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N-BRIDGE HEAD HETEROCYCLIC METHINE CYANINE DYES,[1] SYNTHESIS AND SPECTRAL BEHAVIOUR

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ABSTRACT

Some new key reaction intermediates were used as main entities in the synthesis of N-Bridge Head Heterocyclic indolizino(benzindolizino)[2,3-b] benzpiperidin- Imidazolo [4, 5-b][2, 3, 4-b, j] indolizino- [2, 3-b] benzpiperidin- & Indolizino (benzindolizino)[3, 2-b]-benzpyrimidin-5-one, 2-methyl pyrazolo[3, 2-a] quinolino[1, 5-a] benzpyrimidin-zero-[mono]-methine. Indolizino (benzindolizino) [2,3-b] benz piperidin-benz-piperidino [2,3-d] pyrido [2,1-a] pyridazin-11-one, meso-substituted tri–2[2(4)]-methine cyanine dyes **(9_{a-e}, 12).**. The new synthesised heterocycles key reaction intermediates & related cyanines were identified by elemental & spectral data. The UV-visible absorption spectra of 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.

Keywords: N-Bridge Head Heterocyclic & Methine cyanine synthesis, Spectral Behaviour, Acid-base properties

INTRODUCTION

A variety of N-bridgehead heterocyclic cyanine dyes have been reported as high sensitivity and low fogging, information recording media of high reflectivity and carrier-to-noise ratio, laser disc media, laser-sensitive optical recording material. Besides their use as colorants, **[1].** They have considerable potential for application in energy conversion, **[2].** N-Bridge head heterocyclic cyanine dyes were used as antimicrobial agents **[3 & 4]**, useful for preparing superconducting polymers **[5].**

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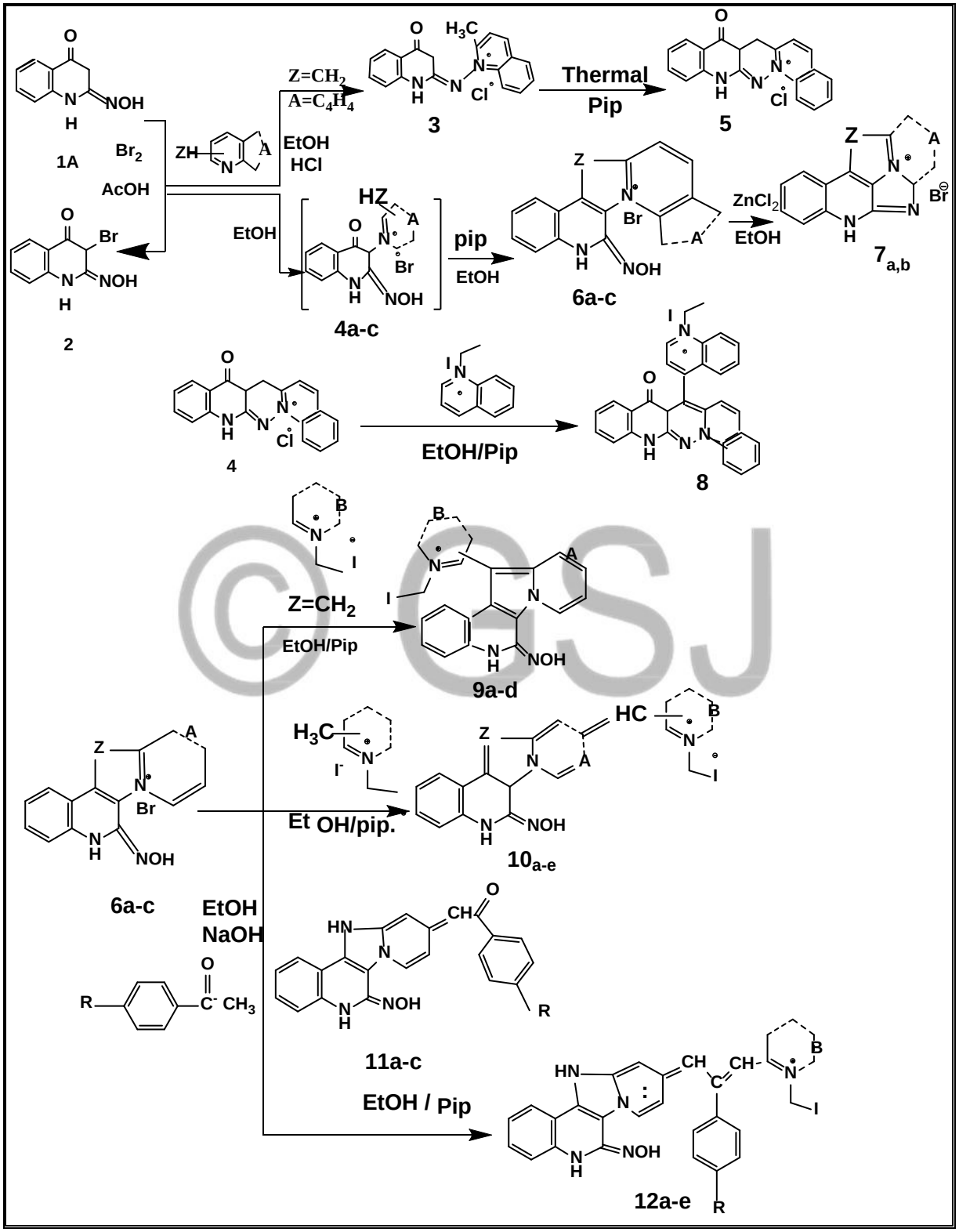
RESULTS AND DISCUSSIONS

SYNTHESIS

Reaction of either 2-oximino-1, 2, 3-tri [H] benzpiperidin-4-one **(1A)** and or its 3-bromo-derivatives **(2)** with 2(4)-methyl (amino) pyridine(quinoline) bases ,in equimolar amounts, in the presence of hydrochloric acid or ethanol afforded 1, 3-di [H]-benzpiperidin-4-one-2(1)-imine--2-methyl-quinolin-1-chloride salt **(3)** and/or 1[H] 2-oximo-benzpiperidin- 4-one-3(1)-2-methyl (amino) pyridin (quinolin)-1-bromide salts **(4a-c).** The later **(3, 4a-c)** undergo Interamolecular heterocyclization in the presence of piperidine to give 6, 12, 16-tri [H]-benz piperidino[2, 3-d] quinolino[2,1-a] pyridazin-11-one-14-chloride salt and 6[H]-5-oximino-indolizino(benzindolizino) [2,3-b]benz-piperidin-13-bromide salts **(5a-c, 6a-e)**. Compounds **(6a-e)** undergo heterocyclization using zinc chloride in ethanol to afford 5[H] Imidazolo[4,5-b] [2,3,4-b,j] indolizino[2,3-b] benzpiperidin-12-bromide salts **(7a-c).** Interaction of 6[H]-5-oximino-indolizino (benz-indolizino)[2,3-b]benzpiperidin-13-bromide salts **(5)** and N-ethyl-quinolin-4-ium-ethiodide salt under thermal piperidine conditions gave 5, 6, di [H]-benzpiperidino [2, 3-d] pyrido[2, 1-a] pyridazin-11-one-zero-12(4)methine cyanine dye **(8)**.The reaction of 6[H]-5-oximino-indolizino (benzindolizino)[2,3-b] benzpiperidin-13-bromide salts and/or 5[H] Imidazolo[4,5-b] [2,3,4-b,j] indolizino[2,3-b] benzpiperidin-12-bromide salt **(6a-e, 7a-c)** with N-Ethyl-[2(4)]-methyl-pyridin-(quinolin)-4(1)[2(4)]--ium iodide salts, in equimolar ratios, under piperidine/Ethanol conditions achieve 6[H] -5-oximino-indolizino (benz indolizino) [2,3-b] benzpiperidin-zero-11 [4(1)] methine and/or 6[H]-5-oximino-indolizino (benzindolizino) [2,3-b] benzpiperidin-mono-2[2(4)] methine cyanine dyes **(9a-c, 10a-c)** and/or 5[H] imidazlo [4, 5-b] [2, 3, 4-b, j] indolizino [2, 3-b] benzpiperidin-zero-10[4(1)]-methine or 5[H] imidazlo [4, 5-b] [2, 3, 4-b, j] indolizino[2,3-b] benzpiperidin-mono-2[2(4)]-methine cyanine dyes **(13a-d 14a-e)** respectively. The reaction of **(6c,7**) with acetophenone derivatives ,in equimolar amounts, under Ethanol/NaOH conditions afforded the key reaction intermediates 6[H]-5-oximino-indolizino(benzindolizino)[2,3-b]benzpiperidine–2[1]-benzoyl-methinyl- and 6[H]- benz-piperidino[2,3-d]pyrido[2, 1-a] pyridazin-11-one-2(1)-benzoyl-methine derivatives **(11a-c ,15).** Fusion of **(11a-c 15)** and 2(4)-methyl-pyridin(quinolin)-2(4)-ium-ethiodide salts in equimolar amounts, under piperidine catalysis afforded 6[H]-5-oximino-indolizino(benz indolizino) [2,3-b]benzpiperidin-meso-substituted-tri–2[2(4)]-methine

and/or 6[H]-benz piperidino [2, 3-d] pyrido[2, 1-a] pyridazin-11- one meso substituted tri-2(2) -methine cyanine dye cyanine dyes **(12a-e,16), Scheme (1A).**

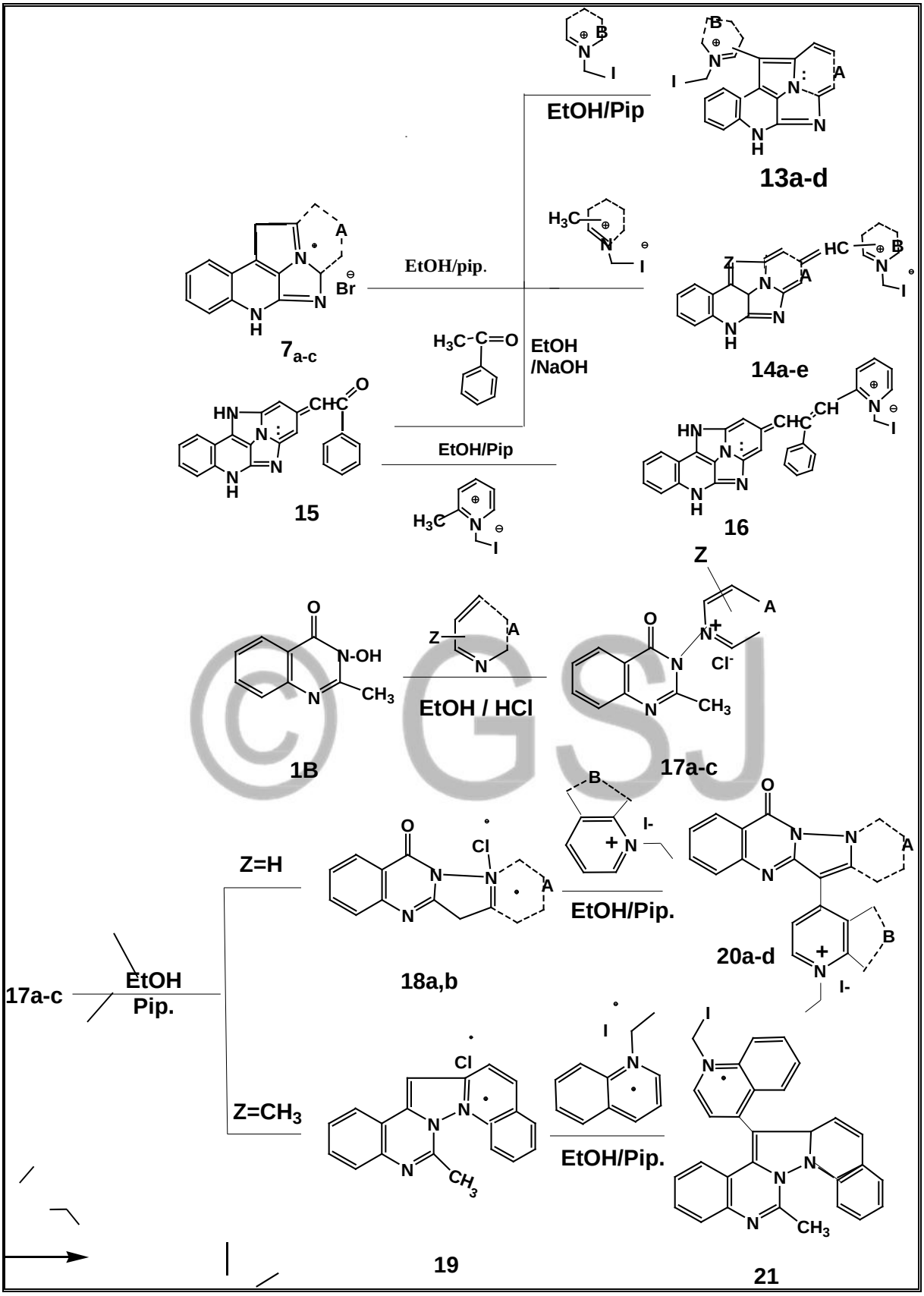


Scheme 1A

Scheme 1 A substituents:

(5, 6, 7a-c): Z = CH_2, A= pyridin-1-ium-bromide (a); Z = CH_2, A= quinolin-1-ium-bromide (b); Z =NH, A= pyridin-1-ium bromide(c), **(9a-d):** A = pyridine, B=pyridin-4-ium salt (a); A = pyridine, B=quinolin-4-ium salt (b); A = pyridine, B=quinolin-1-ium salt (c); A=quinoline, B=quinolin-4-ium salt (d). **(10a-e):** Z=CH, A = pyridine, B=pyridin-2-ium salt (a); Z=CH, A= pyridine, B=quinolin-2-ium salt (b); Z=CH, A= pyridine, B=pyridin-4-ium salt(c); Z=CH, A = quinoline, B=pyridin-4-ium salt (d); Z=NH, A= pyridine, B=pyridin-2-ium salt (e). **(11a-c):** R=H (a); p.NO_2 (b); p.NH_2 (c). **(12a-e)**: R= H, B=pyridin-2-ium salt (a); R= H, B=quinolin-2-ium salt (b); R= H, B=pyridin-4-ium salt (c); R= p.NH_2, B= pyridin-2-ium salt (d); R= p.NO_2, B=pyridin-2-ium salt (e**).**

The reaction of 3-hydroxy-2-methyl-benzpyrimidin-4-one (**1B)** and pyridine (quinoline) and/or 2-methyl-quinoline, in equimolar amount, in presence of ethanol/concentrated hydrochloric acid conditions afforded 2-methyl-benzpyrimidin-4–one-N-pyridin (quinolin)-4(1)-chloride salts **(17a, b,** and **c)** respectively**.** On triturating an ethanolic solution of (**17a-c)** with aqueous KI flowingly by addition of conc.H_2SO_4 liberates iodine vapour on warming. This is a criterion for presence of the chloride anion replaced by iodide analogous. Compounds (**17a-c)** undergo ring closer under piperidine catalysis to afford indolizino (benzindolizino) [3, 2-b]-benzpyrimidin-5-one-13-chloride salt and 2-methyl-pyrazolo[3, 2-a]quinolino[1, 5-a]benzpyrimidin-16-chloride **(18a, b, 19).** Reaction of **(18a, b, 19)** and N-ethyl-pyridin (quinolin)-4(1)-ium-iodide under piperidine catalysis afforded Indolizino (benzindolizino)[3,2-b]-benzpyrimidin-5-one-zero-11 [4 (1)] methine cyanine dyes (**20a-d**, **21)** , **Scheme (1B).**


EtOH/Pip
13a-d
EtOH/pip.
7a-c
EtOH /NaOH
14a-e
15
EtOH/Pip
16
Z
1B
EtOH / HCl
17a-c
Z=H
EtOH/Pip.
20a-d
17a-c
EtOH
Pip.
18a,b
Z=CH3
EtOH/Pip.
19
21

Scheme 1B

Scheme 1 B substituents:

(13a-d): A = pyridine, B= pyridin-4-ium salt (a); A = pyridine, B= quinolin-4-ium salt (b); A = pyridine, B= isoquinolin-1-ium salt (c); A= quinoline, B= quinolin-4-ium salt (d). **(14a-e):** Z =CH, A =pyridine, B= pyridin-2-ium salt (a); Z =CH, A =pyridine, B= quinolin-2-ium salt (b); Z =CH, A =pyridine, B= pyridin-4-ium salt (c); Z =CH, A = quinoline, B= pyridin-4-ium salt (d); Z=N- pyridine, A = pyridine, B= pyridin-2-ium salt (e). **(17a-c):** Z=H, A= N-pyridinium chloride (a); Z=H, A= N-quinolinium chloride (b); Z=CH_3, A= N-quinolinium chloride (c).**(18a, b):** A= N-pyridinium chloride (a); A= N-quinolinium chloride (b). **(20a-d):** A= pyridine, B=pyridin-4-ium salt (a); A= pyridine, B=quinolin-4-ium salt (b); A= pyridine, B=quinolin-1-ium salt (c); A= quinoline, B=quinolin-4-ium salt (d).

The structure of **(3, 4a-c, 5a-c, 6a-e,7a-c,8,9a-c,10a-c, ,11a-c,12a-e, 13a-d 14a-e 15 16,17a,b, c, 18a, b, 19, 20a-d & 21)** was confirmed by elemental analysis, and spectral analysis**, Tables 1,5-7**, **[6-8].**

Table 1: IR &^{1}HNMR Spectral Data of (8, 9a-d, 10a, 11a 12a, 14b, 15, 18 a, 21)

Comp. No	IR (υ KBr cm^{-1})	^{1}HNMR (DMSO, 250 MHz) (ppm)
9a-d,10a-e	2871-2975 (v Et I of heterocyclic salts)	**(8**)1.7(s, 3H, CH_3 of Et I), 3.5 (s, 2H, CH_2 of Et I) 6.8-7.7 (m, 17H, 16H, Ar-H, 1H, NH)
11a,12a	**11a,** 1433 (C=N) 3057- 3060 (stretching C-H) **(12)** 1603 (v C=O) for 2928 (v Et I of heterocyclic salts)	**(9a, 10b)** δ 1.2-1.5 (s, 3H, CH_3 of Et I) for, 3.3- 3.5 (s, 2H, CH_2 of Et I),**(9a)** 8.2-9.2(m,15H, 12H, Ar-H,2H, NH, OH,1H,CH) ,**(10b)** 7.7- 8.6 (m, 18H, 14H, Ar-H, 2H, NH, OH, 2H, 2CH)
13a,14b	**13a, 14b,** 1425-1447(C=N),2856-2921 (Et I of heterocyclic alts), 3443-3429 (NH)	**(12a)** δ1.5-1.6(t, 3H, CH_3 of Et I), 5 (q, 2H, CH_2 , Et I) 8-8.6 (m, 19H, 16H, Ar-H, 2H, 2CH, 1H, NH), 9.1-9.2(d, 2H, 1H, NH, 1H, OH)
15	1433 (C=N), 1615 (C=O),	**(14b)** δ1-1.2 (m, 5H, CH_3CH_2 of Et I), 3.1- 3.3 (s, 2H, CH2) 6.6- 7.8 (m, 14 H, 1H, CH, Ar-H, 1H, NH)
18 a	1702 (C=O) 2850- 2920 (vmax N-chloride)1458-1471 (C=N)	31δ1.7-3.3 (s, 5H, of CH_2CH_3 Et I), 6.5-8 (m, 19H, 15H, Ar., 2H, 2CH, 2H, 2NH)
20a, 21	**(21**) 2921 (v Et I , heterocyclic salts), 3422 (conjugated ring junction tertiary nitrogen).	**(20a):**δ1.2-1.7 (br, 3H, CH_3 of Et I), 3.01 (s, 2H, CH_2 of Et I) 7.5-8 (m, 13H, Ar-H)

COLOUR AND SPECTRAL BEHAVIOUR

5, 6, Di [H]-Benzpiperidino [2, 3-d] pyrido [2, 1-a] pyridazin-11-one-zero-12 (4) methine cyanine dye **(8),** 6[H]-5-oximino-indolizino(benzindolizino) [2,3-b] benzpiperidin-zero-11 [4(1)] methine **(9a-c)**, 6[H]-5-oximino-indolizino (benzindolizino) [2,3-b] benz-piperidin-mono-2[2(4)]methine **(10a-c),** 6[H]-5-oximino-indolizino- (benzindolizino)[2,3-b]benzpiperidin-meso-substituted-tri–2[2(4)]-methine **(12a-e),** 5[H] imidazlo [4, 5-b] [2, 3, 4-b, j] indolizino[2, 3-b]benzpiperidin-zero-10 [4(1)]-methine **(13a-d**), 5[H] imidazlo[4, 5-b][2, 3, 4-b, j]indolizino[2, 3-b]benzpiperidin-mono-2[2(4)]-methine **(14a-e)**, 6[H]-benz piperidino [2, 3-d] pyrido [2, 1-a] pyridazin-11- one meso substituted tri-2 (2)-methine **(16)** Indolizino-(benzindolizino)[3,2-b]benzpyrimidin-5-one-zero-11[4(1)] methine cyanine dyes **(20a-d, 21)** are highly coloured compounds. Their colours in ethanol are easily (partially) soluble in polar (none) organic solvents. On their triturating with conc. H_2SO_4 soluble with liberating iodine vapour on warming. Their ethanolic solutions gave dark violet on basic medium turned to pale violet colour in acidic medium. Their ethanolic solutions gave permanent colour in basic media, which reversibly discharge on acidification**.** The ethanolic solutions of some selected dyes give deep colour in acid media which reversibly discharge on basicfication due to covalent hydration phenomena, **Tables (6, 7).**

The absorption spectra of 6[H]-5-oximino-indolizino(benzindolizino) [2,3-b] benz-piperidin-zero-11[4(1)]methine,6[H]-5-oximino-indolizino (benz indolizino) [2,3-b]benz-piperidin-mono-2[2(4)] methine cyanine dyes **(9a-c**,**10a-c**) in 95% ethanol showed absorption bands batho(hypso)chromically shifted depending upon the nature of heterocyclic quaternary residue **(B)** and the type of substituent **(A).** Thus, the visible absorption spectra of dye **9a** (A = pyridine, B = pyridin-4-ium ethiodide) exhibit (λ_{max} = 460 nm; εmax = 2900 mol^{-1} cm^2). Substitution of (B = pyridin-4-ium ethiodide) in **9a** by (B = quinolin-4- ium ethiodide) **9b** resulted in bathochromic shift of $\Delta\lambda_{max}$ = 10 nm. This is due to more extensive π-delocalization and extra conjugation in the quinoline ring. Additionally, changing the linkage position of quinolin-4-ium salt in dye **9b** to quinolin-1-ium analogue salt in dye **9c** causes hypsochromic shift of $\Delta\lambda_{max}$ = 5 nm. This is attributed to an extended π-delocalization within quinolin-4-ium salt in dye **9b** rather than quinolin-1-ium linkage in dye **9c. Table (7).** Similarly, the visible absorption maximum of dye **10a** (A = pyridine, B = pyridin-2-ium ethiodide) exhibit (λ_{max}= 470nm; ε_{max}=2650$mol^{-1}cm^2$). Substitution of (B= pyridin-2-ium ethiodide) in dye **10a** by (B=

quinolin-2-ium - ethiodide) in dye **10b** causes a bathochromic shift of $\Delta\lambda_{max}$ = 30 nm, accompanied with the appearance of new absorption bands located at longer wavelength λ_{max} = 580 and 670 nm; ε_{max} = 26300, 11500 mol^{-1} cm^2. This is due to the more extensive π-delocalization in dye **10b**, which causes an easier charge transfer from nitrogen ring junction atom as electron sink towards the heterocyclic quaternary moieties via chromophore as electron sink. Additionally, changing the linkage position of pyridin-2-ium in dye **10a** [B= pyridin-2- ium ethiodide] to pyridin-4-ium in dye **10_c** [B= pyridin-4- ium ethiodide] resulted in bathochromic shift of $\Delta\lambda_{max}$ = 10 nm. This is due to an extended π-delocalization within pyridin-4- ium ethiodide causes an easier charge transfer from nitrogen ring junction atom as electron source towards pyridin-4- ium ethiodide. On comparison between the absorption spectra of dyes **(10a**, **10d)**. it was obvious that the later dye **10_d** exhibit absorption band more bathochromic shifted by $\Delta\lambda_{max}$ = 20 nm relative to that band of dye **10a**. This is due to an increase π-delocalization. On the other hand, on comparison of the absorption spectra of dyes **(10a**, **10e)**, (A= pyridine, B= pyridin-2-ium ethiodide), it was obvious that the later dye **(10e**) exhibit absorption band bathochromic shifted by $\Delta\lambda_{max}$ = 5 nm, due to increase electro negativity of nitrogen atom than carbon atom**, Table (7).** The absorption spectra of meso-substituted tri-methine cyanine dyes **(12a-e**) in 95% ethanol showed absorption bands batho(hypso)chromically shifted influenced by the type of heterocyclic quaternary residue **(B)** and the nature of aryl substituents **(R).** Thus, the absorption spectra of (**12a,** R = H, B = pyridin-2-ium ethiodide) exhibit (λ_{max} = 475 nm; ε_{max} =2523 mol^{-1} cm^2). Substitution of (B=pyridin-2-ium ethiodide) in dye **12a** by (B=quinolin-2-ium- ethiodide) in (**12b)** causes bathochromic shift accompanied with the appearance of new absorption bands located at longer wavelength (λ_{max}= 480, 570, 690 nm; ε_{max}= 28574, 2480, 1148 $mol^{-1}cm^2$). This is due to the more extensive conjugation in quinoline ring in dye (**12b).** Changing the linkage position of pyridin- 2-ium in dye (**12a,** B= pyridin-2- ium ethiodide) to pyridin-4-ium in dye (**12c,** B = pyridine-4- ium ethiodide) resulted in bathochromic shift of $\Delta\lambda_{max}$ = 10 nm. This is due to the extended of π-delocalization within pyridin-4- ium linkage causes an easier charge transfer relative to the 2-ium analogue. On the other hand, substitution of (R=H) in dye (**12a)** by (R=4-$NH_{2)}$ in dye (**12d),** resulted in absorption band more bathochromic shift by $\Delta\lambda_{max}$ = 15 nm relative to that band of dye (**12a)**. This is due to an electron donating character of NH_2 group causes an easier charge transfer towards the heterocyclic quaternary residue **(B)** as electron sink. Additionally, substitution of (R =

H) in dye (**12c)** by (R = 4-NO_2) in dye (**12e),** resulted in absorption band hypsochromically shifted by Δ λ_{max} =10 nm accompanied with decreasing in the number of the absorption bands relative to that band of dye (**12c)**. This is due to an electron withdrawing character of NO_2 group in dye **(12e**) causes decreasing in the charge transfer from aryl as electron source towards the heterocyclic quaternary residue **(B)** as electron sink, **Table (5).** The absorption spectra of 5[H] imidazlo[4, 5-b][2, 3, 4-b, j]indolizino[2, 3-b] benz- piperidin-zero-10 [4(1)] & mono-2 [2(4)]- methine cyanine dyes **(13a-d** , **14a-e)** in 95% ethanol showed absorption bands batho (hypso) chromically shifted being influenced by the nature of heterocyclic quaternary residue **(B)** and the type of substituents **(A).**Thus, the absorption spectra of **13a (14a**) [A= pyridine, B = pyridin-4(2)-ium ethiodide] exhibit (λ_{max} = 455(470)nm; ε_{max} = 2540 (2960) $mol^{-1}cm^2$). Substitution of [B=pyridin-4(2)-ium ethiodide] **(13a, 14a)** by (B= quinolin-2-ium-ethiodide) in dye **(13b, 14b)** resulted in bathochromic shift of Δ λ_{max} = 15 (30) nm accompanied with the appearance of new absorption bands located at longer wavelength for dye (**14b**, λ_{max} = 575, 695 nm; ε_{max} = 2751, 2970, 188 $mol^{-1}cm^2$). This is attributed to an extensive π-delocalization within an extra phenyl ring. Changing the linkage position from 4(2)-ium in dye **(13c, 14a**) [B= quinolin-1-ium- (pyridin-2-ium ethiodide] to 1(4)-ium in dye **(13b, 14c)** [B= quinolinium-(4)-pyridin-4-ium ethiodide] resulted in bathochromic shift in absorption band of Δ λ_{max} = 5 (10) nm. This is due to an extended π-delocalization within quinolin-4-ium- (pyridin-4-ium ethiodide causes an easier charge transfer from nitrogen ring junction atom as electron source towards quinolin-4-ium(pyridin-4-ium ethiodide. On comparison between the visible absorption spectra of dye (**14c**, A= pyridine) and (**14d**, A= quinoline), it was obvious that a bathochromic shift of Δλ_{max} = 10 nm accompanied with the appearance of new absorption bands located at longer wavelength for dye (**14d)** if compared with the dye **(14c, 14d)** λ_{max} = 490, 545, 700nm; ε_{max} = 2870, 2520, 1109 $mol^{-1}cm^2$. This is attributed to an increase π-delocalization within an extra phenyl ring. **Table (7).** On comparison between the absorption spectra of dyes 6[H] -5-oximino-indolizino (benzindolizino) [2,3-b] benzpiperidin-zero- 11 [4(1)] and/or –mono-2 [2(4)]-methine **(9a-d, 10a-e)** and 5[H] Imidazolo [4, 5-b] [2, 3, 4-b, j] indolizino [2, 3-b] benzpiperidin-zero-10 [4(1)] and / or mono -2 [2(4)]- methine cyanine dyes **(13a-d, 14a-e),** it was obvious that, dye (**9d,** A= quinoline, B = quinolin-4-ium ethiodide) and (**13d,** A= quinoline, B = quinolin-4-ium ethiodide) showed more bathochromic shift of Δ λ_{max} = 15 nm for dye **(9d)**. This is due to presence of the free electron pair on the nitrogen of

oxime group leading to an easier charge transfer causing an extensive π-delocalization. On comparison between the visible absorption spectra of dyes **(12a**, **16)**, it was obvious that dye **(12a**, λ_{max} = 485nm) showed the more bathochromic shift in the two absorption bands of $\Delta\lambda_{max}$= 10 nm. This is due to the presence of the free electron pair on the oxime nitrogen group in dye (**12a)** leading to an easier of charge transfer causing the extensive π-delocalization. The absorption spectra of dyes **(20a-d, 21)** in 95%ethanol showed absorption bands batho(hypso) chromically shifted depending upon the nature of heterocyclic quaternary residue **(B)** and the type of substituent **(A).** Thus, the absorption spectra of **(20a,** A= pyridine, B=pyridin-4-ium ethiodide) exhibit (λ_{max}= 465 nm; ε_{max}= 2031 mol^{-1} cm^2). Substituting (B=quinolin-4-ium-ethiodide) in dye (**20b)**, exhibit (λ_{max} = 485 nm; εmax = 2641) causing bathochromic shift in absorption band of $\Delta\lambda_{max}$ = 20 nm. This is due to the more extensive π-delocalization and extra conjugation in the quinoline ring. Additionally, changing the linkage position of quinoline -4-ium salt in dye (**20b**) to 1-ium analogue salt in dye (**20c)** causes hypsochromic shift of $\Delta\ \lambda_{max}$ = 10 nm. This is attributed to an extended π-delocalization within quinolin-4-ium salt in dye (**20b)** rather than quinolin-1-ium linkage in dye (**20c).** On comparison of the absorption spectra between dyes **(20c**, **d),** (A= quinoline, B= quinolin-1-ium ethiodide), it was obvious that the later dye **(20d**) exhibit absorption band more bathochromic shifted by $\Delta\lambda_{max}$ = 5 nm relative to that band of dye (**20c), .** This is due to an increase π-delocalization**, Table (7).**

COLOUR CHANGES OF CYANINE DYES WITH ORGANIC SOLVENTS (SOLVATOCHROMISM)

The colour changes of cyanine dyes with solvents (solvatochromism) were previously discussed by **[9, 10]** 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 batho (hypso) chromic positive **(**negative**)** solvatochromism 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 dipolar zwitterionic benzenoid and neutral quinoid forms, **[11]***.* From these finding points of view, the visible absorption spectra of some selected synthesized 6[H] -5-oximino-indolizino (benzindolizino)[2,3-b] benzpiperidine meso-substituted tri–2(2)-methine , 5[H] Imidazolo[4, 5-b][2, 3, 4-b, j]indolizino[2, 3-b] benz- piperidin-mono-2(2)-methine, Indolizino -(benzindolizino) [3,2-b]-benzpyrimidine-5-one-zero-11(4)methine cyanine dyes **(12a**, **14b, 20b)**. The

absorption spectra of such dyes in the wavelength range 350-700 nm, have been studied in different organic solvents **(DMF, EtOH, $CHCl_3$, C_6H_6 and CCl_4) [12],** The colour changes of such dyes with solvents having different polarities are presented and constructed with the intention to illustrate the solvatochromic behaviour of dyes (λ_{max} & ε_{max}) values of the intermolecular charge transfer bands are given in, **Tables (2, 3).** 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 of the solvent is increased. This behavior 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. In point view of light absorption, it was obvious that most of the previous selected cyanine dyes **(12a**, **14b, 20b)** are absorbed the fundamental light absorption (reddish violet- red) as they have got absorption values in the range 400-545nm**,Tables (2,3)**. The selected cyanine dyes might be suggested to be used as photosensitizers in most polar and non polar organic solvents in the (reddish violet-red). Thus, it was obvious that compounds **(12a**, **14b, 20b)** 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.

Table (2): Colour of (10 a, 12 b, 18b) in Organic Solvents

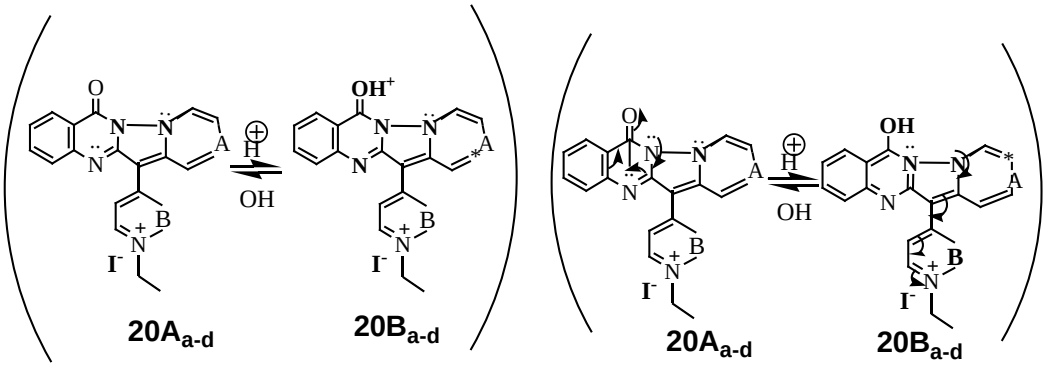
Comp No.	DMF	Et OH	$CHCl_3$	C_6H_6	CCl_4	Alcoholic solution	
						H_2SO_4	NaOH
10a	Dark Brown	Dark brown	Pale Brown	Yellowish Brown	Yellow	Dark Brown	Pale brown
12a	Reddish brown	dark brown	Brown	Pale Brown	Pale Brown	Brown	Light brown
18b	Reddish brown	Dark red	Dark yellow	Yellow	Yellow	Dark Brown	Pale brown

Table (3): Absorption (nm) & Extinction Coefficients ($mol^{-1}cm^{-1}$) Values of (10 a, 12 b, 18b) in pure organic solvents

Comp No.	DMF		EtOH		$CHCl_3$		C_6H_6		CCl_4	
	λ_{max}	ε_{max}	λ_{max}	E_{max}	λ_{max}	ε_{max}	λ_{max}	ε_{max}	λ_{max}	ε_{max}
10a	475	1978	475	2042	465	2164	460	2107	460	1901
12a	475	2860	470	2960	465	2360	460	2104	460	1250
18b	490	1980	485	1866	470	2434	460	1700	455	1889

The absorption spectra of dye **(12a)**, in aqueous universal buffer solution of different values of pH (1.98-10.02) show regular changes with increasing pH of the medium especially in n-$\pi*$ and CT bands**.** The spectral behavior of dye **(12a)** 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} = 470-515 nm. Such dye (**12a)**, in aqueous universal buffer solution reveals absorption of the violet light at λ_{max} = 455 nm at pH = 3.08 and hypsochromic shifted in the absorption of blue light at λ_{max} = 445 nm at pH $\geq$ 7.0 relative to ethanol. The hypsochromic shift of the violet light at pH = 3.08 is due to the presence of quinolin-2-ium 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. **Table (4).** The spectrophotometric determination of dissociation constants pKa values of such dye (**12a)** can be utilized through the variation of the absorbance with pH values**.** Thus, the absorbance pH curves are typical dissociation constant pKa of the dye were determined from the variation of absorbance with pH using the spectrometric half-height limiting absorbance and collector methods**.** The determination of pKa values of dye (**12a)** was listed in **Table (4).** The results showed that pKa value of dye **(12a)** depend upon the nature of such cyanine dye. Thus, pKa values of dye **(12a)** containing quinolinium heterocyclic quaternary residue reveals pKa =4.6, 8.2, This results was suggested that dye (**12a)** is more sensititive as photosensitizers in acidic and causes the high planarity in acidic medium, Some selected dyes exhibit highly coloured in the ethanol acidic-medium discharged on basification. This may be due to **"**Covalent hydration in aqueous solution**.** It is not surprising to find that the acidic ethanolic solution of N-bridge head heterotri (tetra) cyclic and/or fused benzo heterobicyclic moieties substituted with strong electron withdrawing groups (C=NH, C= O) as in dyes **(12a**, **14b, 20b)** give deeping colour solution and discharge on basification in aqueous solution) showed "4-amino pyridinium and/or amidine types resonance "Covalent hydration " in aqueous solution or in dyes (**20a-d), (Equation 1)**. On the other hand, the existence of benzpyrido- NH group as electron donor supplements the directing effect of (C=NH) imino-nitrogen (C=O) and direct the incoming proton of an aqueous medium into such groups leading to a stabilized covalent hydration through the mesomeric effects of either 4-amino-

pyridinium or amidinium types resonance. This phenomenon was studied through dye (**14a),** and the resonance stabilization and the bathochromic shift as the pH of the medium increases. in aqueous solution (highly coloured solution) is due to an electron charge transfer in conjugated mesomeric structures from N-bridge head heterocyclic moiety iminium/ hydroxnium cations moieties as an electron charge transfer in conjugated mesomeric structures **, Table (4).**



Equation A: Covalent Hydration Phenomenon for (20 A, B)

Table (4): Absorption Values of 12a in Universal buffers.

Comp. No.	Absorption Values	Absorption Spectra in Universal Buffer Solutions pH							
		EtOH	1.98	3.08	5.05	6.5	7.64	8.17	10.02	pKa
12a	λ_{max}	470	450	455	455	460	445	435	430	4.6, 8.2
	ε_{max}	2960	2971	2560	3011	2717	2532	2136	2293	
	Abs.	2.96	2.97	2.56	3	2.72	2.5	2.14	2.03	

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 MH_Z spectrophotometer using DMSO d_6 as a solvent and TMs as an internal standard. Chemical shift are expressed as ppm, units. Mass spectra were recorded on a HP Ms 6988 spectrometer and analytical data were determined with a CE 440 Elemental Analyzer- Automatic Injector at Cairo University. The absorption spectra were recorded immediately after preparation of the solutions within the wavelength range (350-800nm) on a 6405 UV/ visible recording spectrophotometer, Aswan faculty of science at 27C$^{\circ}$. Ethanol (95%, ethanol- water 95:5 v/v) was used. pH was measured

on a radelkis OP-208 pH-meter with universal buffer solution. The concentration of the stock solution was about $1x10^{-3}$ and the lower moralities were obtained by accurate dilution.2-Oximino-1,2,3-tri[H]benzpiperidin-4-one & 3-hydroxy–2-methyl- benz pyrimidin-4-one **(1A & 2B)** were prepared according to **[13,14].**

3-Bromo-2-oximino-1,2,3-tri [H] benzpiperidin–4-one (2):.

2-Oximino-1, 2, 3-tri [H] benzpiperidin-4-one **1A** (9g), in 50 ml. AcOH, added (8g). Br_2 in 20 ml. AcOH in 7 min. at 8-10 ^oC, then 100 ml. cold water in 5-10 min. & stir 10 min. filter the crystals and wash first with 25% AcOH, then with 10% AcOH to give compound **2A. Table (5).**

1, 3-Di [H]-Benzpiperidin-4-one-2(1)[imino-N-2-methyl quinolin-1-chloride salt 3:

Ethanolic solution of (**1A)** and quinaldine (0.01mol) in presence of hydrochloric acid was refluxed for 2-4 hrs, filtrate, concentrated and cold. The precipitated product was separated, crystallized from ethanol to give red crystals **Table (4).**

2-Oximino-1,2, 3-tri [H] benzperidin-4-one 3(H)-[2] methyl, amino pyridine (quinolin)- bromide salt 4a-c

Ethanolic solutions of (**2)** and 2-methyl (amino)-pyridine (quinoline) (0.01mol) and few drops of piperidine was refluxed for 1 hour. 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 (**4a-c)**, **Table (5).**

6, 12, 16-Tri [H]-Benz piperidino[2, 3-d] pyrido[2,1-a]-11-one-14- chloride salt 5:

Ethanolic solution of **3** was refluxed for 2-5 min under thermal piperidine. then add 25ml of ethanol on reflux for 1-2 hrs, concentrated, neutralized by acetic acid The precipitated products after dilution with water were separated, filtrated, crystallized from ethanol to give dark red crystals **Table (5).**

5[H] Imidaolo [4, 5-b][2, 3, 4-b, j] indolizino [2, 3-b] benzpiperidin-12- bromide salt 7a,b

Ethanolic solutions of (**6a-c)** and zinc chloride (0.01mol) were refluxed for 4-6 hours filtered hot, concentrated, cooled, the products **5a-c** precipitated on dilution with water were crystallized from ethanol, **Table (5).**

5, 6, Di [H]-Benz piperidino [2, 3-d] pyrido [2, 1-a] pyridazin-11- one-zero-12 (4) methine cyanine dye 8

An ethanolic solution of (**4A)** and quinolin-4-ium ethiodide (0.01mol) was refluxed for 6-8 hrs in presence of few drops of piperidine. 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).**

6[H]-5-Oximino-indolizino(benzindolizino)[2,3-b]benzpiperidin-zero-11[4(1)] methine &6[H]-5-oximino-indolizino (benzindolizino) [2,3-b] benzpiperidin-mono-2[2(4)] methine cyanine dyes (9a-c, 10a-c):

Ethanolic solutions of **(6a,b)** and N-ethyl-pyridin (quinolin)-4(1)-ium-and/or 2(4)-methyl-pyridin(quinolin)-2(4)-ium ethiodide salts (0.01mol) in the presence of few drops of piperidine were refluxed for 6-8 hours. The reaction mixture was 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 (5).**

Table (5): Characterization of (2, 3, 5, 7a-c., 11a-c, 15, 17a-e18a,b,19)

Comp No.	Nature of product			Mol. Formula (M.Wt)	% Calc.(Found)		
	Colour	m.p. °C	Yield %		C	H	N
2	Pale yellow	228	63	$C_9H_6N_2O_2Br$ (255	42.35 (42.33)	2.35 (2.35)	10.98 (10.95).
3	Red	163	48	$C_{19}H_{12}N_3OCl$ (333.5),	68.05 (68.01)	3.59 (3.55	12.59 (12.3).
5	Dark red	173	52	$C_{19}H_{14}N_3OCl$ (335.5)	67.95 (67.91)	4.17 (4.17)	12.51 (12.50)
6a	Pale yellow	220	38	$C_{15}H_{12}N_3OBr$ (330)	(54.54) (54.51)	(3.36) (3.36)	(12.72) (12.76)
6_b	Brown	180	35	$C_{19}H_{14}N_3OBr$ (380)	(59.84) (59.80)	(3.67) (3.67)	(11.02) (11.06)
6c	Pale brown	139	52	$C_{14}H_{11}N_4OBr$ (331)	(50.75) (50.71)	(3.32) (3.32)	(16.91) (16.88)
7a	Dark yellow	171	32	$C_{15}H_{10}N_3Br$ (312)	(57.69) (57.62)	(3.20) (3.20)	(13.46) (13.62)
7b	Dark brown	170	43	$C_{19}H_{12}N_3Br$ (378)	(60.31) (60.38)	(3.1) (3.01)	(11.11) (11.14)
7c	Brown	160	63	$C_{14}H_9N_4Br$ (313)	(53.67) (53.62)	(2.87) (2.83)	(17.85) (17.82)
11a	Brown	135	48	$C_{22}H_{18}N_4O_2$ (369)	74.79 (74.76)	5.14 (5.12)	11.38 (11.35)
11b	Dark brown	143	53	$C_{22}H_{17}N_5O_4$ (414)	66.66 (66.78)	4.34 (4.34)	13.53 (13.50)
11c	Brown	125	58	$C_{22}H_{19}N_5O_2$ (384)	71.87 (71.82)	5.20 (5.20)	14.58 (14.55)

15	Dark brown	184	45	$C_{22}H_{14}N_4O$ (394)	67.00 (67.05)	3.55 (3.50)	14.21 (14.25) .
17a	Green	194	41	$C_{14}H_{12}N_2OCl$ (259.5)	64.73 (64.75)	4.62 (4.62)	10.78 (10.80)
17b	brown	201	37	$C_{18}H_{14}N_2OCl$ (309.5)	69.78 (69.81)	4.52 (4.52)	9.78 (9.04)
17c	Reddish brown	185	35	$C_{19}H_{16}N_2OC$ l (323.5)	70.47 (70.51)	4.94 (4.94)	8.65 (8.67)
18a	Greenish	248	52	$C_{14}H_{10}N_3OCl$ (271.5)	61.87 (61.85)	3.68 (3.68)	15.46 (15.44)
18b	Brownish green	233	54	$C_{16}H_{12}N_3OCl$ (297.5)	64.53 (64.51)	4.03 (4.03)	14.11 (14.12)
19	dark brown	152	41	$C_{19}H_{12}N_3Cl$ (319.5)	71.36 (71.30)	3.75 (3.73)	13.14 (13.12).

6[H]-5-Oximino-Indolizino(benzindolizino)[2,3-b]benzpiperidin-meso-substituted tri–2[2(4)]-methine cyanines dyes (12a-e)

Step (A):i-6[H]-5-Oximino-Indolizino(benzindolizino)[2,3-b]benzpiperidin-2[1]-benzoyl-methinyl derivatives (11a-c)

Ethanolic solutions of **(6c)** and acetophenone derivatives (0.01mol) in the presence of sodium hydroxide were refluxed for 6-8hours. The reaction mixtures were filtrated from unreacted materials. The precipitated products after dilution with water were separated, filtrated, crystallized from the suitable solvent, **Table (5).**

Step (B): Ethanolic solutions mixture of (**11a-c)** and 2(4)-methyl-pyridin(quinolin)-2(4)-ium ethiodide salts (0.01mol) in presence of few drops of piperidine were refluxed for 8 hr,. 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).**

5[H] Imidazolo [4, 5-b][2, 3, 4-b, j] indolizino-[2, 3-b] benzpiperidin-zero-10 [4(1)] Methine cyanine dyes 13a-d

An ethanolic solution (**7a, b)** and N-ethyl-pyridine (quinoline) iodide (0.01mol) in the presence of few drops of piperidine were refluxed for 6-8 hours r. 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).**

6[H] -5-Oximino-indolizino (benzindolizino)[2,3-b] benzpiperidin-mono-2 [2(4)] methine cyanine dyes (14a-e)

Ethanolic solutions of **(7a,b)** and α (γ) picoline and quinaldine] ethiodide salts (0.01mol) in the presence of few drops of piperidine were refluxed for 6-8 hours. The reaction mixture was 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).**

Table 6: Characterization of (8, 9a-d, 10a-e, 13a-d)

Comp No.	Nature of product			Mol.Formula (M.Wt)	% Calc. (Found)			Absorption spectra in 95%EtOH	
	Colour	m.p. °C	Yield %		C	H	N	λ_{max} n. m	ε_{max} Mol $^{-1}$cm^2
8	Brownish red	163	48	$C_{30}H_{23}N_4OI$ (581)	61.96 (61.96)	3.95 (3.95)	9.60 (9.60)	485	2603
9a	Yellow	123	35	$C_{22}H_{19}N_4OI$ (481)	54.77 (53.79)	3.94 (3.92)	11.62 (11.13)	460	2900
9b	Dark Yellow	118	40	$C_{26}H_{21}N_4OI$ (531)	58.63 (57.73)	3.95 (3.95)	10.52 (10.76)	470	2840
9c	Greenish Yellow	138	38	$C_{26}H_{21}N_4OI$ (531)	58.63 (57.42)	31.95 (3.59)	10.52 (11.32)	465	2870
9d	Dark Brown	116	45	$C_{30}H_{24}N_4OI$ (582)	61.84 (60.93)	4.12 (4.12)	9.62 (8.87)	480	2880
10a	Brown	130	41	$C_{22}H_{21}N_4OI$ (483)	55.65 (54.94)	4.23 (4.23)	11.29 (11.41)	470	2650
10b	Violet	185	45	$C_{27}H_{23}N_4OI$ (529)	59.34 (58.95)	4.21 (4.21)	10.26 (10.32)	500 580 670	28500 26300 11500
10c	Brown	183	45	$C_{22}H_{21}N_4OI$ (483)	55.65 (54.84)	4.23 (4.22)	11.29 (11.41)	480	26300
10d	Reddish brown	123	44	$C_{27}H_{23}N_4OI$ (545)	59.34 (58.87)	4.21 (4.21)	10.26 (10.45)	490	2870
10e	Brown	180	47	$C_{22}H_{20}N_5OI$ (496)	53.12 (53.22)	4.02 (4.02)	14.08 (14.06)	475	2690
13a	Brown	122	42	$C_{22}H_{17}N_4I$ (463)	56.90 (57.12)	3.66 (3.65)	12.07 (11.87)	455	2540
13b	brown	119	45	$C_{26}H_{20}N_4I$ (514)	60.69 (60.61)	3.89 (3.87)	10.89 (10.84)	470	2540
13c	Reddish brown	115	43	$C_{26}H_{20}N_4I$ (514)	60.96 (60.90)	3.89 (3.87)	10.89 (10.82)	465	2780
13d	brown	145	33	$C_{26}H_{19}N_4I$ (513)	60.82 (60.89)	3.70 (3.76)	17.78 (17.74)	465	2540

5[H] Imidazolo[4, 5-b][2, 3, 4-b, j] indolizino[2, 3-b] benzpiperidin-zero-10 [4(1)] 13a-d, and mono-2 [2(4)]-methine cyanine dyes (14a-e)

Ethanolic solution of (**7 a, b)** and N-ethyl-pyridin (quinolin)-4(1)-ium ethiodide and/or 2(4)-methyl-pyridin(quinolin)-2(4)-ium ethiodide salts (0.01mol) in presence of few drops of piperidine were refluxed for 6-8 hours. 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 products (**9a-d, 10a-e)**

6[H]-Benzpiperidino [2,3-d] pyrido [2, 1-a] pyridazin-11- one 2(1)-benzoyl-methine 15

Ethanolic solutions of (**7c)** and acetophenone (0.01mol), in presence of sodium hydroxide were refluxed for 6-8 hours. 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 (5).**

6[H]-Benzpiperidino[2,3-d]pyrido [2, 1-a] pyridazin-11- one mesosubstituted tri-2 (2)-methine cyanine dye (16)

Ethanolic solutions of (**15)** and 2(4)-methyl-pyridin (quinolin)-2(4)-ium ethiodide salts (0.01mol) in presence of few drops of piperidine were 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 product after dilution with water were separated, filtrated, crystallized from ethanol, **Table (7)**

2-Methyl–benzpyrimidin-4-one-N-pyridin(quinolin)/2-methyl quinolin)-1- chloride (17a-c) Indolizino (benzindolizino) [3, 2-b]-benz pyrimidin-5-one-13-chloride salts (18a-c) 2-methyl pyrazolo[3, 2-a] quinolino[1, 5-a] benzpyrimidin-16-chloride (19):

Ethanolic solutions of (**1B)** and N-ethyl-pyridin (quinolin)-4(1)-ium ethiodide and/or 2-methyl-quinolin-2-ium ethiodide (0.01mol) in presence of concentrated hydrochloric acid (10ml) was refluxed for 2-3 hr., filtered, concentrated, then poured on ice water to give (**17a-c),** fusion of **(17a-c)** with piperidine for 2-3 min., then add 25ml of ethanol and the reaction mixture was refluxed again for 6-8 hrs. The 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 (**18a,b,19),Table (5).**

Indolizino(benzindolizino)[3,2-b]-benzpyrimidin-5-one-zero-11[4(1)]methine cyanine dyes (20a-d)

Ethanolic solution mixture of (**18a, b)** & N-ethyl-pyridin (quinolin)-4(1)-ium ethiodide (0.01mols) with few drops of piperidine was refluxed for 6-8 hrs. The reaction mixtures were filtrated from unreacted materials. The filtrate was concentrated, and cold. The precipitated product after dilution with water was separated, filtrated, crystallized from ethanol, **Table (7).**

2-Methyl-pyrazolo[3,2-a]quinolino[1,5-a]benzpyrimidin-zero-1[4]methine cyanine dye (21)

Ethanolic solution of (**19)** and N-ethyl- quinolin-4-ium ethiodide (0.01mol) with 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 (7).**

Table (7): Characterization of (12a-d, 14a-e, 16, 20a-d & 21)

Comp No.	Nature of product			Mol.	%Calc .(Found)			Absorption Spectra in 95%EtOH	
	Colour	m.p. °C	Yield %	Formula (M.Wt)	C	H	N	λ_{max} n. m	E max Mol $^{-1}$cm^2
12a	Dark brown	175	53	$C_{30}H_{28}N_5$ OI (399)	62.10 (62.11)	4.84 (4.84)	9.34 (9.31)	475	2523
12b	Reddish violet	197	51	$C_{34}H_{30}N_5$ OI (649)	64.71 (64.74)	4.77 (4.77)	8.63 (8.65)	480 570 690	2874 2480 1148
12c	Reddish brown	177	56	$C_{30}H_{28}N_5$ OI (399)	62.10 (62.11)	4.84 (4.84)	9.34 (9.31)	485	2717
12d	Brownish Red	179	65	$C_{30}H_{27}N_6$ O_3I (644)	57.76 (57.72)	4.35 (4.34)	10.86 (10.82)	490	2583
12e	Brown	170	61	$C_{29}H_{28}N_7$ OI (544)	68.38 (68.31)	5.51 (5.50)	12.86 (12.84)	480	2341
10a	brown	147	31	$C_{23}H_{19}N_4$I (477)	57.74 (56.78)	3.97 (3.96)	11.72 (12.31)	470	2960
14b	Violet	154	48	$C_{27}H_{21}N_4$I (527)	61.37 (62.21)	3.98 (3.97)	10.61 (11.34)	500 575 695	2751 2970 1880
14c	Reddish Brown	151	35	$C_{23}H_{19}N_4$I (477)	57.74 (56.78)	3.97 (3.97)	11.72 (12.21)	480	2750
14d	Violet	191	55	$C_{31}H_{23}N_4$I (577)	64.90 (64.94)	3.98 (3.97)	9.69 (9.68)	490 545 700	2490 2520 1109
14e	Brown	165	32	$C_{22}H_{18}N_5$I (478)	55.12 (55.16)	3.76 (3.74)	14.61 (14.65)	475	2450
16	reddish brown	184	52	$C_{30}H_{25}N_5$I (581)	61.96 (61.96)	4.30 (4.30)	12.04 (12.04),	485	2013

20a	green	212	41	$C_{21}H_{18}N_4OI$ (468)	53.84 (53.81)	3.84 (3.80)	11.96 (11.92)	465	2031
20b	red	205	46	$C_{25}H_{22}N_4OI$ (520)	57.69 (57.65)	4.2 (4.2)	10.76 (10.73)	485	2641
20c	red	182	43	$C_{25}H_{22}N_4OI$ (520)	57.69 (57.64)	4.2 (4.2)	10.76 (10.73)	475	2530
20d	Reddish brown	187	65	$C_{29}H_{26}N_4OI$ (572)	60.83 (60.80)	4.5 (4.5)	9.79 (9.73)	480	2701
21	reddish brown	132	51	$C_{30}H_{23}N_3I$ (551),	65.33 (65.11)	4.17 (4.17)	7.62 (7.60),	435, 485	2120, 2623

SOLVATOCHROMIC AND ACID BASE PROPERTIES:

The organic solvents were used of spectroscopic grade which purified according to the recommended methods **[15]**.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: Accurate volumes 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 recommended by **[16]** 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 obtained 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**.** 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'ṣ mixed with different proportions of organic solvents used. The pH'ṣ of the buffer solutions were checked using Orion pH-meter model (60, A), accurate to ± 0.005 pH units, at 25 ^{0}C.

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