0.02 mol) of 4-amino-3-methyl-1-phenyl-5-(hydroxyl, mercapto or imino)-pyrazole was refluxed in ethanol (50 mL) containing pyridine (20 mL) for 8 h. The reaction mixture changed from a reddish colour to dark brown at the end of the refluxing. It was filtered while hot, precipitated by ice–water mixture and neutralized by concentrated hydrochloric acid. The products were collected, washed with water several times, dried and crystallized from ethanol. The results are listed in Table 1.

4.2.2. Synthesis of 3-iodoethane monoquaternized salts of 4,10-dimethyl-2,8-diphenyl-5,11-dihydro-benzo[2, 3-b; 2′,3′-b′]bispyrazolo[4,5-b]-1,4-(oxa-, thia-, and pyra-)-zine (**4a–c**)

A pure crystallized sample of (**3a–c**) (0.01 mol) and equimolar ratio of iodoethane was heated in a sealed tube till complete fusion. The products were cooled, dissolved in ethanol, filtered to remove impurities, precipitated using ice–water mixture, dried, and crystallized using ethanol. See data in Table 1.

4.2.3. Synthesis of 3,9-iodoethane diquaternized salts of 4,10-dimethyl-2,8-diphenyl-5,11-dihydro-benzo[2, 3-b; 2′,3′-b′]bispyrazolo[4,5-b]-1,4-(oxa-, thia-, and pyra-)-zine (**5a–c**)

This synthesis was established by heating a pure crystallized sample of (**3a–c**) (0.01 mol) and bimolar ratio of iodoethane in a sealed tube till fusion. The products were cooled, dissolved in ethanol, filtered to remove impurities, precipitated using ice–water mixture, dried, and crystallized using ethanol (Table 1).

4.2.4. Synthesis of 10-methyl-3-ethyl-2,8-diphenyl-5, 11-dihydro-benzo[2,3-b; 2′,3′-b′]bispyrazolo[4,5-b]-1,4-(oxa-, thia-, and pyra-)-zine-4[4(1)] monocationic monomethine cyanine dyes (**6a–e**)

A reaction mixture containing equimolar ratios (0.01 mol) of compounds (**4a–c**) and ethyl iodide quaternary salts of pyridine, quinoline, isoquinoline was refluxed in ethanol (30 mL) containing few drops (3–5) of piperidine for 8–10 h. The reaction mixture, which changed from brown to deep brown during the reaction, was filtered while hot to remove unreacted materials, concentrated, cooled, neutralized with glacial acetic acid and precipitated by adding cold water. The precipitate was collected and crystallized from ethanol. The relevant data are given in Table 2.

4.2.5. Synthesis of 10-methyl-3,9-diethyl-2,8-diphenyl-5,11-dihydro-benzo[2,3-b; 2′,3′-b′]bispyrazolo [4,5-b]-1,4-(oxa-, thia-, and pyra-)-zine-4[4(1)] dicationic monomethine cyanine dyes (**7a–e**)

Ethyl iodide quaternary salts of pyridine, quinoline, isoquinoline in equimolar ratios (0.01 mol) were heated under reflux with compounds (**5a–c**) in ethanol (30 mL) containing piperidine (3–5 drops) for 8–10 h. The reaction mixture attained dark brown colour which turns pale violet at the end of the reflux. It was filtered off while hot, concentrated, neutralized with glacial acetic acid and precipitated by adding ice–water mixture. The separated cyanines were filtered, washed with water, and crystallized from ethanol. The results are listed in Table 2.

4.2.6. Synthesis of 3,9-diethyl-2,8-diphenyl-5, 11-dihydro-benzo[2,3-b; 2′,3′-b′]bispyrazolo[4,5-b]-1,4-(oxa-, thia-, and pyra-)-zine-4,10[4(1)]-dicationic bismonomethine cyanine dyes (**8a–e**)

Two different routes are employed to prepare these cyanine dyes.

Route (1): Piperidine (3–5 drops) was added to an ethanolic solution (50 mL) of (**5a–c**) (0.01 mol) and a bimolar ratio of (1-ethyl pyridinum, 1-ethyl quinolinium, 2-ethyl isoquinolinium)-iodide salts (0.02 mol). The mixture was heated under reflux for 8–10 h and changed from brown to violet colours at the end of the reflux. It was filtered while hot, concentrated to half its

volume, cooled, and neutralized with acetic acid. The precipitated dyes were filtered, washed with water, dried and crystallized from ethanol. The data are given in Table 2.

Route (2): The monomethine cyanine dyes (**7a–e**) and equimolar ratios (0.01 mol) of iodoethane quaternary salt of pyridine, quinoline, isoquinoline (0.01 mol) were dissolved in ethanol (30 mL), to which piperidine (3–5 drops) was added. The reaction mixture was refluxed for 3–5 h. It attained a permanent violet colour at the end of the reflux. It was filtered while hot, concentrated, cooled, then neutralized by acetic acid and precipitated by adding cold water. The precipitates were collected and crystallized from ethanol to give the same compounds obtained by route (1), characterized by melting points, mixed melting points, same IR and ^{1}H NMR spectral data (Table 2).

*4.2.7. Synthesis of 4,10-di[2-diethoxyethane]-3,9-diethyl-2,8-diphenyl-5,11-dihydro-benzo[2,3-b;2′,3′,-b′]bispyrazolo[4,5-b]-1,4-(oxa-, thia-, and pyra-)-zine-iodide salts (**9a–c**) as intermediate compounds*

These intermediate compounds were synthesized by refluxing of compound (**5a–c**) (0.01 mol) with triethylorthoformate in 1:2 molar ratios in ethanol (30 mL) containing piperidine (1 mL) for 5–7 h. The dark brown mixture was filtered while hot to remove unreacted materials, concentrated, neutralized with glacial acetic acid and precipitated using cold water. The separated intermediate compounds were filtered, washed with water and crystallized from ethanol. The results are registered in Table 3.

*4.2.8. Synthesis of 10-[2-diethoxyethane]-3,9-diethyl-2,8-diphenyl-5,11-dihydro-benzo[2,3-b; 2′,3′-b′]bispyrazolo[4,5-b]-1,4-(oxa-, thia-, and pyra-)-zine-4[2(4)]-trimethine cyanine dyes (**10a–e**)*

A mixture of equimolar ratios of the intermediate compounds (**9a–c**) (0.01 mol) and *N*-ethyl-α-picolinium iodide, *N*-ethyl-quinaldinium iodide, *N*-ethyl-γ-picolinium iodide (0.01 mol) was heated under reflux in ethanol (30 mL) containing piperidine (3–5 drops) for 8–10 h. The reaction mixture changed its colour from dark brown colour to intense violet at the end of the reflux. It was filtered off while hot, concentrated, neutralized with glacial acetic acid and precipitated by adding cold water. The separated cyanines were filtered, washed with cold water, and crystallized from ethanol. The results are listed in Table 3.

*4.2.9. Synthesis of 3,9-diethyl-2,8-diphenyl-5,11-dihydro-benzo[2,3-b; 2′,3′-b′]bispyrazolo[4,5-b]-1,4-(oxa-, thia-, and pyra-)-zine-4,10[2(4)]-bistrimethine cyanine dyes (**11a–e**)*

Two different routes are employed to prepare these series of cyanine dyes.

Route (1): Piperidine (3–5 drops) was added to an ethanolic solution (50 mL) of (**9a–c**) (0.01 mol) and iodoethane quaternary salts of α-picoline, quinaldine, γ-picoline (0.02 mol). The mixture was heated under reflux for 8–10 h and its colour changed from brown to highly intense violet at the end of the reflux. It was filtered while hot, concentrated to half its volume, cooled, and neutralized with acetic acid. The precipitated dyes were filtered, washed with water, dried and crystallized from ethanol. The data are given in Table 3.

Route (2): The trimethine cyanine dyes (**10a–e**) (0.01 mol) and equimolar ratios of iodoethane quaternary salts of α-picoline, quinaldine, γ-picoline were dissolved in ethanol (30 mL), to which piperidine (3–5 drops) was added. The reaction mixture was refluxed for 3–5 h. It attained a permanent intense violet colour at the end of the reflux. It was filtered while hot, concentrated, cooled, neutralized by acetic acid and precipitated by adding cold water. The precipitates were collected and crystallized from ethanol to give the same compounds obtained by route (1), characterized by melting points, mixed melting points, same IR and ^{1}H NMR spectral data (Table 3).

4.3. Absorption spectroscopy

The electronic visible absorption spectra of the prepared cyanine dyes were examined in 95% ethanol and recorded using 1 cm Qz cell in Shimadzu UV–Visible Recording Spectrophotometer. A stock solution (10^{-3} M) of the dyes was diluted to a suitable volume in order to obtain the required concentrations.

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