Synthesis & Spectral Behaviour of N-Bridge Head Benzpiperidino Methine & Metal Complex Cyanine Dyes

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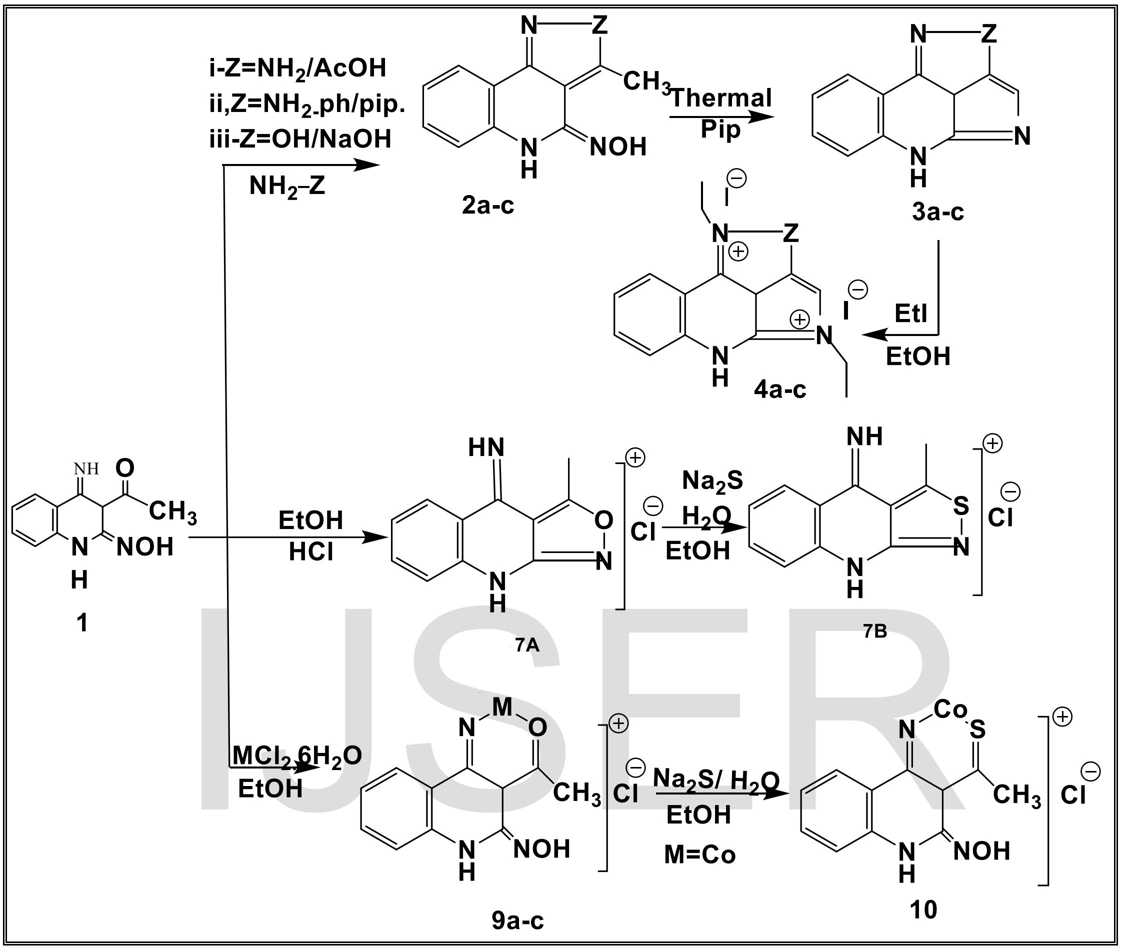
ABSTRACT

3-Acetyl-benzpiperidin-4-imine-2-oxime,2-oximino-benzpiperidin-3-chalcon-4-imine & 2-Oximino-3,3[1,5-diphenyl-pyrazolino]benz piperidin-4-imine derivatives (1,12,17) were used to prepare some interested key reaction heterocyclic intermediates 7[H]-9-methyl-8-oximino-pyrazolo-(isoxazol)[4, 3-e] derivatives 2a-c. 9[H] pyrrolo [4, 3-d] pyrazolo (isoxazol) [5, 6, 7-b, c] benzpiperidine derivatives 3a-c , 9[H] pyrolo [4,3-d] pyrazolo (isoxazolo) [5, 6, 7-b, c] benzpiperidin–1,4-di-ium-ethyl iodide salts 4a-c, 9-methyl-3[H] isoxazolo[3,2-b]benzpiperidin-8-imino–1-ium chloride salt 7 a, 9-methyl- 3[H] isothiazolo [3, 2-b] benzpiperidin-8-imine–1-ium chloride salt 7 b, 6-[H] benz piperidino[4,3-c]1, 3-thiazin-2-metallo complex 10. 2-Oximino-3, 3 [1, 5-diphenyl-pyrazoline]-benzpiperidin-4-imine derivative 17, 2, 3-diphenyl-pyrazolo[1,2-a] pyrazolino [2,3-b] benzpiperidin-5-imine-1-ium-chloride salt 18, 2-aryl-9[H] pyrrolo[2, 3-b]benzpiperidin-4-imine 15a-c. Such key reaction intermediate moieties were used in the synthesis of 9[H] pyrrolo [4,3-d] pyrazolo [5, 6, 7-b, c] benzpiperidin–zero-2 [4(1)]-methine 5a-e, 1[H]benzpiperidin-4-imine-3-methyl-2-oximino-di-5[2]-methine 6A, 3-methyl-1, 9-di [H] pyrrolo [3, 2-b] benzpiperidin-4-imine-zero-2(2)-methine 6B, 3[H] isoxazolo (isothiazolo) [3, 2-b] benzpiperidin-8-imine-mono-9-[1]-methine 8A,B, 6[H] Benzpiperidino[4, 3-c] 1, 3-oxazin-2-metallo–mono-4[4(1)]-methine 9a-d.,1,2,3-tri[H]-2-oximino-benzpiperidin-4-imine-β-styryl-di-3[2(4)] methine 13a-e, 9[H] pyrrolo [2,3-b] benzpiperidin-4-imine-3-styryl-zero-2[2(4)] methine 14, 2-aryl-9[H] pyrrolo [2,3-b]benzpiperidin-4-imine-mono-3[2(4)] methine cyanine dyes 16a-e. & 2,3-diphenyl-pyrazolo[1,2-a]pyrazolino[3,2-b] benzpiperidin–zero-4[(4)]-methine--4-imine 19. The new synthesised heterocycles & their related cyanines were identified and chemically confirmed by elemental & spectral data. The UV-visible absorption spectra of some selected dyes were

investigated in pure & mixed organic solvents to verify molecular complex formation. The UV-visible absorption spectra of such dyes were investigated in aqueous universal buffer solutions.

GRAPHICAL ABSTRACT



Synthetic Routes of Heterocyclic Precursors

KEYWORDS: Benzpiperidino Methine & Metal Complex Cyanine Dyes, Spectral, Solvato-(Media)-chromic Behaviour.

1. INTRODUCTION:

There is growing interest in the synthesis of fused and N-bridgehead heterocyclic dyes to prepare and study their properties of different types[1]. Polymethine cyanine dyes belong to a well-known class of organic compounds, which have been used as photography and information storage, [2] in laser technology [3] and as photo polymerization initiator [4]. Cyanine dyes are easy to synthesize, and show very good optical properties, enhances their photostability and essentially inhibits their decolorization by light [5] they are used as organic photoconductors to their complexation ability and photophysical properties [6]. Recently, they are used as a

new chromofluoroionophore [7].There is currently much interest in the use of the indolizinium chromophores for non-linear optical applications [8] Heterocyclic of benzpiperidin-4-one derivatives is important in biological and medicinal activity [9-12],] and their chemistry has recently received considerable attention. Thus, the object of this investigation is to report the synthesis, absorption spectra, solvatochromic and acid-base behavior of new cyanine dyes incorporating isoxazolo (Isothiazolo) [3, 2-b] benzpiperidin-8- imine, Benz piperidino [2, 3-d] pyrido [2, 1-a] pyridazin -11- one benzpiperidin-4-imino, (Pyrazolo)[5, 6, 7-b, c] benzpiperidin Pyrazolo[1,2-a]pyrazolino [3,2-b] benzpiperidin pyrrolo [3, 2-b] benzpiperidin-4-imino, pyrrolo [2,3-b] benzpiperidin-4-imine, pyrolo [2,3-b] benzpiperidin-4-imine & new stabilized metal complex cyanine dyes covering zero-, mono-,dimethine, styryl types and a correlation has been established between molecular structure and spectral, Solvatochromic behaviors of the synthesized dyes and acid-base behavior were investigated in order to make suitable selections for their applications as photosensitizers.

2. MATERIALS & METHODS

All melting points were uncorrected. IR spectra (KBr) were recorded on a pye Unicam SP1100 spectrophotometer. ^{1}H-NMR spectra were recorded in a Varian EM -390 MHZ spectrophotometer using DMSO d6 as a solvent and TMs as an internal standard. Chemical shift are expressed as ppm, units. The absorption spectra were recorded on a 6405 UV/ visible recording spectrophotometer, Aswan faculty of science at 27C°. 3-Acetyl-2-oximino benzpiperidin-4-imine (1), 2-Oximino-Benzpiperidin-3-chalcone-4-imine 12a-c and their 2-oximino-3, 3-[1,5-diphenylpyrazolino]-benzpiperidin-4-imine derivatives 17 were prepared in a way similar to [30].

2.1 7[H]-9-Methyl-8-oximino-pyrazolo(isoxazol)-[4,3-e]benzpiperidine derivatives (2 a-c,)

An ethanolic solution of 1, and hydrazine hydrate (phenyl hydrazine) and /or hydroxylamine hydrochloride (0.01mol) in the presence of acetic acid, piperidine and/or sodium hydroxide respectively, and crystallized from ethanol to give 2 a-c , Table (5).

2.2 9[H] pyrrolo [4, 3-d] pyrazolo (isoxazol) [5, 6, 7-b, c] benzpiperidine derivatives (3a–c):

Compounds 2 a-c were fused in presence of piperidine for (2min) then add 25ml ethanol, then refluxed for 4-6 hrs. The reaction mixture was filtered off, concentrated, and neutralized by acetic acid. The precipitated products after dilution with water were separated, filtrated, crystallized from ethanol to give 3a-c, Table (5).

2.3 9[H] Pyrolo [4,3-d] isoxazolo (pyrazolo)[5, 6, 7-b, c] benzpiperidin–1, 4-di ethyl iodide salt 4a-c

An ethanolic solution of 3a-c (0.01mol), and ethyl iodide (0.02mol) were refluxed for 4-6 hrs, filtrate and the products were precipitated on dilution with cold water then crystallized from ethanol, Table (5).

*2.4 9[H] Pyrolo [4,3-d] isoxazolo (pyrazolo)[5, 6, 7-b, c] benzpiperidin–zero-2[4(1)]-methine cyanines 5a-*e

An ethanolic solution of 4a-c and pyridinum, quinolinium and isoquinolinium ethiodide (0.01mol) in presence of piperidine was refluxed for 6-8 hrs. The reaction mixtures were filtrated from unreacted materials. The filtrate was concentrated, cold and acidified with acetic acid. The precipitated products after dilution with water were separated, filtrated, crystallized from ethanol, Table (6).

2.5 1[H]benzpiperidin-4-imino-3-methyl-2-oximino-di-5[2]-methine cyanine dye 6A,

Ethanolic mixture of 1 and quinaldine ethiodide (0.01mol) in presence of piperidine was refluxed for 4-6 hours filtered hot, concentrated and cooled. The products precipitated on dilution with water were crystallized from ethanol to give reddish violet crystals of 1[H] benzpiperidine-4-imino-3-methy-2-oximino-di-5 [2]-methine cyanine dye 6A, Table (5).

2.6 3-Methyl-1, 9-di [H] Pyrrolo [3, 2-b] Benzpiperidin-4-imino-zero-2(2)methine cyanine dye 6B

Compound 6A (0.01mol) was fused for 2min in presence of piperidine, then added 25ml of ethanol and refluxed for 4-6 hours filtered hot, concentrated and cooled. The products precipitated on dilution with water were crystallized from ethanol to give reddish violet crystals of 1, 2, 3-tri[H] benzpiperidine-4-imine-3-methyl-2-oximino-di-5 [2]-methine cyanine dye. A product precipitated on dilution with water was crystallized from ethanol to give reddish violet crystals of 6B, Table (6).

2.7 9-Methyl-3[H] Isoxazolium (Isothiazolium) [3, 2-b] Benzpiperidin-8-imino–1-ium chloride salts 7A,B

Ethanolic solution of (1) in presence hydrochloric acid was refluxed for 1-2 hrs. The reaction mixture was filtrated from unreacted materials. The filtrate was concentrated, cold and dried to give dark brown crystals of 3[H] isoxazolo (Isothiazolo) [3, 2-b] benzpiperidino-8- imino-1-ylide chloride 7A, Table (5).

2.8 3[H] Isothiazolo [3, 2-b] benzpiperidino-8- imino-1-ylide chloride, 7B,

A mixture of an ethanolic solution of 7A and aqueous sodium sulphide was refluxed for 1hr. The filtrate was concentrated, cold and dried. The product was precipitated on dilution with water and crystallized from ethanol to give dark green crystals, Table (5).

2.9 6[H] Benzpiperidino-[4, 3-c] 1, 3-oxazin-2-metallo complexs 9a-d

An ethanolic mixture of (1) and metal divalent chlorides (0.01mols) was refluxed for 2-4 hrs. The reaction mixtures were filtrated from unreacted materials. The filtrate was concentrated, cold and dried, Table (5)

2.10 3[H] Isoxazolo (Isothiazolo) [3, 2-b] Benzpiperidin-8-imine mono-9[1] methine cyanine 8A,B

A mixture of ethanolic solutions of (7A, B) and isoquinoline ethiodide (0.01mol) in presence of piperidine was refluxed for 4-6 hours, filtered hot, concentrated, cooled, the products precipitated on dilution with water were crystallized from ethanol, Table (6).

2.11 6[H] Benzpiperidino-[4, 3-c] 1, 3-thazin-2-metallo complexs 10

A mixture of an ethanolic solution of 9c and aqueous sodium sulphide was refluxed for 1hr. The filtrate was concentrated, cold and dried. The product was precipitated on dilution with water and crystallized from ethanol to give dark green crystals 10, Table (6).

2.12 6[H] Benzpiperidino [4, 3-c]1, 3-oxazin-2-metallo–mono-4-[4(1)]-methine cyanine dyes 11a-f

An ethanolic solutions of (9a-d & 10) and pyridinum, quinolinium and isoquinolinium ethiodide (0.01mol) in presence of few drops of piperidine was refluxed for 6-8 hrs. The reaction mixtures were filtrated from unreacted materials. The filtrate was concentrated, cold and acidified with acetic acid. The precipitated products after dilution with water were separated, filtrated, crystallized from ethanol, Table (6).

2.13 2-Oximino-1,2,3-Tri[H]Benzpiperidin-4-imine-β-Styryl-di-3[2(4)]methine cyanine dyes 13a-e

An ethanolic solution of 12a-c & α (γ)-picoline, quinaldine ethiodide (0.01mol) in presence of few drops of piperidine was refluxed for 6-8 hrs. The reaction mixtures were filtrated from unreacted materials. The filtrate was concentrated, cold and acidified with acetic acid. The precipitated products after dilution with water were separated, filtrated, crystallized from the suitable solvent, Table (6).

2.14 9[H] Pyrolo [2,3-b] Benzpiperidin-4-imine-3-Styryl-zero-2-[2(4)] methine cyanine dye 14

Compound 13d (0.01mol). and zinc chloride was refluxed for 2-4 hours, filtered hot, concentrated, cooled, diluted with water where precipitated product separated out ,filtrated, crystallized from the suitable solvent to give product The precipitated product after dilution with water separated out and crystallized from ethanol.Table (6).

2.15 2-Aryl-9[H] Pyrrolo [2, 3-b] Benzpiperidin-4-imine 15a-c.

Compounds (12a-c) were fused in piperidine then added ethanol and refluxed for 6-8 hrs. The precipitated products after dilution with water were separated to give 9[H] -2-aryl pyrolo 2, 3-b] benzpiperidine-4-imine 15a-c

2.16 2-Aryl-9[H]Pyrrolo[2,3-b]Benzpiperidin-4-imine-mono-3-[2(4)]methine cyanine dyes 16a-e

Ethanolic solution of 15 a-c and α (γ)–picoline, quinaldine ethiodide (0.01mol) in the presence of few drops of piperidine was refluxed for 6-8 hrs. The reaction mixtures were filtrated from unreacted materials. The filtrate was concentrated, cold and acidified with acetic acid. The precipitated products after dilution with water were separated, filtrated, crystallized from the suitable solvent to give 16a-e Table (6).

2.17 2,3-Diphenyl-pyrazolo[1,2-a]pyrazolinium-[2,3-b]benzpiperidin-5-imine-1-chloride salt 18

An ethanolic solution of 17 was refluxed in the presence of conc. HCl acid (5ml) for 8 hr., filtered, concentrated, and then poured on ice water to give 18, Table (6).

2.18 2, 3-Diphenyl-Pyrazolo [1, 2-a] Pyrazolino [3, 2-b] Benzpiperidin–Zero-4[(4)]-methine-4-imine cyanine dye 19

Route-1

An ethanolic solution of 17 and quinolinium methiodide (0.01mol) in presence of few drops of piperidine was refluxed for 2-4 hrs. The reaction mixtures were filtrated from unreacted materials. The filtrate was concentrated, cold and

acidified with acetic acid. The precipitated intermediate product (A) after dilution with water was separated, filtrated, crystallized from ethanol. Further refluxing of an ethanolic solutions of A (0.01mol) and zinc chloride for 2-4 hours filtered hot, concentrated, cooled, diluted with water where precipitated product separated out ,filtrated, crystallized from the suitable solvent to give product 19, Table (6).

Route-2

An ethanolic solution of 18 and quinolinium methiodide (0.01mol) in presence of few drops of piperidine was refluxed for 2-4 hrs. The reaction mixtures were filtrated from unreacted materials. The filtrate was concentrated, cold and acidified with acetic acid. The precipitated product 19 after dilution with water separated out, filtrated, crystallized from ethanol. Product 19 has the same m.p and mixed m.p. as obtained in Route-1, Table (6).

2.20 Solvatochromic and Acid-Base Properties:

The organic solvents were used of spectroscopic grade which purified according to the recommended methods [31].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.

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 was 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.

2.21 Preparation of Universal Buffer Solutions:

A modified buffer series derived from [32] was prepared. The constituents are as follows: (a) a solution of 0.4 mo^{-l}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 [32]. This was done by mixing 150 ml of an acid mixture in 250 ml measuring flask with the appropriate volumes of 1.0 mol-dm^{-3} NaOH and completed to the mark with redistilled water. This modification was performed in order to keep an ionic strength constant at all pH's mixed with different proportions of organic solvents used. The pH's of buffer solutions were checked using Orion pH-meter model 60, an accurate to ± 0.005 pH units, at 25 0C.

3. RESULTS AND DISCUSSIONS

3.1 SYNTHESIS

The interaction of 3-acetyl-benzpiperidin-4-imine-2-oxime 1 and hydrazine hydrate (phenyl hydrazine) and/or hydroxylamine hydrochloride in ethanol as solvent in the presence of acetic acid, piperidine and/or sodium hydroxide respectively afforded 7[H]-9-methyl-8-oximino-pyrazolo[4, 3-e] & 9[H] pyrrolo[4, 3-d]pyrazolo[5, 6, 7-b, c]benzpiperidine derivatives 2a-c. The thermal piperidine catalysis of later compounds 2a-c afforded 9[H] pyrrolo [4, 3-d] pyrazolo [5, 6, 7-b, c] benzpiperidine derivatives 3a-c.. Selective quaternization of the later 3 a-c using bimolar ratios of ethyl iodide afforded 9[H] pyrolo[4,3-d] pyrazolo[5, 6, 7-b, c] benzpiperidin–1, 4-yl-ethyl iodide salts 4a-c, On triturating of 4 a-c with conc. sulphuric acid liberated iodine vapor on warming. Reaction of 4 a-c with N-ethyl (pyridinium, quinolinium and isoquinolinium) iodide, in eqiumolar ratios, in presence of piperidine as basic catalyst afforded 9[H] pyrrolo [4, 3-d]pyrazolo [5, 6, 7-b, c] benzpiperidin–zero-2 [4(1)]-methine cyanine dyes 5a-e. Condensation reaction of 1 and quinaldine ethiodide, in equimolar amounts, under thermal piperidine catalysis gave 1[H] benzpiperidin-4-imine-3-methyl-2-oximino-di-5[2]-methine cyanine dye 6A, which undergoes interamolecular cyclocondensation reaction to afford 3-methyl-1, 9-di [H] pyrrolo[3, 2-b] benzpiperidin-4-imine-zero-2(2)-methine cyanine dye 6B.

Compound 6A was soluble in conc. H_2SO_4 to give iodine vapour on warming. On triturating an ethanolic solution of 1 with hydrochloric acid afforded 9-methyl-3[H] isoxazolium [3, 2-b] benzpiperidin-8-imine–1-ium chloride salt 7A, which treated with aqueous sodium sulphide to give 9-methyl-3[H]isothiazolium [3, 2-b] benzpiperidin-8-imin–1-ium chloride salt 7B. Reaction of ethanolic solution (7A, B) and isoquinoline ethiodide, in equimolar ratios, under thermal piperidine catalysis, undergo oxidative elimination reaction to afford 3[H] isoxazolo (isothiazolo) [3, 2-b] benzpiperidin-8-imine-mono-9-[1]-methine cyanine dyes (8A, B) , Scheme 1A . On triturating of 7A with aqueous saturated solution of KI followed by dissolving of the resulted precipitation in conc. H_2SO_4 liberated iodine vapour on warming. This is a criterion for the presence of chloride anion replaced by iodide analogous. 6 [H]Benzpiperidino [4, 3-c] 1, 3-oxazin-2-metallo–mono-4 [4(1)]-methine cyanine dyes 9a-d was conducted via the preparation of key reaction intermediate through addition reaction of an ethanolic solution of 1 with metal divalent chlorides to give 6[H]benzpiperidino-[4, 3-c] 1, 3-oxazin-2-metallo complexs 9a-d,. On triturating of 9c with aqueous sodium sulphide gave 6-[H] benzpiperidino-[4, 3-c]1, 3-thiazin-2-metallo complex 10. Reaction of 9a-d with N-ethyl (pyridinium, quinolinium and isoquinolinium) iodide, equimolar ratios, in the presence of piperidine as basic catalyst afforded 6 [H] benzpiperidino [4, 3-c] 1, 3-oxazin/ thiazin-2-metallo-mono-4 [4(1)] methine cyanine dyes 11a-d Scheme (1A). 1,2,3-Tri[H]-2-Oximino-benzpiperidin-4-imine-3-[2(4)]bis styryl dimethine and 9 [H]pyrrolo [2,3-b] benzpiperidine-4-imine-3-styryl-mono-2[2(4)]-methine cyanine dyes 13a-e & 14 was achieved through the interaction of an ethanolic solution of 1,2,3-tri[H]-3-arylideno benzpiperidin-4-imino-2-oxime derivatives 12a-c and [α(γ)–picoline, quinaldine] ethiodide under piperidine conditions to give 1,2,3-tri[H]-2-oximino-benzpiperidin-4-imine-3-β-styryl di-3[2(4)] methine cyanine dyes 13a-e. Dehydration process was carried out for selected 13d, X=p-OH using zinc chloride to afford 9[H] pyrrolo[2,3-b] benzpiperidin-4-imine-3-styryl-zero-2 [2(4)] methine cyanine dye 14, On the other hand, thermal /piperidine catalysis of 1,2,3-tri[H]-3-arylideno-benzpiperidin-4-imine-2-oxime 12a-c undergoes ring closer to afford 2-aryl-9[H]pyrrolo[2,3-b] benzpiperidin-4-imine 15a-c.. Reaction of ethanolic solution of 15 a-c with α (γ)–picoline or quinaldine ethiodide, in equimolar amount in the presence of piperidine afforded 2-aryl-9[H] pyrrolo [2,3-b] benzpiperidin-4-imine-mono-3[2(4)]methine 16a-e, Scheme 1B. 2-Oximino-benz piperidin-3-chalcone-4-imine 12a-c when interacted

with phenyl hydrazine in ethanol as solvent in the presence of piperidine gave 2-Oximino-3,3-[1,5-diphenyl-pyrazolino]-benzpiperidin-4-imine derivative 17. On triturating of the later 17 with hydrochloric acid in ethanol undergoes ring closer to afford 2, 3-diphenyl-pyrazolo[1,2-a] pyrazolinium[2,3-b]benzpiperidin-5-imin-1-chloride salt 18. On triturating an ethanolic solution of 18 with aqueous KI solution give precipitate which in conc. H_2SO_4 liberating iodine vapour on warming. The appearance of iodine vapour is a criterion for presence of chloride anion replaced by iodide analogous. The reaction of 18 with quinoline methiodide under thermal piperidine catalysis afforded 2, 3-diphenyl-pyrazolo [1,2-a] pyrazolino [3,2-b] benzpiperidin–zero-4[(4)]-methine--4-imine cyanine dye 19, Scheme 1B. 3-Methyl-1, 9-di [H] pyrrolo [3, 2-b] benzpiperidin-4-imine-zero-2 (2) methine , 3[H] isoxazolo (Isothiazolo) [3, 2-b] benzpiperidin-8- imine-mono- 9- [1] methine , 6[H] benz- piperidino- [4, 3-c] 1, 3-oxazin-2-metallo-mono-4[4(1)]-methine, 9[H] pyrolo [4,3-d]isoxazolo (pyrazolo) [5, 6, 7-b, c] benzpiperidin-zero-2[4(1)]-methine, 2, 3-diphenyl-pyrazolo [1, 2-a] pyrazolino [3, 2-b] benzpiperidin–zero-4[(4)]-methine-4-imine cyanine dye, 1[H]2-oximino-benzpiperidin-4-imino-3- β-styryl di-[2(4)] methine, [9[H] pyrolo [2,3-b]benzpiperidin-4-imine-3-styryl-zero-2-[2(4)]methine, 2-aryl-9[H]-pyrrolo-[2,3-b]benzpiperidin-4-imine-mono-3[2(4)] methine (5a-e , 6B, 8a,b 11 a-f, ,13a-e,14,16a-e,19) are easily (partially) soluble in polar (non) organic solvents and concentrated sulphuric acid from which iodine vapour was liberated on warming. In 95% ethanol possess (dark brown to reddish brown), in colour. Their ethanolic solutions exhibited permanent coloured in basic media, which reversibly discharged on acid media Table (1). Other ethanolic solution gave deep colour in acidic medium and discharged on basification. This is due to the appearance of covalent hydration phenomenon in aqueous solution. The structure of (4 a-c, 5 a-e , 6A, B, 7A,B, 8A,B, 9a-c ,11a-f , 13a-e, 14, 15a-c & 16 a-e18, 19) was confirmed by elemental & spectral analyses[13-15],Tables 6.

3.2 SPECTRAL BEHAVIOUR

The absorption spectra of 9[H] pyrolo [4,3-d] isoxazolo (pyrazolo) [5, 6, 7-b, c] benzpiperidin-zero-2[4(1)]-methine cyanine dyes 5a-e in 95% ethanol consists of different absorption bands, their position and molar extinction coefficient being influenced by the type of heterocyclic quaternary residue (A) and nature of aryl substituents (Z), Thus, the absorption spectra of 5 a (Z= O, A= pyridin-4-ium ethiodide) exhibit (λ_{max}= 465 nm; ε_{max} =2437 mol^{-1}cm^{2}). Substitution of (A= pyridin-

4-ium ethiodide) in dye 5 a by (A= quinolin-4-ium ethiodide) in dye 5 b, causes bathochromic shift of $\Delta\lambda_{max}$ = 10 nm. This is due to more extensive π-delocalization or conjugation in dye 5 b. Changing the linkage position of quinoline residue from 4-ium in dye 5b [A= quinolin-4-ium ethiodide] to 1-ium in dye 5c [A=quinolin-1-ium ethiodide] resulted in bathochromic shift in absorption band of $\Delta \lambda_{max}$ = 5 nm. On the other hand, substituting of (Z= O) in dye 5b by (Z= N-Ph) in dye 5d, resulted in bathochromic shift in absorption band of $\Delta \lambda_{max}$ = 15 nm (5d, λ_{max} = 490nm; ε_{max}= 2696 $mol^{-1}cm^2$). This is due to an increase in conjugation within phenyl group causes an easier charge transfer towards the heterocyclic quaternary residue (A) as electron sink. Additionally, substituting of (Z= N-Ph) dye 5d by (Z=N-$COCH_3$) in dye 5e causes hypsochromic shift of $\Delta \lambda_{max}$ = 25 nm, accompanied with decreasing in the absorption bands number [5e, λ_{max} = 465 nm. ε_{max} = 2662 $mol^{-1}cm^2$]. This is due to an electron withdrawing character of N-$COCH_3$ group causing decreasing in the charge transfer from an aryl group as electron source towards heterocyclic quaternary residue (A) as electron sink, Table 6. The absorption spectra of 3-hydroxy-4[H] benzpiperidino[5, 4-d]1, 3-oxazin-2-metallo–mono-10-[4(1)] methine cyanine dyes 11a-f in 95 % ethanol showed different absorption bands, their position and molar extinction coefficient being influenced by the type of heterocyclic quaternary residue (A), nature of both metal and (X) atom. Thus, the absorption spectra of dye 11a [M=Cu, X=O, A= pyridin-4-ium ethiodide] exhibit (λ_{max} =460 nm; ε_{max}= 1909 $mol^{-1}cm^2$). Substituting of (A= pyridin-4-ium ethiodide) in dye 11a by [A= quinolin-4- ium ethiodide] in dye 11b causes bathochromic shift of $\Delta\lambda_{max}$ = 40 nm. 11b, λmax =500 nm; εmax= 2641 $mol^{-1}cm^2$. This is due to more extensive π-delocalization in dye 11b. Changing the linkage position of quinoline residue from 4-ium in dye 11b [A= quinolin-4- ium ethiodide] to 1-ium in dye 11c [A= quinolin-1-ium ethiodide] resulted in hypsochromic shift in absorption band exhibit (λ_{max} = 475 nm; ε_{max} = 2870 $mol^{-1}cm^2$). On the other hand, substituting of (M=Cu) in dye 11 b by (M=Co) in dye 12d causes hypsochromic shift of $\Delta\lambda_{max}$ = 10 nm than those in dye 11b [12d, λ_{max} = 490 nm; ε_{max} =1145 $mol^{-1}cm^2$]. Also, substitution of (M = Cu) in dye 11 b by (M= Ni) in dye 11e resulted in hypsochromic shift of $\Delta \lambda_{max}$ = 30 nm than those in dye 11b. This is due to the vacant orbital increasing gradually from Copper to Cobalt, leading to more extensive π-conjugation. Additionally, substitution of (X=O) in dye 11d by (X=S) in

dye 11f ,the absorption spectra of 11f exhibited λ_{max} = 525nm; ε_{max}= 2744 mol^{-1}cm^{2}and causes bathochromic shift due to more electron donating character of sulpher atom than oxygen atom, Table (6). The absorption spectra of 1,2,3-tri[H]-2-oximino-benzpiperidin-4-imino-β-styryl-di-3[2(4)]methine cyanine dyes 13a-e in 95% ethanol showed absorption bands batho (hypso) chromically shifted depending upon the type of heterocyclic quaternary residue (A) and nature of aryl substituents (X). Thus, the absorption spectra of 13a, [X=H, A= pyridin-2-ium] exhibit [λ_{max} = 465nm; ε_{max} = 2534 mol^{-1}cm^{2}]. Substitution of [A=pyridin-2-ium] in dye 13 a by [A=quinolin-2-ium ethiodide] 13 b resulted in the appearance of new absorption bands located at longer wavelength (λ_{max} = 560, 695 nm; ε_{max} = 2330, 1297 mol^{-1}cm^{2}). This is due to more extensive conjugation in dye 13 b. Changing the linkage position of pyridinium residue from 2-ium in dye 13 a [A= pyridin-2-ium ethiodide] to 4-ium in dye 13c [A= pyridin-4- ium ethiodide] resulted in bathochromic shift in absorption band to exhibit (λ_{max} = 475 nm; ε_{max} = 2554 mol^{-1}cm^{2}) On the other hand, substitution of [X=H] in dye 13 a by [X=P-OH] in dye 13d causes bathochromic shift in absorption band of $\Delta\ \lambda_{max}$ = 15 nm for dye 13d. This is due the electron donating effect of hydroxyl group causing an easier charge transfer towards heterocyclic quaternary residue (A) as electron sink. Additionally, substitution of [X=p.OH] in dye 13d by [X =p.Cl] in dye 13e resulted in hypsochromic shift of $\Delta\ \lambda_{max}$ = 35 nm accompanied with decreasing in absorption band numbers. This is due an electron withdrawing character of chlorine anion causing decreasing in charge transfer from aryl group as electron source towards heterocyclic quaternary residue (A) as an electron sink Table (6) . On comparison between the absorption spectra of acyclic and cyclic dyes 13d 14, it was obvious that the former dye 13d showed a bathochromic shift of $\Delta\lambda_{max}$ = 10 nm. This is due to increasing the intensity of an electron donating character of two OH groups causing an easier charge transfer towards heterocyclic quaternary residue (A) in the case of acyclic dye 13 d as was observed in the absorption spectra of dyes 13 a-e & 14. The absorption spectra of 2-aryl-9[H] pyrolo[2,3-b]benzpiperidin-4-imine-mono-3-[2(4)]-methine cyanine dyes 16 a-e in 95% ethanol showed absorption bands batho (hypso) chromically shifted depending upon the type of heterocyclic quaternary residue (A) and nature of aryl substituents (X). Thus, the absorption spectra of 16 a [X=H, A=pyridin-2-ium] exhibit (λ_{max} 455 nm; ε_{max} 2428 mol^{-1}cm^{2}). Substitution of [A= pyridin-2-ium] in dye 16 a by (B = quinolin-2-ium ethiodide) 16 b causes the

appearance of new absorption in the longer wavelength (λ_{max} = 560, 685 nm; ε_{max} = 2378, 1393 mol^{-1}cm^{2}). This is due to more extensive π-delocalization or conjugation in dye 16b. Changing the linkage position of pyridinium residue from 2-ium in dye 16a [A= pyridin-2-ium ethiodide] to 4-ium in dye 16c [A pyridin-4-ium ethiodide] resulted in bathochromic shift in absorption band to exhibit (λ_{max} = 465nm; ε_{max} = 2418 mol^{-1}cm^{2}). Additionally, substitution of [X=H] in dye 16 a by [X = p-OH] in dye 16d exhibited bathochromic shift in absorption band in dye 16d, λ_{max} = 460nm; ε_{max} = 2800 mol^{-1}cm^{2}. This is due to an electron donating of aryl substituent causes an easier charge transfer towards heterocyclic quaternary residue (A) as an electron sink. Also, substitution of [X = p-OH] in dye 16d by [X= p.Cl] in dye 16e, of an electron withdrawing character resulted in hypsochromic shift of 10 nm than those of an electron donating character accompanied with decreasing in number of the absorption bands 16e, λ_{max}= 450 nm; ε_{max} = 2210 mol^{-1}cm^{2}, causes decreasing in the charge transfer from aryl group as an electron source towards heterocyclic quaternary residue (A) as an electron sink Table 6 .On comparison between the absorption spectra of 3[H] isoxazolo (isothiazolo) [3, 2-b] benz-piperidin-8- imino mono-9-[1]-methine cyanine dyes 8a b in 95% ethanol, it was obvious that the later dye 8b, X=S) showed a bathochromic shift of $\Delta\lambda_{max}$ = 15 nm. Concomitant with an increasing of extinction coefficient of the band relative to the former one 8a, X=O). This is due to that sulpher atom is more electron donating more than oxygen atom of an electro negativity.

3.3 SOLVATOCHROMISM

It was reported that, the colour changes of cyanine dyes with solvents (solvatochromism) were discussed by [16] *to* correlate the effect of structure on molecular orbital energy levels. It is clear that the type of substituents and the solvent polarity change the electron densities of cyanine dyes. Solvatochromic dyes generally exhibit steady bathochromic (positive solvatochromism) or hypsochromic (negative solvate-chromism) shifts in solvents of various polarities. Cyanine dyes are also ascribed a large change in dipole moment upon exitation due to the relative contribution of both dipolar zwitterionic benzenoid and neutral quinoid forms [17, 18]. Therefore, these dyes have been used by various workers to establish empirical relationships of solvent polarity. The solvatochromism is caused by differential solvation of the ground and Franck-Condon excited state, due to the absorption of an electromagnetic radiation in the UV-vis region. If the ground state is more

stabilized than the excited state due to solvation by solvents of increasing polarity, negative solvatochromism is exhibited and vice versa. According to the Franck-Condon principle [19], the time required for molecules to be exited is much smaller than that required to execute vibration or rotation. Therefore, the first excited state of the molecule in solution, called the Franck-Condon excited state has the same solvation pattern as in corresponding ground state, called the equilibrium ground state. The first Franck-Condon excitation state is much more dipolar than the ground state due to intramolecular charge transfer upon excitation. Stabilization of the Franck-Condon excited state before and after relaxation to the equilibrium excited state and the destabilization of the Frank-Condon ground state relative to the equilibrium ground state by differential solvation leads to the positive solvatochromism. Positive solvatochromism is more sensitive to changes in solvent polarity than the corresponding absorption band in suitable cases. From these finding points of view, the absorption spectra of 9[H] pyrrolo [4,3-d]pyrazolo [5, 6, 7-b,c]benz-piperidine–zero-2(4)-methine cyanine dye 5d, 3[H] isoxazolo (isothiazolo)[3,2-b]benzpiperidin-8-imine-mono-9-[1]methine cyanine dye 8a,b, 1,2,3-tri[H]2-oximino-benzpiperidin-4-imine-β-styryl-di-3(2)methine cyanine dye 13d 2-oximo-N-phenyl-pyrazol-4-imine-zeromethine cyanine dye 19. The absorption spectra of (5d, 8a, b 13d &19) in the wavelength range 350-700 nm, have been studied in different organic solvents (DMF, EtOH, CHCl3, C6H6 and carbon tetrachloride) [20].The colour changes of such dyes in solvents having different polarities and (λ_{max} ,ε_{max}) values of the intermolecular charge transfer bands with the intention to illustrate the solvatochromic behaviour of dyes are given in Tables 1. 2. These dyes are showed positive solvatochromism with an increase in solvent polarity, which depend on the structure and the type of dye. This indicates that the polar excited states of these cyanine dyes are stabilized by polarization interaction forces as polarizability of the solvent is increased. This behavior occurs as a result of electrostatic interactions of distributed cationic charges with dipoles of the solvated molecules which leads to formation of specific solvated forms of dyes. In point view of light absorption, it was obvious that most of (5d ,8a,b, 13d &19) are absorbed the fundamental light absorption (reddish violet- red) as they have got absorption values in the range 400-545 nm Table (2) in accordance with the literature´s observations [21,22]. The selected cyanine dyes might be suggested to be

used as photosensitizers in most polar and non polar organic solvents in reddish violet-red region. Thus, it was obvious that dye 15 absorbed blue-green light in carbon tetrachloride λ_{max} = 495 nm., extended and improved to the absorption of green light in EtOH, DMF, $CHCl_3$, benzene λ_{max} = 505-545nm. Blue-green light in carbon tetrachloride λmax=495 nm. Also, compounds (5d ,8a, b,13d &19) absorbed near blue light in benzene, carbon tetrachloride, λ_{max} = 420-465 nm., extended and improved to the absorption of blue-green light in DMF, EtOH, $CHCl_3$ λ_{max} = 475-490 nm. The spectral behavior of 2-oximino-1, 2, 3-tri [H]-benzpiperidin-4-imine-β-styryl-di-3(2)-methine cyanine dye 15d in mixed solvents of different polarities was discussed. The study is performed to trace the possibility of formation of a hydrogen-bonded solvated complex between the solute and solvent molecules. It is also aimed to prove whether the solvent shift in the spectra of such dye in ethanol solutions is due to hydrogen bonding or to more solvating 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 2-oximino-1, 2, 3-tri [H]-benzpiperidin-4-imine-β-styryl-di-3(2)-methine cyanine dye 15d (1x10-4 M) in DMF containing varying amounts of benzene showed that in the presence of 2.26 M of benzene, the spectrum exhibits band located at 465 nm, while presence of 9.04 M benzene the band is shifted to 440 nm with gradual blue shift. Also, an increase in band intensity at fixed wavelength 445 nm. is observed to a certain limit and then decreases with increasing of benzene content. A broken line is obtained on plotting the absorbance against the dielectric constant, and the Δν` versus the D-1/D+1, where ν` = 1/λnm x 107 cm^{-1} and D is dielectric constant of the solvent added, , therefore the band shift is governed by other factors in addition to the dielectric constant of the medium, these factors include solute solvent interactions. The plot of E and ΔE against the mole fraction of benzene results broken line of three segments [23]. Such segments corresponding to an orientation and hydrogen-bond energies. From data in Table (2). The energy of the solute is 66.51 k. cal. $mole^{-1}$ in pure benzene and 58.96 k. cal. mol^{-1}in pure DMF for the two systems respectively. The orientation energy is 1.25 k. cal. $mole^{-1}$ and the hydrogen bond is 3.34 k.cal. $mole^{-1}$. The stability constant of molecular complex which

formed between the solute and benzene molecules is calculated from the relation between the absorbance and molarity benzene at fixed wave length [24]. The log kf is 0.64 [kf = 4.4], where the value of kf is dependent on both the solute and the solvent used, [26.27] The number (n) of the solvent molecules benzene with the solute is computed and recorded in Table (3). Also, ΔG is calculated and recorded in Table 3. The values of kf, ΔG and n indicate that a 1:1 complex is formed.

3.4 MEDIACHROMIC BEHAVIOUR

The ethanolic solution of dye 11f gives a permanent colour in basic medium which is discharged on acidification. This promoted us to study their spectral behavior in different aqueous universal buffer solution in order to ensure optimal pH in the application of these dyes as photosensitizers. The effectiveness of the compounds as photosensitizers increases when they are present in ionic forms (non protonated form) which have higher planarity[25]. The absorption spectra of dye 11f, in aqueous universal buffer solution of different values of pH (3.08-10.02) show regular changes with increasing pH of the medium especially in n-π∗ and CT bands. The spectral behavior of dye 11f in 95% ethanol and/or in aqueous universal buffer solution showed that such dye absorbed the near blue light extended to green light λ_{max} = 475-515 nm. Such dye 11f in aqueous universal buffer solution reveals absorption of the violet light at λ_{max} = 465 nm at pH = 3.08 and hypso (batho) chromic shifted in the absorption of blue light at λ_{max} = 475 nm at pH ≥ 7.0 relative to ethanol. The hypsochromic shift of the violet light at pH = 3.08 is due to the presence of quinolinium ethiodide as strong inductively group causes the protonation of nitrogen atom in such solution of low pH value and therefore the interaction is inhibited and the protonated form does not absorb energy in the visible region. On the other hand, the resulted bathochromic shift as pH of the medium increases is due to the fact that the protonated dye becomes deprotonated and therefore its mesomeric interaction with the rest of molecule becomes high and consequently CT interaction within the free base is facilitated. The spectro-photometric determination of dissociation constants pKa values of such dye 11f can be utilized through the variation of the absorbance with pH values. Thus, the absorbance pH curves are typical dissociation constant pKa of the compounds were determined from the variation of absorbance with pH using the spectrometric half-height limiting absorbance and collector methods, [26-28]. The determination of

pKa values of dye 11f was listed in Table (4). The results showed that pKa value of dye 11f depend upon the nature of such cyanine dye. Thus, pKa values of dye 11f containing quinolinium heterocyclic quaternary residue reveals pKa =7.8, This results was suggested that dye 11f is more sensititive as photosensitizers in acidic and causes the high planarity in acidic medium, On the other hand, the ethanolic of N-bridge head heterotri (tetra)cyclic and/or fused benzo heterobicyclic moieties (8a,b,16a-e & 19) in aqueous solution (acidic medium) exhibit coloured solutions discharged on basification. This may due to that some heterocyclic compounds substituted with an electron-withdrawing group showed a "Covalent hydration phenomenon "in aqueous solutions [29]. It is not surprising to find their acidic ethanolic solution gave such phenomenon. This is due to that such dyes substituting with strong electron withdrawing groups (C=NH, C=O) showed 4-amino pyridinium type resonance "Covalent hydration" in aqueous solution as in dyes (8a,b ,19). On the other hand, the existence of benzpiperidin-NH group as electron donor supplements the directing effect of imino-nitrogen [C=NH] and direct the incoming proton of an aqueous medium into such groups leading to the stabilized form through the mesomeric effects of either 4-amino-pyridinium or amidinium types resonance. The highly coloured solutions in aqueous solution is due to electron charge transfer in conjugated mesomeric structures from N-bridge head heterocyclic moiety iminium/ hydroxnium cations moieties causes the resonance stabilization (Equation A).

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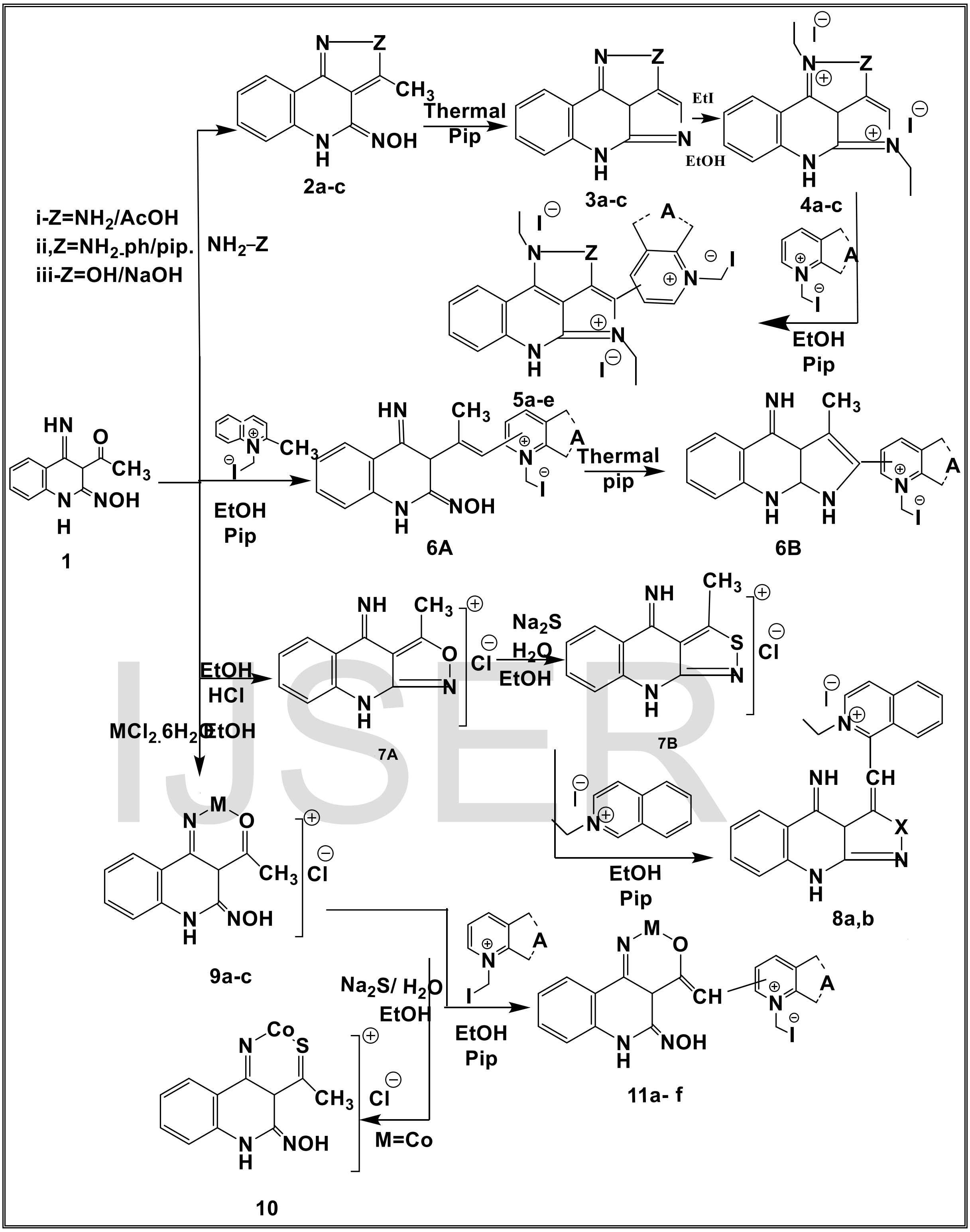
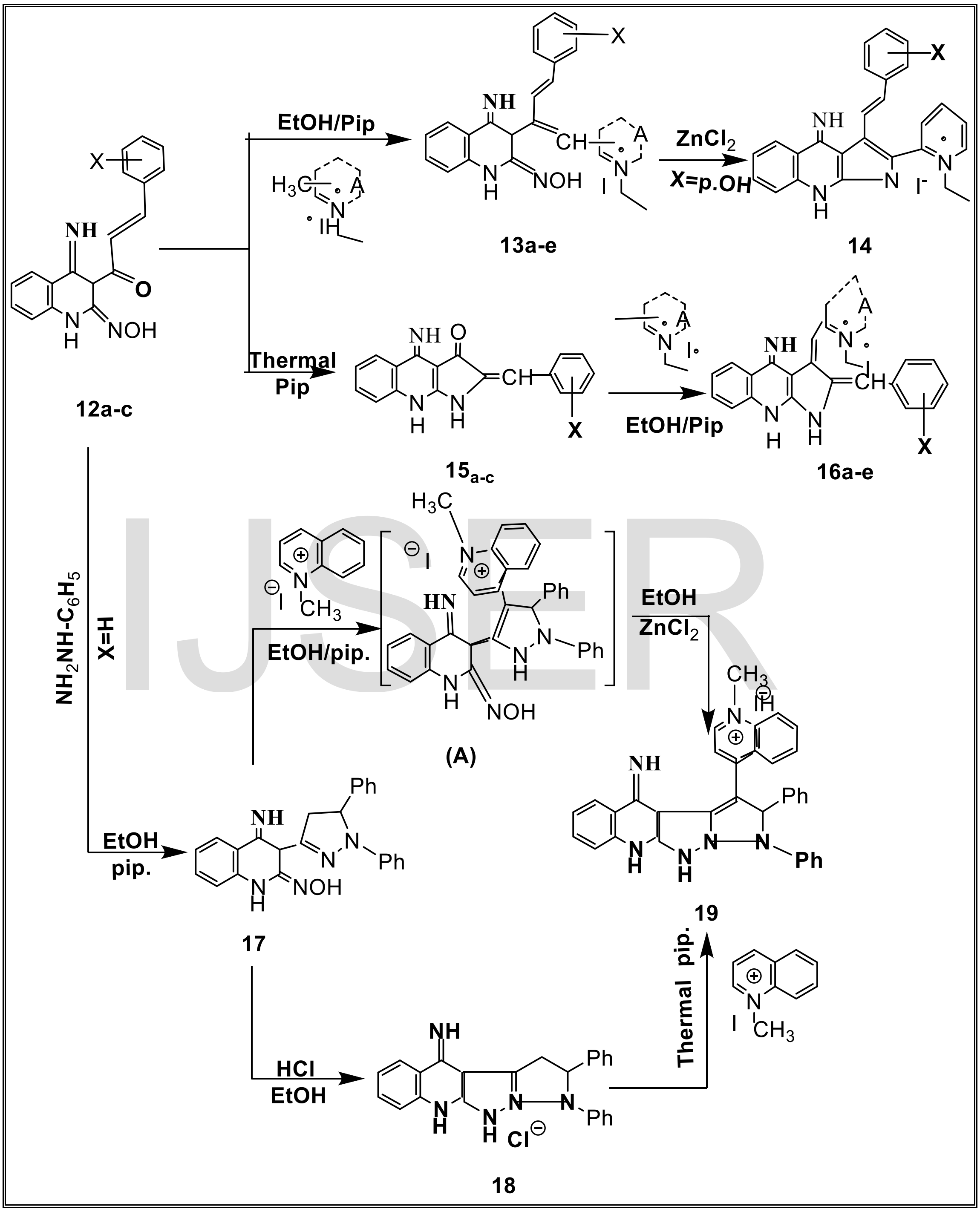


Scheme 1A

Scheme 1A substituents:

(2a-c, 3a-c): Z=N-$COCH_3$ (a); Z=N-ph (b); Z=O (c). (4a-c): Z=N-$COCH_3$ (a), Z=N-Ph (b), Z=O (c). (5a-e):Z=O,A=pyridin-4-ium salt (a); Z=O,A=quinolin-4-ium salt (b); Z=O, A=quinolin-1-ium salt (c); Z=N-Ph, A=quinolin-4-ium salt (d);Z=N-COCH3, A= quinolin-4-ium salt (e). (8A, B): (a), X= O; (b), X= S. (9a- c): M=Cu (a); M=Co (b);

M=Ni (c). (11a-f): X=O, M=Cu, A=pyridin-4-ium salt (a); X=O, M=Cu ,A=quinolin-4-ium salt (b);X=O, M=Cu A=quinolin-1-ium salt (c); X=O, M=Co, A=quinolin-4-ium salt (d); X=O,M=Ni, A=quinolin-4-ium salt (e);X=S, M=Co, A=quinolin-4-ium salt (f)

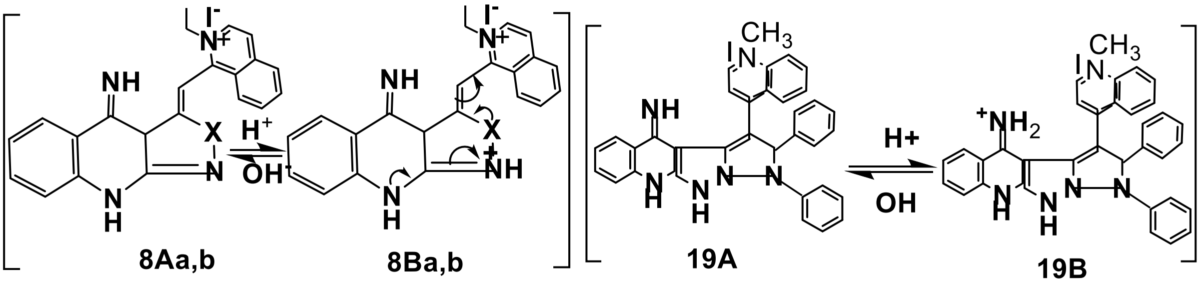


Scheme 1B

<u>Scheme 1 B Substituents</u>

(12a-c): X=H, (a), X=p-OH (b), X=p-Cl (c), (13a-e): X=H; A=pyridin-2-ium salt (a); X=H; A=pyridin-4-ium salt (b); X=H; A=quinolin-2-ium salt (c); X=p.OH;

A=pyridin-2-ium salt (d); X=p.Cl; A =pyridin-2-ium salt (e). (15a-c): X=H (a), X=p.OH (b), X=p.Cl (c).(16a-e):X=H; A=pyridin-2-ium salt (a); X=H; A=pyridin-4-ium salt (b); X=H; A=quinolin-2-ium salt (c); X=p.OH; A=pyridin-2-ium salt (d); X=p. Cl; A =pyridin-2-ium salt (e).



Equation a: Covalent Hydration phenomenon for 8A, B & 19A, B

Table 1: Colour of (5 d, 8A,B, 13 d ,19) in Organic Solvents

Comp. No.	DMF	Et OH	$CHCl_3$	C_6H_6	CCl_4	Ethanolic solution in	
						H_2SO_4	NaOH
5d	Dark red	Dark red	red	reddish Yellow	Orange	Light Yellow	Yellow
8A	Brownish red	Brown	Brown	Pale Brown	Yellow	Deep Red	Pale brown
8B	Greenish brown	Greenish brown	Brown	Pale Brown	Yellow	Deep Red	Pale brown
14d	Reddish brown	Reddish Brown	Dark brown	Brown	Pale brown	Deep Red	Pale brown
19	Reddish violet	Reddish violet	Red	Orange	Pale orange	Reddish violet	Orange

Table 2, 3: Absorption (nm) and extinction coefficients Values (mol^{-1} cm^{-1}) of (5d , 8A,B, 13d, 19) in pure organic solvents &Commutative data of 13d in mixed solvents

Comp No.	**DMF**		**EtOH**		**CHCL$_3$**		**C$_6$H$_6$**		**CCl$_4$**	
	λmax(εmax)		**λmax (εmax)**		**λmax (εmax)**		**λmax (εmax)**		**λmax(Emax)**	
5d	**490**	**2179**	**490**	**2.321**	**480**	**2.531**	**465**	**2.690**	**450**	**2.531**
8a	**475**	**1936**	**475**	**1828**	**460**	**2945**	**450**	**2098**	**440**	**2585**
8b	**490**	**2574**	**490**	**2388**	**480**	**1973**	**465**	**2453**	**450**	**2702**
13d	**485**	**2310**	**480**	**2696**	**470**	**2105**	**460**	**2670**	**455**	**2351**
19	**545**	**2830**	**540**	**2714**	**535**	**2622**	**505**	**2387**	**495**	**2387**

Comp. No.	**Solvent system**	**k.cal.mol-1**					**N**	**Log. Kf (-)**	**Kf**	**-ΔG k.cal. mol-1**
		Exc. G Pure Solvents		**Orient. G**	**H. Bond G**	**Total G**				
13d	**DMF-C6H6**	**66.5 (C$_6$H$_6$)**	**58.9 (DMF)**	**1.25**	**3.34**	**4.59**	**1**	**0.64**	**4.4**	**0.793**

Table 4: Absorption Value of 11f in Universal Buffers

Comp. No.	**Absorption Values**	**Absorption Spectra in**							
		EtOH	**Universal Buffer Solutions pH**						
			3.08	**4.2**	**6.04**	**7.64**	**8.17**	**10.02**	**pKa**
11f	**λmax**	**505**	**465**	**470**	**470**	**475**	**475**	**475**	**7.8**
	εmax	**2657**	**1164**	**1053**	**1219**	**1349**	**2943**	**2865**	
	Abs.	**2.657**	**1.164**	**1.053**	**1.219**	**1.349**	**2.943**	**2.865**	

Table 5: Characterization of (2 a-c, 3 a-c, 6A, 7a,b 9a-c, 10, 15a-c)

Comp. No.	**Colour**	**m.p. C^o**	**Yield %**	**Mol. Formula MS(m/z)**	**Calc.(Found)**		
					C	**H**	**N**
2a	**yellow**	**182**	**48**	**$C_{13}H_{10}N_4O_2$ (254)**	**(61.41) (61.43)**	**(3.93) (3.92)**	**(22.04) (22.06)**
2b	**Pale brown**	**154**	**47**	**$C_{16}H_{12}N_4O$ (276)**	**(69.84) (69.80)**	**(4.34) (4.34)**	**(20.28) (20.28)**
2c	**Pale yellow**	**176**	**45**	**$C_{11}H_7N_3O_2$ (213)**	**(61.97) (61.91)**	**(3.28) (3.28)**	**(19.71) (19.75)**
3a	**Brown**	**150**	**43**	**$C_{13}H_8N_4O$ (236)**	**(66.10) (66.15)**	**(3.38) (3.31)**	**(23.72) (23.71)**
3b	**Reddish brown**	**150**	**42**	**$C_{16}H_{10}N_4$ (258)**	**(74.41) (74.48)**	**(3.87) (3.84)**	**(21.70) (21.74)**
3c	**Dark yellow**	**165**	**35**	**$C_{11}H_5N_3O$ (195)**	**(67.69) (67.64)**	**(2.56) (2.53)**	**(21.53) (21.55)**
4a	**Dark brown**	**146**	**41**	**$C_{15}H_{18}N_3OI_2$ (508)**	**35.43 (35.46)**	**3.54 (3.51)**	**8.26 (8.21)**
4b	**Dark brown**	**153**	**51**	**$C_{20}H_{22}N_4I_2$ (570)**	**47.24 (47.28)**	**3.50 (3.52)**	**9.82 (9.87)**
4c	**Dark yellow**	**168**	**48**	**$C_{17}H_{20}N_4OI_2$ (548)**	**37.22 (37.28)**	**3.64 (3.64)**	**10.21 (10.29)**
6A	**reddish violet**	**218**	**58**	**$C_{24}H_{23}N_4OI$ (509)**	**56.58 (56.50)**	**4.51 (4.50)**	**11.00 (11.05)**
7A	**Brown**	**190**	**67**	**$C_{11}H_9N_2O_2Cl$ (236.5**	**55.58 (55.52)**	**3.80 (3.81)**	**11.83 (11.86)**

7B	**green**	**200**	**47**	$C_{11}H_9N_2O_SCl$ **(252.5)**	**52.27 (52.22)**	**3.56 (3.56)**	**11.08 (11.00).**
9a	**Dark Blue**	**>250**	**75**	$C_{11}H_{11}N_3O_2CuCl$ **(281.5)**	**49.81 (49.78)**	**4.15 (4.17)**	**10.58 (10.50)**
9b	**Pale blue**	**180**	**63**	$C_{11}H_{11}N_3O2CoCl$ **(279.5)**	**50.00 (50.05)**	**4.16 (4.12)**	**10.61 (10.65)**
9c	**Pale green**	**205**	**65**	$C_{11}H_{11}N_3O2NiCl$ **(280.5)**	**50.09 (50.02)**	**4.17 (4.16)**	**10.62 (10.68)**
10	**Dark blue**	**165**	**77**	$C_{11}H_{11}N_3OCoSC$ **(295.5)**	**48.61 (48.61)**	**4.05 (4.02)**	**10.31 (10.35)**
15a	**Pale brown**	**175**	**37**	$C_{18}\ H_{13}N_3\ O$ **(287)**	**57.26 (57.75)**	**4.52 (4.65)**	**14.63 (14.65)**
15b	**Dark brown**	**177**	**45**	$C_{18}\ H_{13}N_3\ O_2$ **(271)**	**60.70 (60.85)**	**4.79 (4.80)**	**15.49 (15.48)**
15c	**Brown**	**182**	**54**	$C_{18}\ H_{12}N_3\ O\ Cl$ **(321.5)**	**67.18 (67.15)**	**3.73 (3.75)**	**13.06 (13.01)**

Table 6: Characterization of (5a-e, 6B, 8A, B, 11a-e, 12 f, 13a-e, 14, 16 a-e 18, 19,)

Comp No.	**Nature of product**			**Mol. Formula (M. Wt)**	**Calc.(Found)**			**Absorption spectra in 95%EtOH**	
	Colour	**m.po C**	**Yield %**		**C**	**H**	**N**	**λmax n. m**	**Emax Mol-1cm2**
5a	**Dark brown**	**156**	**38**	$C_{20}H_{20}N_4OI_2$ **(584)**	**41.09 (41.09)**	**3.42 (3.48)**	**9.58 (9.52)**	**465**	**24370**
5b	**Reddish brown**	**179**	**46**	$C_{24}H_{24}N_4OI_2$ **(636)**	**79.33 (79.39)**	**3.77 (3.70)**	**8.80 (8.86)**	**475**	**2826**
5c	**Reddish brown**	**174**	**39**	$C_{24}H_{24}N_4OI_2$ **(636)**	**79.33 (79.39)**	**3.77 (3.70)**	**8.80 (8.86)**	**470**	**2367**
5d	**Dark red**	**118**	**35**	$C_{29}H_{26}N_5I_2$ **(696)**	**50.00 (50.6)**	**3.16 (3.18)**	**10.05 (10.08)**	**490**	**2372**
5e	**Orange**	**178**	**38**	$C_{28}H_{26}N_5I_2$ **(684)**	**49.12 (49.18)**	**3.80 (3.84)**	**10.23 (10.29)**	**465**	**2662**
6B	**reddish violet**	**187**	**37**	$C_{24}H_{21}N_4I$ **(491),**	**58.65 (58.68)**	**4.27 (4.27)**	**11.40 (11.42),**	**485**	**2646**
8A	**Brownish red**	**183**	**46**	$C_{22}H_{20}N_4OI$ **(482)**	**54.77(54.70)**	**4.14 (4.15)**	**11.61 (11.65),**	**475**	**2511**
8B	**greenish brown**	**187**	**37**	$C_{22}H_{20}N_4SI$ **(498),**	**53.01(53.07)**	**4.01 (4.03)**	**11.24(11.27)**	**490**	**2939**
11a	**Dark Green**	**112**	**38**	$C_{18}H_{18}N_4O_2CuI$ **(477)**	**35.43 (35.46)**	**3.54 (3.51)**	**8.26 (8.21)**	**460**	**1909**
11b	**Reddish Violet**	**145**	**45**	$C_{22}H_{22}N_4O_2CuI$ **(529)**	**47.24 (47.28)**	**3.50 (3.52)**	**9.82 (9.87)**	**500**	**2641**
11c	**Dark Blue**	**150**	**42**	$C_{22}H_{22}N_4O_2CuI$ **(529)**	**37.22 (37.28)**	**3.64 (3.64)**	**10.21 (10.29)**	**475**	**2870**
11d	**Dark red**	**188**	**25**	$C_{22}H_{22}N_4O_2\ NiI$ **(528)**	**41.09 (41.09)**	**3.42 (3.48)**	**9.58 (9.52)**	**490**	**1145**
11e	**Greenish brown**	**177**	**48**	$C_{22}H_{22}N_4O_2CoI$ **(527)**	**79.33 (79.39)**	**3.77 (3.70)**	**8.80 (8.86)**	**480**	**2473**
11f	**Dark red**	**186**	**71**	$C_{22}H_{22}N_4OSCoI$ **(543)**	**79.33 (79.39)**	**3.77 (3.70)**	**8.80 (8.86)**	**525**	**2644**
14a	**Brown**	**174**	**38**	$C_{26}H_{25}N_4OI$ **(523)**	**58.21 (57.75)**	**4.66 (4.65)**	**10.45 (10.63)**	**465**	**2434**

14b	**Dark Violet**	**179**	**48**	**$C_{30}H_{27}N_4OI$ (585)**	**61.43 (60.85)**	**4.61 (4.61)**	**9.56 (9.62)**	**450 560 695**	**2329 2330 1297**
14c	**Reddish Brown**	**182**	**56**	**$C_{26}H_{25}N_4OI$ (523)**	**58.21 (57.75)**	**4.66 (4.65)**	**10.45 (10.63)**	**475**	**2554**
14d	**Dark Brown**	**215**	**45**	**$C_{25}H_{26}N_4O_2I$ (540)**	**55.55 (55.59)**	**4.81 (4.82)**	**10.73 (10.40)**	**480**	**2696**
14e	**Dark Brown**	**159**	**42**	**$C_{26}H_{24}N_4OClI$ (557.5)**	**53.70 (53.21)**	**4.13 (4.13)**	**12.05 (12.32)**	**455**	**2448**
14f	**greenish brown**	**125**	**38**	**$C_{25}H_{24}N_4OI$ (522),**	**57.47(75 .51)**	**4.59 (4.59)**	**10.72 (10.73)**	**470**	**2471**
15	**Reddish brown**	**176**	**48**	**$C_{35}H_{30}N5I$ (646),**	**65.01(65 .08)**	**4.64 (4.64)**	**10.83 (10.83)**	**540**	**2830**
16a	**Dark Brown**	**132**	**36**	**$C_{26}H_{23}N_4I$ (505)**	**60.23 (59.75)**	**4.44 (4.45)**	**10.81 (10.75)**	**455**	**2428**
16b	**Dark Violet**	**140**	**51**	**$C_{30}H_{25}N_4I$ (567)**	**63.36 (62.56)**	**4.40 (4.40)**	**9.85 (10.12)**	**450 460 685**	**2419 2378 1393**
16c	**Dark Brown**	**135**	**38**	**$C_{25}H_{23}N_4I$ (505)**	**60.23 (59.75)**	**4.44 (4.45)**	**10.81 (10.75)**	**465**	**2418**
16d	**Dark Yellow**	**137**	**32**	**$C_{25}H_{23}N_4OI$ (521)**	**57.58 (57.78)**	**4.41 (4.41)**	**10.74 (10.74)**	**460**	**2800**
16e	**Brown**	**142**	**34**	**$C_{25}H_{22}N_4Cl$ I (539.5)**	**55.91 (55.95)**	**4.08 (4.08)**	**10.37 (10.40)**	**450**	**2210**
18	**dark brown**	**160**	**45**	**$C_{25}H_{21}N_4$ (412.5)**	**72.72 (72.75)**	**5.09 (5.09)**	**13.75 (13.57)**	**450**	**2253**

Table 7: IR &1HNMR Spectral Data of some Selected (2b, 5a, 6A, B, 7a, 8A, 9a, 11a, 13a 14, 15c, 16a 18, 19,)

Comp. No	IR ((vKBr) (cm-1)	^{1}HNMR (DMSO, 250 MHz) (ppm)
2b, (4a, 5a),	**1699 (v,C= O),1530 (v,C=NH) for 2b 1483 (v, C= N), 1600 cm-1 (C=O), & 2851-2921 (v Et I of heterocyclic salts) for 5a**	**(2b), 3.5(s, 2H, CH2), 6.6 (m, 9H, Ar-H), 10.6 (S, 1H, NH).**
6A,B	**760-849 (vmax mono sub. Ar.), 1683 (v,C= N),2849-2922 (v Et I of hetero cyclic salts), 3422 (v, 2NH)**	**(8A), δ1.2- 2.1 (s, 3H, of CH3 Et I)), 3.3 (s, 2H, of CH2 Et I)), 6.5- 8.1 (m, 12H,11H,Ar-H, 1H, CH Me I) & 10.7 (s, 2H, 2NH),**
7a 9a,11a	**1580 (vC=C), 3480 (NH) for 7a, 755-821 (v mono sub. Ar.), 599 (v, C=N), 3272-3443 (v, 2NH, OH), 2922 (v Et I heterocyclic salts)**	**(13a) δ 1.2 (s, 3H, CH3 EI), 2.1 (s, 2H, CH2 Et I), 6.4- 7.9 (m, 18H,14H,Ar-H, 3H, 3CH, 1H, NH) , 9.1-9.8 (br, 2H, 1H, NH, 1H, NOH)**
18,19	**1454 (C=N) for 16B, & 2922 (v Me I of heterocyclic salts) for 19.**	**IR ((vKBr) 699-790 (vmax mono subs .Ar, 1697 (v,C= N) 3182-3315 (v, 2NH) for 16, 2852-2922 (v Et I of hetero cyclic salts) for 15c, 16a**