# Heterocyclic Quaternary Schiff Bases in the synthesis of N-Bridge Head Heterocyclic Mero & Zero Methine cyanine dyes

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**ABSTRACT**

Acetylating of Acyclic (cyclic)-N-Aryl [pyrazolinyl (pyridinyl)] Schiff bases quaternary salts **(2a-I, 3A)** resulted in 5-Acetyl-N-Aryl[Pyrazolinyl(Pyridinyl)]pyrolo-[5,4-d] pyrazolin-iodide salts and their Anhydro Bases] **(4a-j)**. Cyclic heterocyclic quaternary salts and related 5-Acetyl derivatives changed into their anhydro bases as cyclic mero cyanine dyes **(3B, 4a-I)** using sodium acetate. The reaction of **(3B)** with pyridine (quinolin)-4(1)-ium-Ethiodide salts afforded substituted N-Aryl [pyrazolinyl (pyridinyl)] pyrolo[5,4-d] pyrazol-zero-5[4(1)] methine cyanine dyes **(6a-c).** The structure of heterocyclic Schiff bases quaternary salts and their 5-Acetyl- N-Aryl [pyrazolinyl (pyridinyl)]-pyrolo[3,2-d]pyrazolin [oxazolin/ imidazolin-6-one]-1-ium-iodide and their heterocyclic Cyclo-mero & zero-5[4(1)] methine cyanine dyes was identified by elemental & spectral data. The UV-visible absorption spectra of some selected dyes was investigated in absolute 95% EtOH, polar (non polar) organic solvents and in universal buffer solutions to investigate the best conditions when these new dyes are applied as photosensitizes

**Key Words:** Heterocyclic Schiff Bases quaternary salts, Cyclo-mero, Zero Methine cyanine dyes Synthesis, Spectral Behaviour, solvatochromic and acid-Base Properties.

## 1.INTRODUCTION

Applications of heterocyclic Schiff bases were useful in perfumery **[1, 2, 3]** and as corrosion inhibitor [**4],** electrochemical sensors **[5]** and in the preparation of various medicines **[6, 7].** The chemistry of pyrazole and its derivatives is particularly interesting because of their potential application in medicinal chemistry as analgesic, antiinflammatory, antipyretic, antiparasitic, antimalarial, antifungal and antimicrobial and as enzyme inhibitory agents **[8].** The development of heterocyclic Schiff bases for the corrosion inhibition, or metal protection in aqueous media, especially in acidic solutions has been the subject of consideration for several investigators. Heterocyclic

containing sulpher, nitrogen and/or oxygen (having one or more active center) were widely used as corrosion inhibitors for various metals in different media. Addition of heterocyclic compounds had been done to improve the metal solution interface (environment) to modify the reactions concerned. [**9].** Electrochemical behaviour of 4-aryl azamethenyl-3-methyl-1-phenyl pyrazolo-5-one and 4-Aryl-azamethenyl-5-chloro-3-methyl-1-phenyl pyrazole as corrosion inhibitors for copper alloy in nitric acid (2 Mol) as corrosion medium was discussed in our lab by **[10].**

## 2.Experimental

2.1 All melting points are uncorrected. Elemental analysis IR, $^{1}$H-NMR & & Mass spectra recorded with Perkin Elmer Infrared 127B , EM-390 90 MHz NMR & a Hp Ms 6988 spectrophotometers at the Micro analytical center (Cairo-University).The visible were recorded on UV-Visible recording spectrophotometer UV-240, and UV-160A. 4-Acetyl-[Bromo-, Amino]-3-Methyl-1-phenyl-Pyrazolin-5-one and 4-acetyl-3-methyl-1-phenyl-pyrazolin-5-one-hetero cyclic Schiff Bases **(1a-g), Table (1)** were prepared in a way similar to **[11-13].**



**Table (1): Characterization of Heterocyclic Schiff Bases (1a-g):**

| Comp. No. | Nature of product | | | Mol. Formula (M.wt) | Analytical analysis % calcd. (found) | | | Absorption Spectra in 95% EtOH | |
|---|---|---|---|---|---|---|---|---|---|
| | M.p. ˚C | Yield % | Colour | | C | H | N | $\lambda_{max}$ (n.m) | $\varepsilon_{max}$ (mol$^{-1}$ cm$^{2}$) |
| **1a** | 185 | 50 | Reddish brown | $C_{18}H_{17}N_3O$ (291) | 74.22 (74.65) | 5.84 (5.90) | 14.43 (14.5) | - | - |
| **1b** | 220 | 49 | Reddish brown | $C_{18}H_{17}N_3O_2$ (307) | 70.36 (70.42) | 5.53 (5.60) | 13.68 (13.70) | 400 | 10500 |
| **1c** | 190 | 53 | Deep brown | $C_{18}H_{17}N_3O_2$ (307) | 70.36 (70.39) | 5.53 (5.50) | 13.68 (13.66) | 430 | 2900 |
| **1d** | 240 | 50 | Ball brown | $C_{19}H_{17}N_3O_3$ (335) | 68.06 (68.11) | 5.07 (5.00) | 12.54 (12.50) | - | - |
| **1e** | 245 | 50 | Reddish brown | $C_{19}H_{17}N_3O_3$ (335) | 68.06 (68.13) | 5.07 (5.12) | 12.54 (12.56) | - | - |
| **1f** | 165 | 55 | Reddish brown | $C_{22}H_{21}N_5O_2$ (387) | 68.22 (68.25) | 5.43 (5.50) | 18.09 (18.12) | 365 445 | 2500 2800 |
| **1g** | 135 | 42 | Reddish brown | $C_{17}H_{16}N_4O$ (292) | 69.86 (69.91) | 5.48 (5.53) | 19.18 (19.22) | - | - |

## 2.2 Synthesis of N-Aryl [pyrazolinyl (pyridinyl)] Schiff bases quaternary iodide salts (2a-i)

An Ethanolic solution of 4-acetyl-3-methyl-1-phenyl-pyrazolin-5-one-heterocyclic Schiff Bases (1a-i) and 3-methyl-1-phenyl-pyrazolin-5-one [2-methyl-oxazolin-5-one] (0.01 mol) in Iodine was refluxed for 1-2 hours, filtered hot, concentrated and cooled. The precipitated solids after dilution with water were collected and crystallized from aqueous ethanol to give products. **Table (2).**

**2.3 Synthesis of 6-methyl-4-phenyl-N-aryl-2-(3-methyl-1-phenyl-pyrazol-5-one)-pyrrolo-[5,4-d] pyrazoline ylide iodide salt & 3-Methyl-1-phenyl- pyrrolo[5,4-d] pyrazol- 3[4(1)] mero cyanine dyes (3A,B).**

A-Compound (2c) was fused in presence of few drops of piperidine for 10 minutes, cooled, dissolved in 30ml ethanol, refluxed for about 3hr., filtered hot, concentrated, cooled and acidified with acetic acid. The solid 6-methyl-4-phenyl N-Aryl-2-(3-methyl-1-phenyl-pyrazol-5-one)-pyrolo-[5, 4-d] pyrazolone iodide salt (3A) was precipitated on dilution with water and crystallized from ethanol. B-A mixture of (3A) 10 m mol and AcONa 20 m mol / NaOH 40 m mol in ethanol 40 ml **[14]** was heated to boiling. The colour was changed to violet and the solid 6-methyl-4-phenyl-N-aryl-2-(3-methyl-1-phenyl-pyrazol-5-one)-pyrolo-[5,4-d] pyrazole (3B) was filtered and washed with water.

**Table (2)**

**Table (2): Characterization of Acyclic Heterocyclic Schiff Bases Quaternary Salts (2a-i):**

| Comp. No. | Nature of product | | | Mol. Formula (M.wt) | Analytical analysis % calcd. (found) | | | Absorption Spectra in 95% EtOH | |
|---|---|---|---|---|---|---|---|---|---|
| | M.p. ˚C | Yield % | Colour of crystal | | C | H | N | $\lambda_{max}$ (n.m) | $\varepsilon_{max}$ ($mol^{-1}$ $cm^2$) |
| **2a** | 130 | 65 | Brown | $C_{28}H_{26}N_5O_2I$ (591) | 65.85 (65.90) | 4.40 (4.44) | 11.84 (11.88) | 365 | 14200 |
| **2b** | 140 | 68 | Brown | $C_{28}H_{26}N_5O_3I$ (607) | 55.35 (55.40) | 4.28 (4.35) | 11.53 (11.56) | 370 | 22000 |
| **2c** | 145 | 78 | Deep brown | $C_{28}H_{26}N_5O_3I$ (607) | 55.35 (55.42) | 4.28 (4.33) | 11.53 (11.50) | 375 | 11200 |
| **2d** | 150 | 67 | Reddish brown | $C_{29}H_{26}N_5O_4I$ (635) | 54.80 (54.85) | 4.09 (4.12) | 11.02 (10.99) | 360 | 12000 |
| **2e** | 155 | 69 | Deep reddish brown | $C_{29}H_{26}N_5O_4I$ (635) | 54.80 (54.88) | 4.09 (4.00) | 11.02 (11.10) | 350<br>420<br>500 | 15000<br>3800<br>3800 |
| **2f** | 135 | 66 | Deep brown | $C_{22}H_{21}N_4O_4I$ (532) | 49.62 (49.66) | 3.95 (4.00) | 10.53 (10.60) | 360 | 17800 |
| **2g** | 155 | 64 | Deep brown | $C_{21}H_{20}N_5O_4I$ (533) | 47.28 (47.31) | 3.75 (3.80) | 13.13 (13.20) | 355 | 14800 |
| **2h** | 145 | 70 | reddish brown | $C_{32}H_{30}N_7O_3I$ (687) | 55.90 (56.00) | 4.37 (4.40) | 14.26 (14.33) | 290<br>375 | 24000<br>8200 |
| **2i** | 115 | 50 | reddish brown | $C_{27}H_{25}N_6O_2I$ (592) | 54.73 (54.70) | 4.22 (4.18) | 14.19 (14.22) | 280<br>370 | 20000<br>7000 |
| **3A** | 140 | 55 | Red | $C_{28}H_{24}N_5O_2I$ | 57.05 | 4.07 | 11.88 | 465 | 2340 |

| | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | | | brown | (589) | (57.01) | (4.1) | (11.82) | | |
| **3B** | 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 |

## 2.4 5-Acetyl-N-Aryl [pyrazolinyl (pyridinyl)] pyrolo [3,2-d]pyrazole-, oxazole-, imidazol-3-one-1-ium-iodide (4a-i):

Mixture of N-Aryl-[3-methyl-1-phenyl-pyrazolin-5-one, pyridinyl] methyl-imine Schiff Bases -methyl-iminium-iodide salts (2a-i, 0.005 mol) with acetic anhydride (10 ml).The reaction mixture was refluxed for 3 hours, and filtered, concentrated and cooled, the solid product was collected and crystallized from ethanol to give **(4a-i), Table (3)**

**Table (3): Characterization of 5- Acetyl Heterocyclic Quaternary Salts of (4a-i ):**

| Comp. No. | Nature of product | | | Mol. Formula (M.wt) | Analytical analysis % calcd. (found) | | | Absorption Spectra in 95% EtOH | |
|---|---|---|---|---|---|---|---|---|---|
| | M.p. ˚C | Yield % | Colour | | C | H | N | $\lambda_{max}$ (n.m) | $\varepsilon_{max}$ (mol$^{-1}$ cm$^2$) |
| **4a** | 125 | 70 | Deep brown | $C_{30}H_{26}N_5O_2I$ (615) | 58.54 (58.60) | 4.23 (4.32) | 11.38 (11.46) | 265 | 26000 |
| **4b** | 165 | 73 | Deep brown | $C_{30}H_{26}N_5O_3I$ (631) | 57.05 (57.15) | 4.12 (4.22) | 11.09 (11.20) | 270 | 31000 |
| **4c** | 160 | 75 | Deep reddish brown | $C_{30}H_{26}N_5O_3I$ (631) | 57.05 (57.18) | 4.12 (4.25) | 11.09 (11.22) | 275 | 25000 |
| **4d** | 135 | 65 | Deep brown | $C_{31}H_{26}N_5O_4I$ (659) | 56.45 (56.55) | 3.95 (4.05) | 10.62 (10.72) | 260 | 26000 |
| **4e** | 145 | 68 | Deep brown | $C_{31}H_{26}N_5O_4I$ (659) | 56.45 (56.56) | 3.95 (4.10) | 10.62 (10.74) | 250 | 29000 |
| **4f** | 120 | 70 | Deep brown | $C_{24}H_{21}N_4O_4I$ (556) | 51.80 (51.92) | 3.78 (3.90) | 10.07 (11.00) | 260<br>340 | 22000<br>13500 |
| **4g** | 130 | 71 | Deep brown | $C_{23}H_{20}N_5O_4I$ (557) | 49.55 (49.70) | 3.59 (3.70) | 12.57 (12.72) | 255 | 26500 |
| **4h** | 150 | 74 | Brown | $C_{34}H_{30}N_7O_3I$ (711) | 57.38 (57.50) | 4.22 (4.35) | 13.78 (13.90) | 275 | 27000 |
| **4i** | 140 | 55 | Brown | $C_{29}H_{25}N_6O_2I$ (616) | 56.49 (56.6) | 4.06 (4.17) | 13.64 (13.80) | 270 | 25000 |

## 2.5 5-Acetyl-Anhydro-N-Aryl [pyrazolinyl (pyridinyl)] Schiff Bases Cyclic Mero Cyanine like (5a-i):

Ethanolic solution of 5-Acetyl-N-Aryl-[3-methyl-1-phenyl-pyrazolin-5-one, pyridinyl] pyrolo [3,2-d]pyrazole-, oxazole-, imidazol-3-one-1-ium-iodide (4a-I, 0.005 mol) in fused sodium acetate (10 ml) was refluxed for 3 hours and filtered, concentrated and cooled, the solid product was collected and crystallized from ethanol to give **(5a-i), Table (4)**

**Table (4): Characterization of 5-Acetyl Anhydro Heterocyclic Schiff Bases (5a-i):**

| Comp. No. | Nature of product | | | Mol. Formula (M.wt) | Analytical Analysis % calcd. (found) | | | Absorption Spectra in 95% EtOH | |
|---|---|---|---|---|---|---|---|---|---|
| | M.p. °C | Yield % | Colour | | C | H | N | $\lambda_{max}$ (n.m) | $\varepsilon_{max}$ ($mol^{-1}$ $cm^2$) |
| **5a** | 210 | 65 | Deep brown | $C_{30}H_{25}N_5O_2$ (487) | 73.92 (74.00) | 5.13 (5.20) | 14.37 (14.44) | 265 | 26000 |
| **5b** | 200 | 68 | Deep brown | $C_{30}H_{25}N_5O_3$ (503) | 71.57 (71.50) | 4.97 (5.00) | 13.92 (14.00) | 270 | 31000 |
| **5c** | 230 | 69 | Deep grey brown | $C_{30}H_{25}N_5O_3$ (503) | 71.57 (71.65) | 4.97 (5.06) | 13.92 (13.86) | 275 | 25000 |
| **5d** | 200 | 60 | Brown | $C_{31}H_{25}N_5O_4$ (531) | 70.06 (70.13) | 4.71 (4.80) | 13.18 (13.25) | 260 | 26000 |
| **5e** | 195 | 61 | Brown | $C_{31}H_{25}N_5O_4$ (531) | 70.06 (70.18) | 4.71 (4.66) | 13.18 (13.08) | 250 | 29000 |
| **5f** | 200 | 64 | Deep brown | $C_{24}H_{20}N_4O_4$ (428) | 67.29 (67.33) | 4.67 (4.60) | 13.08 (13.15) | 260<br>340 | 22000<br>13500 |
| **5g** | 220 | 66 | Deep brown | $C_{23}H_{19}N_5O_4$ (429) | 64.34 (64.41) | 4.43 (4.50) | 16.32 (16.40) | 255 | 26500 |
| **5h** | 205 | 67 | Brown | $C_{34}H_{29}N_7O_3$ (583) | 69.98 (70.10) | 4.97 (5.02) | 16.81 (16.90) | 275 | 27000 |
| **5i** | 195 | 50 | Brown | $C_{29}H_{24}N_6O_2$ (488) | 71.31 (71.38) | 4.92 (5.00) | 17.21 (17.30) | 270 | 25000 |



## 2.6 N-Aryl [pyrazolinyl (pyridinyl)]Pyrolo[5,4-d] pyrazolo--zero-5[4(1)] methine cyanine dyes (6a-c)

Equimolar proportions of (3A) and pyridin(quinolin)-4(1)-ium-ethiodide salts (0.01 mol) were fused in presence of few drops of piperidine for 10 minutes, cooled, dissolved in 30ml ethanol, refluxed for about 5 hr., filtered hot, concentrated, cooled and acidified with acetic acid. The precipitated solids after dilution with water were collected and crystallized from aqueous ethanol to give the corresponding products, **(6a-c), Table (5)**

**Table (5): Characterization data of Heterocyclic-Zero-5[4(1)]Methine (6a-c):**

| Comp. No. | M.p $^0$C | Yield % | colour | Mol. Formula (Mol. wt) | %Calcd(Found) | | | Absorption Spectra in Et-OH | |
|---|---|---|---|---|---|---|---|---|---|
| | | | | | C | H | N | $\Lambda_{max}$ (nm) | $\varepsilon_{max}$ ($cm^2mol^{-1}$) |
| **6a** | 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 |
| **6b** | 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 |
| **6c** | 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 |

## 2.7 Solvatochromic and Acid-Base properties:

For studying the effect of pure solvents in visible region: An accurate volume of the stock solution of dyes was diluted to appropriate volume in order to obtain the required concentration and to eliminate the effect of time. The organic solvents of spectroscopic grade were used according to **[13]**. The absorption spectra of dyes in different organic solvents were recorded within λ nm (350-700 nm) on Jenway Model 6800 Flight Deck UV/Visible recording spectrophotometer using 1cm cell. The stock solution of a dye was in the order $10^{-3}$ mol-$dm^{-3}$. Solutions of low molarities were obtained by accurate dilution.

## 2.8 Preparation of Universal Buffer Solutions:

For 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. A modified buffer series derived from **[16]** was prepared for use in the present investigation. 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. A solution of 0.4 mol-$dm^{-3}$ of boric acid was obtained by dissolving the appropriate weight of the recrystallised acid in redistilled water. 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 (2.05-11.16) was prepared as recommended by **[16].** This was done by mixing 150 ml of the acid mixtures in a 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 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 °C.

## 3. RESULT & DISCUSSION

### 3.1 Synthesis

Selective quaternization of N-Aryl [pyrazolinyl (pyridinyl)] methyl-imine Schiff Bases **(1a-g)** with 3(2)-Methyl-1-phenyl-Pyrazolin [oxazolin]-5-one/ imidazolin-2,5-dione, in Equimolar amount, under presence of iodine afforded N-Aryl [pyrazolinyl (pyridinyl)] methyl-imine Schiff Bases-methyl-imin-ium-iodide salts **(2a-i).** Thermal piperidine catalysis of acyclic ketomethylene heterocyclic Schiff base quaternary iodide salts **(2c)** gave 6-methyl-4-phenyl-N-Aryl-2(3-methyl-1-phenyl-pyrazol-5-one)-pyrolo-[5,4-d] pyrazolin-iodide salt **(3A)** which on treatment with AcONa/ NaOH in ethanol converted into an intense violet anhydro base transformation to afford 6-methyl-4-phenyl-N-Aryl-2(3-methyl-1-phenyl-pyrazol-5-one)-pyrolo-[5,4-d] pyrazolin **(3B).** Acetylating of **(3A) or** Intramolecular heterocyclization ring closure of **(2a-i)** under acetic anhydride afforded 5-Acetyl- N-Aryl [pyrazolinyl (pyridinyl)]pyrolo[3,2-d] pyrazolin[oxazolin /Imidazolin]-1-ium-iodide **(4a-i)** which on treatment with AcONa / NaOH in ethanol transformed into 5-Acetyl-N-Aryl [pyrazolinyl (pyridinyl)] pyrolo[3,2-d] pyrazolin [oxazolin /Imidazolin] anhydro base **(5a-i)** as heterocyclic Cyclo-mero cyanine dyes**[11,12].** On triturating of an ethanolic solution of **(3B, 5a-i)** with aq. solution KI followed by solubility in conc. sulfuric acid give no iodine vapour on warming**.** Fusion of **(3B)** with Acetamide confirmed the formation of the later **(5a-i).** Interaction of **(3B)** and N-ethyl pyridin (quinolin & quinolin)-4(1)-ium iodide salts, in Equimolar ratio, in the presence of piperidine/ethanol resulted in N-Aryl [pyrazolinyl (pyridinyl)]pyrolo [5,4-d] pyrazol-zero-5[4(1)] methine cyanine dyes **(6a-c), Scheme (1).** The structure of (2c, 3A, 4b,5b, f, g, h, I & 6a) was confirmed by elemental and spectral analyses, **[18-21], Tables (1-6)**

The formation of 3-methyl-1-phenyl pyrolo [5, 4-d] pyrazol-mero cyanine **(3B)** was suggested to proceed via liberation of the methylene base **(A)** of an acyclic heterocyclic quaternary salt **(2b)** under basic catalyst through dihydro iodination process. Such methylene base **(A)** expressed a higher nucleophilic character and the nucleophilic attack proceeded stronger & faster on the electron deficient $Sp^2$ carbon atom of pyrazol-5-one to form an intermediate **(B)** which abstract a proton from the $BH^+$ to form an intermediate **(C)** which undergoes dehydration process to form merocyanine **(6b)**.The formation of **(3B)** was suggested to proceed via dehydration ring closer, as a reactive methyl group in **(2b)** readily lose proton to give a methylene base intermediate **(A)** due to the lower basicity of the nuclei in an acyclic

quaternary Schiff base **(2b)** under reaction condition. The latter formed anhydro base is considered as a good nucleophilic reagent and when approached carbonyl carbon of pyrazol-5-one deficiency resulted in an intermediate **(B)** which abstracts a proton then undergoes dehydrogenation process to form mero cyanine dye **(3B), [17].** The formation of **(6a-c)** was suggested to proceed via liberation of a methylene base of **(4c)** under piperidine catalysis to form an intermediate **(A). A** nucleophilic addition reaction between an intermediate **(A)** and pyridin (quinolin)-4(1)-ium-ethiodide followed by oxidative elimination process to afford N-Aryl [pyrazolinyl (pyridinyl)]pyrolo[5,4-d] pyrazolin-zero-3[4(1)] methine cyanine dyes **(6a-c), Equation (1A,B).** The heterocyclic Schiff bases quaternary salts, 5-Acetylated-heterocyclic mero- and zero-5[4(1)]methine cyanine dyes **(4a-I, 5a-I & 6a-c)** possess different colors ranging from (reddish-brown to intense violet) in colours, easily soluble in polar organic solvents and in conc. $H_2SO_4$ liberating Iodine vapour for **(4a-I, 6a-c )** & without liberating for **(5a-i)** on warming. They exhibit green fluorescence in solution depending on the type of substituent present in N-methyl-imin-ium salts or N-heterocyclic residue moieties of **[A or B(Z)]** Their ethanolic solutions gave yellow/ pale brown colour in acidic medium and turned to deep permanent on basification.



**3.2 Spectral Behaviour**

The absorption spectra of **(2a-i)** in 95% ethanol in the visible region showed different absorption bands, their position and molar extinction coefficient being influenced by the type of substituent present in N-methyl-imin-ium salts **(A)** and N-heterocyclic moieties B**(Z)** depending upon the type of N-substituent**.** Thus, the absorption spectra of **(2a, A=N-$C_6H_5$-** & B **(Z)** = 3-methyl-1-phenyl pyrazolin-5-one] exhibit $\lambda_{max}$ 365nm; $\varepsilon_{max}$ 14200 $ol^{-1}$ $cm^2$). Substituting of **A=N-$C_6H_5$-** by **N-o.OH.$C_6H_4$-** and **N-p.OH.$C_6H_4$** in **(2b, 2c)** causes a hypsochromic shifted of $\Delta\lambda$ = 40 nm and with a bathochromic shift of (5-10nm) in absorption band for (**2c)** than **2b, A=**N-o.OH-$C_6H_4$ [$\lambda_{max}$ 400nm; $\varepsilon_{max}$ 10500$mol^{-1}$ $cm^2$,[**2c**, $\lambda_{max}$ 430nm; $\varepsilon_{max}$ 2900$mol^{-1}$ $cm^2$]. **This** is due to the presence of methyl group acting as electron donating inductively effected. On comparison of the absorption spectra of **(2d, 2e)** substituted by **A=N-o(**p).**COOH-$C_6H_4$-** showed a hypsochromic shifted in CT band (5-15nm) less than **(2a) [2d**, $\lambda_{max}$ at 360nm; $\varepsilon_{max}$ 12000 $mol^{-1}cm^2$ and **2e,** $\lambda_{max}$ 350, 420, 500nm; $\varepsilon_{max}$ 15000,3800,3800 $mol^{-1}cm^2$]. This is due to an electron withdrawing character of **A=N-o(**p).**COOH-$C_6H_4$-** groups leads to decreasing the charge transfer of bis. Heterocyclic pyrazolone rings in **(2d, e)** than **(2a).** An increasing the number and intensifies of the absorption bands is due to the partial mixing of the lone pair orbital's of N-Aryl ring substituent with π-system leading to modified set of energy levels and this moves band intensity to hypso-chromically shift. The

absorption spectra of [**(2f,g,** B**(Z)**=3-methyl-1-phenyl pyrazolin-5-one, B**(Z)=** 2-methyl oxazolin-5-one] exhibit ($\lambda_{max}$ at 360 nm; $\varepsilon_{max}$ 17800mol$^{-1}$ cm$^2$) causes a blue shift in the CT band of 10 nm less than **(2b).**The absorption spectra of **(2h**, **A**= imidazolin-2,5-di one**)** showed hypsochromic shift $\Delta\lambda$=15 nm in absorption band ($\lambda_{max}$ 355 nm; $\varepsilon_{max}$ 14800 mol$^{-1}$ cm$^2$) compared with **(2b).** This is attributed to conjugated π-delocalization of the nature heterocyclic ring in **(2b, 2f, 2g)** towards (N-CO & p. COOH) ring and N-atom in position-1(2) for **(2g**,**2f))** of less and more electron withdrawing oxygen electronicatity respectively. The absorption spectra of **(2h & 2i, A= N-C$_6$H$_5$-, B(Z)=**N-3-methyl-1-phenyl pyrazolin-5-one**)** exhibit **2h** [$\lambda_{max}$ 365, 445nm; $\varepsilon_{max}$ 2500, 2800mol$^{-1}$ cm$^2$ and **2i** ($\lambda_{max}$ at 290, 375 nm; $\varepsilon_{max}$ 24000, 8200mol$^{-1}$ cm$^2$) with a bathochromic shift in absorption band of $\Delta\lambda$= (5-25 nm) more than **N-Aryl** substituent of **(2a-e).** This **is** due to the more extensive π-delocalization and extra conjugation in phenyl-pyrazolone ring. Additionally to an increase in electron donating character of methyl group attached to position-3 of pyrazolone ring causes an easier charge transfer towards N-methyl-imin-ium salts through other heterocyclic rings. Substituting of A=**N-C$_6$H$_5$-** by **A**=N-pyridinyl ring in **(2i)** the absorption spectra showed a bathochromic shift in absorption band $\Delta\lambda$= 5 nm and exhibit ($\lambda_{max}$ 280, 370 nm; $\varepsilon_{max}$ 20000, 7000 mol$^{-1}$ cm$^2$) more than **(2a).**This is due to co-operation of hetero-N-pyridinyl ring atom lone pair electrons causes an increasing in electron density and an easier charge transfer towards N-heterocyclic Schiff bases quaternary salts. This is attributed to the partial mixing of the lone pair orbital's of nitrogen atom with π-system pyrazolone heterocyclic ring leading to a modified set of energy levels and this moves band intensity to be in UV region 300nm, for compounds **(2a,d,e,i**, **A** = C$_6$H$_5$**, A** =o.COOH-C$_6$H$_4$**-, A**=N- p.COOH-C$_6$H$_4$**-,** A=N- pyridinyl]**.Table (2).** The absorption spectra of **(6a-c)** in absolute ethanol showed absorption bands batho(hypso)chromically shifted depending upon the nature of heterocyclic moieties A and their linkage position. Thus, the visible absorption maximum of dye **(6b)** [A = quinolin-4-ium ethiodide] showed $\lambda_{max.}$= 485 nm ($\varepsilon_{max,}$ 4950 cm$^2$ mol$^{-1}$ ). Substitution of [A = pyridin-4-ium ethiodide] in dye **(6a)** resulted in hypsochromic shift of $\Delta\lambda_{max.}$ 15 nm, $\lambda_{max.}$ = 470nm ($\varepsilon_{max,}$ 3124 cm$^2$ mol$^{-1}$) for **(6a).** This is due to the more extra conjugated-π-delocalization and in the quinoline ring. Additionally, changing of the linkage position of quinolin-4-ium salt in dye **(6b)** to 1-ium analogue salt in **(6c)** causes hypsochromic shifted of $\Delta\lambda$ = 8 nm $\lambda_{max.}$ = 477 nm ($\varepsilon_{max,}$ 2730 cm$^2$ mol$^{-1}$). This is due to the extened of π- delocalization within quinolin-4-ium ethiodide in **(6b)** rather than quinolin-1-ium linkage in **(6c).**

**3.3 Solvatochromic Behaviour**

The absorption spectra of cyanine dye **(6b),** in $\lambda_{nm.}$ 350-700 nm have been studied in different organic solvents ($H_2O$, DMF, EtOH, and acetone, CHCl3, $C_6H_6$ and $CCl_4$) **[22].** the colour changes of such dyes with solvents having different polarities are presented in **Table (7).** This is constructed with the intention to illustrate the solvatochromic behaviour of these dyes ($\lambda_{max}$ and $\varepsilon_{max}$) values of the intramolecular charge transfer bands are given in **Table (7).** These dyes are showed positive Solvatochromism with increased 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 the polarizability, and 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 lead to formation of specific solvated forms of dyes.

**3.4 Mediachromic Behaviour**

The absorption spectra of an ethanolic solution of zero-5[4(1)]Methine cyanine dye **(6b)** in aqueous universal buffer solution of different values pH (1.98-12.12) show regular changes with increasing the pH of the medium especially in the n- $\pi^*$ and CT bands. The absorption spectra of 3-methyl-1-phenyl-substituted pyrolo [5,4-d] pyrazol-zero-3[4(1)] methine cyanine dye **(6b)** in absolute ethanol showed absorption of blue-green light $\lambda_{max}$= 485 nm. Meanwhile, the absorption spectra in universal buffer solution of this compound (6b) reveals absorption of 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, resulted in hypsochromically shifted if compared with those obvious in ethanol, **Table (8).** In acid (pH ≥ 1.99) medium dye **(6b)** undergo a hypsochromic colour change due to the protonation of the heterocyclic nitrogen atom. In such cases the intramolecular charge transfer (CT) between the heterocyclic donor nitrogen and the aldehydes acceptor carbonyl oxygen does not occur, and the long wave length CT band disappears. A new short wave length is observed, which could be assigned to a localized $\pi^*$ - $\pi^*$ transition. On the other hand, the resulted bathochromic shift as the pH of the medium increases is due to that the protonated compounds becomes deprotonated and their mesmeric interaction with the rest of the molecule becomes high and consequently the CT interaction with the free base is facilitated. The $pK_a$ values were obtained using the standard procedure **[19],** the $pK_a$ values and spectral characteristics of the protonated forms of dye **(6b)** is collected in **Table (8).** Thus, it was obvious that $pK_a$ values, $pK_a$=3.6, 5.6 and 10.8. Thus, it was suggested that this dye **(6b)** is more sensitive as photosensitizers in both acidic and basic medium. This may be due to the presence of N-methyl quinolin-2-/pyridin-4-linkage and the

other quinolin-2-/pyridin-4-ium salts in compound causing the high planarity of the dye molecule.

**Table (6): IR & $^{1}$HNMR & Mass Spectra Data for some selected Heterocyclic compounds:**

| Comp. No. | IR (υ K Br cm$^{-1}$) | $^{1}$HNMR (DMSO,300MHZ) (δ – ppm),m/z M+(Base Peak) |
|---|---|---|
| **2c** | 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 and Het-H) 609 (0.09) 51 (100) |
| **3A** | 1715.5 (υ α, β-unsaturated carbonyl group) in addition to the general bands cited in compound (13b) | showed general signals cited before in compound (13b) δ 2.1004 (s, 2H, CH2), 591 (13.92) 57 (100) |
| **4b** | 3416.28 (υ OH ), 3057.58 (υ stretching CH), 2919.7 (υ heterocyclic quaternary salt), 1771.3-1712.48 (υ 2 $COCH_3$),1589.7 (υ C=C conj.),690.39-836 (υ mono substituted Ar.) ,1496.49 (υ C=N) and (1364,1446.35( υ 2$CH_3$) | $M^+$=672(111) |
| **5b** | 3064.33 (υ stretching CH), 1496.49 (υ C=N), 755.96 (υ mono substituted Ar.), 3430.74(υ OH), 1600.63(υ C=O), 3430.74(υ OH ),(1283.39 , 1368.25, 1448.28 ( υ 3$CH_3$)). | 6.9 – 8.2 (m,15H,14H Ar. + 1H hetero.), (1.166, 1.234 ,1.979 (s, 9H, 3$CH_3$ ),3.431(s, H, OH). $M^+$=503(80) |
| **5f** | 3407.6(υ OH), 692.32- 839.85(υ mono substituted Ar), 1495.53(υ C=N cyclic .),1594.84(υ C=O), 1016.3(υ C-O-C cyclic.), 1275.68-1448.28(υ 3$CH_3$). | 6.6-8.3 (m,10H, 9H Ar. + 1H hetero.) (0.759 ,1.175 2.154(s,9H, 3$CH_3$)3.478(s, 1H, OH). $M^+$=428(80) |
| **5g** | 3419.17(υ OH ),3064.33 (υ stretching CH), (1593.88-1623.77(υ3C=O)), 1494.56(υ C=N cyclic.) 690.39-835(υ mono substituted Ar.),(1290.1, 1370.18, 1452.14(υ 3$CH_3$) | 6.9 – 8.1 ( m, 10H, 9H Ar. + 1H hetero.),1.149 - 2.089( s, 6H ,2$CH_3$),3.45(s,1H, OH ) , 2.17 4-2.229 (s,2H, 2NH). $M^+$=429(77) |
| **5h** | 3062.41(υ stretching CH), 1712.48( υ $COCH_3$) ,(1599.66,1621.84(υ2C=O)),1494.56(υ C=N cyclic.)(1315.21, 1362.46, 1398.14(υ 3$CH_3$)690.39-825.38(υ mono substituted Ar.),1067.41-1121.4(υ C-N-C cyclic.), | 7-8.1(m,15H, H Ar.), 1.236-2.204(s,12H, 4$CH_3$), 3.371-3.436(s, 2H, 2OH), $M^+$=583(93) |
| **5i** | 3063.37(υ stretching CH),(1600.63, 1721.16 (υ2C=O)),1499.38(υ C= N cyclic.),688.46-838.88(υ mono substituted Ar.),1065.48(υ C-N-C cyclic.),(1273.75, 1361.5, 1447.31(υ 3$CH_3$)). | 6.2-8.2(m, 14H, 10H Ar.+ 4H hetero.),1.059-2.051(s, 9H, 3$CH_3$),3.325(s,1H, OH), $M^+$=488(77) |
| **6a** | 3061.7(υ N-ethyl heterocyclic quaternary salts) | δ 7.857(m, 4H,pyridinium -4-yl iodide salt) and δ |

| | | |
|---|---|---|
| | | 3.679 (t, 3H, CH3 of ethyl iodide salts), 760 (4.48) 119 (100) |

**Table (7): Characterized Colour of (6b) and Absorption Values extinction coefficients (λ nm & $mol^{-1}$ $cm^{-1}$) in pure organic solvents:**

| Comp. No. | Colour of (6b) in Pure Organic Solvents | | | | | | | Ethanolic Solution in | |
|---|---|---|---|---|---|---|---|---|---|
| | | | | | | | | $H_2SO_4$ | NaOH |
| | DMF | EtOH | Acetone | $CHCl_3$ | $C_6H_6$ | $CCL_4$ | Water | | |
| | Brown | Brown | Brown | Brown | Brown | Brown | Brown | Brown | Brown |
| | λ max. Є max. $10^3$ | λ max. Є max. $x10^3$ | λ max. Є max. $x10^3$ | λ max. $Є_{max}.x10^3$ | λ max. $(Є_{max}.x10^3)$ | λ max. Є max. $x10^3$ | | | |
| 6b | 485 (4.95) | 480 (4.442) | 460 (4.428) | 470 (4.46) | 465 (4.23) | 470 (4.502) | | | |



**Table (8): The variation of $\lambda_{max}$ ($\varepsilon_{max}$ $x10^3$) and absorbance in $\lambda_{max}$ for (6b) in universal buffer solutions:**

| Comp. No. $\lambda_{max}$ pH | Absorbance In universal buffer solutions at $\lambda_{465}$ | $\lambda_{max}$ ($\varepsilon_{max}$ $x10^3$) |
|---|---|---|
| **1.98** | 2.33 | 480(4.442) |
| **3.25** | 2.338 | 465(4.66) |
| **4.08** | 2.542 | 460(4.678) |
| **5.02** | 2.513 | 465(5.084) |
| **6.07** | 2.767 | 465(5.026) |
| **7.041** | 2.713 | 475(5.59) |
| **8.07** | 2.637 | 470(5.452) |
| **9.08** | 2.614 | 470(5.278) |
| **10** | 2.47 | 460(5.24) |

| | | |
|---|---|---|
| **11.04** | 2.588 | 460(4.962) |
| **12.12** | 2.637 | 465(5.176) |
| $pK_a$ | **3.6 - 5.6 - 10.8** | 480(5.318) |

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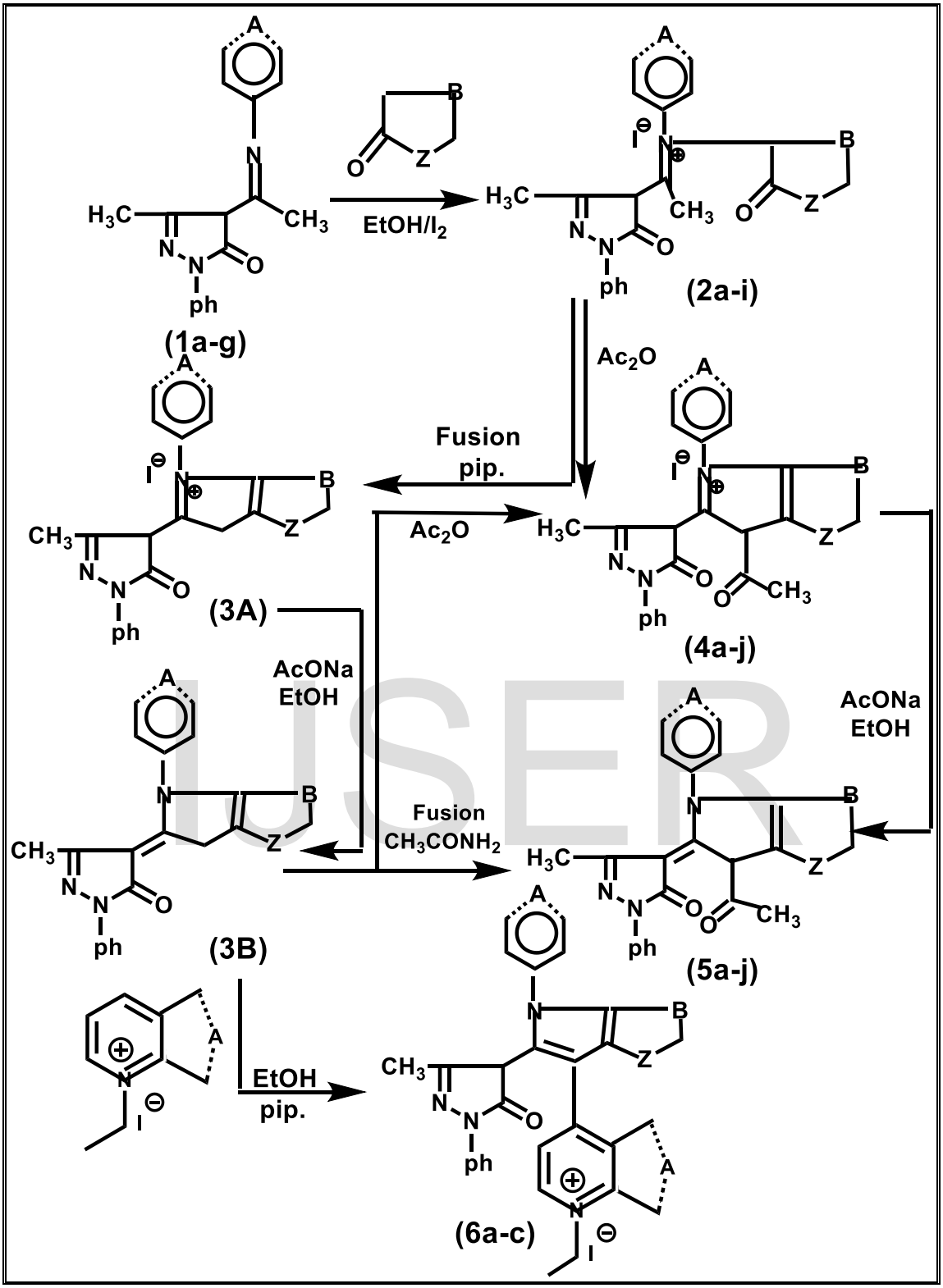
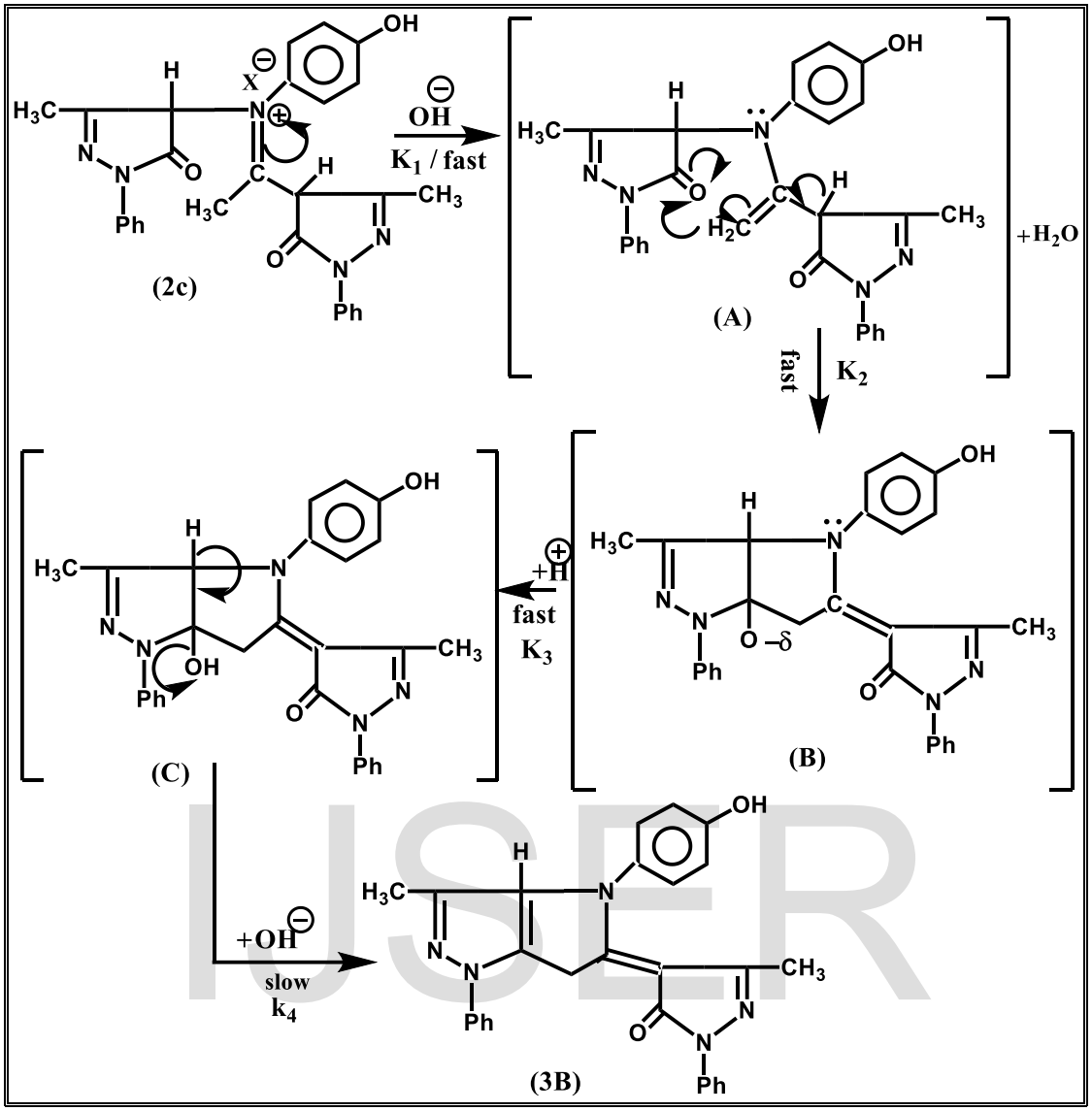



**Scheme (1)**

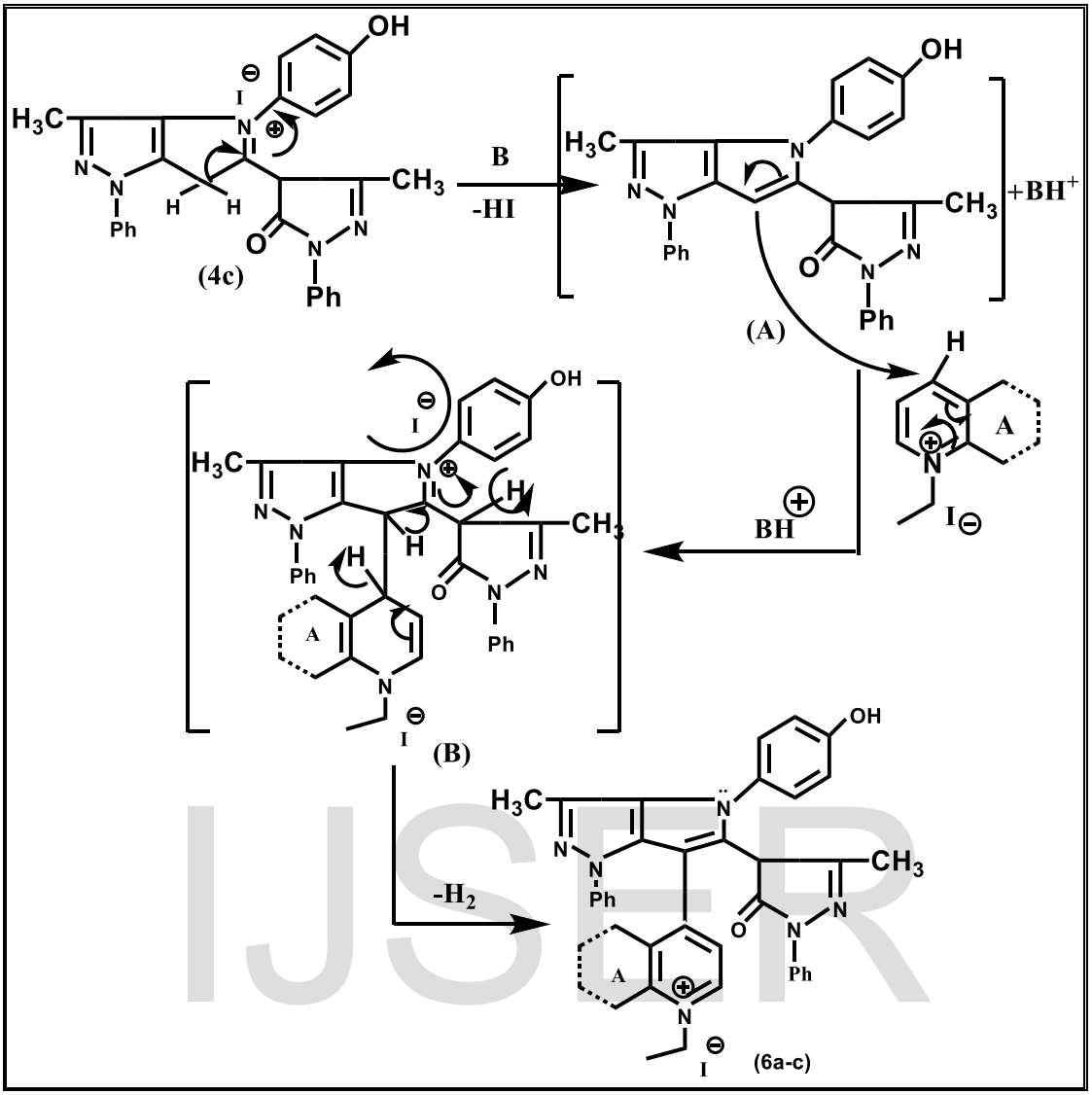
**Schemes (1) Substituents:**

**(1a-g): A**= $C_6H_5$- **(a) A**=o. OH- **$C_6H_4$- (b)**, **A**=p. OH- **$C_6H_4$- (c)**, **A**=o. COOH- **$C_6H_4$- (d)**, **A**=p. COOH-**$C_6H_4$- (e)**, **A**=N-3-Methyl-1-phenyl-pyrazolin-5-one, **A**=o. OH-**$C_6H_4$- (f)**, **A**=N-Pyridinyl, **A**=o. OH- **$C_6H_4$- (g). (2a-i): A= $C_6H_5$-, X=I** (a) **A**=o.

OH- **$C_6H_4$-,X=I** (b), **A**=p. OH-**$C_6H_4$-**, **X=I** (c), **A**=o. COOH-**$C_6H_4$-**, **X=I** (d), **A**=p. COOH- **$C_6H_4$-**, **X=I** (e), **B(Z)** = 3-Methyl-1-phenyl-pyrazolin-5-one**, A**= o.OH-**$C_6H_4$-, X=I** , **B(Z)** = N-2-Methyl-Oxazolin-5-one**,** (f), **A**= o. OH- **$C_6H_4$-, X=I** ,**B(Z)** = Imidazolin--5-one, (g), **A**=N-3-Methyl-1-phenyl-pyrazolin-5-one,**B(Z)** =3-Methyl-1-phenyl-pyrazolin-5-one, **X=I** (h), **A**=N-Pyridinyl**, B(Z)** =3-Methyl-1-phenyl-pyrazolin-5-one, **X=I** (i). **(4a-i): B(Z)** = 3-Methyl-1-phenyl-pyrazolin-5-one, **A**= **$C_6H_5$-, X=I** (a) **A**=o. OH- **$C_6H_4$-**, **X=I** (b), **A**=p. OH- **$C_6H_4$-**, **X=I** (c), **A**=o. COOH-**$C_6H_4$-**, **X=I** (d), **A**=p. COOH- **$C_6H_4$-**, **X=I** (e), **B(Z)** = N-2-Methyl-Oxazole, **A**= o. OH- **$C_6H_4$-,** (f), **B(Z)** = Imidazol-6-one, **A**= o. OH- **$C_6H_4$- (**g), **A**=N-3-Methyl-1-phenyl-pyrazolin-5-one, **B(Z)**=3-Methyl-1-phenyl-pyrazole, **X=I,** (h), **A**=N-Pyridinyl**, B(Z)** =3-Methyl-1-phenyl-pyrazole, **X=I,** (i). **(5a-i): B(Z)** = 3-Methyl-1-phenyl-pyrazolin-5-one, **A= $C_6H_5$-, (a) A**=o. OH- **$C_6H_4$-**, **(b), A**=p. OH- **$C_6H_4$-**, **(c), A**=o. COOH- **$C_6H_4$-**, **(d), A**=p. COOH- **$C_6H_4$-**, **(e),; A**= o. OH-**$C_6H_4$-, B(Z**)=Oxazole **(f) ; A**= o. OH-**$C_6H_4$-,**B(Z)=imidazol-6-one**(g) ;A= A**=N-3-Methyl-1-phenyl-pyrazolin-5-one, **B(Z)** =3-Methyl-1-phenyl-pyrazole**(h) ;A=** N-Pyridinyl**, B(Z)** =3-Methyl-1-phenyl-pyrazole**(i). (6a-c):A**=p. OH- **$C_6H_4$-, B(Z)** = 3-Methyl-1-phenyl-pyrazole, **A**= pyridin-4-ium-iodide (a), **A**=p. OH-**$C_6H_4$-, B(Z)** = 3-Methyl-1-phenyl-pyrazole, **A**=quinolin-4-ium- iodide (b), **A**=p. OH- **$C_6H_4$-, B(Z)** = 3-Methyl-1-phenyl-pyrazole, **A**=quinolin-1-ium-iodide (c)




**Equation (1A): The suggested Formation Mechanism for (3B)**




**Equation (1B): The suggested Formation Mechanism for (6a-c)**