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Benzo[g]quinoline heterocyclic derivative as a typical precursor in the synthesis of new class of cyanine-like dyes

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ABSTRACT

New unsymmetrical cyanine-like dyes have been synthesized including monomethine, dimethine, and tetramethine, containing heterocyclic quinone of benzo[g]quinoline derivative. The new synthesized compounds were identified by elemental analysis, IR and 1H NMR. The UV visible absorption spectra of dyes are also reported.

1. Introduction

Our target in this work employing heterocyclic compound of benzo[g]quinoline derivative as a typical precursor to prepare new heterocyclic cyanine-like dyes related to quinones expected to have a biological activity and other applications. This is due to the fact that quinone derivatives are widely used as fungicides [1,2] and antibacterial agents [2-4]. Also a large number of chemicals derived from quinone as the basic subunit exhibit prominent pharmacological applications such as antimalarial [5] and herbicidal activity [6]. On the other hand, cyanine dyes have been extensively studied over the past century, mainly as photosensitizes for photography [7,8]. In recent decades, other applications such as optical recording and storage media [9,10], visible and near-infrared laser dyes [10-12], biological fluorescent stains and probes [13] cyanine dyes find extensive application as photo sensitizers in the blue green light [14]. Some of these dyes are growth inhibitors to bacteria and to the mitosis of fertilized sea urchin eggs [15]. Additionally, wide applications of quinones can also be found in the field of synthetic new heterocyclic derivatives [16] and cyanine dyes [8,17,18].

In continuation of our interest by cyanine dyes, several types of cyanines by different routes have been synthsised [19-24]. Here, by using a joint theoretical and experimental approach, we demonstrate the correspondence between cyanines and the new class of cyanine-like dyes involving heterocyclic quinone of benzo[g]quinoline derivatives [25,26]. This paper describes the synthesis and spectral behavior of new dimethine, merocyanine, monomethine and tetramethine cyanine-like dyes incorporating 4-amino-2-methyl-5,10-dioxo-1,5,10,11-tetra-hydro-benzo[g]quinoline-3-carbonitrile moiety [27].

2. Experimental

2.1. Instrumentation

All melting points are uncorrected. Elemental analyses were carried out at the Micro analytical center (Assuit-University). The IR (KBr) spectra were determined with Perkin-Elmer Infrared 127B Spectrophotometer (Assuit University). ^{1}H NMR spectra were recorded with a Bruker AMX-250 spectrometer. The electronic absorption spectra were recorded within the wavelength range (350-700 nm) on 6405 UV/Visible recording spectrophotometer, Faculty of Science, Aswan, Egypt. Mass spectra were recorded on an HpMs 6988 spectrometer (Cairo University).

2.2. Synthesis of 4-amino-2-methyl-5,10-dioxo-1,5,10,11-tetrahydrobenzo[g]quinoline-3-carbonitrile (1)

The compound **1** was carried out according to Khalafallah *et al*., 2002 [27].

2.3. Synthesis of 4-amino-5,10-dioxo-1,5,10,11-tetrahydro-benzo[g]quinoline-3-carbonitrile-merocyanine-2(4)mono-methine cyanine- like dye (2a), *4-amino-5,10-dioxo-1,5,10, 11-tetrahydro-benzo[g]quinoline-3-carbonitrile-mero-cyanine-2(4)monomethine cyanine-like dye* (2b), *4-amino-5,10-dioxo-1,5,10,11-tetrahydro-benzo[g]quinoline-3-carbo nitrile-merocyanine-2(1)monomethine cyanine- like dye* (2c)

An ethanolic solution of equimolar amount of compound **1** and 1-ethyl(pyridinium, quinolinium and/or isoquinolinium) salts (0.01 mol) were refluxed for 7-8 hr, in the presence of piperidine (3-5 drops), filtered hot, concentrated and acidified with acetic acid.

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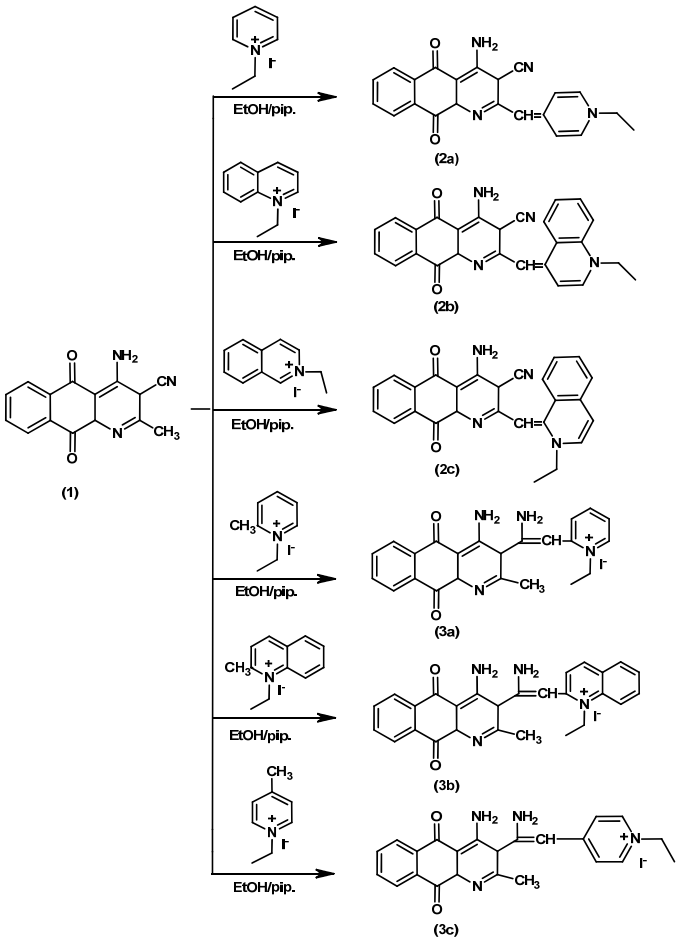


Scheme 1

The precipitated products after dilution with water filtered off and crystallized from ethanol to give the corresponding products (Scheme 1, Tables 1, 2).

2.4. Synthesis of 4-amino-2-methyl-5,10-dioxo-1,5,10,11-tetra-hydrobenzo[g]quinoline meso-substituted-3(2) dimethine cyanine-like dye (3a), *4-amino-2-methyl-5,10-dioxo-1,5,10,11-tetra-hydrobenzo[g]quinoline meso-substituted-3(2)dimethinecyanine-like dye* (3b), *4-amino-2-methyl-5,10-dioxo-1,5,10,11-tetra-hydrobenzo[g]quinoline meso-substituted-3(4) dimethine cyanine-like dye* (3c)

Equimolar amounts of compound **1** and 2-methyl quaternary salts (α(γ)-picoline and/or quinaldine) ethyl iodide (0.01 mol) were dissolved in ethanol (30 mL) then piperidine (3-5 drops) was added. The reaction mixture was refluxed for 8 hr, filtered hot, concentrated cooled and acidified with acetic acid. The precipitated products after dilution with water were collected and crystallized from aqueous ethanol (Scheme 1, Tables 1 and 2).

2.5. Synthesis of 4-amino-2-formyl-5,10-dioxo-1,5,10,11-tetrahydrobenzo[g]quinoline-3-carbonitrile (4)

The compound **1** was refluxed for 12-15 hr, with selenium dioxide (0.02 mol) in dioxane (20 mL). The reaction mixture was filtered hot from selenium metal. The filtrate was allowed to cool and the filtrate was concentrated and the separated product dilution with water and cooling was filtered off, washed with water, and crystallized from ethanol (Scheme 2, Tables 1 and 2).

2.6. Synthesis of 4-amino-5,10-dioxo-1,5,10,11-tetra-hydro benzo[g]quinoline-2(2) dimethine cyanine- like dye (5a), *4-amino-5,10-dioxo-1,5,10,11-tetra-hydrobenzo[g] quinoline-2(2) dimethine cyanine- like dye* (5b), *4-amino-5,10-dioxo-1,5,10,11-tetra-hydrobenzo[g]quinoline-2(4) dimethine cyanine-like dye* (5c)

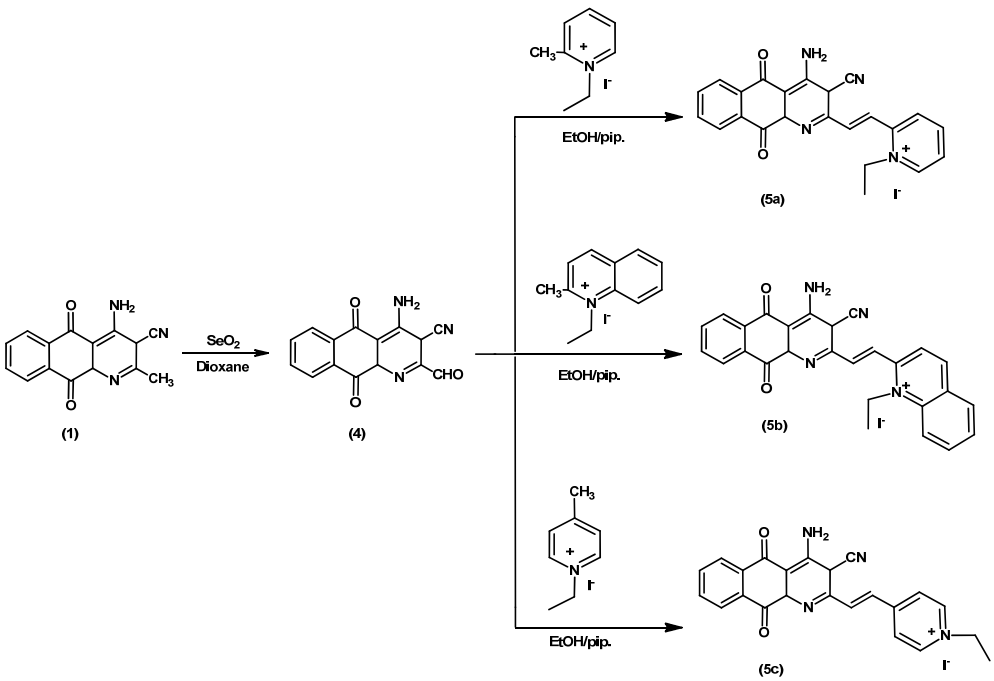
Equimolar amounts of compound **4** and 2-methyl heterocyclic quaternary salts (α(γ)-picoline and/or quinaldine) ethyl iodide (0.01 mol) were dissolved in ethanol (30 mL) then piperidine (3-5 drops) was added .The reaction mixture was refluxed for 8 hr, filtered hot, concentrated cooled and acidified with acetic acid. The precipitated products after dilution with water were collected and crystallized from aqueous ethanol (Scheme 2, Tables 1 and 2).

2.7. Synthesis of intermediate compounds (6a-e)

Equimolar amounts of compound **4** and acetaldehyde, acetone and/or acetophenone derivatives were refluxed with 30 mL ethanol and (3-5 drops) of piperidine for 6-8 hr, filtered hot, concentrated, cooled and acidified with acetic acid. The precipitated products after dilution with water were collected and crystallized from aqueous ethanol (Scheme 3, Tables 1 and 2).

Table 1. Characterization of compounds (**2a-7g**).

Compound No	Yield, %	M.P., °C	Mol. Formula, (M.wt., g)	Elemental Analysis, % Calculated (Found)			Mass, *m/z*
				C	H	N	
2a	70	> 300	$C_{22}H_{18}N_4O_2$ (370.41)	71.35 (71.47)	4.86 (4.78)	15.14 (15.22)	370
2b	75	240	$C_{26}H_{20}N_4O_2$ (420.47)	74.29 (74.37)	4.76; (4.71)	13.33. (13.25)	420
2c	80	> 300	$C_{26}H_{20}N_4O_2$ (420.47)	74.29 (74.38)	4.76 (4.67)	13.33 (13.42)	420
3a	60	300	$C_{23}H_{23}N_4O_2I$ (514.37)	53.70 (53.57)	4.47 (4.40)	10.90 (10.93)	514
3b	70	200	$C_{27}H_{25}N_4O_2I$ (564.43)	57.44 (57.39)	4.43 (4.52)	9.93 (9.88)	564
3c	65	200	$C_{23}H_{23}N_4O_2I$ (514.37)	53.70 (53.53)	4.47 (4.42)	10.90 (10.91)	514
4	50	300	$C_{15}H_9N_3O_3$ (279.25)	64.52 (64.59)	3.23 (3.29)	15.05 (15.12)	279
5a	60	185	$C_{23}H_{19}N_4O_2I$ (510.33)	54.12 (54.19)	3.73 (3.78)	10.98 (10.90)	510
5b	65	230	$C_{27}H_{21}N_4O_2I$ (560)	57.86 (57.95)	3.75 (3.62)	10.00 (9.91)	560
5c	60	300	$C_{23}H_{19}N_4O_2I$ (510.33)	54.12 (54.15)	3.73 (3.75)	10.98 (10.94)	510
6a	60	185	$C_{17}H_{11}N_3O_3$ (305.29)	66.89 (66.99)	3.61 (3.88)	13.77 (13.69)	305
6b	65	230	$C_{18}H_{13}N_3O_3$ (319.32)	67.71 (67.85)	4.08 (4.13)	13.17 (13.23)	319
6c	58	300	$C_{23}H_{15}N_3O_3$ (381.39)	72.44 (72.52)	3.94 3.88)	11.02 (11.10)	381
6d	49	220	$C_{24}H_{17}N_3O_4$ (411)	70.07 (70.12)	4.14 (4.19)	10.22 (10.16)	411
6e	62	222	$C_{23}H_{14}N_4O_5$ (426.39)	64.79 (64.72)	3.29 (3.36)	13.15 (13.11)	426
7a	55	>300	$C_{31}H_{25}N_4O_2I$ (612)	60.78 (60.69)	4.09 (4.18)	9.15 (9.19)	612
7b	75	260	$C_{35}H_{27}N_4O_2I$ (662)	63.44 (63.55)	4.08 (4.13)	8.46 (8.43)	662
7c	51	265	$C_{31}H_{25}N_4O_2I$ (612)	60.78 (60.71)	4.09 (4.22)	9.15 (9.20)	612
7d	75	260	$C_{36}H_{29}N_4O_3I$ (692)	62.43 (62.52)	4.19 (4.23)	8.09 (8.16)	692
7e	62	263	$C_{35}H_{26}N_5O_4I$ (707)	59.41 (59.48)	3.68 (3.56)	9.90 (9.82)	707
7f	52	260	$C_{29}H_{23}N_4O_2I$ (586)	59.39 (59.45)	3.93 (3.87)	9.56 (9.49)	586
7g	57	260	$C_{30}H_{25}N_4O_2I$ (600)	60 (59.95)	4.17 (4.17)	9.33 (9.31)	600



Scheme 2

Table 2. IR and ^{1}H NMR spectral data of compounds **2a-c**, **3a-b**, **4**, **5a-b**, **6a-d**, and **7a-g**.

Compound No	IR (cm^{-1})	^{1}H NMR (δ, ppm)
2a	2200 (C≡N), 2900-2800 (N-C_2H_5 of heterocyclic group), 3400-3100 (NH_2), 1650 (Quinone ring)	1.00 (t, 3H, CH_3), 2.00 (s, 2H, NH_2), 2.69 (q, 2H, CH_2), 4.81 (s, 1H, Quinone), 5.60-6.46 (m, 5H, CH + 4H, Pyridine ring), 7.64-792 (m, 4H, Ar), 2.85 (s, 1H, CH-CN).
2b	2215 (C≡N), 2900-2800 (N-C_2H_5 of heterocyclic group), 3400-3100 (NH_2), 1690 (Quinone ring).	1.13 (t, 3H, CH_3), 2.00 (s, 2H, NH_2), 3.10 (q, 2H, CH_2), 4.81 (s, 1H, Quinone), 5.50-8.05 (m, 11H, CH + Heterocyclic-H + Ar-H), 2.86 (s, 1H, CH-CN).
2c	2220 (C≡N), 2900-2800 (N-C_2H_5 of heterocyclic group), 3400-3100 (NH_2), 1650 (Quinone ring)	-
3a	1495 (C=N), 2924 (ethyl iodide of heterocyclic salt), 3400-3100 (NH_2), 1600-1590 (Quinone ring)	1.71 (s, 3H, CH_3), 1.00 (t, 3H, CH_3 (Ethyl iodide)), 2.00 (s, 4H, $2NH_2$), 2.59 (q, 2H, CH_2 (Ethyl iodide)), 4.81 (s, 1H, Quinone), 4.52-6.17 (m, 5H, CH + Pyridine ring), 7.63-8.05 (m, 4H, Ar-H), 2.85 (s, 1H, CH-CN).
3b	2922 (Ethyl iodide of heterocyclic salt), 1497 (C=N), 3400-3100 (NH_2), 1600-1580 (Quinone ring)	-
4	2200 (C≡N), 2922 (Ethyl iodide of heterocyclic salt), 3400-3100 (NH_2), 1598 (Quinone ring), 1718 (CHO)	2.00 (s, 2H, NH_2), 4.81 (s, 1H, Quinone), 7.63-8.05 (m, 4H, Ar-H), 9.68 (s, 1H, CHO), 2.86 (s, 1H, CH-CN).
5a	1500 (C=N), 1595 (Conjugated C=C), 2220 (C≡N), 2923 (Ethyl iodide of heterocyclic salt), 3450-3350 (NH_2), 1600 (Quinone ring)	1.00 (t, 3H, CH_3), 2.00 (s, 2H, NH_2), 2.59 (q, 2H, CH_2), 4.81 (s, 1H, Quinone), 5.04-6.39 (m, 6H, CH=CH + Pyridine ring), 7.64-8.05 (m, 4H, Ar-H), 2.85 (s, 1H, CH-CN).
5b	1500 (C=N), 1595 (Conjugated C=C), 2200 (C≡N), 2922 (Ethyl iodide of heterocyclic salt), 3450-3350 (NH_2), 1600 (Quinone ring)	-
6a	1595 (Conjugated C=C), 2200 (C≡N), 3450-3350 (NH_2), 1600 (Quinone ring), 1700 (C=O)	2.00 (s, 2H, NH_2), 4.81 (s, 1H, Quinone), 6.29-8.05 (m, 6H, CH=CH + Ar-H), 9.68 (s, 1H, CHO), 2.85 (s, 1H, CH-CN).
6b	1595 (Conjugated C=C), 2200 (C≡N), 3450-3350 (NH_2), 1600 (Quinone ring), 1700 (C=O)	-
6c	1595 (conjugated C=C), 2200 (C≡N), 3450-3350 (NH_2), 1620-1600 (Quinone ring), 1718 (C=O)	2.00 (s, 2H, NH_2), 4.81 (s, 1H, Quinone), 7.22-8.05 (m, 11H, CH=CH + Ar-H), 2.86 (s, 1H, CH-CN).
6d	1595 (Conjugated C=C), 2200 (C≡N), 3450-3350 (NH_2), 1620-1600 (Quinone ring), 1700 (C=O)	2.00 (s, 2H, NH_2), 4.81 (s, 1H, Quinone), 3.73 (s, 3H, OCH_3), 6.96-8.05 (m, 10H, CH=CH + Ar-H), 2.82 (s, 1H, CH-CN).
7a	1487 (Cyclic C=N),1595 (Conjugated C=C), 1620-1600 (Quinone ring), 2200 (C≡N), 3450-3350 (NH_2), 2900 (Ethyl iodide of heterocyclic salt)	0.9 (t, 3H, CH_3), 2.00 (s, 2H, NH_2), 1.4 (q, 2H, CH_2), 4.81 (s, 1H, Quinone), 6.51-9.30 (m, 16H, CH=CH-C=CH + heterocyclic H + Ar-H), 2.82 (s, 1H, CH-CN).
7b	1487 (cyclic C=N),1595 (conjugated C=C), 1620-1600 (Quinone ring), 2200 (C≡N), 3450-3350 (NH_2), 2900 (ethyl iodide of heterocyclic salt)	0.9 (t, 3H, CH_3), 2.00 (s, 2H, NH_2), 1.4 (q, 2H, CH_2), 4.81 (s, 1H, Quinone), 6.51-8.90 (m, 18H, CH=CH-C=CH + heterocyclic H + Ar-H), 2.80 (s, 1H, CH-CN).
7d	1595 (Conjugated C=C), 1487 (Cyclic C=N), 2200 (C≡N), 3450-3350 (NH, NH_2), 1620-1600 (Quinone ring), 2929-2921 (Ethyl iodide of heterocyclic salt)	-
7f	1595 (Conjugated C=C), 1487 (cyclic C=N), 1620-1600 (Quinone ring), 2200 (C≡N), 2929-2921 (Ethyl iodide of heterocyclic salt), 3450-3350 (NH_2)	0.9 (t, 3H, CH_3), 2.00 (s, 2H, NH_2), 1.4 (q, 2H, CH_2), 4.81 (s, 1H, Quinone), 6.51-8.90 (m, 14H, CH=CH-CH=CH + heterocyclic H + Ar-H), 2.84 (s, 1H, CH-CN).
7g	1595 (Conjugated C=C), 1487 (Cyclic C=N), 2200 (C≡N), 3450-3350 (NH_2), 1620-1600 (Quinone ring), 2929-2921 (Ethyl iodide of heterocyclic salt)	-

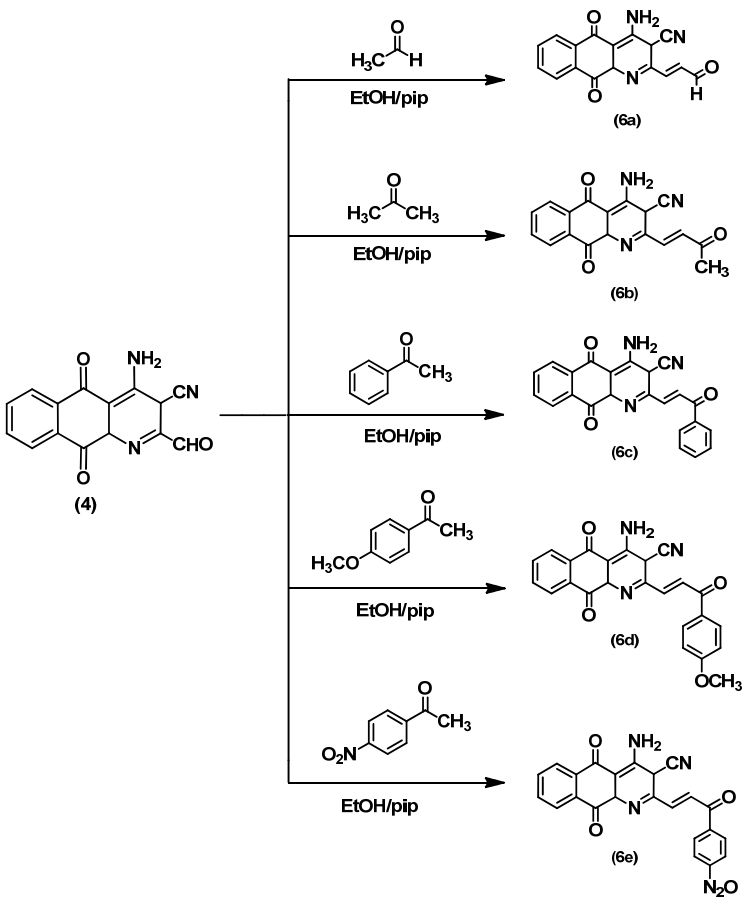
2.8. Synthesis of 4-amino-5,10-dioxo-1,5,10,11-tetrahydro benzo[g]quinoline-3-carbonitrile-meso-substituted-2(2) tetra methine cyanine-like dye (7a), *4-amino-5,10-dioxo-1,5, 10,11-tetrahydrobenzo[g]quinoline-3-carbonitrile-meso-substituted- 2(2) tetramethine cyanine-like dye* (7b), *4-amino-5,10-dioxo-1,5,10,11-tetrahydrobenzo[g]quinoline-3-carbonitrile-meso-substituted- 2(4)tetramethine cyanine-like dye* (7c), *4-amino-5,10-dioxo-1,5,10,11-tetrahydrobenzo [g] quinoline -3-carbonitrile-meso-substituted-2(2)tetra methine cyanine-like dye* (7d), *4-amino-5,10-dioxo-1,5,10, 11-tetrahydrobenzo[g]quinoline-3-carbonitrile-meso-substituted-2(2)tetramethine cyanine-like dye* (7e), *4-amino-5,10-dioxo-1,5,10,11-tetrahydrobenzo[g]quinoline-3-carbonitrile-meso-substituted-2(2) tetramethine cyanine-like dye* (7g)

Equimolar amounts of compounds **6a-e** and 2-methyl heterocyclic quaternary salts (α(γ)-picoline and/or quinaldine) ethyl iodide with (3-4 drops) of piperidine and 30 mL ethanol refluxed for 8 hr, then filtered hot, concentrated cooled and acidified with acetic acid. The precipitated products after dilution with water filtered off and crystallized from aqueous ethanol (Scheme 4, Tables 1 and 2).

3. Results and discussion

3.1. Synthesis

Reaction of equimolar ratios of 4-amino-2-methyl-5,10-dioxo-1,5,10,11-tetra-hydrobenzo[g]quinoline-3-carbonitrile compound **1** [27] with heterocyclic quaternary salts of (pyridinum, quinolinium and isoquinolinium) ethyl iodide in the presence of piperidine as basic catalyst afforded the desired 4-amino-5,10-dioxo-1,5,10,11-tetrahydrobenzo[g]quinoline-3-carbonitrile-merocyanine2[4(1)] monomethine cyanine-like dyes **2a-c** (Scheme 1). Treating on the latter compounds **2a-c** by conc. H_2SO_4 resulted in liberating no iodine vapor on warming. This is due to that the above reaction between the compound **1** and heterocyclic quaternary salts of (pyridinum, quinolinium and/or isoquinolinium) ethyl iodide was suggested to proceed through oxidative elimination via liberation of hydrogen followed by hydrogen iodide molecules. On the other hand, reaction of compound **1** with active methyl heterocyclic quaternary salts (α(γ)-picolines and/or quinaldine)ethyl iodide gave the corresponding 4-amino-2-methyl-5,10-dioxo-1,5,10,11-tetra-hydrobenzo[g]quinolin-meso-substituted-3[2(4)] dimethine cyanine-like dyes **2a-c** (Scheme 1).



Scheme 3

The active methyl group in compound **1** is oxidized using equimolar ratios of compound **1** and selenium dioxide in presence of dioxane as a solvent afforded the intermediate compound 4-amino-2-formyl-5,10-dioxo-1,5,10,11-tetrahydro benzo[g]quinoline-3-carbonitrile **4** [28,29] (Scheme 2).

Reaction of compound **4** with active methyl heterocyclic quaternary salts [α (γ)-picolines and/or quinaldine] ethyl iodide gave the corresponding 4-amino-5,10-dioxo-1,5,10,11-tetrahydrobenzo[g]quinoline-3-carbonitrile-2[2(4)]dimethine cyanine-like dyes **5a-c** (Scheme 2). The reaction was suggested to proceed through condensation reaction between the formyl group of the compound **4** and active methyl group of heterocyclic quaternary salts [α(γ)-picolines and/or quinaldine] ethyl iodide involving dehydration process.

Condensation reaction of equimolar ratios of compound **4** and acetaldehyde, acetone and/or acetophenone derivatives between the formyl group of the former compound and active methyl group of the latter ones in the presence of piperidine as basic catalyst and ethyl alcohol as solvent takes placed to afford the intermediate compounds **6a-e**, (Scheme 3). The reaction of latter compounds **6a-e** with quaternary heterocyclic salts (α (γ)-picolines and/or quinaldine) ethyl iodide in presence of piperidine as basic catalyst and ethanol as solvent gave the corresponding 4-amino-5,10-dioxo-1,5,10,11-tetra-hydrobenzo [g]quinoline-3-carbonitrile-meso-substituted-2[2(4)]-tetra-methine cyanine-like dyes **7a-g**, (Scheme 4).

The newly synthesized cyanine-like dyes **2a-c**, **3a-c**, **5a-c** and **7a-g** are highly colored compounds, easily soluble in polar organic solvents giving a green fluorescence but sparingly soluble in non-polar solvents. Compounds **3a-c**, **5a-c** and **7a-g** are soluble in conc. H_2SO_4 liberating iodine vapor on warming.

3.2. Spectral behavior

The electronic absorption spectral features (λ_{max} and ε_{max} values) of the newly synthesized cyanine-like dyes **2a-c**, **3a-c**, **5a-c** and **7a-g** in ethanol solution are depicted in (Table 3).

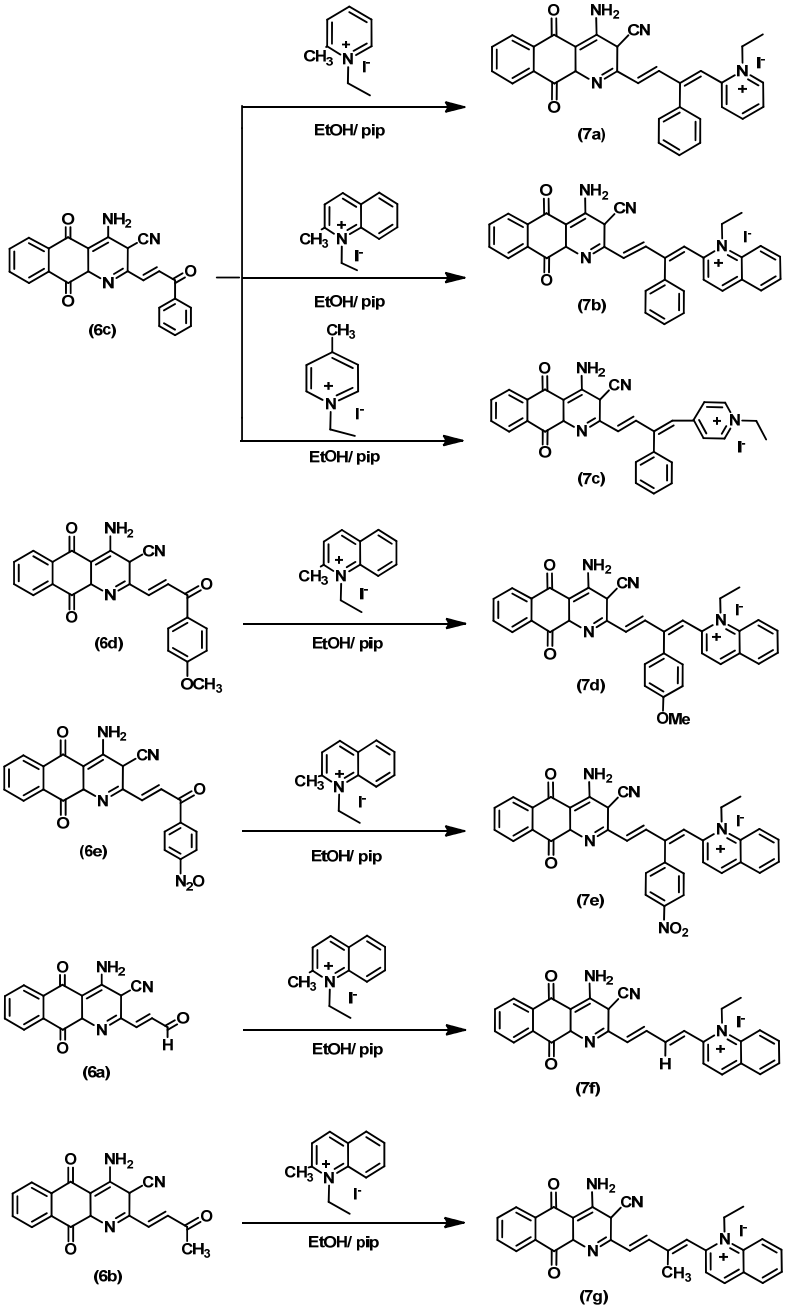
The visible absorption spectra of 4-amino-5,10-dioxo-1,5,10,11-tetra-hydrobenzo[g]quinone-3-carbonitrile mero-cyanine-2[4(1)] monomethine cyanine-like dyes **2a-c** in 95% ethanol undergo bathochromic or hypsochromic shifts depending on the nature of the quaternary salts residue and their linkage position. Thus, the electronic absorption spectra of compound **2a** which incorporating a heterocyclic of *N*-ethyl pyridin-4-ium, showed λ_{max} at 465 nm. Substitution of a heterocyclic of *N*-ethyl pyridin-4-ium in compound **2a** by a heterocyclic of *N*-ethyl quinolin-4-ium in compound **2b** resulted in a bathochromic shift of $\Delta\lambda_{max}$ = 5 nm and appearance of a new absorption band, so compound **2b**, exhibited λ_{max} = 470, 540 nm. This is due to the more extensive π-delocalization and extra conjugation within the extra phenyl ring in quinolinium ring in compound **2b**.

Additionally, changing the linkage position from 4-ium in compound **2b** which incorporating a heterocyclic of *N*-ethyl quinolin-4-ium to 1-ium in compound **2c** which incorporating a heterocyclic of *N*-ethyl isoquinolin-1-ium causes a hypso-chromic shift of $\Delta\lambda_{max}$ = 40, 5 nm, so compound **2c**, showed λ_{max} = 430, 535 nm.

Table 3. The electronic absorption spectra of new synthesized cyanine-like dyes (**2a-c**), (**3a-c**), (**5a-c**) and (**7a-g**) in 95% EtOH *.

Compound	**λ_{max}, nm (ε_{max} mol^{-1}.cm^{-1})**						
Merocyanine monomethine cyanine-like dyes, **2a-c**	**2a** 465 (2210)		**2b** 470 (2424) 540 (1451)		**2c** 430 (1869) 535 sh (1507)		
Meso-substituted dimethine cyanine-like dyes, **3a-c**	**3a** 430 (1655) -		**3b** 580 (723) 690 (226)		**3c** 450 (2029)		
Dimethine cyanine-like dyes, **5a-c**	**5a** 455 (1865)		**5b** 570 (2628) 660 (876)		**5c** 455 (2064) -		
Meso-substituted-tetramethine cyanine-like dyes, **7a-g**	**7a** 430 (1588)	**7b** 520 (724) 555 (481) 600 (657) 690 (379)	**7c** 490 (2402)	**7d** 525 (1366) 560 (1975)	**7e** 455 (1.068)	**7f** 510 (2150) 550 (1715)	**7g** 520 (2152) 555 (1719)

* sh = shoulder of absorption band.



Scheme 4

This is due to the more extensive π-delocalization within 4-ium rather than 1-ium linkage position, (Table 3).

The electronic absorption spectra of 4-amino-2-methyl-5,10-dioxo-1,5,10,11-tetrahydrobenzo[g]quinolin-meso-substituted-3[2(4)]dimethine cyanine-like dyes **3a-c** and 4-amino-5,10-dioxo-1,5,10,11-tetrahydrobenzo[g]quinoline-3-carbonitrile-2[2(4)]dimethine cyanine-like dyes **5a-c** in 95% ethanol exhibited absorption band which become more intense and with strong red shift on increasing the conjugation of quaternary heterocyclic residue.

The absorption spectra of compound **3a** quaternary heterocyclic residue of 1-ethyl pyridinium-2-ium salt had absorbed maxima at 430 nm. Replacing on the pyridyl residue by quinoline analogue, compound **3b**, the absorption band becoming more high intense concomitant with an increasing in the number of absorption band and showing strong red shift of $\Delta\lambda_{max}$ = 150, 260 nm, λ_{max} = 580, 690 nm. This is due to the more extensive π delocalization within the molecule through the extra phenyl ring for compound **3b**.

Additionally, changing the linkage position of heterocyclic quaternary residue from 2-ium in compound **3a** to 4-ium in compound **3c** resulted in a bathochromic shift of $\Delta\lambda_{max}$ = 30 nm (**3c**) quaternary heterocyclic residue of 1-ethyl quinolinium 4-ium salt λ_{max} = 450 nm. This is due to the increasing of the extension conjugation of 4-linkage pyridine moiety better than 2-linkage analogous, (Table 3).

Also the absorption spectra of compound **5a** quaternary heterocyclic residue of pyridinium 2-ium ethyl iodide had absorption maxima at 445 nm. On replacing quaternary heterocyclic residue of pyridinium 2-ium ethyl iodide in compound **5a** by quaternary heterocyclic residue of quinolinium-2-ium ethyl iodide in compound **5b** causes the strong red shift of $\Delta\lambda_{max}$ = 125 nm, concomitant with the appearance of a new absorption band at λ_{max} = 660 nm. This is due to the more extensive π-delocalization within the molecule.

Additionally, changing the linkage position of heterocyclic quaternary residue from 2-ium in compound **5a** to 4-ium in compound **5c** resulted in a bathochromic shift of $\Delta\lambda_{max}$ = 10 nm **5c** λ_{max} = 455 nm. This is due to the increasing of the extension conjugation of 4-linkage pyridine moiety better than 2-linkage analogous, (Table 3).

The visible absorption spectra of 4-amino-5,10-dioxo-1,5,10,11-tetrahydrobenzo[g]quinoline-3-carbonitrile-meso-substituted-2[2(4)]-tetramethine cyanine-like dyes **7a-g** in 95% ethanol showed absorption band undergo batho (hypso) chromically shifted depending upon the heterocyclic quaternary residue, their linkage position and the substituted derivatives. Thus, the absorption spectra of compound **7a** quaternary heterocyclic residue of 1-ethyl pyridin-2-ium ethyl iodide showed λ_{max} = 430 nm. Substituting of heterocyclic quaternary residue 1-ethyl pyridin-2-ium ethyl iodide in compound **7a** by quaternary heterocyclic residue of 1-ethyl quinolin-2-ium ethyl iodide in compound **7b** resulted in strong bathochromic shift of $\Delta\lambda_{max}$ = 90 nm concomitant with the increasing number of absorption bands, **7b**, λ_{max} = 690, 600, 555, and 520 nm. This is due to the more extensive π delocalization within the extra phenyl ring in compound **7b**.

Additionally, changing the linkage position from 2-ium linkage position in compound **7a**, quaternary heterocyclic residue of 1-ethyl pyridin-2-ium ethyl iodide to 4-ium in compound **7c**, quaternary heterocyclic residue of 1-ethyl pyridin-4-ium ethyl iodide resulted in a remarkable bathochromic shift of $\Delta\lambda_{max}$ = 60 nm, if compared with compound **7c**, λ_{max} = 490 nm. This is due to the increasing of the extension conjugation of 4-linkage pyridine moiety better than 2-linkage analogous, (Table 3). On the other hand, substitution of C_6H_5- in compound **7b** by C_6H_4-NO_2 in compound **7e** resulted in a hypsochromic shift of $\Delta\lambda_{max}$ = 65 nm accompanied with the disappearance of the other absorption bands. This is due to the strong electron withdrawing effect of NO_2 group. Also, substitution of C_6H_4-NO_2 in compound **7e** by C_6H_4-OCH_3 in compound **7d** causes a bathochromic shift of $\Delta\lambda_{max}$ = 70 nm accompanied with the appearance of a new absorption band located at 560 nm. This is due to the electron donating effect of CH_3O group (Table 3).

4. Conclusion

New unsymmetrical cyanine-like dyes have been prepared incorporating heterocyclic quinone of benzo[g]quinoline derivative and were identified by chemical and spectroscopic evidences (Elemental analyses, UV, IR, ^{1}H-NMR and MS spectra).

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