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Microwave Assisted Synthesis and Solvato (Media)-Chromic Behaviour of Some New Series Photosensitizing Dyes

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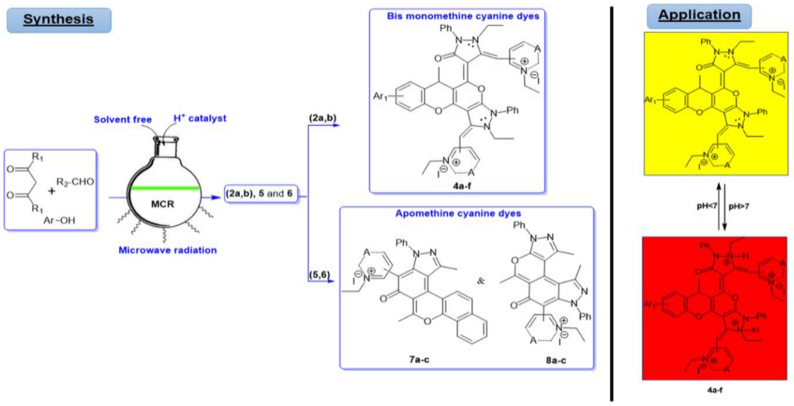
ABSTRACT

The motivation in the synthetic process of new benzo[7',8'] chromeno [2',3':4,5]pyrano [2,3-c] pyrazol, benzo[7,8] chromeno[4,3-e]indazole and pyrazolo[4',3':5,6] pyrano[4,3-e] indazole heterocyclic moieties and related cyanine dyes is to improve the specific characterization, photosensitization behavior, and probable application in the field of biology, medical Science, technology and physics. A new efficient and simple one-pot synthesis of three component reaction were performed for the synthesis of new mono and zero methine cyanine dyes under solvent free microwave condition to provide a green technique, shorter reaction times, high efficiency reactions and high yield product for the synthesis. Such Heterocyclic and related dyes were identified by elemental and spectral analysis. The absorption and emission spectra were investigated in 95% Ethanol to attempt and throw some light on the influence of such new heterocyclic nuclei and to compare or evaluate spectral behaviors. Acid-Base properties (halochromic) in aqueous solutions universal buffer of some selected cyanine dyes were studied to determine the better PH for these photosensitizers.

Graphical abstract



Highlights:

- New bismonomethine and zeromethine cyanine dyes developed by one pot reaction techniques under microwave irradiation and avoiding toxic organic solvent to achieve the green aspect of the process (ecofriendly).
- The intensity of the color of cyanine dyes is depending basically on increasing or decreasing л-delocalization conjugation in the dye molecule.
- Increasing number of charge transfers give better photosensitizers
- Dyes which have more conjugated charge transfer pathways have lower energy gap (E_{0-0}) than those which have one conjugated charge transfer pathway.

Changing the color of the dyes from acidic to basic medium give the opportunity of these dyes to be used as an indicator in analytical chemistry.

Keywords: Synthesis, Photosensitizing dyes, Solvato(media)-chromic behaviour, Photophysical properties.

INTRODUCTION

Cyanine's exhibit large extinction coefficients and moderate fluorescence quantum yields, leading to widespread applications in various fields of science, technology, engineering, pharmacology and medicine such as photo sensitizers, stains, fluorescent labels, indicator, solar energy conversion, laser technology and sensors [1-4]. cyanine's have been extensively used as probes for nucleic acids among other biological systems [5] increased fluorescent intensity when bound to the biological molecule, they have been applied in some biomedical fields [6], including gel staining [7] and developed for numerous applications in photographic processes and more recently as fluorescent probes for bio-molecular labeling and imaging [8-13] which present great potential to be developed into biological fluorescent probes. Microwave synthesis technique for cyanine dyes is an efficient tool depends upon using of dry media reactions avoiding organic solvents during the reactions in organic synthesis leads to a clean, efficient, and economical technology (green chemistry). There is an increasing interest in the use of environmentally benign reagent sand procedures. Or, in other words, the absence of solvents coupled with the high yields and short reaction times often associated with reactions of this type make these procedures very attractive for synthesis. A microwave is a form of electromagnetic energy, which falls at the lower end of the electromagnetic spectrum and is defined in a measurement of frequency as 300 to 300,000 Megahertz, corresponding to wavelengths of 1 cm to 1 m [14]. The microwave region of the electromagnetic spectrum lies between infrared and radio frequencies [15, 16]. Historically, chemists thought that compounds reacted in the liquid state or dissolved [17]. This has made solvents common in chemical synthesis, however, many compounds used as solvents were found to be environmentally unfriendly. The problem associated with waste disposal of solvents has been overcome by performing reactions without a solvent under microwave irradiation (MWI)[18]. In recent years, the entry of microwave ovens in the chemistry laboratory has made it possible to carry out many transformations with greater efficiency and ease of workup [19-22]. The future for the application of microwave technology looks bright because of its efficiency and its potential to contribute to clean products. In the present discussion, we describe three component system reaction as a direct and simple method for the synthesis of new series of cyanine dyes by dry reaction techniques coupled with microwave activation, Studies and comparative studies of absorption and emission spectral-structural behavior, and acid-base properties of some selected synthesized dyes.

MATERIALS AND METHODS

Physical and Chemical Properties Determinations: All melting points are uncorrected elemental analysis was carried out at the Analytical Services Laboratory (Textile Engineering, Chemistry and

Science Department-North Carolina State University) and the Micro analytical center (Cairo University). The IR (νKBr) spectra were determined with Perkin Elmer Infrared 127ß spectrophotometer (Cairo-University) and Thermo Electron FTIR with Nexus 470 bench and Continuum Microscope (NCSU). ^{1}H-NMR spectra were recorded with a Bruker AMX-250 spectrometer (Cairo University). Mass spectra were recorded on a HpMs 6988 spectrometer (Cairo University). The absorption spectra were recorded immediately after preparation of the solutions within the wavelength range (350-700) on 6405 UV/Visible recording spectrophotometers, Faculty of Science, Aswan. Emission spectra were recorded by fluor log spectrophotometer (NC State University).

Synthesis and structural characterization: The required intermediates and final compounds were synthesized using the standard synthetic protocols. The procedures for the synthesis of intermediates and target dyes along with their structural characterization data are given below.

Synthesis of 1, 3-bis(3-methyl-5-one-1-phenyl-4-hydro-pyrazol-4-yl) propane-1,3-dione 1: A mixture of 1-phenyl 3-methyl pyrazol-5-one (2mmol) and diethylmalonate (1 mmol) in acetic acid (20 mL) and sodium acetate (0.01 g) were refluxed for 8 h. The mixture was allowed to cool, filtered and poured on crushed ice. The solid thus separated was collected by filtration and recrystallized from petroleum ether gives the pure crystals, table**1**.

Synthesis of substituted 4-(1,6-dimethyl-3-phenyl-chromeno[2',3':4,5]pyrano[2,3-c]pyrazol-5(6H)-ylidene)-3-methyl-1-phenyl-pyrazol-5(4H)-one2a, b: A mixture of compound **1** (1 mmol), 1-naphthol or 2-naphthol (1mmol), aldehyde (1 mmol) and (13N) sulfuric acid (0.08 ml) was irradiated in microwave oven for 5 min at 200 watts under solvent free conditions. The resulting mixture cooled and extracted with chloroform. The combined organic layers dried over Na_2SO_4, and filtered. After removing the solvent, the compound purified by recrystallization from petroleum ether were presented in table1.

Synthesis of substituted 2-ethyl-5-(2-ethyl-3-methyl-5-oxo-1-phenyl-1H-pyrazol-2-ium-4(5H)-ylidene)-3-phenyl-5,6-di[H]-3H-chromeno[2',3':4,5]pyrano[2,3-c]pyrazol-2-iumiodide-bis-1,6-mono[4(1)]methine cyanine dyes 4a-f : Started by the reaction**2a, b** (1mmol) and Ethyl iodide (2mmol) in microwave oven for 4 min at 119 watts. The reaction mixture was allowed to cool, poured on ethanol and filtered. The solid thus separated was collected by filtration and recrystallized from diethyl ether to form **3a, b** as dark yellow orange crystals. Followed by the reaction of **3a, b** (1 mmol) withpyridine [quinolin]-4(1)-ium-ethiodide salts (2mmol) in the presence of 2-3 drops of piperidine in microwave oven for 5 minutes at 119 watts. The product was dissolved in hot ethanol and filtered to recover the unreacted material. The reaction mixture cooled and poured on crushed ice. The solid thus separated was collected by filtration and recrystallized from diethyl ether, table1.

Synthesis of 5,13-dimethyl-3-phenyl-3,5b-di[H]-benzo[7,8]chromeno[4,3-e] indazol-1(2H)-one5: A mixture of 4-formyl-3-methyl-1-phenyl-5-one pyrazole (1 mmol), 1-naphthol (1mmol), acetyl acetone (1 mmol) and (13N) sulfuric acid (0.09 ml) in presence of a few mL of ethanol, was irradiated in microwave oven for 8 min at 119 watts. The product was extracted with ethyl acetate and the combined organic layers dried over Na_2SO_4, and filtered. After removing the solvent, the solid thus separated was collected by filtration and recrystallized from hexanes gives the pure crystals, table1.

Synthesis of 1,5,10-trimethyl-3,8-diphenyl-8,10b-di[H]-3H-pyrazolo[4',3':5,6]pyrano[4,3-e] in dazol-6(7H)-one 6: The reaction of 4-formyl-3-methyl-1-phenyl-5-one pyrazole(1 mmol), 4-H-3-methyl-1-phenyl-5-one pyrazole (1mmol), acetyl acetone (1 mmol) and (13N) sulfuric acid (0.09 ml) in presence of a few mL of 1,4-dioxane were irradiated in microwave oven for 8 minutes at 119 watts. The product was dissolved in hot ethanol and neutralized by saturated solution of Na_2CO_3 then extracted with ethyl acetate and the combined organic layers dried over Na_2SO_4, and filtered. After removing the solvent, the solid thus separated was collected by filtration and recrystallized from petroleum ether, table1.

Synthesis of 5, 13-dimethyl-3-phenyl-benzo [7,8]chromeno [4,3-e]indazol-1-one-2-zero [4(1)] methane cyanine dyes 7a-c: Mixture of **5**(1mmol) and pyridine[quinolin]-4(1)-ium-ethiodide salts (1 mmol) in presence of 2-3 drops of piperidine was irradiated in microwave oven for 8 min at 200 watts. The reaction mixture was poured on crushed ice and neutralized with glacial acetic acid. The solid thus separated was collected by filtration and recrystallized from petroleum ether, table1.

Synthesis of 1,5,10-trimethyl-3,8-diphenyl-pyrazolo[4',3':5,6]pyrano[4,3-e]indazol-6-one-7- zero [4(1)]methine cyanine dyes 8a-c: Mixture of **6** (1mmol) and pyridine [quinolin]-4(1)-ium-ethiodide salts (1 mmol) in presence of 2-3 drops of piperidine was irradiated in microwave oven for 8 min at 200 watts. The reaction mixture was poured on crushed ice and neutralized with glacial acetic acid. The solid thus separated was collected by filtration and recrystallized from petroleum ether, table1.

Table 1: Characterization data for **(1)**, **(2a, b)**, **(3a, b)**, **(4a-f)**, **(5)**, **(6)**, **(7a-c)** and **(8a-c).**

Comp No.	**Nature of Products**				**% Calcd. (Found)**		
	M.p. °C	**Yield %**	**Color**	**Mol. Formula (Mol. Wt.)**	**C**	**H**	**N**
1	117	72	Yellow	$C_{23}H_{20}N_4O_4$ (416.4)	66.34 (66.22)	4.84 (4.92)	13.45 (13.44)
2a	122	75	Yellow	$C_{35}H_{26}N_4O_3$ (550.6)	76.35 (76.30)	4.76 (5.78)	10.18 (10.19)
2b	118	89	Yellow	$C_{35}H_{26}N_4O_3$ (550.6)	76.35 (76.37)	4.76 (4.75)	10.18 (10.12)
3a	115	84	Orange	$C_{39}H_{36}I_2N_4O_3$ (562.5)	54.31 (54.32)	4.21 (4.25)	6.50 (6.52)
3b	113	92	Orange	$C_{39}H_{36}I_2N_4O_3$ (562.5)	54.31 (54.30)	4.21 (4.22)	6.50 (6.46)
4a	79	97	red	$C_{53}H_{50}I_2N_6O_3$ (1072.8)	59.34 (59.31)	4.70 (4.87)	7.83 (7.79)
4b	90	69	red	$C_{61}H_{54}I_2N_6O_3$ (1172.93)	62.46 (62.49)	4.64 (4.65)	7.16 (7.13)
4c	85	65	red	$C_{61}H_{54}I_2N_6O_3$ (1172.93)	62.46 (62.45)	4.64 (4.68)	7.16 (7.20)
4d	92	96	red violet	$C_{53}H_{50}I_2N_6O_3$ (1072.8)	59.34 (59.37)	4.70 (4.71)	7.83 (7.89)
4e	98	96	Violet	$C_{61}H_{54}I_2N_6O_3$ (1172.93)	62.46 (62.44)	4.64 (4.63)	7.16 (7.13)
4f	100	69	Red	$C_{61}H_{54}I_2N_6O_3$ (1172.93)	62.46 (62.45)	4.64 (4.67)	7.16 (7.14)
5	125	58	Brown	$C_{26}H_{20}N_2O_2$ (392.45)	79.57 (79.55)	5.14 (5.14)	7.14 (7.15)
6	107	69	Red	$C_{26}H_{22}N_4O_2$ (422.47)	73.92 (73.96)	5.25 (5.24)	13.26 (13.28)
7a	160	84	Red	$C_{33}H_{26}IN_3O_2$ (623.48)	63.57 (63.58)	4.20 (4.19)	6.74 (6.75)
7b	180	92	Red	$C_{37}H_{28}IN_3O_2$ (673.54)	65.98 (66.01)	4.19 (4.22)	6.24 (6.21)
7c	165	85	Red	$C_{37}H_{28}IN_3O_2$ (673.54)	65.98 (65.96)	4.19 (4.21)	6.24 (6.25)
8a	127	88	Violet	$C_{33}H_{28}IN_5O_2$ (653.51)	60.65 (6.62)	4.32 (4.33)	10.72 (10.75)
8b	120	90	Red violet	$C_{37}H_{30}IN_5O_2$ (703.57)	63.16 (63.02)	4.30 (4.33)	9.95 (10.01)
8c	130	72	Red	$C_{37}H_{30}IN_5O_2$ (703.57)	63.16 (63.12)	4.30 (4.31)	9.95 (9.98)

Absorption and fluorescence spectroscopy: The electronic visible absorption and fluorescence spectra of the synthesized dyes were examined in 95% ethanol and recorded using 1cm Qz cell by using 10^{-4} M concentration of the dye.

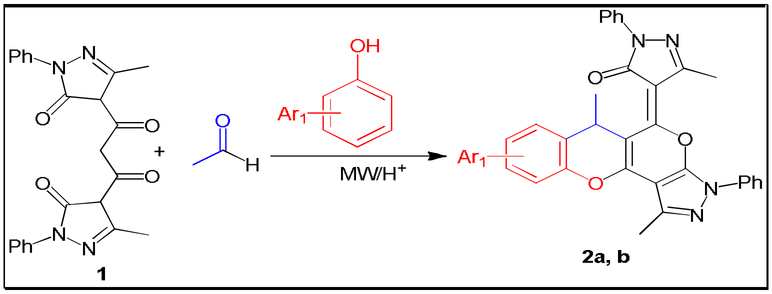
Spectral behavior in aqueous universal buffer solutions: The stock solution of the dye was of the order 10^{-3} M. An accurate volume of the stock solution was added to 5 ml of the buffer solution in 10 mL measuring flask, then completed to the mark with redistilled water. The pH of such solution was checked then the electronic absorption spectra of the dyes in different pH solutions were recorded within a wavelength range (350-700 nm) using 1cm Qz cell.

RESULTS AND DISCUSSION

It is of interesting to attempt and throw some light on such synthesis and their physico-chemical studies. the purpose of the present investigation was to evaluate ecofriendly, simple, Highly efficient, high yielding and green technique for the synthesis of poly substituted chromeno pyrano [2,3-c]pyrazol, chromeno pyrano[2,3-c]pyrazole, benzo chromeno pyrano[2,3-c]pyrazol-di[H]-benzo[7,8]chromeno[4,3-e]indazole and pyrazolo pyrano[4,3-e] Indazole by using three component reaction procedure (one pot synthesis). The reactions were performed under solvent free condition by using microwave irradiation to achieve the green aspect of the process. The poly substituted chromeno pyrano [2,3-c] pyrazol, chromeno pyrano[2,3-c] pyrazole, benzo chromeno pyrano[2,3-c] pyrazole, di[H]-benzo[7,8]chromeno[4,3-e] indazole and pyrazolo pyrano[4,3-e] indazole moieties represents a main synthetic entities for the synthesis of heterocyclic cyanine dyes as a criterion of photosensitization effect with the hope to permit an improvement of synthetic routes suggesting the formation mechanistic pathways. Considering their spectral studies, the absorption spectra would extend the available range of long wavelength absorbing material depending on nature of heterocyclic residue, their linkage positions, and type of both substituents. The most traditional and promising approach is how to reach the goal and trend in order to systematize such dyes according to their quite different physico-chemical features and shed some light upon a possible color-chemical structure relationship in order to permit a criterion for their use as photosensitizes. There is a great interest in the synthesis of some new mono, zero and mero-methine cyanine dyes. One of the main bottlenecks to the development of such multi-property material is to pertain and search of new methodology including three components system reactions and in solvent-free microwave irradiation, the details are as follows:

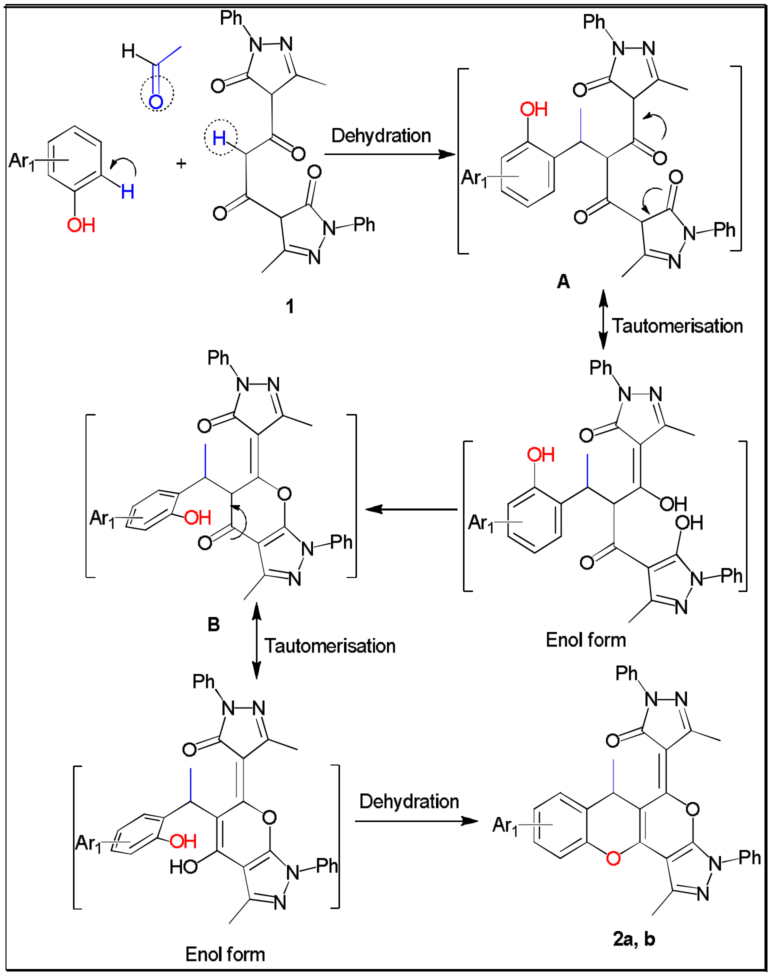
Synthesis

Bis monomethine cyanine dyes based on benzo chromeno [2',3':4,5]pyrano[2,3-c]pyrazole(4a-f): The precursor compounds substituted 4-(1,6-dimethyl-3-phenyl-chromeno[2',3':4,5]pyrano[2,3-c]pyrazol-5(6H)-ylidene)-3-methyl-1-phenyl-pyrazol-5(4H)-one **2a, b** were prepared by cyclo-condensation reaction of1, 3-bis(3-methyl-5-one-1-phenyl-4-hydro-pyrazol-4-yl) propane-1,3-dione**1**, 1-naphthol or 2-naphthol and acetaldehyde in concentrated sulfuric acid catalysis to afford**2a,b**respectively, **Scheme 1.**



Scheme 1: Synthetic routes of **2a, b**. Where**,** Ar_1=2,3-C_4H_4**(2a)**;Ar_1**=**3,4-C_4H_4**(2b)**

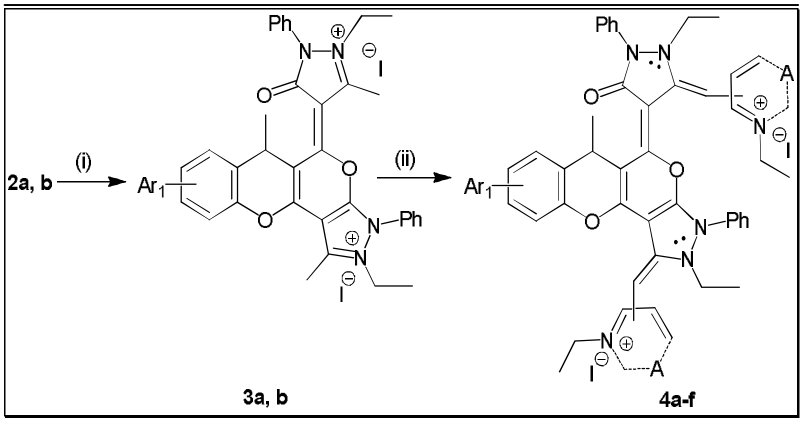
The formation of substituted 4-(1,6-dimethyl-3-phenyl-chromeno[2',3':4,5]pyrano[2,3-c]pyrazol-5(6H)-ylidene)-3-methyl-1-phenyl-pyrazol-5(4H)-one **2a, b** was suggested to proceed through loss of three water molecules in acidic medium. First dehydration involves removal hydrogen atom from active methylene group in compound **1**, other hydrogen atom from position 2 (1) in case of 1-naphthol (2-naphthol) and oxygen from acetaldehyde to form intermediate **A** followed by cyclo-condensation by dehydration of other water molecule from hydroxyl group in 1-naphthol (2-naphthol) and hydrogen from the enol in intermediate compound **A** to form intermediate **B** which dehydrate to form the target polycyclic compounds **2a, b**. Equation **1**.



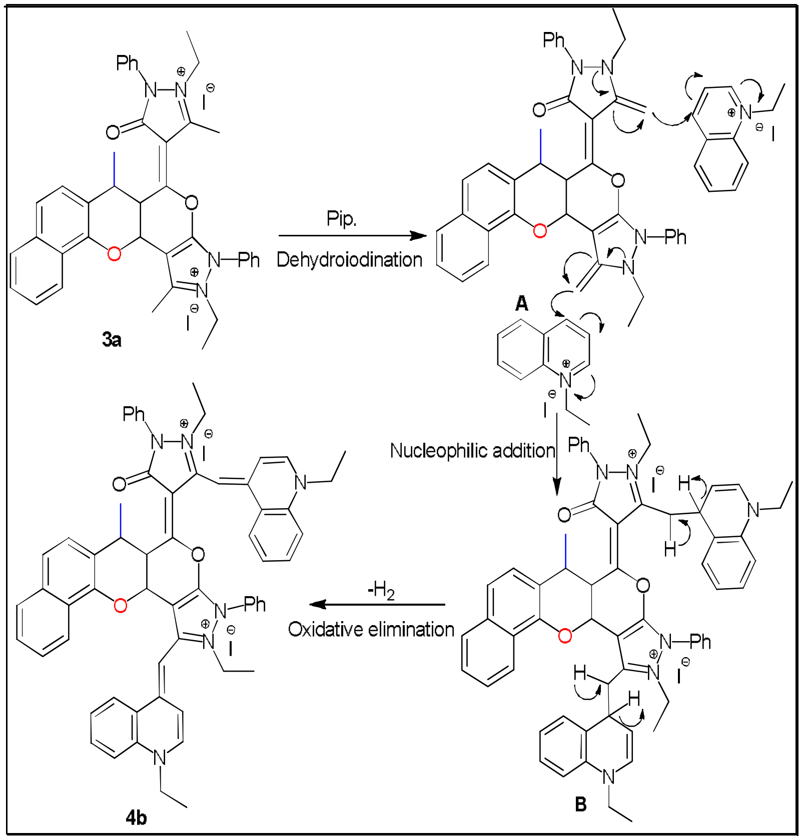
Equation 1. Suggested Formation Mechanism of **2a, b**

Compounds **2a, b** was irradiated in microwave oven with two mole of ethyl iodide to afford2-ethyl-5-(2-ethyl-3-methyl-5-oxo-1-phenyl-1H-pyrazol-2-ium-4(5H)-ylidene)-1,6-dimethyl-3-phenyl-5,6-di[H]-3H-chromeno[2',3':4,5]pyrano[2,3-c]pyrazol-2-ium iodide**3a, b** respectively. Finally, dehydrogenation reaction of quaternized salts **3a, b** in microwave oven by the reaction with2mole of active hydrogen quaternary salt such as pyridin[quinolin]-4(1)-ium-ethiodide saltsto affordsubstituted 2-ethyl-6-methyl-3-phenyl-chromeno[2',3':4,5]pyrano[2,3-c]pyrazol-5(6H)-ylidene)-1-ethyl-2-phenyl-pyrazolidin-3-one bis-4,5-mono[4(1)]methine- cyanine dyes **4a-f**, Scheme**2.**

The formation mechanism of 1-ethyl-4-(2-ethyl-1-mono-[4(1)]methine-6-methyl-3-phenyl-benzo [5,6'] chromeno[2',3':4,5]pyrano[2,3-c]pyrazol-5(6H)-ylidene)-5-mono-[4(1)]methine-2-phenylpyrazolidin-3-one cyanine dye**4b**was suggested to proceed through oxidative elimination following by dehydro halogenation processes under basic conditions. Thus, compound **3a**was easily lose a proton or changed into anhydro-base under piperidine catalyzed to form an intermediate nucleophile **A.** A nucleophilic addition reaction process would occur between an intermediate **A** and N-ethyl-heterocyclic-iodide salts in ethanol to form nucleophilic addition intermediate **B.** The later intermediate **B** undergoes oxidative elimination to give the desired dye **4b**, Equation**2.**



Scheme 2. Synthetic routes of dyes **4a-f.** Where,Ar$_1$=2, 3-C_4H_4**,** A=1-ethyl pyridin-4-ium salt **(a)**;Ar$_1$=2, 3-C_4H_4, A=1-ethyl-quinolin-4-ium salt **(b)**; Ar$_1$=2, 3-C_4H_4, A=2-ethyl-quinolin-1-ium salt **(c)**;Ar$_1$=3, 4-C_4H_4**,** A=1-ethyl pyridin-4-ium salt **(d)**;Ar$_1$=3, 4-C_4H_4,A=1-ethyl-quinolin-4-ium salt **(e)**; Ar$_1$=3, 4-C_4H_4,A=2-ethyl-quinolin-1-ium salt **(f)**;(i)Ethyl iodide (2mole), MW., 119 watts, 4 mins. (ii)=(pyridin[quinolin]-4(1)-ium-ethiodide salts), MW., 119 watts, 5mins. And Piperidine.



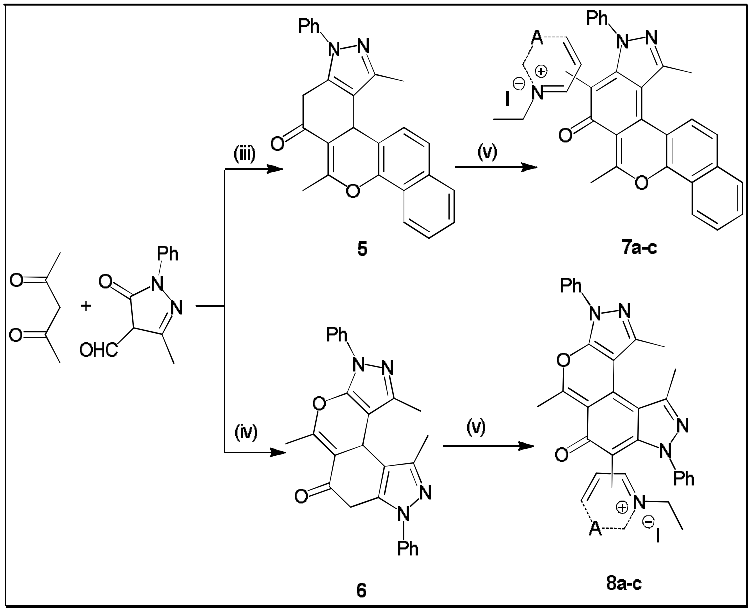
Equation 2. Suggested Formation Mechanism of **4b**

The structures of **1, 2a** and **(4a-f)** was confirmed by spectral data analysis IR, ^{1}H-NMR and mass. Thus, FT-IR (ν^{KBr} cm^{-1}) showed general absorption bands at: 3124 (CH aromatic), 2945 (CH stretch for CH_3), 1715 (C=O), 1503 (C=C aromatic), 1456 (C=N), 756 (phenyl substituent) for **(1)**;3067 (CH Aromatic), 2920 (CH stretch for CH_3), 1802 (C=O), 1498 (C=C aromatic), 1455 (C=N), 756 (phenyl substituent) for (**2a)**;3063(CH Aromatic), 2920 CH for alkyl (hetero cyclic quaternary salt), 1708 (C=O), 1594 (C=C aromatic), 1499 (C=N), 753 (phenyl substituent) for dye **(4a);** 3061(CH aromatic), 2976 (CH for alkyl heterocyclic quaternary salt), 1710 (C=O), 1595 (C=C aromatic), 1499 (C=N), 758 (phenyl substituent) for dye **(4b)**; 3061(CH aromatic), 2924 (CH for alkyl heterocyclic quaternary salt), 1699 (C=O), 1595 (C=C aromatic), 1499 (C=N), 754 (phenyl substituent) for dye **(4d);** 3067 (CH aromatic), 2930 (CH for alkyl heterocyclic quaternary salt), 1710 (C=O), 1595 (C=C aromatic), 1497 (C=N), 752 (phenyl substituent) for dye **4e** and 3070 (CH aromatic), 2924 (CH for alkyl heterocyclic quaternary salt), 1705 (C=O), 1596 (C=C aromatic), 1499 (C=N), 754 (phenyl substituent) for dye**(4f)**.^{1}H-NMR ($CDCl_3$, 500 MHz) spectra showed signals at δ 1.6 (S, 6H, 2CH_3-pyrazolo), 3.36 (S, 2H, CH for pyrazole), 3.62 (S, 2H, CH_2), 7.1-7.6 (m,10H, Aromatic) for **(1)**;signals at δ2.2 (S, 6H, 2CH_3-pyrazole), 3.4 (S, 3H, CH_3-pyrane), 7.1-7.8 (m,16H, Aromatic) for **(2a)**;signals at δ1.26 (S, 3H, CH_3-pyrane), 1.26-1.47 (t, 12H, 4CH_3), 2.15-2.39 (q, 6H,J=7 Hz, 3CH_2), 4.2 (q, 1H,J=8 Hz, CH-pyrane), 5.4 (S, 2H, 2=CH), 7-8.1 (m, 29H, Aromatic) for dye**(4b)**and signals at δ1.17 (S, 3H,CH_3-pyrane), 1.48-1.61 (t, 6H,J=15 Hz, 2CH_3-pyrazole), 1.96-2.15 (t, 6H,J=6.5 Hz, 2CH_3-quaternary salt), 2.79-2.91 (q, 6H,J=7 Hz, 3CH_2-pyrazole), 3.22-3.38 (q, 2H,J=7.5 Hz, CH_2 quaternary salt), 3.6 (S, 2H, 2=CH),4.2 (q, 1H,J=7.8 Hz, CH-pyrane), 7-8.1 (m, 24H, Aromatic) for dye **(4d)**.Mass spectra confirmed a molecular formula agree with a molecular ion peaks at m/z=415and base peak at m/z=77 for compound**(1)**;a molecular ion peaks at m/z=551 and base peak at m/z=77 for (**2a)**;a molecular ion peaks at m/z=1173and base peak at m/z=77for dye **(4b)**;a molecular ion peaks at m/z=1073 and base peak=77 for dye **(4d)**.

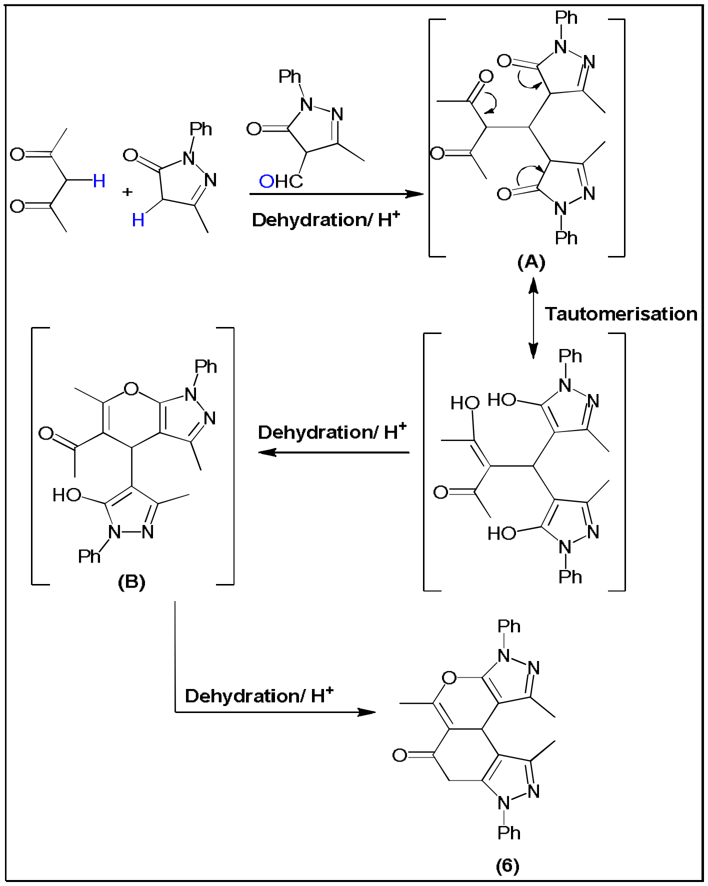
Zero methinecyanine dyes based on benzo [7,8] chromeno[4,3-e]indazole(7a-c) and pyrazoio [4',3':5,6]pyrano[4,3-e] indazole(8a-c): Direct cyclo-condensation reaction for three components system reaction in one pot step by removal of three water molecules between1-phenyl 3-methyl-4-formyl pyrazol-5-one, acetyl acetone and 1-naphthol or 4-H-3-methyl-1-phenyl-pyrazol-5-oneby 1:1:1 molar ratio in concentrated sulfuric acid catalysis in microwave oven at appropriate time at 119 watt under solvent-free conditions afforded 5,13-dimethyl-3-phenyl-3,5b-dihydrobenzo [7,8] chromeno [4,3-e]indazol-1(2H)-one **5**and 1,5,10-trimethyl-3,8-diphenyl-8,10b-dihydro-3H-pyrazolo [4',3':5,6] pyrano[4,3-e]indazol-6(7H)-one **6**respectively followed by the reaction of**5, 6** with active hydrogen compounds such as pyridine [quinolin]-4(1)-ium-ethiodide salts with active hydrogen quaternary salts such as pyridine [quinolin]-4(1)-ium-ethiodide salts under piperidine catalysis in microwave oven at appropriate time at 200 watt under solvent-free conditions afforded 5,13-dimethyl-3-phenyl-benzo [7,8]chromeno[4,3-e]indazol-1-one-2-zero-[4(1)]methine cyanine dyes **7a-c** and1,5,10-trimethyl-3,8-diphenyl-pyrazolo[4',3':5,6]pyrano[4,3-e]indazol-6-one-7-zero-[4(1)]methine cyanine dyes **8a-c**respectively, **Scheme 3.**

Formation of 1,5,10-trimethyl-3,8-diphenyl-8,10b-dihydro-3H-pyrazolo[4',3':5,6]pyrano[4,3-e] indazole-6(7H)-one **6** was suggested to proceed through loss of three water molecules in acidic medium. First dehydration involves removal hydrogen from active methylene group of 4-H-3-methyl-1-phenyl-5-one pyrazole, other hydrogen from active methylene group in acetyl acetone and oxygen form formyl group of 4-formyl-3-methyl-1-phenyl-5-oneform intermediate **(A)** followed by cyclo condensation by dehydration of other water molecule from the two hydroxyl group from Enol form of the intermediate **(A)** to form intermediate **(B)** followed by intramolecular dehydration of water molecule to form 1,5,10-trimethyl-3,8-diphenyl-8,10b-dihydro-3H-pyrazolo[4',3':5,6] pyrano[4,3-e]indazol-6(7H)-one **6, Equation (3).**

The structures of **5, 6, (7a-c)** and **(8a-c)** was confirmed by spectral data analysis IR, ^{1}H-NMR and mass. Thus, FT-IR (ν^{KBr} cm^{-1}) showed general absorption bands at: 2923 (CH for CH_3), 1708 (C=O), 1400-1700 (C=C aromatic), 1498 (C=N), 752 (phenyl substituent) for **(5)**;FT-IR γ (Cm^{-1}): 3067 (CH



Scheme 3. Synthetic routes for dyes **7a-c** and **8a-c**. Where, A = 1-ethyl pyridin-4-ium salt(**a**); 1-ethyl-quinolin-4-ium salt(**b**); 2-ethyl-quinolin-1-ium salt(**c**); (iii)1-naphthol,MW, 8 mins. and 13N sulfuric acid;(iv)4-H-3-methyl-1-phenyl-pyrazol-5-one, MW, 8 mins. and13N sulfuric acid and(v)(pyridine [quinolin]-4(1)-ium-ethiodide salts), MW, 10 min. and Piperidine.



Equation 3. Formation mechanism of **(6)**

aromatic), 2924 (CH of alkyl heterocyclic quaternary salt), 1712 (C=O), 1400-1700 (C=C aromatic), 1499 (C=N), 752 (phenyl substituent).for **(6);** 3061, (CH aromatic), 2966 (CH of heterocyclic quaternary salt), 2930 (CH of alkyl), 1710 (CO),1400-1600 (C=C aromatic), 1493 (C=N), 759 (phenyl substituent) for dye **(7b);** 3063 (CH aromatic), 2921 (CH of alkyl), 2856(CH of hetero cyclic quaternary salt), 1704 (C=O), 1400-1700 (C=C aromatic), 1491 (C=N), 752 (phenyl substituent) for dye **(8a)**; 3067 (CH aromatic), 2925 (CH of alkyl), 2853 (CH of heterocyclic quaternary salt), 1709 (C=O), 1400-1700 (C=C aromatic), 1498 (C=N), 756 (phenyl substituent) for dye **(8b)**; 3063 (CH aromatic), 2925 (CH of alkyl), 2854 (CH of hetero cyclic quaternary salt), 1707 (C=O), 1400-1700 (C=C aromatic), 1499 (C=N), 756 (phenyl substituent) for dye **(8c)**. ^{1}H-NMR ($CDCl_3$, 500 MHz) spectra showed signals at δ 1.99-2.26 (S, 6H, 2CH_3-Pyrazole), 2.33-2.47 (S,3H, CH_3-Pyrane), 3.42 (S, 2H, 2CH), 7.18-7.93 (m, 10H, Aromatic) for compound **(6);** signals atδ1.17 (S, 3H, CH_3-pyrazole), 2.38 (t, 3H, J=8 Hz,CH_3-Ethyl),2.53 (S, 3H, CH_3-Pyrane), 3.39 (S, 1H, CH), 3.78-3.98 (q, 2H,J=7.2 Hz, CH_2-Ethyl), 6.76-8.05 (m, 17H, Aromatic) for dye **(7b)**;signals at δ0.93 (S, 6H, 2CH_3-Pyrazole), 1.26-1.68 (t, 3H,J=7.4 Hz, CH_3), 2.14-2.23 (q, 2H, J=8 Hz CH_2), 4.6 (S, 1H, CH), 5.5 (S, 1H, CH pyrane), 7.1-8 (m, 16H, Aromatic) for dye **(8b)**.Mass spectra confirmed a molecular formula agree with a molecular ion peaks at m/z=395 and base peak at m/z=77 for **(5)**;a molecular ion peaks at m/z=422and base peak at m/z=77 for **(6)**;a molecular ion peaks at **m/z=**673and base peak at m/z=60for dye **(7b)**; a molecular ion peaks at m/z=707 and base peak=240 for dye **(8b)**.

Table 2. Summary of features for normalized absorption and emission spectra of compounds **4a-f**, **6, 7a-c** and **8a-c** in ($1x10^{-4}$ M) ethanol. Where, N (compound number), λ_{max} (maximum absorption wavelength), ε_{max} (Maximum molar extinction coefficient), E_{max}(maximum emission wavelength), I (intersection of absorption and emission spectra) and E_{0-0} (HOMO-LUMO gap).

Dye	**λ_{max} (nm)**	**ε_{max} ($10^4 cm^2 mol^{-1}$)**	**E_{max}(nm)**	**Stock shift (nm)**	**I (nm)**	**E_{0-0} (ev)**
4a	447	0.4138	565	118	542	2.28753
4b	524	0.8961	590	66	545	2.27494
	437	0.7902	-	-	-	-
4c	478	1.0388	549	71	518	2.39352
	367	0.7311	-	-	-	-
4d	449	0.3376	537	88	502	2.46980
4e	623	0.4577	661	38	642	1.93122
	524	1.0007	-	-	-	-
	412	0.7265	-	-	-	-
4f	457	1.0544	566	109	543	2.28332
5	429	0.3220	575	146	546	2.27077
7a	506	0.8813	564	58	543	2.28332
7b	445	1.3069	-	-	-	-
	527	0.8644	608	81	568	2.18282
7c	434	1.2975	-	-	-	-
	517	0.8637	579	62	551	2.25017
8a	441	0.4403	542	101	503	2.46489
8b	434	1.7831	596	162	535	2.31746
	$627_{(S)}$	0.1185	-	-	-	-
	347	1.0264	-	-	-	-
8c	487	0.5654	581	94	525	2.36160

Photo-physical properties (Spectral Characterizations)

Normalized absorption spectral behavior in ethanol: Substituted 2-ethyl-5-(2-ethyl-3-methyl-5-oxo-1-phenyl-1H-pyrazol-2-ium-4(5H)-ylidene)-3-phenyl-5,6-di[H]-3H-chromeno[2',3':4,5] pyrano [2,3-c]pyrazol-2-ium iodide-bis-1,6-mono[4(1)]methine cyanine dyes**(4a-f)**;5,13-dimethyl-3-phenyl-benzo[7,8]chromeno[4,3-e]indazol-1-one-2-zero[4(1)]methine cyanine dyes **(7a-c)**and1,5,10-trimethyl-3,8-diphenyl-pyrazolo[4',3':5,6]pyrano[4,3-e]indazol-6-one-7-zero[4(1)] methine cyanine dyes**(8a-c)**are highly colored compounds. Their color in ethanolic solution are ranging from reddish to intense violet, easily (partially) soluble in polar (non) organic solvents exhibiting colored solutions (red/violet) concomitant with slight or intense greenish-red fluorescence depending upon the solvent used. The absorption spectra of bis monomethine **(4a-f)** and zeromethine **(7a-c), (8a-c)**cyanine dyesin 95% ethanol showed absorption bands batho(hypso)chromically shifted depending upon the nature of heterocyclic quaternary residue A and their linkage position. Thus, the visible absorption maximum of dyes**(4b), (4e), (7b)** and **(8b)** are bathochromically shifted to those of dyes **(4a)**, **(4d)**, **(7a)** and **(8a)** by $\Delta\lambda_{max}$ = 73 nm, 174 nm, 87 nmand186nm respectively. This is due to the more extensive π-delocalization and extra conjugation in the quinoline ring. Additionally, changing the linkage position of [A = quinolin-4-ium ethiodide] in dyes **(4b), (4e), (7b)** and **(8b)** to the 1-ium analogue salt in **(4c), (4f), (7c)** and **(8c)** resulted in hypsochromic shift by $\Delta\lambda_{max}$ = 46 nm, 174nm, 15 nm, 140 nm respectively. This can be related to decreasing the length of conjugated π-delocalization in quinolin-1-ium in dyes(**4c), (4f), (7c)**and**(8c)** than those quinolin-4-ium analogous in dyes(**4b), (4e), (7b)** and **(8b)** respectively, table**[2]**.

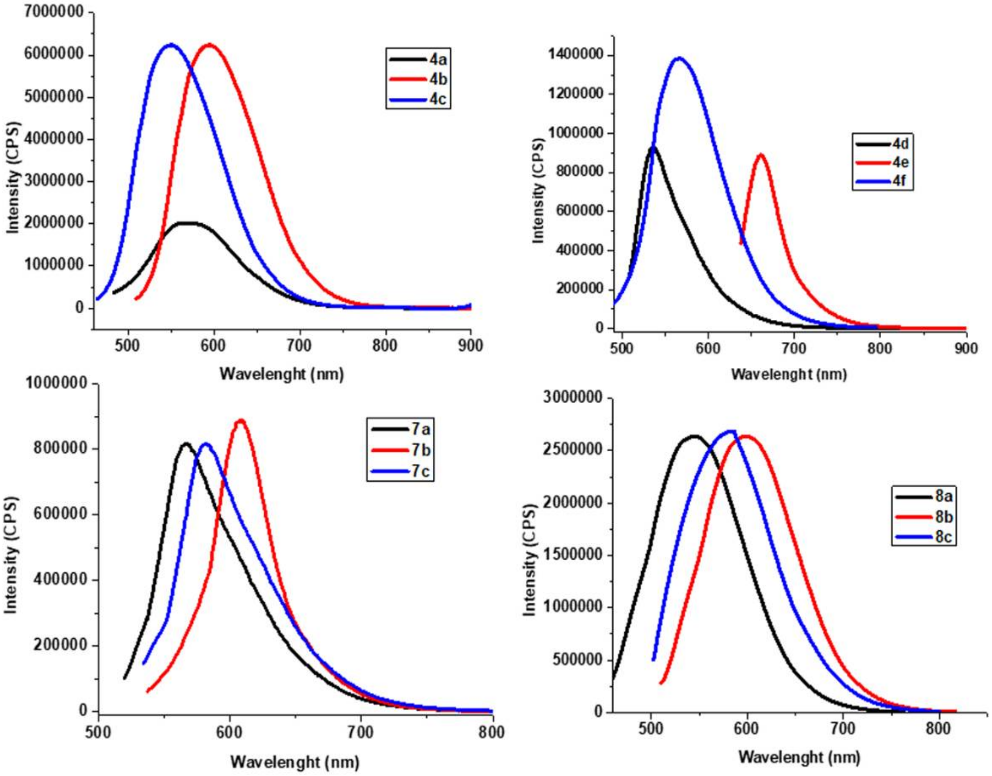
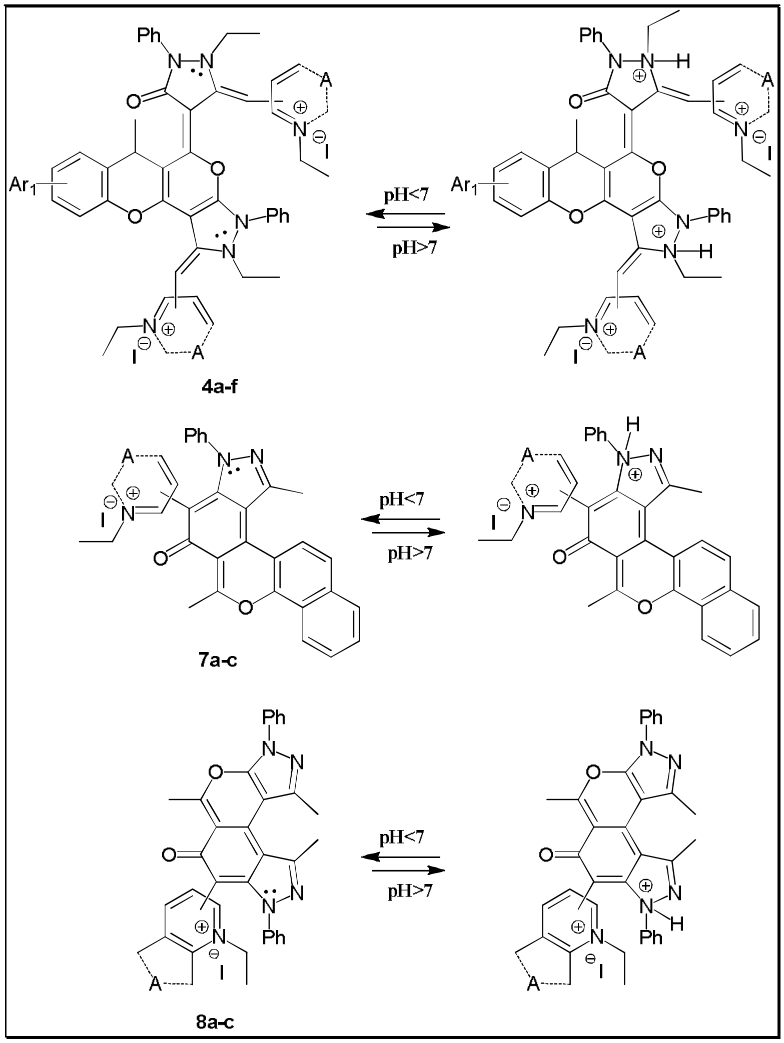


Figure 1. Emission and fluorescence spectra for dye **(4a-f)**, **(7a-c)** and **(8a-c)** in ethanol (1x10^{-4} M).

Table 3. Values of absorption (nm) and extinction coefficients (mol^{-1}cm^{-1}) of dyes **4b, 4c**, **4e**, **7b** and **8a**in aqueous universal

Comp	**Universal buffer**															
	2.5		4.5		5.5		7		8		9.3		10.6		11.9	
	λ_{max}	ε_{max}	λ_{max}	ε_{max}	λ_{max}	ε_{max}	λ_{max}	ε_{max}	λ_{max}	ε_{max}	λ_{max}	ε_{max}	λ_{max}	ε_{max}	λ_{max}	ε_{max}
4b	399	7926	400 514	8921 6588	401 516	9472 8347	407 517	7943 8194	404 519	10412 9150	404 525	10445 9084	410 536	10510 8921	410 539	10117 9183
4c	369	7052	386	10103	-	-	439	9307	-	-	442	8571	443	8907	444	8401
4e	380	5120	401 514	7833 7005	400 516	6399 6825	404 516 616	6849 7939 3080	403 524 621	8259 7579 3686	405 526 622	8136 8660 3236	408 533 626	8283 8710 3506	410 535 630	8136 8742 3727
7b	490	3873	497	4222	492	5228	499	4927	499	5031	500	5834	502	6184	512	6337
8a	400	11969	406	11062	407	11718	409	11920	418	11865	419	12521	431	12821	430	12674

Emission fluorescence spectra and excitation energy: The emission fluorescence spectra showed that the amount and wavelength of the emitted energy depend on both the fluorophore and the chemical environment of the fluorophore. The emission of the relaxed excited state relative to the ground state sometimes called the HOMO-LUMO gap was measured from the intersection of the normalized absorption and emission spectra of dyes**(4a-f), (7a-c)** and **(8a-c).**The emission spectra for the dyes were recorded in 95 % ethanol and the results are depicted in, Table 2., Fig.1. We noticed that, dyes **(4b), (4c), (4e), (4f), (7a, c)** and **(8a, c)** achieved lower excitation energy (E_{0-0}) and higher emission maxima compared to dyes **(4a)**, **(4d)**,**(7b)** and **(8b)** respectively. This change in the emission maxima and the excitation energy depend basically on the type of substituents and the nature of heterocyclic quaternary salt (A, B) which have a great effect on the number of π-conjugations in fluorophore.



Equaton 4. Protonation and deprotonation of dyes **(4a-f)**, **(7a-c)** and **(8a-c)** in acidic and basic mediums respectively.

Halochromic evaluation study: This is a useful study for the spectral behavior of cyanine dyes in different aqueous universal buffer solution to ensure optimal pH in the application of these dyes as photosensitizers and to evaluate the possibility of uses and/or applications of these dyes as indicators in acid/base titrations in analytical chemistry. The effect of the dyes as photosensitizers increases when they are present in the ionic form (non-protonated form) which has higher polarity and therefore more conjugation [23]. We noticed that, the absorption spectra of dyes **4b, 4c**, **4e**, **7b** and **8a** in aqueous universal buffer solution in different values of pH **(2.5**, **4.5**, **5.5**, **7**, **8**, **9.3**, **10.6**, **11.9)** showed hypsochromic shift (negative halochromism) in the acidic medium due to the protonation of the heterocyclic nitrogen atom of heterocyclic quaternary salts and other lone pair of electron of non-quaternate nitrogen atom of the donor part. In such cases the intramolecular charge transfer (CT) between the lone pair of heterocyclic donor nitrogen and the heterocyclic acceptor nitrogen atoms does not occur and the long wavelength CT band disappears as shown for dyes **4a-f**in equation **4**. A new short wavelength band is observed which could be assigned to a localized π–π* transition as well as showed bathochromic shift (positive halochromism) with increasing the pH due to that the protonated dyes become deprotonated and intern support the lone pairs of electrons of the heterocyclic ring system and increase its mobility for mesomeric interaction with the rest of the molecule becomes high and consequently the CT interaction with the free base is facilitated. The results are depicted in table3, Fig. **2 (a-d)**.

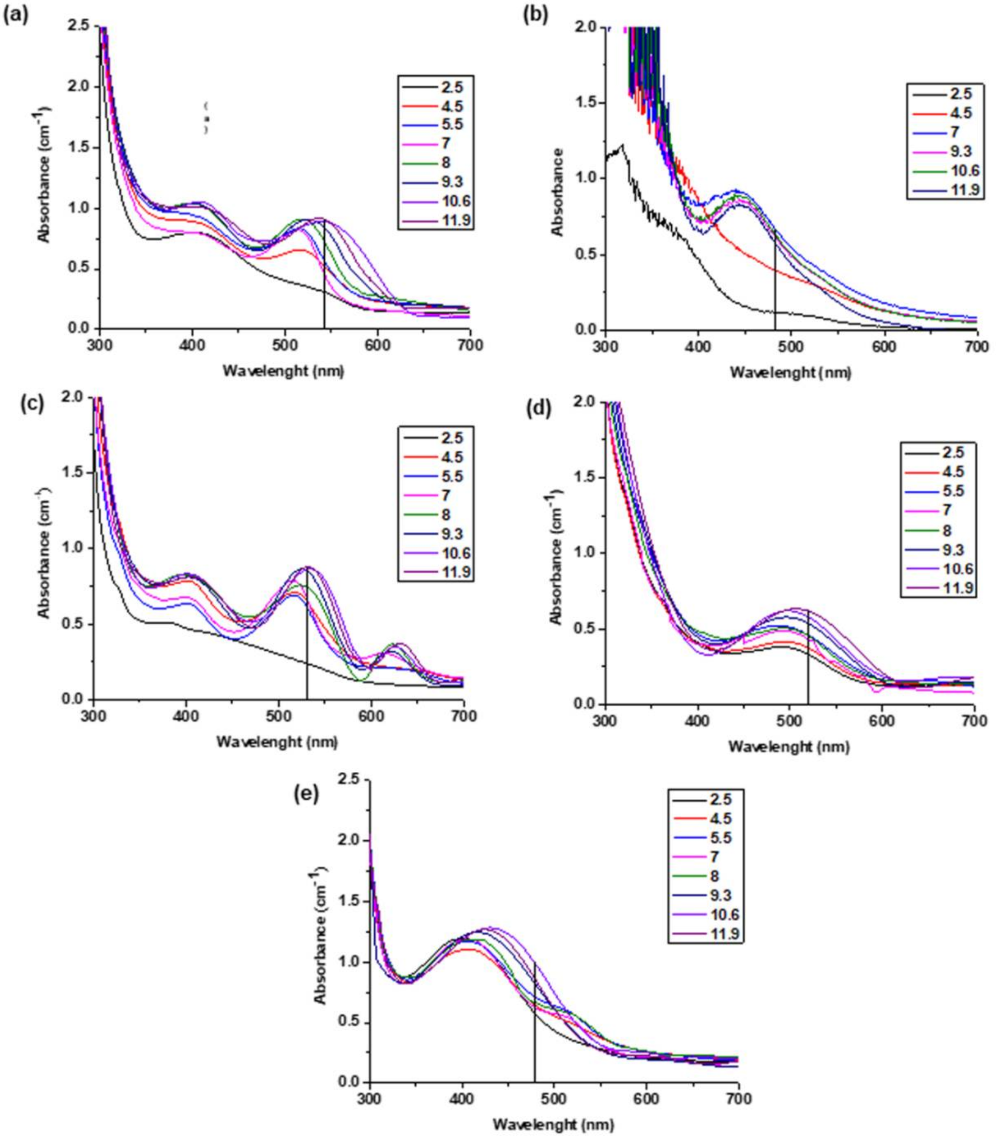
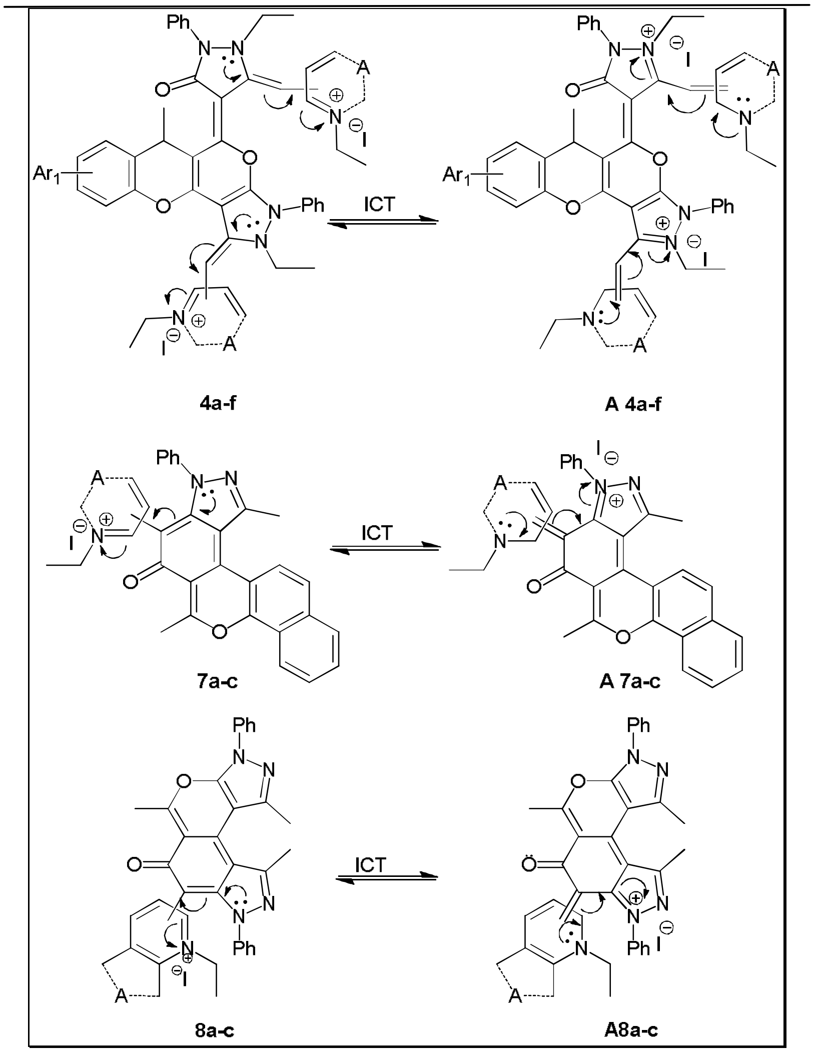


Figure 2. **(a-e).**UV-visible spectra of dyes**(4b), (4c), (4e), (7b)**and **(8a)** respectively in different aqueous universal buffer solutions

Table 4. The variation of absorbance in λ_{max} characteristic for each selected dye **4b, 4c**, **4e**, **7b** and **8a** in different universal buffer solutions

Dye	**Absorbance**				
λ_{max}	**4b**	**4c**	**4e**	**7b**	**8a**
pH	λ_{542}	λ_{483}	λ_{532}	λ_{520}	λ_{479}
2.5	0.3113	0.1163	0.5387	0.3354	0.5643
4.5	0.4244	0.3933	0.6517	0.3780	0.6424
5.5	0.4777	-	0.6162	0.4490	0.7134
7	0.5173	.6703	0.6801	0.4277	0.6211
8	0.7375	-	0.7440	0.4632	0.7063
9.3	0.844	0.6063	0.8505	0.5342	0.8199
10.6	0.8952	0.6276	0.8647	0.5839	0.9904
11.9	0.913	0.5744	0.8789	0.6195	0.8697
pK$_a$	7.7	8.2 10.1	7.6	4.8 8.9	4.9 9



Equation 5. Suggested Mesmeric CT for dyes **(4a-f)**, **(7a-c)**and **(8a-c)**

Acid dissociation (pk_a) determination: Several methods had been adopted for spectrophotometric estimation of the dissociation constants of weak acids [24] but the procedure which depend on plotting the absorbance at settled wavelength versus pH values had been used[25] and S-shaped curves were obtained. For all S-shaped curves, the horizontal portion to the left corresponded to the acidic form of the indicator while the upper portion to the right corresponded to the basic form. Since the pk_a value was defined as the pH value for which one half of the indicator (dye) is in the basic form and the other half in the acidic form. This point (pk_a value) was determined by the intersection of the S-curve with horizontal line midway between the left and right segments [26], table **[4]**.

APPLICATION

New heterocyclic moieties and related cyanine dyes have been developed by microwave irradiation to provide simple, efficient, high yield and convenient one pot techniques. Moreover, avoiding toxic organic solvent in the preparation of these dyes under MWI achieve the green aspect of the process (ecofriendly).

CONCLUSIONS

New heterocyclic moieties and related cyanine dyes have been developed by microwave irradiation to provide simple, efficient, high yield and convenient one pot techniques. Moreover, avoiding toxic organic solvent in the preparation of these dyes under MWI achieve the green aspect of the process (ecofriendly). The electronic visible absorption spectra of the synthesized cyanine dyes in 95% ethanol solution underwent to give bathochromic and/or hypsochromic shifted bands depending on the following factors:a) Increasing or decreasing л-delocalization conjugation in the dye molecule b) Presence of electron pushing or electron pulling groups c) Higher or lower planarity of the dye molecule. So, increasing number of charge transfers give better photosensitizers than those which have one conjugated charge transfer pathway as well decreasing HOMO-LUMO gap (E_{0-0}). We noticed that, changing the color of the synthesized dyes from acidic to basic medium give the opportunity of these dyes to be used as an indicator in analytical chemistry as well as the intensity of the color of the synthesized dyes is due to two suggested mesomeric structures producing a delocalized positive charge over the conjugated system as shown in, Equation **5**.

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