Heterocyclic Schiff Bases as Main Entity In Methine & Metal Complexes Cyanine Dyes Synthesis

A. I. M. Koraiem[1], M. M. Gommaa[2], H. A. El-Damarany[3], M. H. Yosry[4]

Chemistry Department, Aswan-faculty of Science, Aswan, Egypt

Abstract: *Heterocyclic Schiff bases (1a-g) was prepared and employed in the synthesis of substituted ketomethylene acyclic (cyclic) heterocyclic quaternary iodide salts and acyclic pyrazolo and/or cyclic substituted pyrrolo[5, 4-d] pyrazolin-mero-2(4), pyrrolo [5, 4-d] pyrazolo-zero-3[4(1)]methine and pyrrolo[5, 4-d] pyrazolo or pyrazol [4, 5-d] dioxine (thiazine/ oxazine) metal complex cyanine dyes (2a-d, 3A, B, 4a-d & 5a, b, 6A, B & 7a-c, 8a-c, 11a-d, 12, 13a-d, 14a, b & 17). The new synthesized cyanines and their metal chelator complex dyes were identified by elemental & spectral analyses, The absorption spectra and solvatochromic behaviours of the newly selected synthesised dyes was investigated in pure organic solvents, as well as in aqueous universal buffer solutions.*

Keywords: Heterocyclic ketomethylene, Schiff Bases iodide salts, cyanine dyes synthesis, spectral , Solvatochromic Behaviour and Acid-Base Properties

1. Graphical Abstract
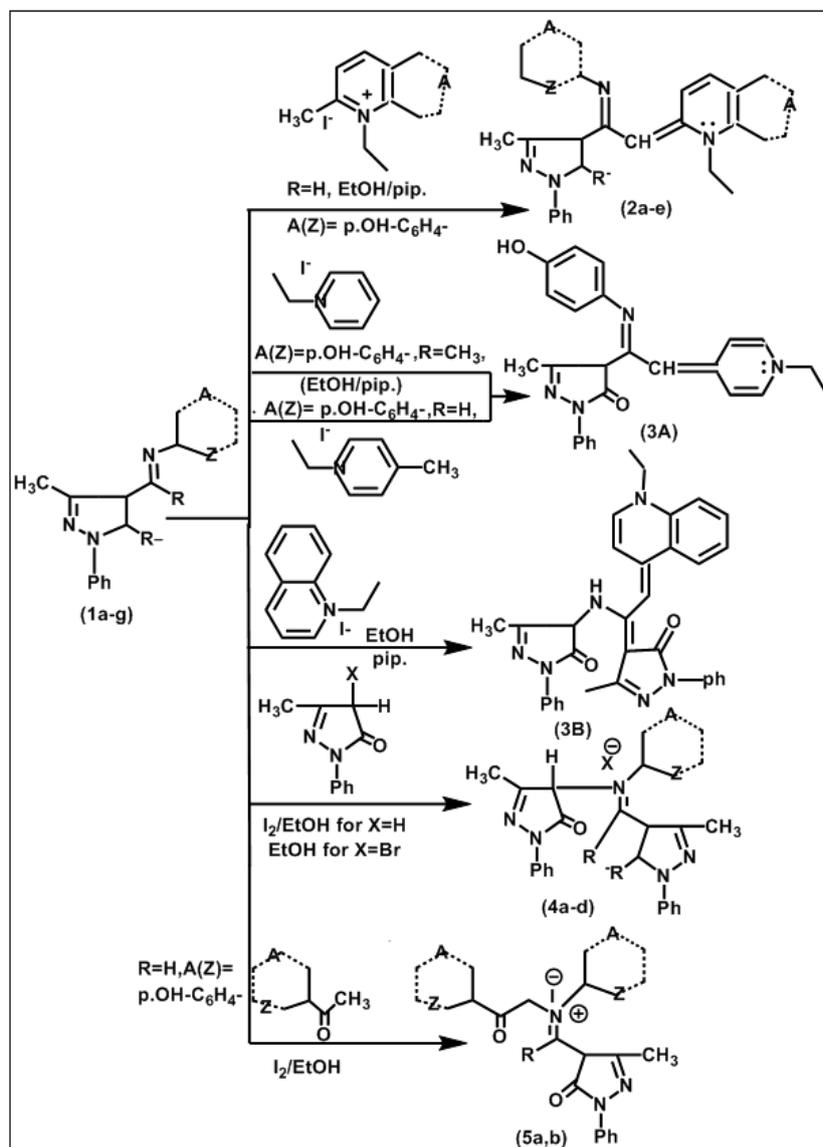
1. Introduction

Design molecular structure of cyanine dyes had attracted an increasing attention as materials for various purposes. They were used as photographic sensitizers [1, 2], colour photography [3] heat-developable photosensitizing materials [4]. Cyanine dyes were used in high speed recording CD [5], in preparation of optical filter dyes [6], in manufacturing of blue filter to laminate of an organic electroluminescent element, and colour filter showed highly pure light emission [7]. It was of interest to examine the reactivity of both acyclic (cyclic) ketomethylene heterocyclic Schiff bases quaternary iodide salts as main heterocyclic alternative precursors in cyanine dye synthesis with respect to their ring closure in order to systemize such dyes according to their quite different physico-chemical features. It was found that the formation of such dyes was sensitive to the reaction conditions and structure of the substrates. In this paper, we suggested the ring closure mechanism for reaction of both acyclic (cyclic) ketomethylene heterocyclic Schiff bases quaternary iodide salts based on the base catalysis and substituent effects.

2. Materials and Methods

All melting points are uncorrected. Elemental analysis IR, ^{1}H-NMR & & Mass spertra recorded with Perkin Elmer Infrared 127B , EM-390 90 MHz NMR & a Hp Ms 6988 spectrophotometers at the Micro analytical centre (cairo-University).The visible were recorded on UV-Visible recording spectrophotometer UV-240, and UV-160A. 3-Methyl-(5-Chloro-3-methyl)-1-phenyl pyrazolin-5-one-4-carboxaldehyde. 4-Acetyl -3-methyl-1-phenyl -pyrazolin-5-imino (one) & their substituted keto methylene heterocyclic quaternary iodide salts, 3-Methyl-1-phenyl-pyrazoline-5-one (Schiff) iso Schiffbases (1a-g), 3-methyl-1-phenyl-pyrazolin-5-one-4[α, β-unsaturated ketone] and 3-methyl-1-phenyl-pyrazolin-six membered chelated nucleus precursors 4-amino-3-methyl-1-phenyl-pyrazolin-5-one, 3-methyl-1-phenyl-pyrazolin-5-one-4-carboxylic acid (10a, b &15) were prepared in accordance to those cited prospective references [21-27].

3. Synthesis

3-Methyl-1-phenyl & 5-chloro-3-methyl-1-phenyl-pyrazolin-5-one-mero-4(1) [2 (4)] cyanine dyes (2a-d, 3A, B):
Ethanolic solution of acetyl (formyl) Schiff bases (1a-g) and pyridin(quinolin)-4(1)-ium /or 2(4)-Methyl-N-ethyl-pyridin(quinolin)-2(4)-ium ethiodide salts to which piperidine was added were refluxed for 3-5 h. The reaction mixtures were filtered hot, concentrated and cooled and acidified with acetic acid. The products (2a-d, 3A, B) after dilution with water were collected and recrystalised from aqueous ethanol. Table (1).

Substituted Acyclic Ketomethylene Heterocyclic Schiff Bases Quaternary Iodide salts (4a-d, 5a, b):

Route (A):
Ethanolic solution of Schiff bases (1a, g, 0.01 mol) and acetophenone; 4-acetyl-3-methyl-1-phenyl-pyrazolin-5-one and 3-methyl-1-phenyl-pyrazoline-5-one (0.01 mol) in the presence of Iodine was refluxed for 1-2 hours, The reaction mixtures were filtered hot, concentrated and cooled.The precipetated solids after dilution with water were collected and crystallized from aqueous ethanol to give (4a-d, 5a, b).

Route (B):
Ethanolic solution of Schiff bases (1a, g, 0.01 mol) and 4-bromo-3-methyl-1-phenyl-pyrazolin-5-one (0.01 mol) were refluxed for 1-2 hours, The reaction mixtures were filtered hot, concentrated and cooled The precipetated solids after dilution with water were collected and crystallized from aqueous ethanol to give the corresponding products (4a-d) The ethanolic solution of the products on triturating with solution of KI in water gave the same m.p. and mixed m.p. of the products obtained in Route (A).Table(2).

6-Methyl-4-phenyl-N-aryl-2(3-methyl-1-phenyl-pyrazolin-5-one)-pyrrolo[5, 4-d] pyrazolin- iodide salt (6A):
Compuond (4b) was fused in presence of few drops of piperidine for 10 minutes, cooled, dissolved in 30ml ethanol, refluxed for 3hr., The reaction mixtures were filtered hot, concentrated, coold and acidified with acetic acid. 6-Methyl-4-phenyl-N-aryl-2(3-methyl-1-phenyl-pyrazol-5-one)-pyrrolo [5, 4-d] pyrazolin-2-ium iodide salt (6A) was precipitated on dilution with water and crystallized from ethanol, Table (2).

3-Methyl-1-phenyl-pyrrolo[5, 4-d]pyrazol-mero-3[4(1)] cyanine dyes (6B):
Synthetic route of the anhydro base trasformation (6B) was prepared in a way similar to prospective reference [28]: A mixture of compound (6A, 10 m mol) and Na Ac 20 m mol and/or NaOH 40 m mol in ethanol 40 ml was heated to boiling. The colour changed to violet and a precipitate form was filtered and washed with water after cooling the reaction mixture. Table (2).

Pyrrolo[5, 4-d] pyrazol-zero-3[4(1)] methine cyanine dyes (7a-c)
Ethanolic solution of of (15A) and N-methyl (0.01 mol) were fused in presence of few drops of piperidine for 10 minutes, refluxed for 5 hr., The reaction mixtures were filtered hot, concentrated, coold and acidified with acetic acid. The precipetated solids after dilution with water were collected and crystallized from aqueous ethanol to give (7a-c), Table (2).

Substituted pyrrolo[5, 4-d] pyrazol-Metal chelator complex dyes (8a-c):
Ethanolic solution mixtures of (15A) and metal divalent chloride (Co, Ni, Cu) were refluxed for 2-3 h, The reaction mixtures were filtered hot, keeping over night, metal complexes mono methine cyanine dyes (8a-c) separated out, filtered and washed with ethanol followed by ether. Table (2).

3-Methyl-1-phenyl-pyrazolin-5-one- mero-4(4) cyanine dyes precursors (9a, b):

To an ethanolic solution of (2b) and N-methyl pyridin(quinolin)-4(1)-ium ethiodide salts (0.01 mol), piperidine (3-5 drops) was added. The reaction mixtures were refluxed for 2-3 h., filtered hot, concentrated and cooled and acidified with acetic acid. The precipetated solids after dilution with water were collected and crystallized from aqueous ethanol to give (9a, b) .

3-Methyl-1-phenyl -pyrazolin-5-one-metal chelator complex (10a, b):

Ethanolic solution mixtures of 3-methyl-1-phenyl pyrazolin-5-one-4-carboxaldehyde and/or 4-acetyl -3-methyl-1-phenyl -pyrazolin-5-one and metal divalent chloride (Co, Ni, Cu) were refluxed for 2-3 h, The reaction mixtures were filtered hot, keeping over night, metal complexes mono methine cyanine dyes (8a-c) separated out, filtered and washed with ethanol followed by ether. Table (1).

3-Methyl-1-phenyl-pyrazol[4, 5-d]dioxin-metal-complex cyanine dyes (11a-d)

An ethanolic solution of (9a, b) and metal divalent chloride (Co^{++}, Ni^{++}, Cu^{++}) in (1:1) ratios was refluxed for 2-3 hours, The reaction mixture was filtered hot, keeping over night, metal complexes mono methine cyanine dyes (11a-d) separated out, filtered and washed with ethanol followed by ether. Table (3)

3-Methyl-1-phenyl-pyrazol[4, 5-d]thiazin-metal-complex cyanine dye (12)

An ethanolic solution of (11a) and 1% Na_2S solution was refluxed for one hour, The reaction mixture was filtered hot, concentrated and cooled and acidified with acetic acid. The precipetated solids after dilution with water were collected and crystallized from aqueous ethanol to give (12).

3-Methyl-1-phenyl-pyrazol[4, 5-d]oxazin-metal-complex cyanine dyes (13a-d &14a-b)

An ethanolic solution of (10a, b, 11a-e) and of p-OH anilline (0.01 mol) was refluxed for 2-3 hours, The reaction mixture was filtered hot and washed with ethanol to give dyes (13a-d &14a, b), Table (3)

3-Methyl-1-phenyl-pyrazol[4, 5-d]dioxin(thiazin/oxazin) metal-complex cyanine dye (16)

An ethanolic solution of (15) and metal divalent chloride (Co^{++}, Ni^{++}, Cu^{++}) in (1:1) ratios was refluxed for 2-3 hours, The reaction mixture was filtered hot, keeping over night, metal complexes mono methine cyanine dyes (16) separated out, filtered and washed with ethanol followed by ether. Table (3)

3-Methyl-1-phenyl-pyrazol[4, 5-d] oxazin-metal-complex cyanine dye (17)

An ethanolic solution of (16) and of p-OH anilline (0.01 mol) was refluxed for 2-3 hours, The reaction mixture was filtered hot and washed with ethanol, dyes (13a-d 14a, b & 17) separated out, Table (3)

Solvatochromic and acid base properties:

The organic solvents were used of spectroscopic grade which purified according to the recommended methods [29]

The absorption spectra of dyes in different organic solvents were recorded within the wavelength (350-700 nm) on 6405 UV/Visible recording spectrophotometer using 1cm cell. The stock solution of the dye was of the order 10^{-3} mol-dm^{-3}. Solutions of low molarities used in spectral measurements were obtained by accurate dilution.

1-Preparation of dyes solution:

1-Studying the effect of pure solvents in the UV and visible range: An accurate volume of the stock solution of the dyes were diluted to appropriate volume in order to obtain the required concentration. The spectra were recorded immediately after mixing in order to eliminate as much as possible the effect of time. 2-Studying the spectral behaviour in mixed solvents in the visible region: -An accurate volume of the stock solution (10^{-3} mol-dm^{-3} in ethanol) of the dyes were placed in10 ml measuring flask containing the required volume of ethanol, then completed to the mark with the other solvent. 3-Studying the spectral behaviour in aqueous universal buffer solutions:-An accurate volume of the stock solution was added to 5ml of the buffer solution in 10 ml measuring flask, then completed to the mark with redistilled water. The pH of such solution was checked before spectral measurements.

II- Preparation of universal buffer solutions:

A modified buffer series derived from [30] was prepared. The constituents are as follows: (a) A solution of 0.4 mol-dm^{-3} of each of phosphoric and acetic acid was prepared by accurate dilution of A. R. concentrated stock. (b) A solution of 0.4 mol-dm^{-3} of boric acid was obtaind by dissolving the appropriate weight of the recrystallized acid in redistilled water.(c) A stock acid mixture was prepared by mixing equal volumes of three acids in large bottle.The total molarity of the acid was thus maintained at 0.4 mol-dm^{-3}. A series of buffer solutions with pH values ranging from (1.98-12.12) was prepared as recommended by [30]. This was done by mixing 150 ml of the acid mixtures in a 250 ml measuring flask with the appropriat volumes of 1.0 mol-dm^{-3} NaOH and completed to the mark with redistilled water. This modification was performed in order to keep the ionic strength constant at all pH's mixed with different proportions of organic solvents used. The pH's of the buffer solutions were checked using Orion pH-meter model (60, A), accurate to ± 0.005 pH units, at 25 ^{0}C

4. Results and Discussions

Piperidine catalysis of 3-methyl-1-phenyl-pyrazolin-5-one Schiff (Isoschiff) bases (1a-g) and 2(4)-methyl-N-ethyl-pyridin(quinolin)-4(1)-ium salts analogous, in equimolar ratios, achieved 3-methyl-1-phenyl and/or 5-chloro-3-methyl-1-phenyl-pyrazolin-5-one mero-4(1)[2(4)] cyanine dyes (2a-d & 3A, B). The formation of 3-methyl-1-phenyl-pyrazolin-5-one mero-4(1)[2(4)] cyanine dye (3A) was chemically confirmed by the interaction of (1d), (R=CH_3, A(Z)=p-OH-C_4H_4) and pyridin-4-ium iodide salt under the same conditions to give the same m.p. & mixed m.p. as obtained in the former reactions.. The interaction of Schiff bases (1a, f) with 3-methyl-1-phenyl-pyrazolin-5-one and/or acetophenone; 4-acetyl-3-methyl-1-phenyl-pyrazolin-5-one in the presence of Iodine (Route-a) and/or with 4-bromo-3-methyl-1-phenyl-pyrazolin-5-one, in equimolar proportions,

in ethamol (Route-b) gave substituted acyclic (cyclic) ketomethylene heterocyclic Schiff bases quaternary iodide salts (4a-c & 5a, b). The products (X=Br) on triturating with solution of KI in water gave the same m.p. and mixed m.p.as obtained in Route (a), Scheme (1A) The formation of mero-4(1) [2(4)] cyanine dyes was suggested to proceed through Route a where the liberation of acyclic methylene base (4a-d & 7) under piperidine catalysis, followed by approaching via nucleophilicity character to the heterocyclic Schiff bases (Equation 1) or Route b where the liberation of acyclic methylene base of pyridin-4-ium-iodide salt under piperidine catalysis, followed by approaching via nucleophilicity character to the heterocyclic quaternary salt (Equation 1) followed by the oxidative elimination step through dehydrogenation and dehydroiodination. Piperidine catalyzed of acyclic ketomethylene heterocyclic Schiff base quaternary iodide salts (4b) gave 6-methyl-4-phenyl-N-aryl-2(3-methyl-1-phenyl-pyrazol-5-one)-pyrrolo-[5, 4-d] pyrazolin-2-ium- iodide salt (6A) The later compound was trasformed into an anhydro base (6B) using NaAc and/or NaOH in ethanol [7]. The colour changed to violet and their ethanolic solution on triturating with solution of KI in water gave no iodine vapour in warming with conc.sulfuric acid to give 3-Methyl-1-phenyl-substituted pyrrolo[5, 4-d] pyrazolin-mero-3[4(1)] cyanine dye (6B). The formation of 3-methyl-1-phenyl-pyrrolo[5, 4-d]pyrazol-mero-cyanine (6B) was suggested to proceed in accordance to those described in prospective reference [8] via firstly the liberation of the methylene base (A) of an acyclic heterocyclic quaternary salt (4b) under the effect of basic catalyst through dehydroiodination process. Such methylene base (A) expressed a higher nucleophilic character and the nucleophilic attack proceeded stronger & faster on the electron deficient of pyrazolin-5-one carbonyl Sp^2 carbon atom to form an intermediate (B) which abstract a proton from the BH^+ to form the latter intermediate (C). Such later intermediate (C) undergoes dehydration process to form the desired merocyanine (6B).The formation of (6B) was suggested also to proceed via dehydration ring closer, as a reactive methyl group in (4b) readily lose proton to give a methylene base intermediate (A). In general, a methylene base will liberated from the cation more readily due to the lower basicity of the nuclei in an acyclic quaternary Schiff base (4b) under reaction condition. The latter formed anhydro base is considered as a good nucleophilic reagent and when approached pyrazol-5-one carbonyl carbon deficiency resulted in an intermediate compound (B) which abstract a proton, then undergoes dehydrogenation process to form desired mero cyanine dye (15) Equation (2), Interaction of (6A, B) and 1-ethyl pyridin (quinolin)-4(1)-ium iodide salts , in equimolar ratio, under basic catalysis resulted in the formation of pyrrolo[5, 4-d] pyrazolin-zero-3[4(1)] methine cyanine dyes (7a-c). The reaction of (6A) with metal divalent chloride (Co^{++}, Ni^{++}, Cu^{++}) afforded metal chelator complex dyes (8a-c), Scheme (1B), Table (2). The formation of pyrrolo[5, 4-d] pyrazolin-zero-3[4(1)] methine cyanine dyes (7a-c) was suggested to proceed via nucleophilic addition reaction between active methylene group of (6A) and heterocyclic ring carbon of pyridin (quinolin)-ium ethiodide involving oxidative elimination followed by dehydrobromination (iodination) processes to afford desired dyes (7a-c). Our approaches in the synthesis of metal chelator complex dyes was started by synthesis of

3-methyl-1-phenyl-pyrazolin-5-one-4[α, β-unsaturated ketone] and 3-methyl-1-phenyl-pyrazolin-5-one-4(4) mero cyanine dyes and/or preparation of 3-methyl-1-phenyl-pyrazolo[4, 5-d] and 3-methyl-4-formyl-1-phenyl-pyrazolo[4, 5-d] oxazinium chloride salts (9a, b, 10a, b &15) as a new key raction intermediate precursors. Thus, reaction of (9a, b & 10a, b) with metal divalent chlorides (CuCl₂, NiCl₂, CoCl₂) in equimolar ratio, in absolute ethanol gave an intermediate compound from which on refluxing with ethanol achieved 3-methyl-1-phenyl-pyrazoline chelated nucleus (11a-c, 16). The formation of (11a-c) was chemically confirmed by direct interaction of (10b) and 1-ethyl-quinolin-4-ium iodide salt in , equimolar amount, under piperidine catalysis to afford the same m.p. and mixed m.p.as obtained in the former chelation process. On trituration of ethanolic solution of (11a) with Na₂S solution afforded 3-methyl-1-phenyl-pyrazolo[4, 5-d]thiazin- metal complex cyanine dyes (12). Direct interaction of (10a, b, 11&16) and p.hydroxy aniline in , equimolecular amount, under thermal basic conditions achieved metal chelator complex dyes (13a-d, 14a, b &17).On triturating of the later compounds with saturated solution of KI followed by dissolving of the resulted in conc. H₂SO₄ liberated iodine vapour on warming. This is a criterion for the presence of the chloride anion replaced by iodide analogous, Scheme (2), Tables (2, 3).

The structure of (2a-d & 3A, B, 4a-d, 5a, b, 6A, B , 7a-c, 8a-c , 9a, b, 10a, b, 11a-c, 12, 13a-d, 14a, b, 15, 16 &17) was characterized & identified by elemental & spectral data (IR, ¹HNMR & Mass spectra), Tables (1-4). [9-12]

3-Methyl-1-phenyl-pyrazolin-5-one-mero-4(1)[2(4)] & 5-chloro-3-methyl-1-phenyl- pyrazolin mero-substituted pyrrolo[5, 4-d] pyrazolin-mero-2(4)-, substituted pyrrolo [5, 4-d] pyrazol-zero-3[4(1)]methine, pyrrolo[5, 4-d] pyrazole metal chelator complex dyes heterocyclic metal complexes pyrazol[4, 5-d] dioxin (thiazin/ oxazin) metal complex cyanine dyes (2a-d, 3A, B, 5a, b, 6B, 7a-c, 11a-d, 12, 13a-d , 14a-b, 16, & 17) are easily soluble in polar organic solvents possess (dark brown to reddish brown)in colour. Their ethanolic solutions exhibited permanent coloured in basic media which reversibly discharged on acidification and in concentrated sulphuric acid from which iodine vapor was not liberated on warming. Table (2, 3).

The absorption spectra of (1e, d, f) in absolute ethanol showed absorption bands batho (hypso) chromically shifts depending upon the nature of acyclic R moieties. Thus, the absorption spectra of (1a) (R= H) showed absorption band located at $\lambda_{max,}$ 520 nm. ($\varepsilon_{max,}$ 1154 cm² mol⁻¹). Substituting of R = H by CH₃ group in (1d) causes hypsochromic shift of $\Delta \lambda$ = 40 nm. at λ_{max} 480 nm. ($\varepsilon_{max,}$ 2596 cm² mol⁻¹). The hypsochromic shift of absorption band in dye (1d) is due to the presence of methyl group acting as electron donating inductively effect .Substituting of C=O by C-Cl in dye (1e) causes hypsochromic shift of $\Delta \lambda$ = 10 nm. λ_{max} 510 nm. ($\varepsilon_{max,}$ 2237 cm² mol⁻¹). This is due to the presence of Cl atom which acts as electron-withdrawing atom. Substituting of aryl by heterocyclyl in dye (1d) causes bathochromic shift of $\Delta \lambda$ =10 nm. at λ_{max} 530 nm. ($\varepsilon_{max,}$ 2578 cm² mol⁻¹). The bathochromic shift of absorption band in dye (1d) is

due to an electron-donating character of heterocyclic ring and increasing π-delocalized conjugation.

The absorption spectra of (2a-d, 3A, B) in absolute ethanol showed absorption bands batho(hypsho) chromically shifts depending upon the nature of heterocyclic moieties A, their linkage position and the nature of the substituting in Schiff's bases. Thus, absorption maximum of dye (2a) [A = quinolin-4-ium ethiodide] showed λ_{max} at 515nm (ε_{max}, 18550 cm^2 mol^{-1}). Substituting of [A = pyridin-4-ium ethiodide] in dye (3A) resulted in hypshochromic shifted of $\Delta \lambda$ 25 nm, at λ_{max}= 490 nm (ε_{max}, 9230cm^2 mol^{-1}) for (3A). This is due to the more extensive π- delocalization and an extra conjugation in quinoline ring. Additionally, changing of the linkage position of pyridin-4-ium salt in dye (3A) to pyridin-1-ium analogue salt in dye (2d) causes hypshochromic shifted of $\Delta \lambda$ = 10 nm at λ_{max} 480 nm (ε_{max}, 5890 cm^2 mol^{-1}). This is due to an extended of π-delocalization within pyridin-4-ium ethiodide in dye (3A) rather than pyridin-1-ium linkage in dye (2d). On comparison between the absorption spectra of dye (2a & 2c), it was obvious that dye (2c) showed absorption band more bathochromic shifted by $\Delta \lambda$ = 15 nm λ_{max} 530 nm (ε_{max}, 27510 cm^2 mol^{-1}). relative to that band in dye (2a). This may be due to an electron withdrawing character of NO$_2$ in dye (2c). Also, changing of the linkage position of p-OH in dye (2a) to o-OH analogue in dye (2b) causes hypsochromic shifted of $\Delta \lambda$ = 5 nm λ_{max} 510 nm (ε_{max}, 20430 cm^2 mol^{-1}). This is due to an easer charge transfer from OH group to the nitrogen aza atom in dye (2b). On comparison between the absorption spectra of dye (2a, 3B), it was obvious that the later dye showed absorption band more bathochromic shifted $\Delta \lambda$ = 15 nm λ_{max} 530 nm (ε_{max}, 28340 cm^2 mol^{-1}) relative to that band in dye (2a). This may be due to an electron withdrawing character of oxo group in dye (3B) than those of chlorine atom in dye (2a). The absorption spectra of (4a-d, 5a, b) showed absorption bands batho (hypso)chromically shifted depending upon the nature of both 4 , 5-di-substituted aryl (heterocyclyl) moieties. Thus, the absorption spectra of (4a) (R= H) showed absorption band located at λ_{max}, 440 nm. (ε_{max}, 1940 cm^2 mol^{-1}). Substituting of R=H by CH$_3$ group in (4b) causes hypsochromic shifted of $\Delta \lambda$ = 40 nm. λ_{max}, 400 nm. (ε_{max}, 1830 cm^2 mol^{-1}). The hypsochromic shifted of absorption band in (4b) is due to the presence of methyl group acting as electron donating inductively effected .Substituting of 5-position C=O by C-Cl in (4d) causes bathochromic shifted of $\Delta \lambda$ = 20 nm. λ_{max} 460 nm. (ε_{max}, 2237cm^2 mol^{-1}). The bathochromic shift of absorption band in dye (4d) is due to the mesomeric effect of chloride atom. Substituting of aromatic by hetero- cyclic amine in (4c) causes bathochromic shifted of $\Delta \lambda$ = 10 nm. λ_{max}450 nm. (ε_{max}, 2154 cm^2 mol^{-1}). The bathochromic shift of absorption band in dye (4c) is due to the presence electron-withdrawing character of heterocyclic ring. Substituting pyrazolone ring in dye (4a) by phenyl ring in dye (5a) causes hypsochromic shift of $\Delta \lambda$ = 5 nm. λ_{max}435 nm. (ε_{max}, 1981 cm^2 mol^{-1}). The hypthochromic shift of absorption band in dye (5a) is due to the resonance effect of the phenyl ring. The absorption spectra of dyes (7a-c) in absolute ethanol showed absorption bands batho (hypsho) chromically shifted depending upon the nature of heterocyclic moieties A, and their linkage position. Thus, the absorption maximum of dye

(7b, A = quinolin-4-ium ethiodide] showed λ_{max}= 485 nm (ε_{max}, 4950 cm^2 mol^{-1}). Substituting [A = pyridin-4-ium ethiodide] in dye (7a) resulted in hypshochromic shift of $\Delta \lambda_{max}$ 15 nm, λ_{max} = 470 nm (ε_{max}, 3124 cm^2 mol^{-1}) for dye (7a). This is due to the more extensive π-delocalization and an extra conjugation in the quinoline ring. Additionally, changing of the linkage position of quinolin-4-ium salt in dye (7b) to quinolin-1-ium analogue in dye (7c) causes hypsochromic shifted of $\Delta \lambda$ = 8 nm λ_{max} = 477 nm (ε_{max} 2730 cm^2 mol^{-1}). This is due to an extened of π-delocalization within quinoline-4-ium ethiodide in dye (7b) rather than quinolin-1-ium linkage in dye (7c). The absorption spectra of (8a-c) in absolute ethanol showed absorption bands batho(hypso)- chromically shifted depending upon the nature of metal divalent ion. Thus, the absorption maximum of (8a), M = Cu^{+2} showed λ_{max} 490 nm (ε_{max}, 1703 cm^2 mol^{-1}). Substituting of metal divalent M = Cu^{+2} in dye (8a) by M = Co^{+2} / Ni^{+2} in dyes (8b, c) resulted in bathochromic shifted by $\Delta \lambda$ = 20(15)nm. This is due to the vacant orbital increasing gradually from Copper to Cobalt leading to an extensive π-conjugation. The absorption spectra of dyes (13a-d , 14a, b, 17,) showed absorption bands batho(hypso)-chromically shifted depending upon the nature of 4(5)-heterocyclic moieties A, phenyl ring, , R=H , CH$_3$) and nature of divalent metal. Thus, the visible absorption maximum of dye (13b) [A =quinolin-4-ium ethiodide] showed λ_{max} 530 nm (ε_{max}, 2792 cm^2 mol^{-1}). Substituting of [A = pyridin-4-ium ethiodide] in dye (13a) resulted in hypsochromic shifted of $\Delta \lambda_{max}$ 10 nm, λ_{max} =520m (ε_{max}, 2126 cm^2 mol^{-1}) for dye (13a). This is due to an extensive π-delocalization and an extra conjugation in quinoline ring. Additionally, changing of heterocyclic moiety in dye (13b) by phenyl ring (p-OH –C$_4$H$_4$) in dye (17) causes hypsochromic shifted of $\Delta \lambda$ = 30 nm λ_{max} 490 nm (ε_{max}, 2771 cm^2 mol^{-1}). This is due to the presence of electron-withdrawing character of phenyl ring in dye (17). On comparison of the absorption spectra of dyes (13b , 14b) , it was obvious that the later dye showed absorption band more hypsochromic shifted by $\Delta \lambda$ = 45 nm λ_{max} 485 nm (ε_{max}, 2474 cm^2 mol^{-1}) relative to that band of dye (13b). This may be due to the presence of methyl group acting as electron donating inductively effected. On comparison between the absorption spectra of dyes (14a, b) , it was obvious that (14a) dye showed absorption band more bathochromic shifted by $\Delta \lambda$ = 50 nm λ_{max} 520 nm (ε_{max}, 2518 cm^2 mol^{-1}) relative to that band of dye (14b). This may be due to the presence of electron-withdrawing character of hydrogen atom. Also, substituting of metal divalent M = Cu^{+2} in dye (13b) by M = Co^{+2} / Ni^{+2} in dyes (13c, d) resulted in bathochromic shifted by $\Delta \lambda$ = 15/ 10nm. This is due to the vacant orbital increasing gradually from Copper to Cobalt, leading to the more extensive π-conjugation. On comparison between the absorption spectra of dyes (11b, 12), it was obvious that dye (11b) showed absorption band more bathochromic shifted by $\Delta \lambda$ = 10 nm λ_{max} 460 nm (ε_{max}, 2168 cm^2 mol^{-1}) relative to that band of dye (12) λ_{max} 450 nm (ε_{max}, 2051cm^2 mol^{-1}). This may be due to the lower electronegativity of sulphur atom in dye (12) causing the more extensive of π-conjugation relative to the oxygen atom in dye (11b) characterized with more electron negativity. On comparison between the absorption spectra of dyes metal complexes and pyrazolo (4, 5-d) heterocyclic metal chelate mono-4[4(1)] methine (9a, b, 11a-d), it was found that these

dyes have λ_{max}. higher than dyes of 4-formyl (acetyl)-pyrazol-5-one chelated complexes and pyrazolo (4, 5-d) heterocycles metal chelate mono-4[4(1)] methine. This is due to the electron donation in dyes (9a, b , 11a-d) is from heterocyclic quaternary anhydro base moiety acting as electron source to heterocyclic metal chelator acting as electron sink (Tables 5-8).

The solvatochromic behaviour of (1a, 2a, 4a , 7b & 17) in the wavelength range 350-700 nm, have been studied in different organic solvents (H₂O, DMF, EtOH, acetone, CHCl₃, C₆H₆ and CCl₄) [13]. The colour changes of such dyes with solvents having different polarities are constructed with the intention to illustrate (λ_{max} and ε_{max}) values of the intramolecular charge transfer bands, Tables (5-7). These dyes are showed positive solvatochromism with increase solvent polarity, which depend on the structure and the type of dye. This indicates that the polar excited states of such dyes are stabilized by polarization interaction forces as the polarizability of the solvent is increased. This behaviour occurs as a result of electrostatic interactions of the distributed cationic charges with the dipoles of the solvated molecules which leads to formation of specific solvated forms of dyes Tables (5-7).The spectral behaviour of some selected cyanine dyes in mixed solvents of different polarities was studied to perform trace the possibility of the formation of a hydrogen-bonded solvated complex between the solute and solvent molecules & to prove whether the solvent shift in the spectra of these dyes in ethanol solutions is due to hydrogen- bonding or to more salvation effect. The complexes which are liable to form in solution are those of dyes capable of forming stable hydrogen bond between solute and solvent. The effect of addition of successively increasing amounts of polar solvents on the absorption spectra of cyanine dyes in solvent of low and high polarities is discussed. Thus, the absorption spectra of dye (2a, 1×10^{-4}) in EtOH containing varying amounts of water is shown. The increases proportion of water added give an increase in the dielectric constant of the medium and leads to an increase in the solute solvent hydrogen bonding. This type of oxygen n-electrons atom causes a blue shift of the CT band. Thus, on plotting the absorbance at λ_{max} nm versus the mole fraction of EtOH and water solvents reveals that the absorbance increases sharply as the mole fraction of EtOH increases up certain limit and then decreases accompanied with red shift in λ_{max}. On plotting the energy against the mole fraction of H₂O, a broken line with three segments is obtained. From this plotting, the energies in pure water are 58.61 k.cal.mole⁻¹ for dye (2a). The stability constant of the molecular complex which formed between the solute and EtOH molecules is calculated from the molarities of EtOH. The log k_f is ($k_f = 0.74$) for dye (2a) and the number of sovent molecules (n) of EtOH equal to one and $–\Delta G = 164.9$ k. cal. mol⁻¹ for dye (2a), Tables (5-7). The values of k_f, ΔG and n indicate that a 1:1 complex is formed.

The ethanolic solution of (1a, g, 2a, d, 4a, 7b & 17) gave a permanent colour in basic medium which is discharged on acidification. This promoted us to study their spectral behaviour in different aqueous universal buffer solution to ensure optimal pH in the application of these dyes as photosensitizers. The effectiveness of dyes as photosensitizers increases when they are present in the ionic

forms (non protonated form) which have higher planarity The absorption spectra of selected Schiff bases and their cyanine dyes (1a, 2a, 4a, 7b & 17) in aqueous universal buffer solution of different values pH (1.98-12.12) show regular changes with increasing pH of the medium especially in the n- $\pi\overset{*}{\circ}$ and CT bands. The spectral behaviour of (1a, g, 2a, 4a, 7b &17) in absolute ethanol and in aqueous universal buffer solution showed that such dyes absorbed green light at (λ_{max} range 520 , 515 nm, 500) nm, Such dyes in aqueous universal buffer solution reveal the absorbtion of violet light $\lambda_{max}= 410$ nm at pH =1.98 with hypsochromic shift in the absorption of blue-green light ($\lambda_{max} = 495$ nm at pH ≥ 7.0) relative to ethanol for heterocyclic schiff bases (1a, g), violet light ($\lambda_{max} = 420$ nm at pH ≥ 1.99) extended to the absorption of blue-green light ($\lambda_{max}= 490$ nm at pH ≥ 7.00), with hypsochromic shifts if compared with those obvious in ethanol for dye (2a) , blue light region ($\lambda_{max}= 440$ nm at pH ≥1.99), extended to blue green light region , ($\lambda_{max}= 480$ nm at pH ≥10.00) for dye (4a) , blue-green light ($\lambda_{max}= 485$ nm)., blue light ($\lambda_{max} = 460$ nm at pH ≥ 1.99) extended to the absorption of blue – green light ($\lambda_{max}= 490$ nm at pH ≥ 3.00), for dye (7b) & violet light ($\lambda_{max}= 435$ nm) and/or reveals absorption of violet light ($\lambda_{max}= 410$ nm at pH ≥ 1.99) extended to blue light ($\lambda_{max} = 460$ nm at pH ≥ 8.0) for dye (17).The hypsochromic colour change shifts at pH ≥ 1.98 is due to the protonation of the azomethine nitrogen atom is protected by acid medium. In such cases the intramolecular charge transfer (CT) between the azomethine donor nitrogen and the acceptor carbonyl oxgen atom does not occur and long wave length CT band disappears. A new short wave length is observed, which could be assigned to a localized π^{*}-π^{*} transition.. On the other hand, the resulted bathochromic shift as the pH of the medium increases is due to that the protonated dye becomes deprotonated and their mesomeric interaction with the rest of the molecule enhanced & becomes high and consequently the CT interaction with the free base is facilitated. The spectrophotometric determination of dissociation constants pK_a values of heterocyclic schiff bases and their dyes (1a, g, 2a, 4a, 7b &17) can be utilized through the variation of the absorbance with pH values Thus, the absorbance-pH curves are typical dissociation constant pK_a of dye was determinted from the variation of absorbance with pH using the spectrometric half- height limiting absorbance and collector methods . The results in Tables (8, 9) showed that the pKa values of dyes (1a)= 2.4, 7.6 & 10.4, (2a) = 4.2 & 8.5. , (4a) = 2.4 & 4.8, (7b), 3.6, 5.6 &10.8, (17)= 3.2 & 9. The presence of pyridin(quinolin)-2(4)-ium salts in a dye causes high planarity of dye molecule. It was suggested that, selected dyes might be more sensitive as photosensitizers in both acidic and basic mediums [14-20].

References

[1] K.Morimoto, ; T. Hioki, and Y.Yabuki, , Jpn. Kokai Tokkyo Koho JP (2000), 162, 729; C. A. (2000), 133, 4, 51111.

[2] E.Delaey; F.Vanlaar; D.Devos; A.Kamuhabwa; P. Jacobs, and P. J.De Witte , Photochem. Photoboil., (2000). 55(1), 27- 36

[3] J.Ito, and K.Miyazawa, , Eur. Pat. Appl. Ep, (2000), 1, 048, 976; C. A. 133, No. 24, 342415.

[4] K. Kato, and Y.Yabuki, , Jpn. Kokai Tokkyo Koho JP (2000), 221, 631; (2000), C. A. 133. 13, 185448.

[5] N.Satio, , Jpn. Kokai Tokkyo Koho JP 2000, 94, 834; (2000). C. A. 132, 19, 258222,

[6] T.Harada, ; T.Yamada; R.Suzuki, ; Y. Yabuki and J.Nishijaki, , PET Int. appl. WO (2000).23, 829; C. A. 132, No. 22, 200771

[7] R. Kobayashi, .; Y.Shiraishi, and T.Kawaguchi, , Jpn. Kokai Tokkyo Koho JP (2000), 309, 726; (2000), C. A. 133 No. 25, 357351.

[8] A. I. M. Koraiem, .; H. A. Shindy, and R. M.Abu El-Hamd, , Chem. Papers (2000), 54(2) 78-86, .

[9] L. J Bellamy, The infrared spectra of complex molecules, London: Methuen, (1962).

[10] T. J.Batterham, "^{1}HNMR spectra of simple heterocycles" Wiley New York, (1973).

[11] F.Sheinman, , Nuclar magnetic resonance of complex Molecules, (1970), 1.Braunschweig: Vieweg and Sohn GmbH, .

[12] Q. N. Porter, and J.Baldas, "Mass Spectrometry of Heterocyclic Compounds" Wiely, New York, (1971).

[13] R. C. Weast and M. J.Astle, , CRC Hand book of Chemistry and Physics, 61 st. Edn. (CRC press, Inc.) (1980-1981).56,

[14] M. R.Mahmoud, ; Z. H. Khalil and R. M.Issa, , Acta. Chim. Acad. Sci. Hung, (1975). 87(2), 121-5,

[15] I. M.Issa; R. M.Issa, ; M. S. El-Ezaby, and Y. Z.Ahmed, , Phys. Chem., (1969). 242, 169-75.

[16] I. M Issa; R. M.Issa, ; M. S. El-Ezaby and Y. Z.Ahmed, Phys. Chem., (1970).13, 1293-305.

[17] I.Bassiouni, M. Sc.Thesis Assiut University, (1960).

[18] J. C.Colleter, , Ann. Chim., (1960)5, 415-67.

[19] R.Foster, Molecular Association, 2nd ed., London, Academic Press, (1975).

[20] M.Mitewa, ; N.Mateeva; L.Antonov and T.Deligeorier, Dyes Pigments, (1995).27(3), 219-25.

[21] F. M.Abd El Latif; A. S. Maghraby and A. I. M.Koraiem, Jour. Chem. Soc. Pak. (1993), 15, (1).

[22] A. I. M.Koraiem, Dyes and Pigments, (1990).12, 77-96.

[23] S. K.Mohanty; R.Sridhar; Sy. Pad. S.Manava, ; Ra. O. Sundarr and A. S., Mittra, Indian J. Chem., (1977), 15b, 1146-1147.

[24] M. S Khaikin; I. I Levkoev and V. A Kukhtin, Zh. Organ. Khim., (1965), 1(1), 133-136, .

[25] M. S Khaikin; D. B.Shamil'skaya, ; I. I.Levkoev and V. A.Kukhtin, , Zh. Nauchn, I. Prikl. Fotogr. Kinematog. (1966), 4(1) 12-13.

[26] A. M. M. El-Kodey, M. Sc. Thesis, Aswan-Faculty of Science , ASWAN University, (2002).

[27] N. S.Salah El-Dean, M. Sc. Thesis, Aswan-Faculty of Science ASWAN University University, (1998).

[28] D. G.Krotkko; V.Fedotov, and A. I.Tolmache, Dyes and pigments, (2005), 65, 183-189,

[29] J. A. Reddick and W. B.Banger, Techiques of Chemistry, Organic Solvents (A Weiss Berger, ed.), 3rd ed. N. Y. Wiley (1970). 11; and Organkum, 9th ed. Berlin: DVW (1979).

[30] H.T.S.Britton, , Hydrogen Ions (Chapman and Hall), London, 4th edn., p. 313, 1952).
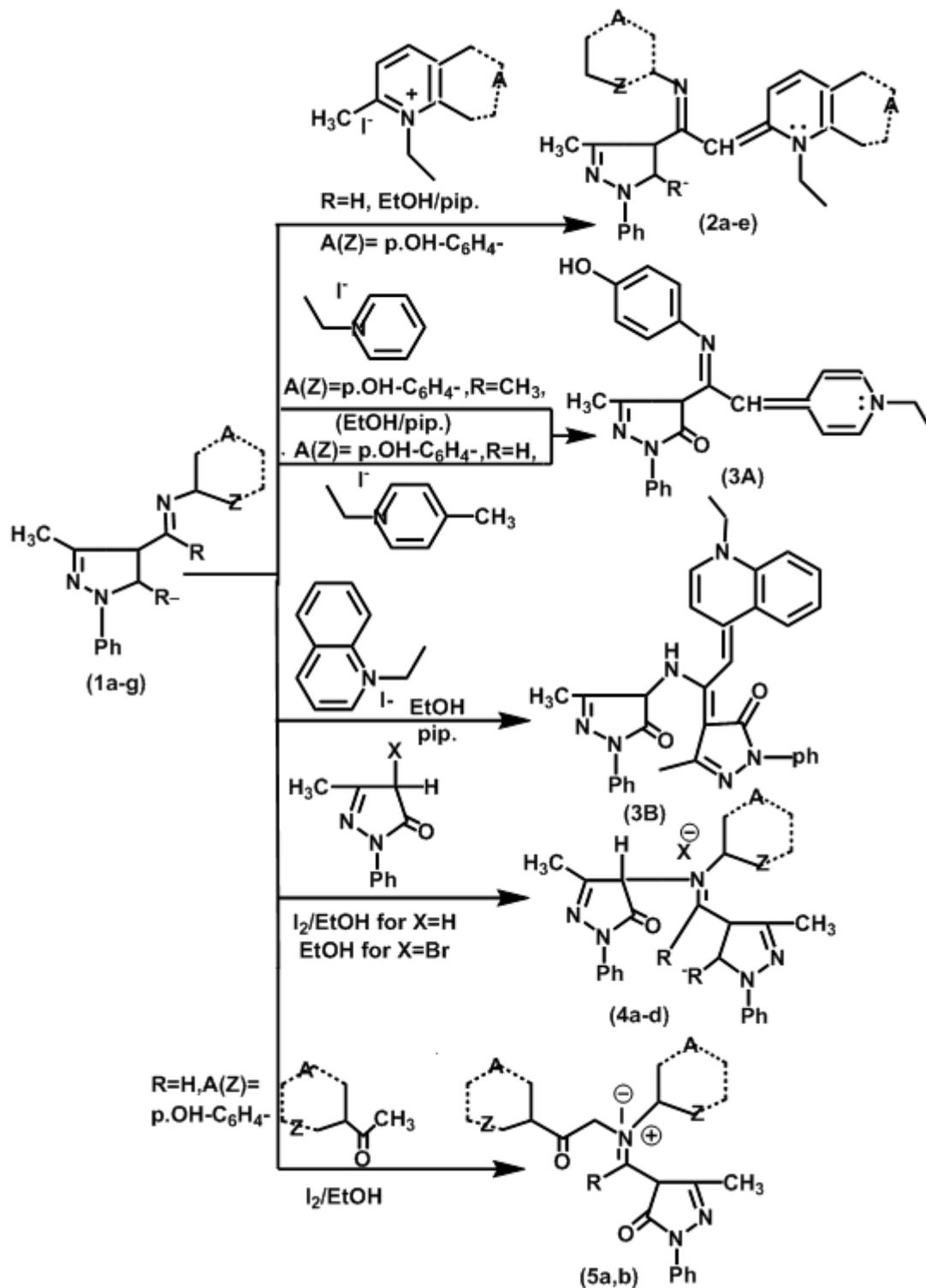
Scheme (1A)
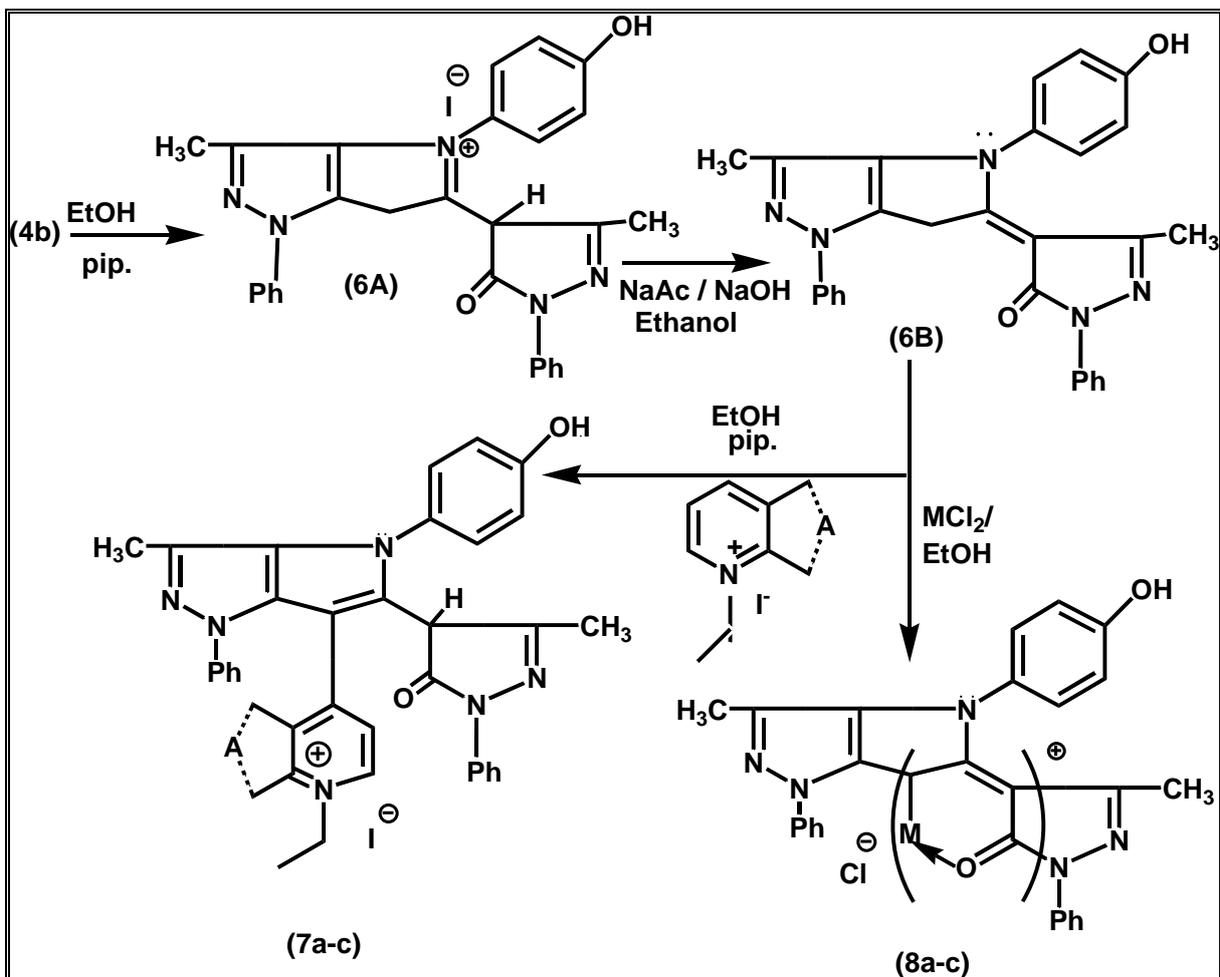
Scheme (1B)
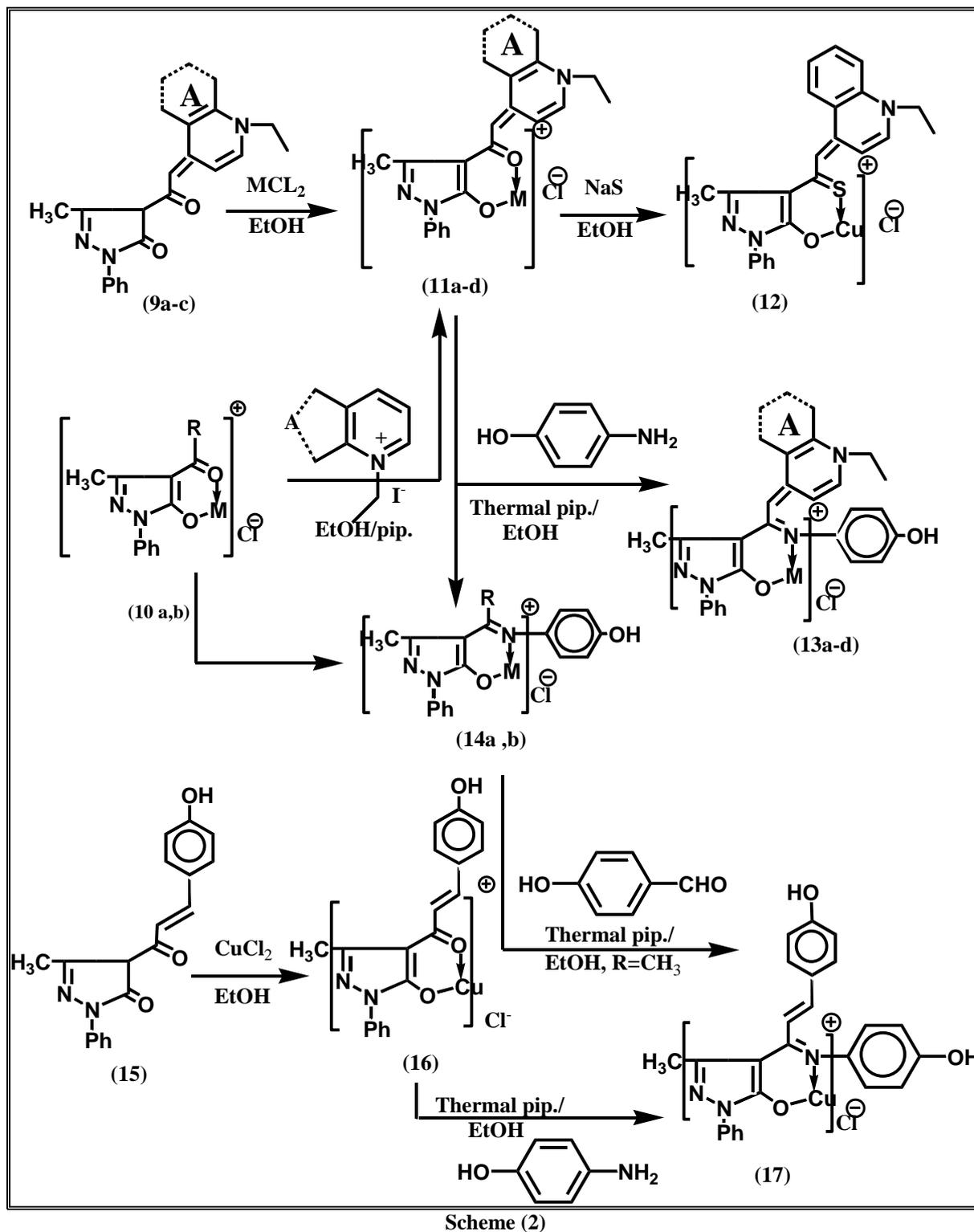
Scheme (2)

Scheme (1A, B & 2) Substituents:

(1a-g):A(Z)=p-OH-C_6H_4-, R(R⁻)=H(C=O)(a), A(Z)=o-OH-C_6H_4-, R(R⁻)=H(C=O).(b), A(Z)=p-NO_2-C_6H_4-, R(R⁻)=H(C=O).(c) A(Z)=p-OH-C_6H_4-, R(R⁻)=CH_3(C=O).(d), 3-methyl-1-phenyl-pyrazolin-5-one, R(R⁻)=H(C=O).(e), A(Z)=5-chloro-3-methyl-1-phenyl-pyrazole, R(R⁻)=H (Cl) (f). A(Z)=3-methyl-1-phenyl-pyrazoline, R=CH_3, R⁻=(C=O) (g). (2a-e) R=p-OH, A=C_6H_4-(a), R =o-OH- A=C_6H_4 (b), R =p-NO_2-A=C_6H_4-(c), R=p-OH, A=H(d), 5-chloro-3-methyl-1-phenyl-pyrazole A=C_6H_4, (e). (4a-d):A(Z)=p-OH-C_6H_4-R (R⁻)=H(C=O), X=I(a), A(Z)=p-OH-C_6H_4-R(R⁻)=CH_3(C=O), X=Br (b) A(Z)=3-methyl-1-phenyl-pyrazolin-5-one, R(R⁻)=H(C=O) X=I (c), 3-methyl-1-phenyl-pyrazolin-5-one, R(R⁻)=H(Cl) X=Br (d)., (5a, b): A(Z)= C_6H_5-R=H(a) A(Z)=3-methyl-1-phenyl-pyrazolin-5-one , R=H(b), (7a-d) R=p-OH, A=C_6H_4-(a), R=o-OH-A=C_6H_4 (b), R =p-NO_2- A=C_6H_4-(c), R=p-OH, A=H (8a, b): A(Z)=p-OH-C_6H_4-(a) A(Z)=3-methyl-1-phenyl-pyrazolin-5-one (b), (9a, b):N-Ethyl-pyridin-4-ium(a), N-Ethyl-quinolin-4-ium (b), N-Ethyl-quinolin-1-ium(c)., (10a, b):R=H, M=Cu^{+2} (a); R=CH_3, M=Cu^{+2} (b), (11a-d): A=H, M= Cu^{+2}(a), A=C_4H_4, M=Cu^{+2} (b); A=C_4H_4, Co^{+2} (c); A= C_4H_4, M =Ni^{+2}

(d). (**1**3a-d) : A=H, M=Cu^{+2}, (a), A=C$_4$H$_4$, M=Cu^{+2} (b); A=C$_4$H$_4$, Co^{+2}, (c); A=C$_4$H$_4$, M =Ni^{+2}, (d), (14a, b):R=H(a), R=CH$_3$ (b).

Equation 1

Equation2
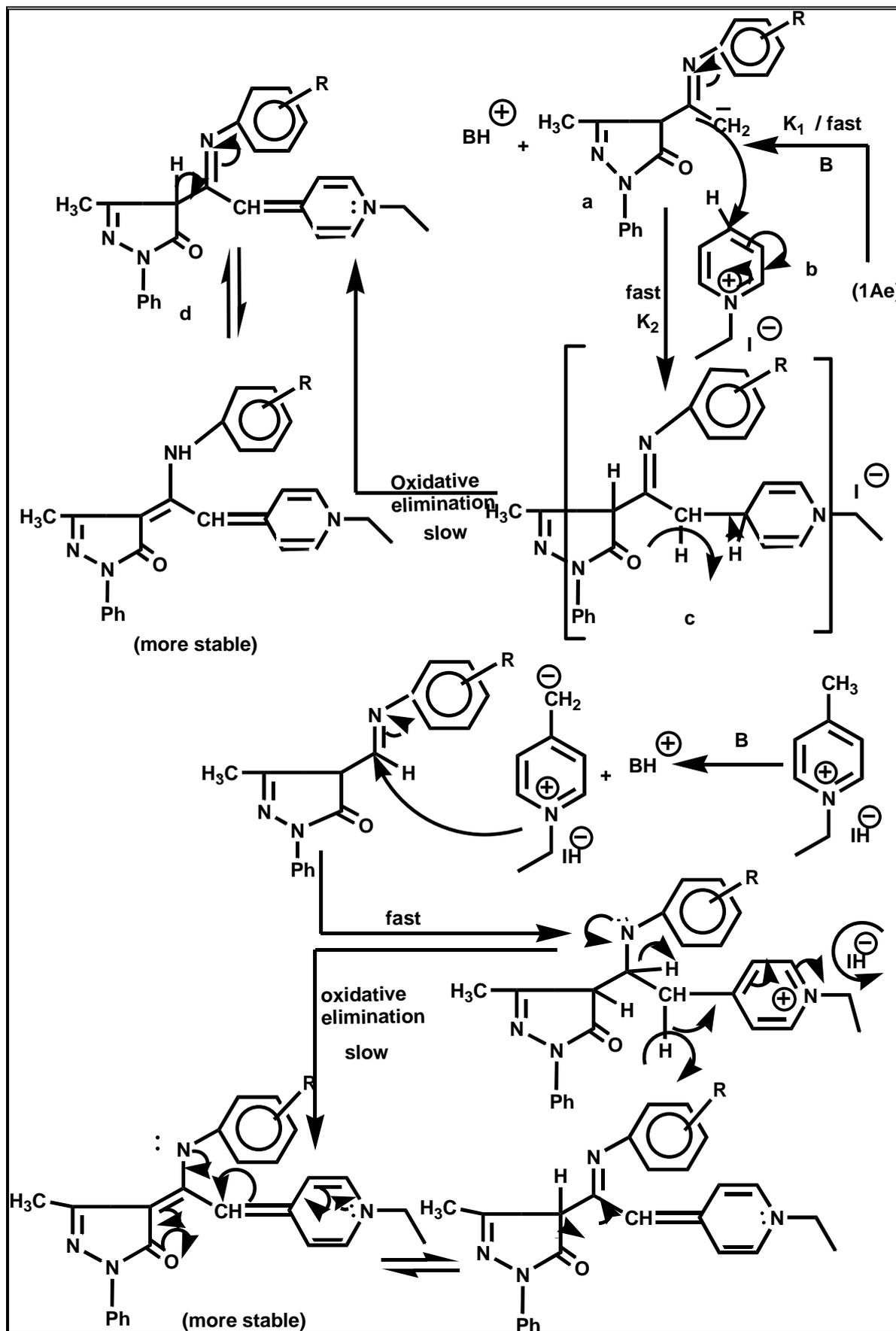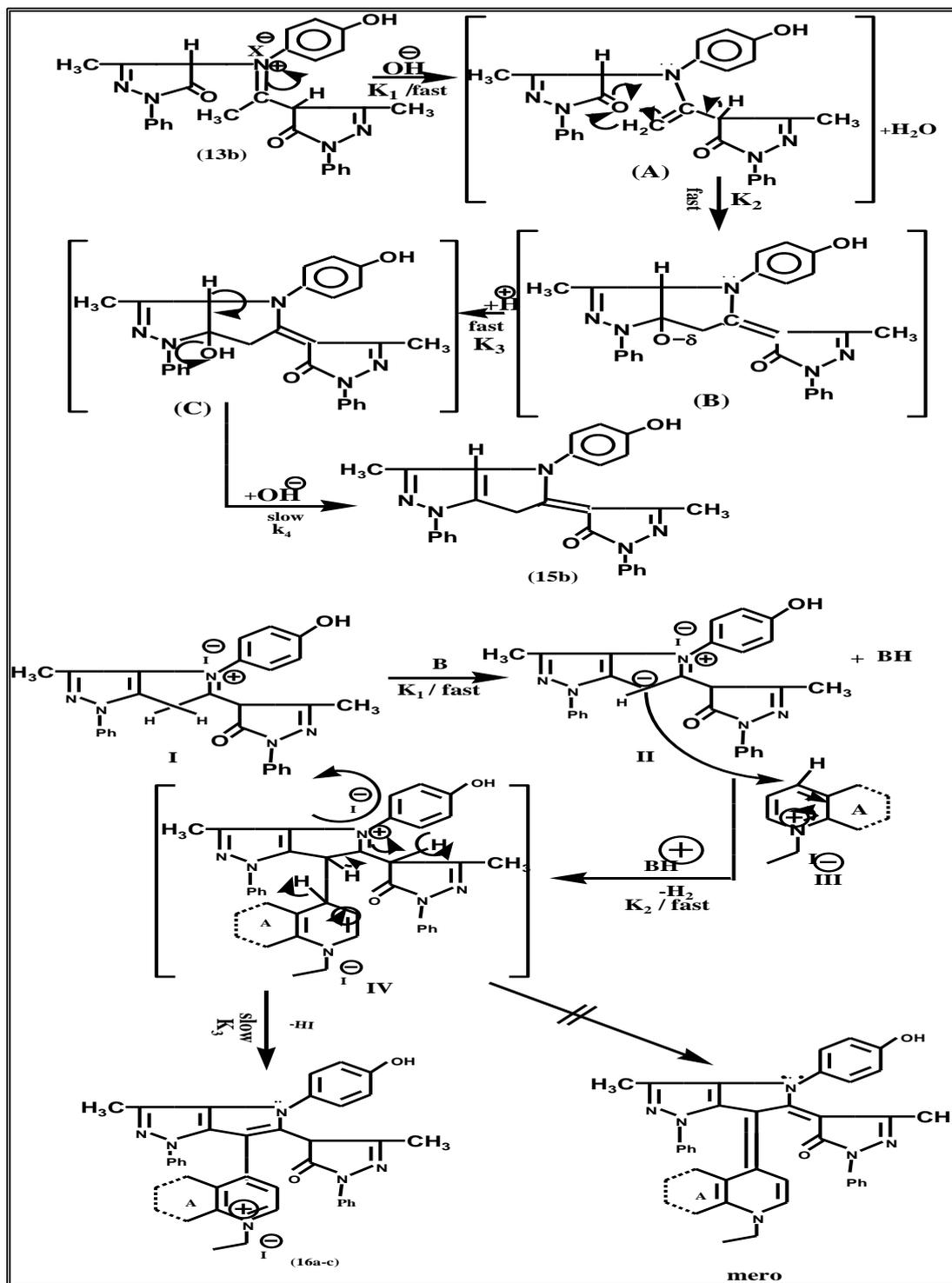
Table 1: Characterization data of (1d, e, g, 2a-d & 3A, B)

Comp. No.	M.P. ^{0}C	Yield %	Colour	Mol.Formula (Mol. wt)	% Calcd. (Found)			Absorption Spectra in Et-OH	
					C	H	N	λ_{max} (nm)	ε_{max} (cm^2 mol^{-1})
1d	120	74	orange	$C_{21}H_{19}N_5O_2$ (373)	67.6 (67.5)	5.09 (5.13)	18.99 (19.05)	530	2596
1e	270	65	brown	$C_{17}H_{15}N_3O_2$ (293)	69.6 (70)	5.11 (5.08)	14.33 (14.27)	520	2219
1g	120	72	light brown	$C_{18}H_{17}N_3O_2$ (307)	70.4 (70.45)	5.5 (5.48)	13.7 (13.77)	480	2237
2a	165	82	Red voilet	$C_{28}H_{24}N_4O_2$ (448)	(75.21) 75	(4.98) 5.36	(12.65) 12.5	515	18550
2b	138	77	Red voilet	$C_{28}H_{24}NO_2$ (448)	(75.28) 75	(5.41) 5.36	(12.82) 12.5	510	20430
2c	142	74	Red voilet	$C_{28}H_{23}N_5O_3$ (461)	(73.2) 72.89	(5.22) 4.99	(14.96) 15.18	530	27510
2d	142	50	Brown	$C_{24}H_{22}N_4O_2$ (398)	(71.89) 72.36	(6.1) 5.53	(14.25) 14.07	480	5890
3A	175	62	Brown red	$C_{24}H_{22}N_4O_2$ (398)	(72.2) 72.36	5.63 5.53	(14.34) 14.07	490	9230
3B	194	83	Red voilet	$C_{28}H_{23}N_4O_4Cl$ (466.5)	(71.8) 72.03	(4.89) 4.93	(11.86) 12	530	28340

Table 2: Characterization data of (4a, b, 5a, b, d, 6A, B, 7a-c & 8a-c)

Comp. No.	M.P. ^{0}C	Yield %	Colour	Mol.Formula (Mol. wt)	%Calcd.(Found)			Absorption Spectra in Et-OH	
					C	H	N	λ_{max} (nm)	ε_{max} (cm^{2}mol$^-$)
4a	140	77	brown	$C_{27}H_{24}N_5O_3I$ (593)	54.64 (55.01)	4.05 (4.26)	11.80 (12.03)	440	1940
4b	130	78	Red brown	$C_{28}H_{26}N_5O_3I$ (607)	55.35 (54.86)	4.28 (4.01)	11.53 (11.28)	400	1830
4c	165	68	Brown orange	$C_{31}H_{28}N_7O_3I$ (673)	55.27 (55.02)	4.60 (4.72)	14.56 (15.02)	450	2154
4d	142	73	brown	$C_{27}H_{23}N_5O_2ClI$ (611.5)	52.98 (52.28)	3.76 (3.56)	11.45 (11.56)	460	2250
5a	150	72	green	$C_{25}H_{21}N_3O_3I$ (538)	55.76 (56.04)	3.9 (4.13)	7.81 (8.05)	435	1981
5b	170	62	Light brown	$C_{29}H_{26}N_5O_4I$ (635)	54.8 (55.01)	4.09 (3.96)	11.02 (11.36)	440	2033
6A	140	55	Red brown	$C_{28}H_{24}N_5O_2I$ (589)	57.05 (57.01)	4.07 (4.1)	11.88 (11.82)	465	2340
6B	120	63	violet	$C_{28}H_{23}N_5O_2$ (461)	72.89 (73.13)	5.00 (4.96)	15.18 (15.72)	520	2532
7a	220	64	brown	$C_{34}H_{30}N_6IO_2$ (681)	59.91 (60.15)	4.41 (4.36)	12.33 (12.56)	470	3124
7b	240	62	Deep brown	$C_{38}H_{32}N_6IO_2$ (731)	62.38 (62.07)	4.38 (4.26)	11.49 (11.84)	485	4950
7c	230	58	brown	$C_{38}H_{32}N_6IO_2$ (731)	62.38 (62.13)	4.38 (4.40)	11.49 (11.05)	477	2730
8a	158	71	Deep brown	$C_{28}H_{23}N_5O_2CuCl$ (560)	60 (59.32)	4.11 (4.02)	12.5 (12.36)	490	1703
8b	175	63	brown	$C_{28}H_{23}N_5O_2COCl$ (555.43)	60.49 (59.87)	4.14 (4.36)	12.60 (13.02)	510	1553
8c	162	58	Reddish brown	$C_{28}H_{23}N_5O_2NiCl$ (555.19)	60.52 (61.02)	4.14 (4.18)	12.61 12.74	495	1523

Table 3: Characterization data of (9a, b, 11a-d , 12, 13a-d, 14a, b, 16, 17):

Comp. No.	M.P. ^{0}C	Yield %	Colour	Mol.Formula (Mol. wt)	%Calcd.(Found)			Absorption Spectra in Et-OH	
					C	H	N	λ_{max} (nm)	ε_{max} (cm^{2}mol$^-$)
9a	105	68	light brown	$C_{18}H_{17}N_3O_2$ (307)	69.87 (70.36)	5.36 (5.54)	13.85 (13.68)	430	645
9b	110	73	brown	$C_{23}H_{21}N_3O_2$ (371)	73.86 (73.95)	5.45 (5.32)	12.03 (11.76)	440	1962
11a	130	72	brown	$C_{18}H_{16}N_3O_2CuCl$ (405)	53.33 (53.96)	3.95 (3.85)	10.37 (10.25)	430	350
11b	150	68	brown	$C_{23}H_{20}N_3O_2CuCl$ (469)	58.02 (57.86)	3.96 (4.06)	9.23 (9.16)	460	2148
11c	110	38	brown	$C_{22}H_{18}N_3O_2CoCl$ (450.43)	58.61 (58.86)	4.00 (4.09)	9.32 (9.54)	480	1746
11d	120	41	brown	$C_{22}H_{18}N_3O_2 NiCl$ (450.19)	58.64 (59.2)	4.00 (3.69)	9.33 (9.45)	470	1709
12	115	64	Yellow brown	$C_{22}H_{18}N_3OSCuCl$ (471)	56.05 (55.67)	3.82 (4.14)	9.17 (9.53)	450	2091
13a	160	70	brown	$C_{24}H_{21}N4O_2CuCl$ (496)	58.06 (58)	4.23 (4.02)	11.29 (11.59)	520	2128
13b	160	61	Deep brown	$C_{29}H_{25}N4O_2CuCl$ (560)	61.54 (61.29)	4.21 (3.99)	10.26 (11.06)	530	2792
13c	100	52	Red voilet	$C_{28}H_{23}N4O_2CoCl$ (541.43)	62.06 (61.59)	4.25 (395)	10.34 (98)	545	2434
13d	120	43	Red voilet	$C_{28}H_{23}N4O_2NiCl$ (541.19)	62.09 (62.47)	4.25 (4.51)	10.35 (9.99)	540	2051
14a	300	52	Deep brown	$C_{17}H_{14}N_3O_2CuCl$ (391)	52.17 (51.85)	3.5 (3.41)	10.74 (11.03)	535	2518
14b	300	58	Red brown	$C_{18}H_{16}N3O_2CuCl$ (405)	53.33 (53.58)	3.95 (4.08)	10.37 10.28	485	2474
16	195	45	Yellow	$C_{19}H_{15}N_2O_3CuCl$ (418)	54.55 (55)	3.59 (3.28)	6.7 (7.05)	450	1.899
17	290	63	Light brown	$C_{25}H_{20}N_3O_3CuCl$ (509)	58.94 (59.14)	3.93 (4.12)	8.25 (8.52)	490	2771

Table 4: IR , ^{1}HNMR & Mass Spectral Data of some Selected Compounds (1d, 2a, 4b, 6A, 7a, 9b, 11b, 13b)

Comp No	IR υ KBr (cm^{-1})	^{1}HNMR (DMSO, 250 MHz) (ppm) & M. Sp. [M$^+$ (Base peak 100%)]	Comp No	IR υ KBr (cm^{-1})
1d	2336.7 (υ C=N) , 1620.4 (υ C=O) , 2922.8 (υ CH$_3$) , 757.9 (υ mono sub.Ar), 689.8 (υ di-substituted Ar)	δ 1.1863 (s, 3H, CH$_3$), δ 6-8 (m, 14H, Ar-H & Het-H), δ10.15 (s, H, OH), m/z =307(216)	7a	3061.7(υ N-ethyl heterocyclic quaternary salts)
2a	1647.7 (υ C=C) , 2337.1 (υ C=N) , 1738.5 (υ C=O) , 752 (υ mono subs tituted Ar), 755 (N-Ethyl tertiary amine)	δ 1.1564 (s, 3H, CH$_3$), δ 6-8 (m, 14H, Ar-H and Het-H), δ 1.55(t, 3H, CH$_3$ of ethyl), δ 3.37ppm (q, 2H, CH$_2$ of Ethyl), δ 3.89 (s, 1H, 4-H of pyrazolone) m/z =449 (55)	9b	1707 cm^{-1} (υ C=O), 615.6cm^{-1} (υ C=C), m/z =371(57)
4b	2282.3 (υ C=N), 1720.4 (υ C=O), 757.2 (υ mono substituted aromatic)	δ 1.1496, 1.1625 (s, 3H, CH$_3$), δ 6.856 (s, 1H, CH of pyrazol-5-one) and at δ 7.481 (m, H, Ar-H &Het-H), m/z =609 (51)	11b	1711.7 cm^{-1} (υ C=O), 627.1cm^{-1} (υ C=C), , m/z =469(57)
6A	1715.5 (υ α, β-unsaturated C=O) in addition to the general bands cited in (6b)	δ 2.1004 (s, 2H, CH$_2$), m/z =591(57) 7a δ 7.857(m, 4H, pyridin-4-ium -iodide salt) & δ 3.679 (t, 3H, CH$_3$ of Ethyl iodide salts), m/z =760(119)	13b	2370.5 cm^{-1} (υ C=N), 1619.2 m^{-1} (υC=C), 2922.7 m^{-1} (υ OH), m/z =560(85)

Table 5: Colour of (1a, 2a, 4a, 7b & 17) in Pure Organic Solvents

Comp No.	Water	DMF	EtOH	Acetone	CHCl$_3$	C$_6$H$_6$	CCL$_4$	Etanolic Solution in	
								H$_2$SO$_4$	NaOH
1a	Brownish-Red	Red	Red	Brownish-Red	Brownish-Red	brown	brown	yellow	Intense brown
2a	Red	Red violet	Intense red	Red	Violet	Violet	Violet	yellow	Intense red
4a	yellow	brown	brown	Yellow brown	brown	yellow	yellow	Yellow brown	Green brown
7b	Brown	Brown	Brown	Brown	Brown	Brown	Brown	Brown	Brown
17	Grey violet	Deep brown	Brown	Light Brown	Brown	Violet	Violet	Greenish brown	Grey violet

Table 6: Values of Absorption (nm.) & Exitenction coefficients (mol^{-1} cm^{-1}) of (1a, 2a, 4a, 7b & 17) in Pure Organic Solvents

Comp. No.	Water		DMF		Et-OH		Acetone		CHCl$_3$		C$_6$H$_6$		CCL$_4$	
	$\lambda_{max.}$	$\epsilon_{max.}$ x10^3	$\lambda_{max.}$	$\epsilon_{max.}$ x10^3	$\lambda_{max.}$	$\epsilon_{max.}$ x10^3	$\lambda_{max.}$	$\epsilon_{max.}$ x10^3	$\lambda_{max.}$	$\epsilon_{max.}$ x10^3	$\lambda_{max.}$	$\epsilon_{max.}$ x10^3	$\lambda_{max.}$	$\epsilon_{max.}$ x10^3
1a	510	1.141	530	1.091	520	1.154	525	1.078	530	0.891	435	2.108	430	2.185
2a	430	0.731	520	1.472	515	1.855	515	1.608	410	0.801	420	0.960	420	1.071
	490	1.405							525	1.314	520	1.323	520	1.224
4a			440	2.042	435	1.940	430	1.963	440	1.947	440	1.991	435	1.978
7b			485	4.95	480	4.442	460	4.428	470	4.46	465	4.23	470	4.502
17			495	2.641	500	2.771	485	2.614	95	2.672	485	2.528	480	2.516

Table 7: Commutative data for selected cyanine dye (2a) in mixed solvents

Comp. No.	Mixed System	Excitation G (K.cal. mol^{-1}) Pure Solvents		Orientation G. K.cal. mol^{-1}	H-bond G. K.cal. mol^{-1}	Total G. K.cal. mol^{-1}	n	Log K$_f$	K$_f$	($\pm$)ΔG. K.cal. mol^{-1}
		EtOH	H$_2$O							
2a	Et-OH-H$_2$O	**55**	58.61	0.24	3.37	3.61	1	0.132	0.74	-164.9

Table 8: Characterization of Absorption Value of (1a, 2a, 4a, 7b & 17) in Universal Buffer Solutions:

Comp. No.		1a	2a	4a	7b	17
pH	λ_{max}	520	515	435	480	500
	ϵ_{max} x10^3	1.154	1.855	1.940	4.442	2.771
1.98	λ_{max}	410	420	410	465	450
	ϵ_{max} x10^3	1.961	13.10	2.129	4.6	6.77
3.25	λ_{max}	440	420	460	460	460
	ϵ_{max} x10^3	2.163	9.53	2.476	4.678	6.19
4.08	λ_{max}	440	490	430	465	560
	ϵ_{max} x10^3	2.194	10.32	2.192	5.084	7.53
5.02	λ_{max}	430		450	465	
	ϵ_{max} x10^3	2.082		2.526	5.026	
6.07	λ_{max}	430	490	440	475	560
	ϵ_{max} x10^3	2.046	17.05	2.231	5.59	8.15
7.041	λ_{max}	410	490	440	470	560
	ϵ_{max} x10^3	1.950	13.97	2.140	5.452	7.80
8.07	λ_{max}	430	490	445	470	565
	ϵ_{max} x10^3	2.011	12.93	2.103	5.278	6.79
9.08	λ_{max}	430	490	450	460	565
	ϵ_{max} x10^3	1.975	15.26	2.228	5.24	8.23
10	λ_{max}	440	490	450	460	570
	ϵ_{max} x10^3	2.062	13.75	2.284	4.962	9.29
11.04	λ_{max}	450		460	465	
	ϵ_{max} x10^3	2.279		2.390	5.176	
12.12	λ_{max}	445		460	480	
	ϵ_{max} x10^3	2.133		2.394	5.318	

Table 9: Variation of Absorbance in λ_{max} for Selected Dyes in Universal Buffer Solutions

pH / Comp. No. λ_{max}	1a λ_{500}	2a λ_{490}	4a λ_{450}	7b λ_{465}	17 λ_{500}
1.98	1.204	0.395	1.932	2.33	0.935
3.25	1.73	0.546	2.474	2.338	1.422
4.08	1.707	1.032	2.03	2.542	1.793
5.02	1.673		2.526	2.513	1.475
6.07	1.6	1.705	2.174	2.767	0.864
7.041	1.177	1.397	2.091	2.713	0.834
8.07	1.616	1.293	2.077	2.637	0.894
9.08	1.308	1.526	2.228	2.614	
10	1.242	1.375	2.254	2.47	2.822
11.04	1.695		2.336	2.588	
12.12	1.654		2.399	2.637	2.84
pK$_a$	2.4 7.6, 10.4	4.2 , 8.5	2.4 , 4.8	3.6, 5.6 , 10.8	3.2 , 9.0