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Novel Heterocyclic Quinone Photosensitizing Dyes, their biological and spectral studies

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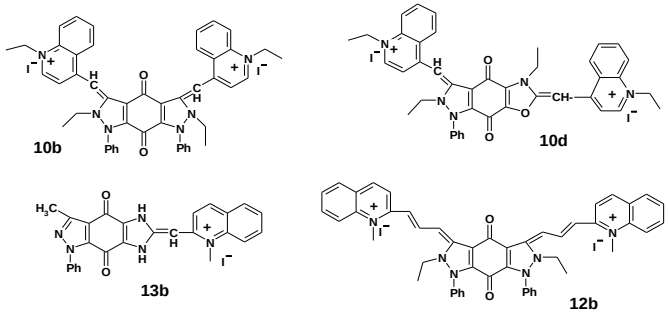
ABSTRACT

A novel symmetrical/ unsymmetrical bis-mono (and/or bis-tri)methine photosensitizing dyes 10a-d and 12a-d were prepared from the new key intermediate compound derivatives7a and 7b namely as 3,5-Dimethyl-1,7-diphenylpyrazolo[4,3-f]indazole-4,8(1H,7H)-dione and 3,6-dimethyl-1-phenyl- 1H-oxazolo [4,5-f'] indazole-4,8-dione respectively(Schemes 1,2,3). Also, new unsymmetrical of different mono methine 13a-c, 14a-c and bis-monomethine 15 cyanine dyes were prepared from the new other key intermediate compound 7c namely as 3-methyl-1-phenylimidazo [4,5-f]indazole-4,6,8(1H,5H,7H)-trione (Scheme 1, 4). Structural determination of the new compounds was carried out by elemental analysis, IR, ^{1}H NMR, mass spectral data. The structure-photosensitization relationship of such dyes was discussed on the basis of their spectral behavior as criteria of photosensitizing effect. Finally, the antimicrobial activity of some selected novel dyes was investigated in vitro using a wide spectrum of microbial strains.

Graphical Abstract:



Highlights

- Synthesis and characterization of novel cyanine dyes.
- Antimicrobial activity with highest potency towards the microorganism *Halobiforma haloterrestris*

Keywords: heterocyclic quinone, bis-monomethine, bis-trimethine, antimicrobial activity.

INTRODUCTION

New development methine cyanine dyes have attracted much attention in literature in order to prepare heterocyclic compounds for synthesis and study the behavior of different types of cyanine dyes [1-7]. In recent work our interest to the synthesis of heterocyclic quinone cyanine dyes which was extended to our previous work [8] due to that the involving heterocyclic quinone compounds represent an important class of biologically active molecules [9], displays various biological activities, including antifungal, antitumor [10-14], antimalarial, [11, 15], antineoplastic [16], anticoagulant [17] and herbicidal activity [18]. Structure–activity relationship studies on quinoid compounds indicated that number and position of nitrogen (N) atoms substituted in heterocyclic ring are considerably important factors to affect the biological activities [19]. Generally, increasing the number of substituent of nitrogen atoms in the ring enhance the activities. On the other hand, cyanine dyes are used as spectral sensitizers in photographic emulations [20], probes for the physical state and membrane potential of liposome and synthetic bi layers [21], as well as potential sensitizers for photodynamic therapy [22]. They were used as inhibitors of cell-growth and division [23], and as tumor-cell specific photosensitizes with reduced skin photoxicity and damage to normal tissue [24]. In recent years, they have been used in DNA minor groove binding studies [25] and in the interaction with nucleic acids [26-29]. Also, they were used as contrast agents in biomedical optical imaging [30]. The objective of this investigation is to synthesize, study the visible absorption spectra and antimicrobial activity of some selected new cyanine dyes. A correlation has been established between molecular structure and spectral behavior of the synthesized compounds.

MATERIALS AND METHODS

Synthesis of 4-Acetyl-3-methyl-1-phenyl-1*H*-5(4H) pyrazol-one (1), mono (1-methylpyridinium) mono(2-(3-methyl-5-oxo-1-phenyl-4,5-dihydro-1*H*-pyrazol-4-yl)-2-oxoethan-1-ide) monoiodide (2): Such compounds were prepared according to respective references [31, 32] and [8] respectively.

Synthesis of 3-Methyl-5-oxo-1-phenyl 4,5-dihydro-1*H*-pyrazole-4-carboxylic acid (3): Compound **(2)** (4.21g 0.01 mol) was dissolved in ethanol 30 mL and plates of sodium hydroxide was added. The reaction mixture was refluxed for 8h., filtered hot, concentrated and cooled. The solid obtained was triturated with cold, conc. HCl and the product was collected and recrystallized from ethanol to give the corresponding product **(3)** (Table 1), (Scheme1).

Synthesis of 4,4'- carbonyl bis(3-methyl-1-phenyl-1 *H*-pyrazol- 5(4*H*)-one)(5a), 2-methyl-4-(3-methyl-5-oxo-1-phenyl-4,5-dihydro-1*H*-pyrazole-4-carbonyl)oxazol-5(4*H*)-one(5b) and/or 5-(3-methyl-5-oxo-1-phenyl-4,5-dihydro-1*H*-pyrazole-4-carbonyl)imidazolidine-2,4-dione (**5c):** A mixture of compound 3 (0.01 mol) and compound [3-methyl-1-phenyl-1*H*-pyrazol—5(4*H*)-one **(4a)**, 2-methyl-oxazol-5(4*H*)--one **(4b)** and/or imidazolidine-2,4-dione (4c**)**] (0.01 mol) were dissolved in acetic acid in the case of **(4a), (4c)** and / or acetic anhydride for **(4b)**. The reaction mixture was refluxed for 5 h., filtered hot, concentrated and cooled. The precipitated solids were collected and crystallized from aqueous ethanol to give **(5a-c)** (Table 1), (Scheme 1)

Synthesis of the intermediate compounds (6a-c): To compounds **(5a-c)** (0.01 mol) dissolved in ethanol 30 mL and catalytic amount of piperidine was added. The reaction mixture was refluxed for 5h., filtered hot, concentrated, cooled and acidified with acetic acid. The precipitated solids were collected and crystallized from aqueous ethanol to give **(6a-c)** (Table 1), (Scheme1).

Synthesis of 3,5-Dimethyl-1,7-diphenylpyrazolo[4,3-*f*]indazole-4,8(1*H*,7*H*)-dione (7a), 3,6-dimethyl-1-phenyl- 1*H*-oxazolo4,5-*f'*]indazole-4,8-dione (7b) and 3-methyl-1-phenylimidazo [4,5-*f*]indazole-4,6,8(1*H*,5*H*,7*H*)-trione (7c): Equimolar ratios of compounds **(6a-c)** (0.01 mol) and formaldehyde (0.01 mol) were dissolved in ethanol 20 ml and catalytic amount of piperidine was added. The reaction mixture

was refluxed for 8 h., filtered hot, concentrated and cooled. The precipitated product was collected and crystallized from ethanol to give **(7a-c)** (Table-1), (Scheme 1).

Synthesis of 2,6-diethyl-3,5-Dimethyl-4,8-dioxo-1,7-diphenyl-1,4,7,8-tetrahydropyrazolo[4,3-*f*] indazole-2,6-diium iodide (8a) and/or 2,6-diethyl-3,6-Dimethyl-4,8-dioxo-1-phenyl-4,8-dihydro-1*H*-oxazolo[4,5-*f*]indazole-2,5-diium iodide (8b): A mixture of compounds (7a),(7b) (0.01 mol) and ethyl iodide (0.02 mol) were refluxed in ethanol for 2 h., on a water bath, filtered hot, concentrated, cooled. The precipitated solids were collected after dilution with water and crystallized from ethanol to give the corresponding compounds **(8a)** and **(8b)** (Table 1), (Scheme 2).

Synthesis of 2-ethyl-3-methyl-4,6,8-trioxo- 1-phenyl-1,4,5,6,7,8-hexahydroimidazo[4,5-*f*]indazol--2-ium iodide (9): A mixture of compound **(7c)** (0.01 mol) and ethyl iodide (0.01 mol) were refluxed in ethanol for 2 h., on a water bath, filtered hot, concentrated, cooled. The precipitated solids were collected after dilution with water and crystallized from ethanol to give the corresponding compound **(9)** (Table 1)**, (**Scheme 2).

Synthesis of 4,4'-(2,6-diethyl-4,8-dioxo-1,7-diphenyl-1,2,6,7-tetrahydropyrazolo[4,3-*f*]indazole-3,5(4*H*,8*H*)-diylidene)bis(methan-1-yl-1ylidene)bis(1-ethylpyridinium)iodide cyanine dye(10a), 4,4'-(2,6-diethyl-4,8-dioxo-1,7-diphenyl-1,2,6,7-tetrahydropyrazolo[4,3-*f*]indazole-3,5(4*H*,8*H*)-diylidene) bis(methan-1-yl-1-ylidene)bis(1-ethylquinolinium)iodide cyanine dye (10b), 1,1'-(2,6-diethyl-4,8-dioxo-1,7-diphenyl-1,2,6,7-tetrahydropyrazolo[4,3-*f*]indazole-3,5(4*H*,8*H*)-diylidene)bis (methan-1-yl-1ylidene)bis(2-ethylisoquinolinium)iodide cyanine dye (10c)and 4,4' –(2,5-diethyl-4,8-dioxo-1-phenyl-1*H*-oxazolo[4,5-*f*]indazole-3,6(2*H*,4*H*,5*H*,8*H*)-diylidene)bis(methan-1-yl-1-ylidene)bis(1-ethylquinolinium)iodide cyanine dye (10d): Equimolar ratios of compounds **(8a,8b)** (0.01 mol) and N-methyl heterocyclic quaternary salts [N-methyl (pyridinium, quinolinium and/or isoquinolinium) iodide] (0.02 mol) were dissolved in ethanol 30 mL and catalytic amount of piperidine was added. The reaction mixture was refluxed for 8 h., filtered hot, concentrated and cooled. The solid was triturated with cold dilute acetic acid and the solid product was collected and recrystallized from ethanol to give the titled products **(10a-d)** (Table 1), (Scheme 2).

Synthesis of ethoxyethene,3-(2,2-diethyl)-5-ethoxy-2,6-diethyl-4,8-dioxo-1,7-diphenyl-1,4,7,8-tetra hydropyrazolo[4,3-f]indazole-2,6-diium diiodide salt(11a) and ethoxyethene,3-(2,2-diethyl)-6-ethoxy-2,5-diethyl-4,8-dioxo-1-phenyl-4,8-dihydro-1*H*-oxazolo[4,5-*f*]indazole-2,5-diium diiodide salt (11b): To a mixture of compounds **(8a,8b)** (0.01 mol) and triethylorthoformate (0.01 mol) dissolved in ethanol 30 mL and catalytic amount of piperidine was added. The reaction mixture was refluxed for 8h., filtered hot, concentrated and cooled. The solid was triturated with cold dilute acetic acid and the solid product was collected and recrystallized from ethanol to give the titled products **(11a,11b)** (Table 1), (Scheme 3).

Synthesis of 2,2'-(1*E*,1'*E*,3*E*,3'*Z*)-3,3'-(2,6-diethyl-4,8-dioxo-1,7-diphenyl-1,2,6,7-tetrahydropyrazolo [4,3-*f*]indazole-3,5(4*H*,8*H*)-diylidene)bis(prop-1-ene-1-yl-3-ylidene)bis(1-methylpyridinium)iodidecay nine dye(12a), 2,2'-(1*E*,1'*E*,3*E*,3'*Z*)-3,3'-(2,6-diethyl-4,8-dioxo-1,7-diphenyl-1,2,6,7-tetrahydro pyra zolo[4,3-*f*]indazole-3,5(4*H*,8*H*)-diylidene) bis (prop-1-ene-1-yl-3-ylidene)bis(1-methyl quinolinium) iodide cyanine dye (12b), 4,4'-(1*E*,1'*E*,3*E*,3'*Z*)-3,3'-(2,6-diethyl-4,8-dioxo-1,7-diphenyl-1,2,6,7-tetra hydro pyrazolo[4,3-*f*]indazole-3,5(4*H*,8*H*)-diylidene)bis(prop-1-ene-1-yl-3-ylidene)bis(1-methyl pyridi nium) iodide cyanine dye (12c)and 2-((*E*)-2-((*E*)-2,5-diethyl-3-((*E*)-3-(1-methylquinolinium-2-yl)ally lidene)-4,8-dioxo-1-phenyl-2,3,4,5,6,8-hexahydro-1*H*-oxazolo[4,5-*f*]indazol-6-yl)vinyl)-1-methylquino linium iodide cyanine dye (12d): To a mixture of compounds **(11a,11b)** (0.01 mol) and 2(4)-methyl quaternary salts [N-methyl α (γ)-picolinium and quinaldinium] iodide (0.02 mol) dissolved in ethanol 20 mL and catalytic amount of piperidine was added. The reaction mixture was refluxed for 12 h., filtered hot, concentrated and cooled. The precipitated product was collected and crystallized from ethanol to give **(12a-d)** (Table 1), (Scheme 3).

Synthesis of 2-(3-methyl-1-phenylimidazo [4,5-*f*]indazole-4, 8(1*H*, 5*H*, 7*H*)-dione (methan-1-yl-1ylidene)(1-methylpyridinium)iodide cyanine dye (13a), 2-(3-methyl-1-phenylimidazo [4,5-*f*] indazole-4, 8(1*H*,5*H*,7*H*)-dione (methan-1-yl-1ylidene)(1-methylquinolinium)iodide cyanine dye (13b) and 4-(3-methyl-1-phenylimidazo [4,5-*f*]indazole-4, 8(1*H*,5*H*,7*H*)-dione (methan-1-yl-1ylidene) (1-methylpyridinium)iodide cyanine dye (13c): To a mixture of compound **(7c)** (0.01 mol) and 2(4)-methyl quaternary salts [N-methyl α (γ)-picolinium and/or quinaldinium] iodide (0.01 mol) dissolved in ethanol 20 ml and catalytic amount of piperidine was added. The reaction mixture was refluxed for 8 h., filtered hot, concentrated and cooled. The solid was triturated with cold dilute acetic acid and the solid product was collected and recrystallized from ethanol to give the titled products **(13a-c) (**Table 1), (Scheme 4).

Synthesis of 1-ethyl-4-((2-ethyl-4,6,8-trioxo-1-Phenyl-1,2,6,7-tetrahydroimidazo[4,5-*f*]indazol-3(4*H*, 5*H*, 8*H*)-ylidene)methyl)pyridinium iodide cyanine dye (14a) 1-ethyl-4-((2-ethyl-4,6,8-trioxo-1-Phenyl-1,2,6,7-tetrahydroimidazo[4,5-f]indazol-3(4*H*, 5*H*, 8*H*)-ylidene)methyl) qunolnium iodide cyanine dye (14b) and 2-ethyl-1-((2-ethyl-4,6,8-trioxo-1-Phenyl-1,2,6,7-tetrahydroimidazo[4,5-*f*]indazol-3(4*H*, 5*H*, 8*H*)-ylidene)methyl)pyridinium iodide cyanine dye (14c) : Equimolar ratios of compound **(9)** (0.01 mol) and N-methyl heterocyclic quaternary salts [N- ethyl (pyridin-4-ium, quinolin-4-ium and/or isoquinolin-1-ium) iodide] (0.01 mol) dissolved in ethanol 20 mL and catalytic amount of piperidine was added. The reaction mixture was refluxed for 8 h filtered hot, concentrated and cooled. The solid was triturated with cold, dilute acetic acid and the solid product, was collected and recrystallized from ethanol to give the corresponding products **(14a-c)** (Table 1), (Scheme 4).

Synthesis of 1-ethyl-4-(((*E*)-2-ethyl-6((1-methylpyridinium-4-yl)methylene)-4,8-dioxo-1-phenyl-1,2, 6,7-tetrahydroimidazo[4,5-*f*]indazol-3(4*H*, 5*H*, 8*H*)-ylidene)methyl)pyridinium iodide cyanine dye (15):To a mixture of compound **(14a)** (0.01 mol) and 4-methyl heterocyclic quaternary salt (γ-picolinium methyl iodide) (0.01 mol) were dissolved in ethanol 25 mL and catalytic amount of piperidine was added. The reaction mixture was refluxed for 8 h., filtered hot, concentrated and cooled. The solid was triturated with cold, dilute acetic acid and the solid product was collected and recrystallized from ethanol to give the titled product **(15)**, (Table 1), (Scheme 4).

Characterization of synthesized Compounds: Melting points (M P.) were measured using melting point apparatus & are uncorrected. Elemental analyses were carried out at the Micro analytical center (Cairo-University). The IR (ν^{KBr}) spectra were determined with Perkin Elmer Infrared 127ß spectrophotometer (Cairo-University). ^{1}H NMR spectra were recorded with a Bruker AMX-250 SpBruker AMX-500 spectrometer, with TMS as an internal standard. Mass spectra were recorded on an HpMs 6988 spectrometer (Assuit University). The electronic absorption spectra were recorded within the wavelength range (350-700) on 6405 UV/Visible recording Spectrophotometer, Faculty of Science, Aswan University, Aswan.

Table 1. Characterization data of the synthesized compounds 3, (3), (5a-c), (6a-c), (7a-c), (8a), (8b), (9), (10a-d), (11a),(11b), (12a-d), (13a-c),(14a-c) and (15)

Compound No.	Mol. Formula Mol. Wt.	% CHN analysis Calculated [a] (%) (Found (%))			Yield (%)	M. P. [c] (°C): .
		C	H	N		
3	$C_{11}H_{10}N_2O_3$ 218	60.55 (60.70)	4.59 (4.75)	12.84 (12.79)	70	158-160
5a	$C_{21}H_{18}N_4O_3$ 374	67.38 (67.56)	4.81(4.60)	14.97 (14.78)	62	138-140
5b	$C_{15}H_{13}N_3O_4$ 299	60.20 (60.59)	4.35 (4.59)	14.05 (13.87)	67	135-137
5c	$C_{14}H_{12}N_4O_4$ 300	56.00(56.24)	4.00 (3.79)	18.67(18.49)	60	144-146
6a	$C_{21}H_{16}N_4O_2$	70.79 (70.93)	4.49(4.76)	15.73 (15.92)	65	174-176

	356					
6b	$C_{15}H_{11}N_3O_3$ 281	64.06 (64.34)	3.92(3.76)	14.95 (14.78)	61	198-200
6c	$C_{14}H_{10}N_4O_3$ 282	59.57 (59.78)	3.55 (3.43)	19.86 (19.78)	54	168-170
7a	$C_{22}H_{16}N_4O_2$ 368	71.74 (71.95)	4.35 (4.20)	15.22(15.04)	65	185-187
7b	$C_{16}H_{11}N_3O_3$ 293	65.53(65.89)	3.75 (3.65)	14.33(14.29)	71	160-162
7c	$C_{15}H_{10}N_4O_3$ 294	61.22 (61.42)	3.25(3.40)	19.05 (18.87)	54	210-212
8a	$C_{26}H_{26}N_4O_2I_2$ 680	45.88 (45.63)	3.82 (3.58)	8.24 (8.44)	75	193-195
8b	$C_{20}H_{21}N_3O_3I_2$ 605	39.67 (39.80)	3.47 (3.32)	6.94 (6.79)	71	198-200
9	$C_{17}H_{15}N_4O_3I$ 450	45.33 (45.49)	3.33 (3.22)	12.44 (12.26)	69	230-232
10a	$C_{40}H_{40}N_6O_2I_2$ 890	53.93 (53.78)	4.49(4.35)	9.44(9.25)	74	170-173
10b	$C_{48}H_{44}N_6O_2I_2$ 990	58.18 (58.30)	4.44(4.53)	8.49(8.66)	69	165-169
10c	$C_{48}H_{40}N_6O_2I_2$ 990	58.18(57.90)	4.44(4.59)	8.49 (8.72)	67	180-183
10d	$C_{42}H_{39}N_5O_3\ I_2$ 915	55.08(55.18)	4.26(4.40)	7.65 (7.75)	59	170-173
11a	$C_{36}H_{46}N_4O_6I_2$ 884	48.87 (48.65)	5.20 (5.41)	6.35 (6.22)	69	150-152
11b	$C_{30}H_{41}N_3O_7I_2$ 809	44.50 (44.43)	5.07(4.90)	5.19 (5.34)	77	160-162
12a	$C_{42}H_{40}N_6O_2I_2$ 914	55.14 (55.22)	4.38 (4.61)	9.19 (9.28)	66	180-182
12b	$C_{50}H_{44}N_6O_2I_2$ 1014	59.17 (59.33)	4.34 (4.45)	8.28 (8.42)	77	200-202
12c	$C_{42}H_{40}N_6O_2I_2$ 914	55.14 (55.34)	4.38 (4.55)	9.19 (9.33)	68	180-182
12d	$C_{44}H_{39}N_5O_3I_2$ 939	56.23 (56.42)	4.15 (4.20)	7.46 (7.53)	72	160-162
13a	$C_{22}H_{18}N_5O_2I$ 511	51.66 (51.42)	3.52(3.71)	13.70 (13.83)	76	198-200
13b	$C_{26}H_{20}N_5O_2I$ 561	55.62(55.42)	3.57(3.70)	12.48 (12.29)	68	180-182
13c	$C_{22}H_{18}N_5O_2I$ 511	51.66(51.80)	3.52 (3.44)	13.70(13.87)	71	190-192
14a	$C_{24}H_{22}N_5O_3I$ 555	51.89(51.63)	3.96(4.11)	12.61(12.54)	74	145-147
14b	$C_{28}H_{24}N_5O_3I$ 605	55.54 (55.34)	3.97 (3.70)	11.57 (11.61)	69	152-154
14c	$C_{28}H_{24}N_5O_3I$ 605	55.54 (55.66)	3.97(3.87)	11.57 (11.70)	67	133-135
15	$C_{31}H_{30}N_6O_2I_2$ 772	48.19(48.37)	3.89(3.66)	10.88 (10.76)	78	155-158

Antibiotic susceptibility: The effects of the synthesized ten compounds were tested against some microorganisms. Tested microorganisms were obtained from the Department of Botany culture collection, Faculty of Science, Aswan University, Aswan, Egypt). Each of the ten compounds was dissolved in ethyl alcohol (96%). Sterile discs of 6 mm diameter were prepared from Whatman filter paper. Each of the ten

compounds was carried on the discs in a concentration of 20 microgram/disc and was dried. The susceptibility of the organisms to the ten compounds was determined by distributing the discs on surface-seeded nutrient agar medium according to [33]. Plates were incubated overnight at 37ºC. The susceptibility which appears as an inhibition zone around the disc was measured and recorded in comparison to standard antibacterial and antihaloarchaeal inhibitors and respectively. The following microorganisms were used.

The gram-positive bacteria are *Bacillus cereus, Staphylococcus aureus, S. citrus* and an unidentified isolate, and gram-negative bacteria is *Pseudomonas aeuroginosa*, *Pseudomonas putida, Escherichia coli*, *Serratia sp*. and from *halophilic archaea* which are microorganisms related to *eucaryota* more than they are related to *eubacteria* and they were formerly called *halobacteria* [34, 35], *Halobiforma haloterrestris.*

RESULTS AND DISCUSSION

Dye synthesis: Thermal basic hydrolysis of the key intermediate compound 3-methyl-1-phenyl-pyrazolin-5-one-ketomethyllene-4(1)-pyridinium iodide salt **(2)** using aqueous ethanolic solution of sodium hydroxide gave the corresponding sodium salt of 3-methyl-1-phenylpyrazolin-5-one 4-sodium carboxylate which on triturating with conc. HCl, the free 3-methyl-1-phenylpyrazolin-5-one-4-carboxylic acid **(3)** is formed.

The hydrolysis process may be suggested to proceed as β bond cleavage of 3-methyl-1-phenyl-pyrazolin-5-one-ketomethyllene-4(1)-pyridinium iodide salt **(2)** following direct approach of nucleophilic OH^- (electrophilic H^+) reagents to the stabilized fractional carbonyl carbonium deficiency and methylene carbanion to form the corresponding 3-methyl-1-phenyl pyrazolin-5-one-4-sodium carboxylate and 1-methyl-pyridin-1-ium iodide salt. Such mechanism was confirmed by the identification of the latter reported heterocyclic quaternary iodide salt which gives iodine vapor on warming with conc. H_2SO_4. The EI-mass spectrum exhibited at *m/z* =216 [M-2] a molecular ion $(M)^+$ however auxiliary peak was found at m/z = 200 [M-H_2O-CH_3], base peak at *m/z* = 174 [M-CO_2] [36].

Reaction of compound **(3)** with equimolar ratios of [3-methyl-1-phenyl-1*H*-pyrazol—5(4*H*)-one 4a, 2-methyl-oxazol-5(4*H*)--one **(4b)** and/or imidazolidine-2,4-dione **(4c)** using acetic acid as a solvent in the case of(4a, 4c)andacetic anhydride in the case of **(4b)** achieved the corresponding biheterocyclic carbonyl compounds **5A (a-c)** namely as 4,4' – carbonyl bis (3-methyl-1-phenyl-1 *H* –pyrazol- 5(4 *H*)-one) **(5a)**, 2-methyl-4-(3-methyl-5-oxo-1-phenyl-4,5-dihydro-1*H*-pyrazole-4-carbonyl)oxazol-5(4*H*)-one **(5b)** and/or 5-(3-methyl-5-oxo-1-phenyl-4,5-dihydro-1*H*-pyrazole-4-carbonyl)imidazolidine-2,4-dione **(5c)**. The latter compounds **5A (a-c)** undergo ring closure via the formation of their corresponding enol form compounds 5B (a-c) under basic catalyst to afford the corresponding intermediate compounds **(6a-c)**. The EIMS of compound **(6a)** afforded the molecular ion peak at m/z 358$(M+2)^+$, corresponding to the molecular formula $C_{21}H_{16}N_4O_2$ and a base peak at 330 (100%), corresponding to $(M+2\text{-}CO)^+$.

Such compounds **(6a-c)** when reacted in equimolar ratios with formaldehyde under piperidine catalysis achieved the corresponding bis heterocyclic quinone system **(7a-c)**, (Scheme 1**)**. The EIMS of compound **(7a)** exhibited the molecular ion peak at m/z 370 $(M+2)^+$ (5%)corresponding to the molecular formula $C_{22}H_{16}N_4O_2$ followed by the consecutive loss of [CO] as indicated by peaks of m/z 342 and 314.

The formation of **(7a-c)** was suggested to proceed via acid catalyzed of compound 3-methyl-1-phenylpyrazol-5-one-4-carboxylic acid **(3)** increasing the electrophilic character of carbonyl –carbonium deficiency and its susceptibility to be attack by nucleophilic 4-methylene carbanion resulted from hydrogen ion abstract **(2)** to form the suggested bis heterocyclic tri-one as key intermediate compounds **(5A)**. The latter intermediate compounds were enolated and dehydrated under piperidine catalysis to give the corresponding intermediate compounds **(6a-c)** which on condensation with formaldehyde under basic condition achieved the desired bis heterocyclic benzdione.

Selective quaternization of compounds 3,5-Dimethyl-1,7-diphenylpyrazolo[4,3-*f*]indazole-4,8(1*H*,7*H*)-dione **(7a)**, 3,6-dimethyl-1-phenyl- 1*H*- oxazolo[4,5-*f*'] indazole-4,8-dione **(7b)** and 3-methyl-1-phenyl imidazo [4,5-*f*]indazole-4,6,8(1*H*,5*H*,7*H*)-trione **(7c)** using ethyl iodide in ethanol afforded the corresponding compounds 2,6-diethyl-3,5-Dimethyl-4,8-dioxo-1,7-diphenyl-1,4,7,8-tetrahydropyra zolo [4,3-*f*]indazole-2,6-diium iodide **(8a)** and/or 2,6-diethyl-3,6-Dimethyl-4,8-dioxo-1-phenyl-4,8-di hydro-1*H*-oxazolo[4,5-*f*]indazole-2,5-diium iodide **(8b)** and /or 2-ethyl-3-methyl-4,6,8-trioxo- 1-phenyl-1,4, 5,6,7,8-hexahydroimidazo[4,5-*f*]indazol-2-ium iodide **(9)** respectively. Reaction of equimolar ratios of compounds **(8a)** and **(8b)** with N-ethyl heterocyclic quaternary salts [N-ethyl (pyridin-4-ium, quinolin-4-ium and/or isoquinolin-1-ium) iodide] under ethanol/piperidine condition afforded the corresponding compounds 4,4' –(2,6-diethyl-4,8-dioxo-1,7-diphenyl-1,2,6,7-tetrahydropyrazolo[4,3-*f*]indazole-3,5(4*H*, 8*H*)-diylidene) bis (methan-1-yl-1ylidene)bis(1-ethylpyridinium)iodide cyanine dye **(10a),** 4,4'-(2,6-diethyl-4,8-dioxo-1,7-diphenyl-1,2,6,7-tetrahydropyrazolo[4,3-*f*]indazole-3,5(4*H*,8*H*)-diylidene)bis (meth an-1-yl-1-ylidene)bis(1-ethylquinolinium)iodide cyanine dye **(10b)**, 1,1'–(2,6-diethyl-4,8-dioxo-1,7-diphenyl-1,2,6,7-tetrahydropyrazolo[4,3-*f*]indazole-3,5 (4*H*,8*H*)-diylidene)bis (methan-1-yl-1ylidene) bis (2-ethylisoquinolinium)iodide cyanine dye **(10c)** and 4,4' –(2,5-diethyl-4,8-dioxo-1-phenyl-1*H*-oxazolo [4,5-*f*]indazole-3,6(2*H*,4*H*,5*H*,8*H*)-diylidene)bis(methan-1-yl-1-ylidene)bis(1-ethylquinolinum)iodide cyan ine dye **(10d)** respectively, (Scheme 2).

Reaction of equimolar ratios of compounds **(8a)** and **(8b)** with bimolar ratios of triethyl ortho formate in ethanol and few drops of piperidine gave the intermediate compounds ethoxyethene,3-(2,2-diethyl)-5-ethoxy-2,6-diethyl-4,8-dioxo-1,7-diphenyl-1,4,7,8-tetrahydropyrazolo[4,3-f]indazole-2,6-diium diiodide salt **(11a)** and ethoxyethene,3-(2,2-diethyl)-6-ethoxy-2,5-diethyl-4,8-dioxo-1-phenyl-4, 8-dihydro-1*H*-oxazolo[4,5-*f*]indazole-2,5-diium diiodide salt **(11b)**. Reaction of the latter Compounds **(11a)** and **(11b)**in equimolar ratios with 2(4)-methyl heterocyclic quaternary salts [N-methyl (α (γ)-picolinium and / or quinaldinium) iodide] in bimolar ratios afforded the corresponding compounds 2,2'-(1*E*,1'*E*,3*E*,3'*Z*)-3,3'-(2,6-diethyl-4,8-dioxo-1,7-diphenyl-1,2,6,7-tetrahydropyrazolo[4,3-*f*]indazole-3,5(4*H*,8*H*)-diylidene) bis (prop-1-ene-1-yl-3-ylidene)bis(1-methylpyridinium)iodide cyanine dye **(12a)**, 2,2'-(1*E*,1'*E*,3*E*,3'*Z*)-3,3'-(2,6-diethyl-4,8-dioxo-1,7-diphenyl-1,2,6,7-tetrahydropyrazolo [4,3-*f*]indazole-3,5(4*H*,8*H*)-diylidene)bis (prop-1-ene-1-yl-3-ylidene)bis(1-methylquinolinium)iodide cyanine dye **(12b)**, 4,4'-(1*E*,1'*E*,3*E*,3'*Z*)-3,3'-(2,6-diethyl-4,8-dioxo-1,7-diphenyl-1,2,6,7-tetrahydropyrazolo [4,3-*f*]indazole-3,5(4*H*,8*H*)-diylidene)bis (prop-1-ene-1-yl-3-ylidene) bis(1-methylpyridinium)iodide cyanine dye **(12c)** and 2-((*E*)-2-((*E*)-2,5-di ethyl-3-((*E*)-3-(1-methylquinolinium-2-yl)allylidene)-4,8-dioxo-1-phenyl-2,3,4,5,6,8-hexahydro-1*H*-oxa zolo [4,5-*f*]indazol-6-yl)vinyl)-1-methylquinolinium iodide cyanine dye **(12d)**, respectively, (Scheme 3).

On the other hand, reaction of equimolar ratios of dye **(7c)** with 2(4)-methyl heterocyclic quaternary salts [N-methyl (α (γ)-picolinium and/or quinaldinium) iodide] under piperidine/ethanol catalysis afforded 2-(3-methyl-1-phenylimidazo [4,5-*f*]indazole-4, 8(1*H*, 5*H*, 7*H*)-dione (methan-1-yl-1ylidene)(1-methyl pyridi nium)iodide cyanine dye **(13a)**, 2-(3-methyl-1-phenylimidazo [4,5-*f*]indazole-4, 8(1*H*,5*H*,7*H*)-dione (methan-1-yl-1ylidene)(1-methylquinolinium)iodide cyanine dye **(13b)**, and 4-(3-methyl-1-phenylimidazo [4,5-*f*]indazole-4, 8(1*H*,5*H*,7*H*)-dione (methan-1-yl-1ylidene)(1-methylpyridinium)iodide cyanine dye **(13c)**. Also, compound **(9)** undergo a reaction with N-ethyl heterocyclic quaternary salts [N-ethyl (pyridin-4-ium, quinolin-4-ium and/or isoquinolin-1-ium) iodide] in equimolar ratios and in presence of ethanol under piperidine catalysis afforded the corresponding 1-ethyl-4-((2-ethyl-4,6,8-trioxo-1-Phenyl-1,2,6,7-tetrahydroimidazo[4,5-*f*]indazol-3(4*H*, 5*H*, 8*H*)-ylidene)methyl)pyridinium iodide cyanine dye **(14a)** 1-ethyl-4-((2-ethyl-4,6,8-trioxo-1-Phenyl-1,2,6,7-tetrahydroimidazo[4,5-f]indazol-3(4*H*, 5*H*, 8*H*)-ylidene) methyl) qunolnium iodide cyanine dye **(14b)** and 2-ethyl-1-((2-ethyl-4,6,8-trioxo-1-Phenyl-1,2,6,7-tetrahydroimidazo[4,5-*f*] indazol-3(4*H*, 5*H*, 8*H*)-ylidene)methyl)pyridinium iodide cyanine dye **(14c)**, (Scheme 4). Further reaction of equimolar ratios of compound **(14a)** and N-methyl (γ)-picolinium iodide under piperidine / ethanol catalysis afforded the corresponding compound 1-ethyl-4-(((*E*)-2-ethyl-6((1-methylpyridinium-4-yl)methylene)-4,8-dioxo-1-phenyl-1,2,6,7-tetrahydroimidazo[4,5-*f*]indazol-3(4*H*, 5*H*,

8*H*)-ylidene) methyl)pyridinium iodide cyanine dye **(15)**, (Scheme 4).The spectral characteristics of the synthesized compounds in this study are as follows.

Analytical and Spectral Data of synthesized compounds

3-Methyl-5-oxo-1-phenyl 4,5-dihydro-1*H*-pyrazole-4-carboxylic acid (3): Yield: 70%; m.p.158-160^{o}C; Anal. calcd. for $C_{11}H_{10}N_2O_3$: C, 60.55; H, 4.59; N, 12.84 %. Found: C, 60.70, H, 4.75, N, 12.79%; IR (cm^{-1}): 1495 (C=N), 1700 (C=O), 3445 (OH of carboxyl group); ^{1}H-NMR (500 MHz, $CDCl_3$, δ/ ppm): 2.12 (s, 1H, pyrazol), 1.18 (s, 3H, CH_3), 7.35-7.90 (m, 5H, Ar-H); MS (*m/z*): 218 (M-2).

4,4' – carbonyl bis(3-methyl-1-phenyl-1 *H* –pyrazol- 5(4*H*)-one) (5a): Yield: 62%; m.p. 138-140^{o}C; Anal. calcd. for $C_{21}H_{18}N_4O_3$: C, 67.38; H, 4.81; N, 14.97 %. Found: C, 67.56, H, 4.60, N, 14.78%; IR (cm^{-1}): 1487 (cyclic C=N), 1720 (C=O); ^{1}H-NMR (500 MHz, $CDCl_3$, *δ*/ ppm): 0.9 (s, 6H, $2CH_3$), 3.3 (s, 2H, CH of two pyrazol rings), 7.00-7.64 (m,10H Ar).

2-methyl-4-(3-methyl-5-oxo-1-phenyl-4,5-dihydro-1*H*-pyrazole-4-carbonyl) oxazol-5(4*H*)-one (5b): Yield: 67%; m.p. 135-137^{o}C; Anal. calcd. for $C_{15}H_{13}N_3O_4$: C, 60.20; H, 4.35; N, 14.05 %. Found: C, 60.59, H, 4.59, N, 13.87%; ^{1}H-NMR (500 MHz, $CDCl_3$, δ/ ppm): 0.9 (s, 6H, $2CH_3$),3.3 (s, 1H, CH of pyrazol ring), 3.2 (s,1H, CH of oxazol ring), 7.00 -7.64 (m, 5H Ar).

5-(3-methyl-5-oxo-1-phenyl-4,5-dihydro-1*H*-pyrazole-4-carbonyl)imidazolidine-2,4-dione(5c): Yield: 60%; m.p. 144-146 ^{o}C; Anal. calcd. for $C_{14}H_{12}N_4O_4$: C, 56.00; H, 4.00; N, 18.67 %. Found: C, 56.24, H, 3.79, N, 18.49%; IR (cm^{-1}): 1487 (cyclic C=N), 1720-1690 (C=O); ^{1}H-NMR (500 MHz, $CDCl_3$, *δ*/ ppm): 0.9 (s, 3H, CH_3), 3.3 (s, 1H, CH of pyrazol ring), 4.43 (s, 1H, CH of imidazol ring), 2.0 (s, 1H, NH), 8.0 (s, 1H, NH between two carbonyl), 7.00 -7.64 (m, 5H Ar).

The intermediate compound (6a): Yield: 65%; m.p. 174-176^{o}C; Anal. calcd. for $C_{21}H_{16}N_4O_2$: C, 70.79; H, 4.49; N, 15.73 %. Found: C, 70.93, H, 4.76, N, 15.92%; IR (cm-1): 1249-1165 (C-O-C cyclic), 1487 (cyclic C=N), 1711 (C=O); ^{1}H-NMR (500 MHz, $CDCl_3$, *δ*/ ppm): 2.79 (s, 6H, $2CH_3$), 7.02-7.3 (m, 10H Ar); MS (*m/z*): 358(M+2) $^{+}$.

The intermediate compound (6b): Yield: 61%; m.p. 198-200^{o}C; Anal. calcd. for $C_{15}H_{11}N_3O_3$: C, 64.06; H, 3.92; N, 14.95 %. Found: C, 64.34, H, 3.76, N, 14.78%; IR (cm-1): 1249-1165 (C-O-C cyclic), 1487 (cyclic C=N), 1720-1690 (C=O), 3400-3100 NH); ^{1}H-NMR (500 MHz, $CDCl_3$, δ/ ppm): 3.20 (s, 3H, CH_3), 2.04 (s, 2H, 2NH), 7.02-7.3 (m, 5H Ar).

The intermediate compound (6c): Yield: 61%; m.p. 168-170^{o}C; Anal. calcd. for $C_{14}H_{10}N_4O_3$: C, 59.57; H, 3.55; N, 19.86 %. Found: C, 59.78, H, 3.43, N, 19.78%.

3,5-Dimethyl-1,7-diphenylpyrazolo[4,3-*f*]indazole-4,8(1*H*,7*H*)-dione (7a): Yield: 65%; m.p. 185-187^{o}C; Anal. calcd. for $C_{22}H_{16}N_4O_2$: C, 71.74; H, 4.35; N, 15.22%. Found: C, 71.95, H, 4.20, N, 15.04%; IR (cm-1): 1487 (cyclic C=N), 1650 (quinone ring); ^{1}H-NMR (500 MHz, $CDCl_3$, *δ*/ ppm): 2.79 (s, 6H, $2CH_3$), 7.3-7.89 (m, 10H Ar); MS (m/z): 370 (M+2) $^{+}$.

3,6-dimethyl-1-phenyl- 1*H*- oxazolo[4,5-*f*'] indazole-4,8-dione (7b): Yield: 71%; m.p. 160-162^{o}C; Anal. calcd. for $C_{16}H_{11}N_3O_3$: C, 65.53; H, 3.75; N, 14.33%. Found: C, 65.89, H, 3.65, N, 14.29.

3-methyl-1-phenylimidazo [4,5-*f*]indazole-4,6,8(1*H*,5*H*,7*H*)-trione (7c): Yield: 54%; m.p. 210-212^{o}C; Anal. calcd. for $C_{15}H_{10}N_4O_3$: C, 61.22; H, 3.25; N, 18.67 %. Found: C, 61.42, H, 3.40, N, 18.87%; IR (cm^{-1}): 1487 (cyclic C=N), 1720-1690 (C=O), 3400-3100 (NH); ^{1}H-NMR (500 MHz, $CDCl_3$, δ/ ppm): 3.22 (s, 3H, CH_3), 2.00 (s, 2H, 2NH), 7.03-7.95 (m, 5H Ar).

2,6-diethyl-3,5-Dimethyl-4,8-dioxo-1,7-diphenyl-1,4,7,8-tetrahydropyrazolo[4,3-*f*]indazole-2,6-diium iodide (8a): Yield: 75%; m.p. 193-195^{o}C; Anal. calcd. for $C_{26}H_{26}N_4O_2I_2$: C, 45.88; H, 3.82; N, 8.24 %. Found: C, 45.63, H, 3.58, N, 8.44%; IR (cm^{-1}): 1487 (cyclic C=N), 1650 (quinone ring), 2923-2800 (N-$C_2H_5$of heterocyclic); ^{1}H-NMR (500 MHz, $CDCl_3$, δ/ ppm): 2.79 (s, 6H, $2CH_3$), 1.00 (t, 6H, $2CH_3$ of N-ethyl), 2.69 (q, 4H, $2CH_2$ of N-ethyl), 6.66-8.81 (m, 10H, Ar).

2,6-diethyl-3,6-Dimethyl-4,8-dioxo-1-phenyl-4,8-dihydro-1*H*-oxazolo[4,5-*f*]indazole-2,5-diium iodide (8b): Yield: 71%; m.p. 198-200^{o}C; Anal. calcd. for $C_{20}H_{21}N_3O_3I_2$: C, 39.67; H, 3.47; N, 6.94 %. Found: C, 39.80, H, 3.32, N, 6.79%.

4,6,8-trioxo-1-phenyl-1,4,5,6,7,8-hexahydroimidazo[4,5-*f*]indazol-2-ium iodide (9): Yield: 69%; m.p. 230-232^{o}C; Anal. calcd. for $C_{17}H_{15}N_4O_3I$: C, 45.33; H, 3.33; N, 12.44 %. Found: C, 45.49, H, 3.22, N, 12.26%; IR (cm^{-1}): 1498 (cyclic C=N), 2923-2850 2880 (N-C_2H_5 of heterocyclic), 1700-1685 (C=O), 3400-3100 (NH); ^{1}H-NMR (500 MHz, $CDCl_3$, δ/ ppm): 1.20 (s, 3H, CH_3), 1.00 (t, 3H, CH_3 of ethyl iodide), 2.59(q, 2H, CH_2 of ethyl iodide), 6.00 (s, 2H, 2NH), 6.66 -7.18 (m, 5H, Ar).

4,4'–(2,6-diethyl-4,8-dioxo-1,7-diphenyl-1,2,6,7-tetrahydropyrazolo[4,3-*f*]indazole-3,5(4*H*,8*H*)-diylI dene)bis(methan-1-yl-1ylidene)bis(1-ethylpyridinium)iodide cyanine dye (10a): Yield: 74%; m.p. 70-173^{o}C; Anal. calcd. for $C_{40}H_{40}N_6O_2I_2$: C, 53.93; H, 4.49; N, 9.44%. Found: C, 53.78, H, 4.35, N, 9.25%; IR (cm^{-1}): 1482 (cyclic C=N), 1640 (quinone ring), 2920-2880 (N-C_2H_5); ^{1}H-NMR (500 MHz, $CDCl_3$, δ/ ppm): 5.20 (s, 2H, 2CH), 0.9 (t, 6H, $2CH_3$ of N-ethyl), 2.55 (q, 4H, 2CH2 of N-ethyl), 1.461(t, 6H, $2CH_3$ of N-C_2H_5I), 3.60 (q, 4H, $2CH_2$ of N-C_2H_5I), 6.67-8.76 (m, 18H, Ar +Het.).

4,4'–(2,6-diethyl-4,8-dioxo-1,7-diphenyl-1,2,6,7-tetrahydropyrazolo[4,3-*f*]indazole-3,5(4*H*,8*H*)-diyli dene)bis(methan-1-yl-1-ylidene)bis(1-ethylquinolinium)iodide cyanine dye (10b): Yield: 69%; m.p. 165-169^{o}C; Anal. calcd. for $C_{48}H_{44}N_6O_2I_2$: C, 58.18; H, 4.44; N, 8.49%. Found: C, 58.30, H, 4.53, N, 8.66%; IR (cm^{-1}): 1487 (cyclic C=N), 1650 (quinone ring), 2923-2800 (N-C_2H_5); ^{1}H-NMR (500 MHz, $CDCl_3$, δ/ ppm): 5.30 (s, 2H, 2CH), 1.00 (t, 6H, $2CH_3$ of N-ethyl), 2.69 (q, 4H, $2CH_2$ of N-ethyl),1.51 (t, 6H, $2CH_3$ of N-C_2H_5I), 3.77 (q, 4H, $2CH_2$ of N-C_2H_5I), 7.03-8.90 (m, 22H, Ar +Het.).

1,1'–(2,6-diethyl-4,8-dioxo-1,7-diphenyl-1,2,6,7-tetrahydropyrazolo[4,3-*f*]indazole-3,5(4*H*,8*H*)-diyli dene)bis (methan-1-yl-1ylidene)bis(2-ethylisoquinolinium)iodide cyanine dye (10c): Yield: 67%; m.p. 180-183^{o}C; Anal. calcd. for $C_{48}H_{40}N_6O_2I_2$: C, 58.18; H, 4.44; N, 8.49 %. Found: C, 57.90, H, 4.59, N, 8.72%.

4,4'–(2,5-diethyl-4,8-dioxo-1-phenyl-1*H*-oxazolo[4,5-*f*]indazole-3,6(2*H*,4*H*,5*H*,8*H*)-diylidene)bis (met han-1-yl-1-ylidene)bis(1-ethylquinolinium)iodide cyanine dye (10d): Yield: 59%; m.p. 170-173^{o}C; Anal. calcd. for $C_{42}H_{39}N_5O_3$ I_2: C, 55.08; H, 4.26; N, 7.65 %. Found: C, 55.18, H, 4.40, N, 7.75%; IR (cm^{-1}): 1487 (cyclic C=N), 1650 (quinone ring), 2923-2800 (N-C_2H_5) .

Ethoxyethene,3-(2,2-diethyl)-5-ethoxy-2,6-diethyl-4,8-dioxo-1,7-diphenyl-1,4,7,8tetrahydropyrazolo [4,3-f]indazole-2,6-diium diiodide salt (11a): Yield: 69%; m.p. 150-152^{o}C; Anal. calcd. for $C_{36}H_{46}N_4O_6I_2$: C, 48.87; H, 5.20; N, 6.35 %. Found: C, 48.65, H, 5.41, N, 6.22%.

Ethoxyethene,3-(2,2-diethyl)-6-ethoxy-2,5-diethyl-4,8-dioxo-1-phenyl-4, 8-dihydro-1*H*-oxazolo[4,5-*f*] indazole-2,5-diium di iodide salt (11b): Yield: 77%; m.p. 160-162^{o}C; Anal. calcd. for $C_{30}H_{41}N_3O_7I_2$: C, 44.50; H, 5.07; N, 5.19 %. Found: C, 44.43, H, 4.90, N, 5.34%.

2,2'-(1*E*,1'*E*,3*E*,3'*Z*)-3,3'-(2,6-diethyl-4,8-dioxo-1,7-diphenyl-1,2,6,7-tetrahydropyrazolo[4,3-*f*]inda zole-3,5(4*H*,8*H*)-diylidene)bis(prop-1-ene-1-yl-3-ylidene)bis(1-methylpyridinium) iodidecyanine dye (12a): Yield: 66%; m.p. 180-182^{o}C; Anal. calcd. for $C_{42}H_{40}N_6O_2I_2$: C, 55.14; H, 4.38; N, 9.19 %. Found:

C, 55.22, H, 4.61, N, 9.28%; IR (cm^{-1}): 1480 (cyclic C=N), 1635 (quinone ring), 2922-2882(N-C_2H_5); ^{1}H-NMR (500 MHz, $CDCl_3$, δ/ ppm): 0.91 (t, 6H, $2CH_3$, N-ethyl), 2.50 (q, 4H, $2CH_2$, N-ethyl), 2.83 (s, 6H, $2CH_3$, CH_3I), 6.56-7.72 (m, 24H, Ar +Het.+ CH).

2,2'-(1*E*,1'*E*,3*E*,3'*Z*)-3,3'-(2,6-diethyl-4,8-dioxo-1,7-diphenyl-1,2,6,7-tetrahydropyrazolo[4,3-*f*] indazole-3,5(4*H*,8*H*)-diylidene)bis(prop-1-ene-1-yl-3-ylidene)bis(1-ethylquinolinium)iodidecyanine dye (12b): Yield: 77%; m.p. 200-202^{o}C; Anal. calcd. for $C_{50}H_{44}N_6O_2I_2$: C, 59.17; H, 4.34; N, 8.28 %. Found: C, 59.33, H, 4.45, N, 8.42%; IR (cm^{-1}): 1485 (cyclic C=N), 1640 (quinone ring), 2924-2880 (N-C_2H_5); ^{1}H-NMR (500 MHz, $CDCl_3$, *δ*/ ppm): 1.00 (t, 6H, $2CH_3$, N-ethyl), 2.69 (q, 4H, $2CH_2$, N-ethyl), 2.85 (s, 6H, 2CH3, CH_3I), 5.50-7.12 (m, 28H, Ar +Het.+ CH).

4,4'-(1*E*,1'*E*,3*E*,3'*Z*)-3,3'-(2,6-diethyl-4,8-dioxo-1,7-diphenyl-1,2,6,7-tetrahydropyrazolo[4,3-*f*] indazole-3,5(4*H*,8*H*)-diylidene)bis(prop-1-ene-1-yl-3-ylidene)bis(1-methylpyridinium)iodide cyanine dye (12c):Yield: 68%; m.p. 180-182^{o}C; Anal. calcd. for $C_{42}H_{40}N_6O_2I_2$: C, 55.14; H, 4.38; N, 9.19 %. Found: C, 55.34, H, 4.55, N, 9.33%; ^{1}H-NMR (500 MHz, $CDCl_3$, δ/ ppm): 1.00 (t, 6H, $2CH_3$, N-ethyl), 2.69 (q, 4H, $2CH_2$, N-ethyl), 2.75 (s, 6H, $2CH_3$, CH_3I), 5.95-7.18 (m, 23H, Ar +Het.+ CH).

2-((*E*)-2-((*E*)-2,5-diethyl-3-((*E*)-3-(1-methylquinolinium-2-yl)allylidene)-4,8-dioxo-1-phenyl-2,3,4, 5,6, 8-hexahydro-1*H*-oxazolo[4,5-*f*]indazol-6-yl)vinyl)-1-methylquinolinium iodide cyanine dye (12d): Yield: 72%; m.p. 160-162^{o}C; Anal. calcd. for $C_{44}H_{39}N_5O_3I_2$: C, 56.23; H, 4.15; N, 7.46%. Found: C, 56.42, H, 4.20, N, 7.53%.

2-(3-methyl-1-phenylimidazo [4,5-*f*]indazole-4, 8(1*H*, 5*H*, 7*H*)-dione (methan-1-yl-1ylidene)(1-methyl pyridinium)iodide cyanine dye (13a): Yield: 76%; m.p. 198-200^{o}C; Anal. calcd. for $C_{22}H_{18}N_5O_2I$: C, 51.66; H, 3.52; N, 13.70 %. Found: C, 51.42, H, 3.71, N, 13.83%; IR (cm^{-1}): 1498 (cyclic C=N), 1594 (C=C), 1716-1695 (C=O), 3400-3100 (NH).

2-(3-methyl-1-phenylimidazo [4,5-*f*]indazole-4, 8(1*H*,5*H*,7*H*)-dione (methan-1-yl-1ylidene)(1-methyl quinolinium)iodide cyanine dye (13b): Yield: 68%; m.p. 180-182^{o}C; Anal. calcd. for $C_{26}H_{20}N_5O_2I$: C, 55.62; H, 3.57; N, 12.48 %. Found: C, 55.42, H, 3.70, N, 12.29%; IR (cm^{-1}): 1498 (cyclic C=N), 1594 (C=C), 1716-1698 (C=O), 3400-3100 (NH); ^{1}H-NMR (500 MHz, $CDCl_3$, δ/ ppm): 1.85 (s, 3H, CH_3),2.85 (s, 6H, $2CH_3$, N-CH_3I), 2.33 (s, 2H, 2NH), 6.54 -7.12 (m, 12H, Ar +Het.+CH).

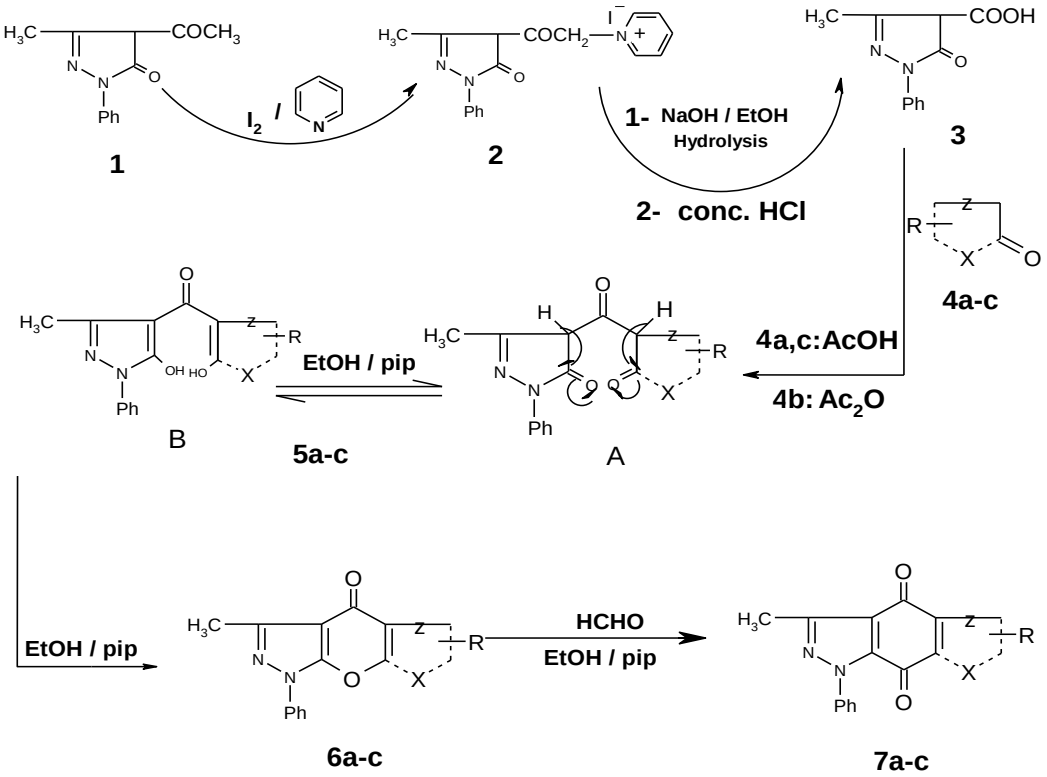
4-(3-methyl-1-phenylimidazo [4,5-*f*]indazole-4, 8(1*H*,5*H*,7*H*)-dione (methan-1-yl-1ylidene)(1-methyl pyridinium)iodide cyanine dye (13c): Yield: 71%; m.p. 190-192^{o}C; Anal. calcd. for $C_{22}H_{18}N_5O_2I$: C, 51.66; H, 3.52; N, 13.70%. Found: C, 51.80, H, 3.44, N, 13.87%; IR (cm^{-1}): 1498 (cyclic C=N), 1590 (C=C), 1713-1685 (C=O), 3400-3100 (NH).

1-ethyl-4-((2-ethyl-4,6,8-trioxo-1-Phenyl-1,2,6,7-tetrahydroimidazo[4,5-*f*]indazol-3(4*H*, 5*H*, 8*H*)-ylid ene)methyl) pyridinium iodide cyanine dye (14a): Yield: 74%; m.p. 145-147^{o}C; Anal. calcd. for $C_{24}H_{22}N_5O_3I$: C, 51.89; H, 3.96; N, 12.61%. Found: C, 51.63, H, 4.11, N, 12.54%; IR (cm^{-1}): 1498 (cyclic C=N), 2920-2889 (N-C_2H_5), 1700-1685 (C=O), 3400-3100 (NH); ^{1}H-NMR (500 MHz, $CDCl_3$, δ/ ppm): 1.09 (t, 3H, CH_3, N-ethyl), 2.45 (q, 2H, CH_2, N-ethyl), 1.15 (t, 3H, CH_3, C_2H_5I), 3.44 (q, 2H, CH_2, C_2H_5I), 6.00 (s, 2H, 2NH), 6.01 -7.22 (m, 10H, Ar + Het. + CH).

1-ethyl-4-((2-ethyl-4,6,8-trioxo-1-Phenyl-1,2,6,7-tetrahydroimidazo[4,5-f]indazol-3(4*H*, 5*H*, 8*H*)-ylid ene)methyl) qunolnium iodide cyanine dye (14b): Yield: 69%; m.p. 152-154^{o}C; Anal. calcd. for $C_{28}H_{24}N_5O_3I$: C, 55.54; H, 3.97; N, 11.57 %. Found: C, 55.34, H, 3.70, N, 11.61%; ^{1}H-NMR (500 MHz, $CDCl_3$, δ/ ppm): 1.20 (s, 3H, CH_3), 1.00 t, 3H, CH_3, N-ethyl), 2.59 (q, 2H, CH_2, N-ethyl), 1.13 (t, 3H, CH_3, C_2H_5I), 3.39 (q, 2H, CH_2 , C_2H_5I), 6.00 (s, 2H, 2NH), 5.94 -7.22 (m, 12H, Ar + Het.+CH).

2-ethyl-1-((2-ethyl-4,6,8-trioxo-1-Phenyl-1,2,6,7-tetrahydroimidazo[4,5-*f*]indazol-3(4*H*, 5*H*, 8*H*)-ylidene)methyl)pyridinium iodide cyanine dye (14c): Yield: 67%; m.p. 133-135 ^{o}C; Anal. calcd. for $C_{28}H_{24}N_5O_3I$: C, 55.54; H, 3.97; N, 11.57 %. Found: C, 55.66, H, 3.87, N, 11.70%.

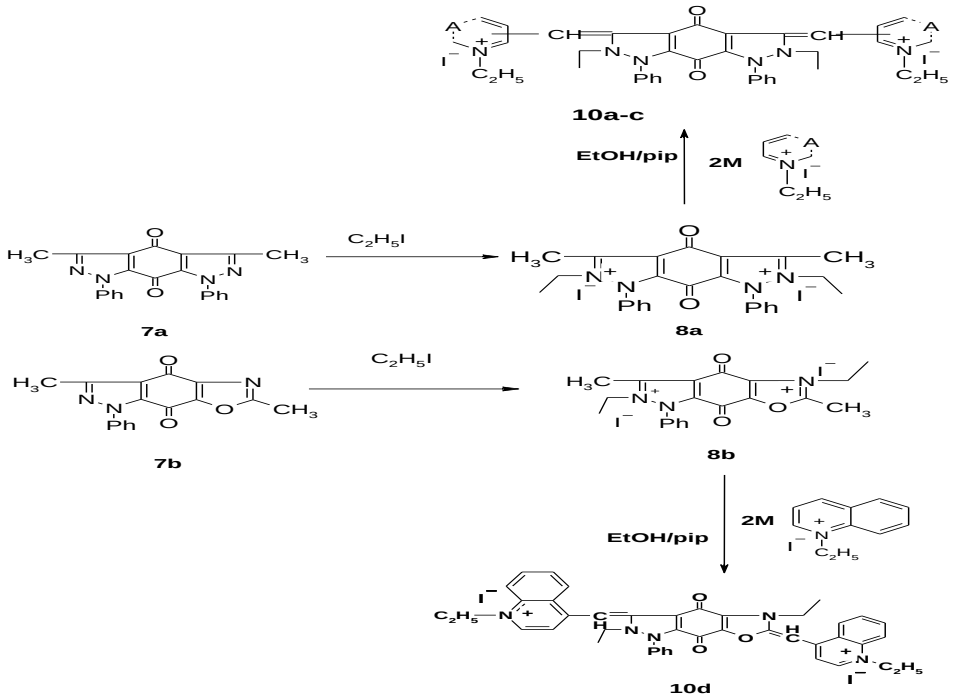
1-ethyl-4-(((*E*)-2-ethyl-6((1-methylpyridinium-4-yl)methylene)-4,8-dioxo-1-phenyl-1,2,6,7-tetrahydroimidazo[4,5-*f*]indazol-3(4*H*, 5*H*, 8*H*)-ylidene)methyl)pyridinium iodide cyanine dye (15): Yield: 78%; m.p. 155-158^{o}C; Anal. calcd. for $C_{31}H_{30}N_6O_2I_2$: C, 48.19; H, 3.89; N, 10.88 %. Found: C, 48.37, H, 3.66, N, 10.76%; ^{1}H-NMR (500 MHz, $CDCl_3$, δ/ ppm): 3.64 (s, 3H, CH_3 of N-methyl iodide), 1.42 (q, 2H, CH_2 of N-ethyl iodide), 1.02 (t, 3H, CH_3 of N-ethyl iodide), 6.11 (s, 2H, 2NH), 5.45 -9.48 (m, 15H, Ar + Het. + 2CH).



Reaction Scheme1 for the Synthesis of Compounds **(2, 3, 4a-c, 5a-c, 6a-c and 7a-c)**

Compound	R[X(Z)]
4a, 5a,6a,7a	3-methyl-1-phenyl-(1H)pyrazole-5(*4H*) -one
4b, 5b,6a,7b	2-methyl-oxazole
4c, 5c,6c,7c	imidazol-2-one

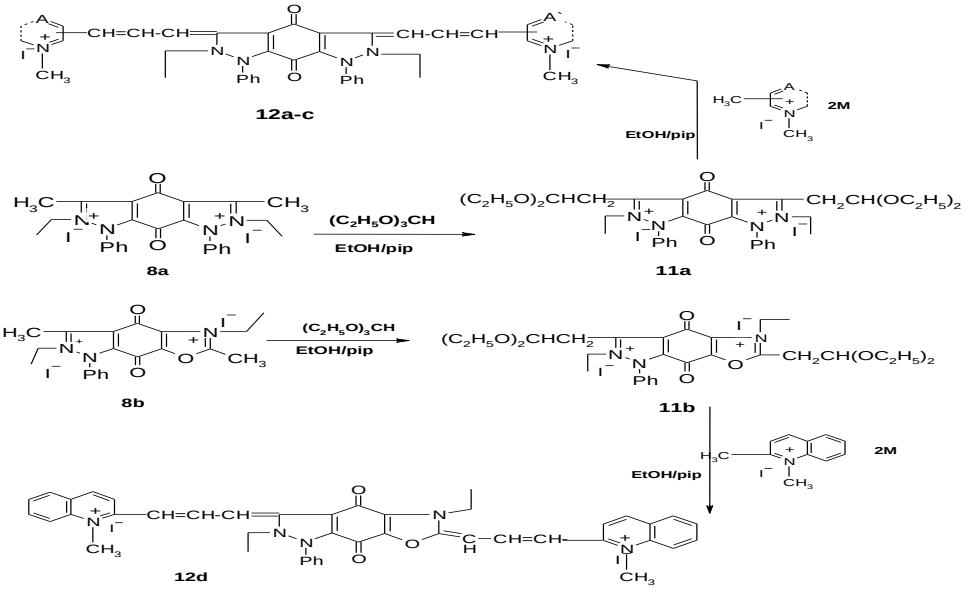
Scheme 1



Reaction Scheme 2 for the Synthesis of Compounds (8a,8b and 10a-d):

Compound	A=A`
10a	N-Ethyl pyridin-4-ium iodide
10b	N- Ethyl quinolin-4-ium iodide
10c	N- Ethyl isoquinolin-1-ium iodide

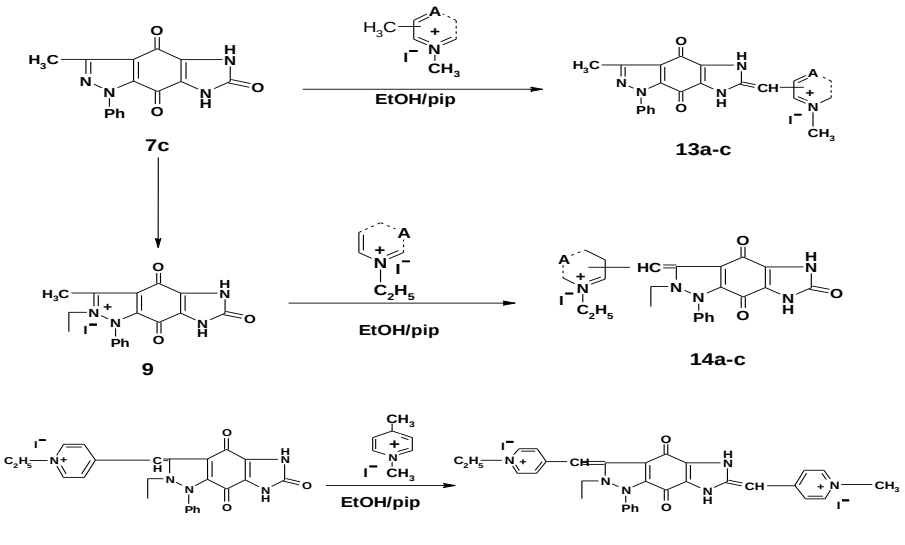
Scheme 2



Reaction Scheme 3 for the Synthesis of Compounds (11a,11b and 12a-d):

Compound	A=A`
12a	N-Methyl pyridin-2-ium iodide
12b	N-Methyl quinolin-2-ium iodide
12c	N-Methyl pyridin-4-ium iodide

Scheme 3



Reaction Scheme 4 for the Synthesis of Compounds **(9, 13a-c, 14a-c and 15):**

Compound	A
13a	N- Methyl pyridin-2-ium iodide
13b	N- Methyl quinolin-2-ium iodide
13c	N- Methyl pyridin-4-ium iodide
14a	N- Ethyl pyridin-4-ium iodide
14b	N- Ethyl quinolin-4-ium iodide
14c	N- Ethyl isoquinolin-1-ium iodide

Scheme 4

Correlation Between Colour and Structure of the Cyanine Dyes

Absorption spectra data in ethanol:The electronic absorption spectra of synthesized cyanine dyes of compounds **(10a-d), (13a-c), (14a-c, 15)** and **(12a-d)** in 95% ethanol showed absorption bands bathochromically (hypsochromically) shifted depending upon the nature of heterocyclic R[X(Z)], heterocyclic quaternary residue A, A` and their linkage position.Thus, electronic absorption spectra of dye **(10a)** [R[X (Z)] = 1-phenylpyrazole, A = A` = pyridine-4-ium] showed λ_{max} = 505, 540 nm. Substitution of [A = A` = pyridine-4-ium] in dye 10aby [A = A` = quinoline-4-ium] in dye **(10b)** resulted in bathochromic shift of $\Delta\lambda_{max}$ = 30 nm. This is attributed to the more extensive π-delocalization within quinoline-4-ium salt, (Table 1). Changing the linkage position of the quinolinium residue from 4-ium in dye 10bto 1-ium in dye **(10c)** resulted in hypsochromic shift of absorption band of $\Delta\lambda_{max}$ = 50 nm. This is due to the increasing in the conjugation of the quinolinium in the 4-ium linkage relative to 1-ium analogue. Substitution of R[X(Z)] = 1-phenylpyrazole nuclei in dye **(10b)** by oxazole nuclei in dye **(10d)** resulted in hypsochromic shift of absorption band of $\Delta\lambda_{max}$ = 35 nm. This is due to the more electro negativity of oxygen atom presence in oxazole ring in dye **(10d).**

The electronic absorption spectra of **(13a-c)** in 95% ethanol showed absorption bands batho (hypso) chromically shifted depending upon the nature of heterocyclic quaternary residue A and their linkage position. Thus, electronic absorption spectra of dye **(13a)** [A = pyridine-2-ium] showed λ_{max} = 470 nm. Substitution of [A = pyridin-2-ium] in dye **(13a)** by [A = quinolin-2-ium] in dye **(13b)** resulted in bathochromic shift of $\Delta\lambda_{max}$ = 35 nm accompanied with the appearance of new absorption band at longer wave length 595 nm. This is attributed to the more extensive π-delocalization within quinoline-2-ium salt, (Table 2). Changing the linkage position of pyridinium residue from 2-ium in dye **(13a)** to 4-ium in dye **(13c)** resulted in a remarkable bathochromic shift of absorption band $\Delta\lambda_{max}$ = 25 nm. This is due to the increasing in the conjugation of the pyridinium in the 4-ium linkage relative to 2-ium analogue.

The visibleabsorption spectra of **(14a-c)** in 95% ethanol showed absorption bands batho(hypso) chromically shifted depending upon the nature of heterocyclic quaternary residue A and their linkage position. Thus, electronic absorption spectra of dye **(14a)** [A = A` = pyridine-4-ium] showed $\lambda_{max}$ = 475 nm. Substitution of [A = A` = pyridin-4-ium] in dye **(12a)** by [A = A` = quinolin-4-ium] in dye **(14b)** resulted in bathochromic shift of $\Delta\lambda_{max}$ = 45 nm. This is attributed to the more extensive π-delocalization within quinolin-4-ium salt, (Table 2). Changing the linkage position of the quinolinium residue from 4-ium in dye **(14b)** to 1-ium in dye 14c resulted in hypsochromic shift of absorption band of $\Delta\lambda_{max}$ = 40 nm. This is due to the increasing in the conjugation of the quinolinium in the 4-ium linkage relative to 1-ium analogue.

On comparison between the electronic absorption spectra of compound **(15)** and compounds **(13c** and **14a)**. It was obvious that compound (**15)** showed bathochromic absorption band located at λ_{max} =510 nm if compared with absorption spectra of compounds **(13c)** at λ_{max} = 495 nm and at 475 nm for compound **(14a)**. This is attributed to the more extensive π-delocalization within the two pyridin-4-ium moieties in (**15)** rather than one pyridin-4-ium moiety in compounds **(13c, 14a)**.

The visible absorption spectra of **(12a-d)** are influenced by the heterocyclic R[X(Z)], heterocyclic quaternary residue A, A` and their linkage position. Thus, electronic absorption spectra of dye **(12a)** [R[X(Z)] = 1-phenylpyrazolin, A = A` = pyridine-2-ium] showed λ_{max} = 510 nm. Substitution of [A = A` = pyridin-2-ium] in dye **(12a)** by [A = A` = quinoline-2-ium] in dye 12bresulted in bathochromic shift of $\Delta\lambda_{max}$ = 40 nm. This can be attributed to the more extensive π-delocalization within quinoline-2-ium salt, (Table-2). Changing the linkage position of pyridinium residue from 2-ium in dye **(12a)** to 4-ium in dye **(12c)** resulted in slight bathochromic shift of absorption band of $\Delta\lambda_{max}$ = 5 nm accompanied with the appearance of a new absorption band at λ_{max} = 495 nm. This is due to the increasing in the conjugation of pyridinium in the 4-ium linkage relative to 2-ium analogue. On the other hand, changing the nuclei R[X(Z)] from R[X(Z)] = 1-phenylpyrazolin in dye **(12b)** to R[X(Z)] = oxazolin nuclei in dye **(12d)** resulted in bathochromic shift of absorption band accompanied with splitting of absorption band of $\Delta\lambda_{max}$ = 35 nm. This is due to the resonance of oxygen atom presence in oxazolin ring in dye **(12d).**

On comparison between the visible absorption spectra of the reported compounds ref.[8] which were namely as 1-phenyl-benzo[4,5-b]pyrazolo-4,7-dione 3[4(1)]monomethine cyanine dyes, 1-phenyl-benzo [4,5-b]pyrazolo-4,7-dione 3[4(1)]monomethine cyanine dyes and 1-phenyl-benzo[4,5-b]pyrazolo-4,7-dione 3[2(4)]trimethine cyanine dyes and the recent work cyanine dyes **(10a-d)**, cyanine dyes **(14a-c)** and or cyanine dyes **(12a-d)**. Generally, it was obvious that building the extra pyrazoline, oxazoline and /or imidazole nuclei at the other side of quinone ring in the former reported compounds ref. [8] resulted in the formation of unsymmetrical mono-3[4(1)] methine cyanine dyes **(14a-c)** and symmetrical bis mono (tri) methine cyanine dyes **(10a-d)** and **(12a-d)** involving bis heterocyclic quinone system leading to the multiplicity of charge transfer, the extra activity, the more extensive π-delocalization and flowingly the stronger bathochromic shift of wavelength of the absorption bands. So, for example, on comparison between the visible absorption spectra of the reported compounds unsymmetrical 1-phenyl-benzo[4,5-b]pyrazolo-4,7-dione 3[4(1)] monomethine cyanine dyes and the correspondence unsymmetrical cyanine dyes **(14a-c)**. It was obvious that the reported compound which contained N-methyl quinoline-4-ium salt showed absorption band at λ_{max} = 480 nm where the correspondence recent compound **(14b)** which contained N-ethyl quinolin-4-ium salt and extra imidazolone nuclei showed strong bathochromic shift of $\Delta\lambda_{max}$ = 40 nm . On the other hand, the correspondence recent compounds **(10b), (10d)** which contained bis-N-ethyl quinolin-4-ium salts and extra pyrazolin and/or oxazolin nucleus showed strong bathochromic shift of $\Delta\lambda_{max}$ = 55, 20 nm respectively.

Also, on comparison between the visible absorption spectra of the reported compounds 1-phenyl-benzo[4,5-b]pyrazolo-4,7-dione 3[2(4)]trimethine cyanine dyes ref. [8] and recent synthesized cyanine

dyes **(12a-d)**, it was obvious that the reported compound (for example) which contained N-methyl quinolin-2-ium salt, showed absorption bands at λ_{max} = 500, 530, 670 nm ref. [8]. While the visible absorption spectra of the recent correspondence cyanine dye **(12d)** (for example) which contained bis-N-methyl quinolin-2-ium salts and extra oxazolin nuclei exhibited strong bathochromic shift of $\Delta\lambda_{max}$ = 25, 30, 10 nm respectively with the appearance of the new bathochromic absorption bands at 480, 585, 635 nm.

Table 2. Absorption spectral data of new cyanine dyes (**10a-d), (12a-d), (13a-c), (14a-c)** and **(15)** in 95% ethanol

Compound	λ_{max} nm	ε_{max} X 10^{-3} cm^{-1} mol^{-1}
10a	505	4.48
10b	535	4.83
10c	485	2.55
10d	500	4.49
12a	510	4.51
12b	520, 555, 595	8.98, 8.90, 5.97
12c	495, 515 s	3.75, 7.24
12d	480, 525, 560, 585 s, 635 s, 680 s	5.58, 5.93, 6.93, 5.44, 2.60, 1.7152
13a	470	2.02
13b	530, 560, 595	7.82, 8.62, 5.26
13c	495, 600 s	2.68, 2.68
14a	475	2.35
14b	520	3.25
14c	480	2.24
15	510	3.12

s = shoulder

APPLICATIONS

Antimicrobial activity of some selected cyanine dyes: The activities of three started compounds and the corresponding their seven cyanine dyes 3,5-Dimethyl-1,7-diphenylpyrazolo[4,3-*f*]indazole-4,8(1*H*,7*H*)-dione **(7a)**, 3,6-dimethyl-1-phenyl- 1*H*- oxazole [4,5-*f*'] indazole-4,8-dione **(7b)** and 3-methyl-1-phenyl imidazo[4,5-*f*]indazole-4,6,8(1*H*,5*H*,7*H*)-trione **(7c)**,4,4' –(2,6-diethyl-4,8-dioxo-1,7-diphenyl-1,2,6,7-tetra hydropyrazolo[4,3-*f*]indazole-3,5(4*H*,8*H*)-diylidene)bis(methan-1-yl-1-ylidene)bis(1-ethylquinolinium) iodide cyanine dye **(10b)**, 1,1' –(2,6-diethyl-4,8-dioxo-1,7-diphenyl-1,2,6,7-tetrahydropyrazolo[4,3-*f*] indazole-3,5 (4*H*,8*H*)-diylidene)bis (methan-1-yl-1ylidene)bis(2-ethylisoquinolinium)iodide cyanine dye **(10c)** and 4,4' –(2,5-diethyl-4,8-dioxo-1-phenyl-1*H*-oxazolo[4,5-*f*]indazole-3,6 (2*H*,4*H*,5*H*,8*H*)-diylid ene)bis(methan-1-yl-1-ylidene)bis(1-ethylquinolinium)iodide cyanine dye **(10d)**, 2-(3-methyl-1-phenyl imidazo [4,5-*f*]indazole-4, 8(1*H*, 5*H*, 7*H*)-dione (methan-1-yl-1ylidene)(1-methylpyridinium)iodide cyanine dye **(13a)**, 2-(3-methyl-1-phenylimidazo [4,5-*f*]indazole-4, 8(1*H*,5*H*,7*H*)-dione (methan-1-yl-1ylidene)(1-methylquinolinium)iodide cyanine dye (13b), 2,2'-(1*E*,1'*E*,3*E*,3'*Z*)-3,3'-(2,6-diethyl-4,8-dioxo-1,7-diphenyl-1,2,6,7-tetrahydropyrazolo [4,3-*f*]indazole-3,5(4*H*,8*H*)-diylidene)bis(prop-1-ene-1-yl-3-ylide ne)bis(1-methylpyridinium)iodide cyanine dye (12a), 2,2'-(1*E*,1'*E*,3*E*,3'*Z*)-3,3'-(2,6-diethyl-4,8-dioxo-1,7-diphenyl-1,2,6,7-tetrahydropyrazolo [4,3-*f*]indazole-3,5(4*H*,8*H*)-diylidene)bis(prop-1-ene-1-yl-3-ylidene) bis(1-methylquinolinium)iodide cyanine dye **(12b)** were tested against a wide spectrum of Gram positive bacteria; *Bacellus cereus, Staphylococcus aureus, S. citrus* and an unidentified isolate, and Gram negative bacteria; *Pseudomonas aeroginosa, Pseudomonas putida, Escherichia coli, Serratia sp*. and from

halophilic archaea formerly called *halobacteria Halobiforma haloterrestris* (Table 3). Several organic compounds are well known to have antimicrobial activity against many species of bacteria and other microorganisms [37-41]. These compounds are useful in treatment and/or control of human, animal, and plant diseases. The present investigation was carried out to determine the antimicrobial activity of these ten compounds. Thus, the 4,4' –(2,6-diethyl-4,8-dioxo-1,7-diphenyl-1,2,6,7-tetrahydropyrazolo[4,3-*f*]indazole-3,5(4*H*,8*H*)-diylidene)bis(methan-1-yl-1-ylidene)bis(1-ethylquinolinium)iodide cyanine dye **(10b)**, 1,1' –(2,6- diethyl-4,8-dioxo-1,7-diphenyl-1,2,6,7-tetrahydropyrazolo[4,3-*f*]indazole-3,5 (4*H*,8*H*)-diylidene)bis (methan-1-yl-1ylidene)bis(2-ethylisoquinolinium)iodide cyanine dye **(10c)** and 4,4' –(2,5-diethyl-4,8-dioxo-1-phenyl-1*H*-oxazolo[4,5-*f*]indazole-3,6 (2*H*,4*H*,5*H*,8*H*)-diylidene)bis(methan-1-yl-1-ylidene)bis(1-ethylquinolinium)iodide cyanine dye **(10d)** showed antimicrobial activity against the tested microorganisms, where the amount of the activity is dependent on the structure of the dye. Thus, compound **(10d)** has more activity towards both Gram positive and gram negative bacteria than compounds **(10b)** and **(10c)**. This is due to the compound **(10d)** contains the N-quinolinium heterocyclic in addition to an oxazole heterocyclic ring which increases the activity. Oxazolidinons are used as an active synthetic antibiotic with a unique mechanism of bacterial protein synthesis inhibition [42-45] and exhibited broad spectrum of antibacterial activity including activity against drug–resistant gram positive bacteria as well as several anaerobes and Mycobacterium tuberculosis. Also,2,2'-(1*E*,1'*E*,3*E*,3'*Z*)-3,3'-(2,6-diethyl-4,8-dioxo-1,7-diphenyl-1,2,6,7-tetrahydropyrazolo[4,3-*f*]indazole-3,5(4*H*,8*H*)-diylidene) bis(prop-1-ene-1-yl-3-ylide ne)bis(1-methylquinolinium)iodide cyanine dye **(12b)** and 2-(3-methyl-1-phenylimidazo [4,5-*f*]indazole-4, 8(1*H*,5*H*,7*H*)-dione (methan-1-yl-1ylidene)(1-methylquinolinium)iodide cyanine dye **(13b)**,[including A= quinolinium-2-ium salt moiety] showed antimicrobial activity with highest potency against the tested microorganisms. Substituted of A= 1-ethyl quinolinium-2-ium salt in **(12b)** and/ or **(13b)** by A= 1-ethyl pyridinium-2-ium salt in **(11a)** exhibit biological inactive against the tested microorganisms. Finally, it was observed that all above tested cyanine dyes compounds **(10b), (10c), (10d), (13b) and (12b)** showed antimicrobial activity with highest potency towards the microorganism *Halobiforma haloterrestris* in comparison with the other tested microorganism (Table 3).

Table 3. Antibacterial activities of tested compounds expressed as size (mm) of inhibition zone

Compound No. / **Test organism**	**10b**	**10c**	**10d**	**12b**	**13b**	**Ampicillin**
1- Bacteria						
Staphylococcus aureus	10	8	10	9	9	+
S. citrus	9	9	12	11	10	+
Bacellus cereus	10	9	11	9	10	+
Unidentified isolate	10	8	12	12	10	+
Pseudomonas aeroginosa	-	-	-	-	-	+
Pseudomonas putida	-	-	-	-	-	+
Escherichia coli	-	-	-	-	-	+
Serrata sp.	-	-	-	-	-	+
2- Archaea						**Novobiocine**
Halobiforma aloterrestris	24	15	30	30	20	+

CONCLUSIONS

All the observations and analytical spectra in this paper support the synthesis of new symmetrical and unsymmetrical mono, bis-mono (and/or bis-tri) methine photosensitizing dyes. The absorption spectra of the synthesized dyes were investigated in 95 % ethanol. The results indicated that the color of these dyes

depends on the terminal groups and the length of conjugation within the structure. Thus, the more the length of conjugation (bis tri methine dyes) the stronger the bathochromic wavelength of absorption bands than those of (bis mono methine dyes). Also, the color of these dyes depends on the nature of their heterocyclic and heterocyclic quaternary salt and their linkage position. The antimicrobial activity of some selected synthesized novel dyes was investigated in vitro using a wide spectrum of microbial strains which dependent on the structure of dye. So, such compounds **(10b)**, **(10c)**, **(10d)**, **(12b)** and **(13b)** showed antimicrobial activity with highest potency towards the microorganism *Halobiforma haloterrestris* in comparison with the other tested microorganism.

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