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The use of *N*-bridgehead heterocyclic indolizinium ylide in the synthesis of aza-cyanine dyes

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Abstract

The reaction of 3-methyl-8-oxime-1-phenylpyrazolo [4,5-*d*]indolizinium (bezoindolizinium) ylide iodide with 2(4)-methyl substituted heterocyclic quaternary salts give 8[2(4)]-aza-monomethine cyanine dyes. Meanwhile, the reaction with carbonyl compounds followed by reaction with 2-methyl quinolinium methiodide salts afforded 5(2)-aza-trimethine cyanine dyes. On the other hand, the reaction of 5-formyl-2-methyl-4-phenylpyrazolo[4,5-*d*]indolizinium (benzoindolizinium) ylide iodide with hydroxylamine hydrochloride followed by reaction with *N*-methyl heterocyclic quaternary salts afforded the corresponding 5[4(1)]-aza-dimethine cyanine dyes. These new compounds are characterized with elemental analyses, visible absorption, IR, ^{13}C NMR, ^{1}H NMR and mass spectroscopy. The correlations between the structure and spectral properties of these dyes have been studied.

Keywords: Indolizinium ylide; Aza-cyanine; Aza-monomethine; Aza-trimethine; Aza-dimethine

1. Introduction

There is growing interest by our group in the synthesis of *N*-bridgehead heterocyclic compounds in view of their use in the synthesis of cyanine dyes [1–4]. Aza-cyanine dyes have potential applicability in non-linear optics, as optical sensors, and in physiology/biochemistry areas [5–7]. Also, they are used as organic photoconductors to their complexation ability and photophysical properties [8–11]. Recently, they are used as a new chromofluoroionophore [12–14]. There is currently much interest in the use of the indolizinium chromophores for non-linear optical applications [15].

This paper will describe the synthesis and spectral behaviour of new indolizinium aza-cyanine dyes having a pyrazolo[4,5-*d*]indolizinium ring moiety.

2. Experimental

All melting points are uncorrected. Elemental analyses were carried out at the Microanalytical center (Cairo University). The IR (ν^{KBr}) spectra were determined with Perkin Elmer Infrared 127ß spectrophotometer (Cairo University). ^{1}H NMR spectra were recorded with a Bruker AMX-250 spectrometer. ^{1}H NMR and ^{13}C NMR 2D spectra were measured with a Bruker AMX-400 spectrometer and with TMS as an internal standard. Mass spectra were recorded on an HpMs 6988 spectrometer (Cairo University). The electronic absorption spectra were recorded within the wavelength range (350–700) on 6405 UV/visible recording spectrophotometer (Faculty of Science, Aswan).

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2.1. Synthesis of 3-methyl-1-phenyl-4-[2-methyl-N-pyridin(quinolin)-1-ium iodide] pyrazol-5-one **3a**,**b**

A mixture of compound 3-methyl-1-phenyl pyrazol-5-one **1** (0.01 mol), iodine and α-picoline (quinaldine) (0.01 mol) was refluxed in methanol for 5 h, filtered hot, concentrated, and cooled. The precipitated solids were collected, washed with ethanol and crystallized from aqueous ethanol.

(**3a**): Yield 85%; m.p. 125–127 °C, Anal. cald for $C_{16}H_{16}N_3OI$ (393): C, 48.86; H, 4.07; N, 10.69. Found: C, 49.03; H, 4.21; N, 10.87.
(**3b**): Yield 89%; m.p. 130–133 °C, Anal. cald for $C_{20}H_{18}N_3OI$ (443): C, 54.18; H, 4.06; N, 9.48. Found: C, 54.39; H, 4.25; N, 9.27.

2.2. Synthesis of 2-methyl-4-phenyl pyrazolo[4,5-d]indolizinium(benzoindolizinium) ylide iodide salts **4a**,**b** according to [16]

A mixture of compounds **3a**,**b** (0.01 mol) was dissolved in ethanol (30 ml) and piperidine (3–5 drops) was added. The reaction mixture was refluxed for 5 h, filtered hot, concentrated, cooled and acidified with acetic acid. The precipitated solids were collected and crystallized from aqueous ethanol.

(**4a**): Yield 79%; m.p. 160–163 °C, Anal. cald for $C_{16}H_{14}N_3I$ (375): C, 51.20; H, 3.73; N, 11.20. Found: C, 51.45; H, 3.65; N, 11.37.
(**4b**): Yield 75%; m.p. 168–170 °C, Anal. cald for $C_{20}H_{16}N_3I$ (425): C, 56.47; H, 3.77; N, 9.88. Found: C, 56.67; H, 3.95; N, 10.07.

2.3. Synthesis of 2-methyl-5-oxime-4-phenyl pyrazolo[4,5-d]indolizinium (benzo indolizinium)-iodide **5a**,**b**

To a solution of compounds (**4a**,**b**) (0.01 mol) in ethanol, 10 ml of conc. HCl acid was added. The mixture was cooled to 0 °C. Saturated solution of sodium nitrite was added and conc. hydrochloric acid was also added drop by drop to the mixture until the nitroso fumes appeared, the mixture was allowed to stand and precipitated by ice-water. The precipitated product was collected and crystallized from ethanol to give **5a**,**b**.

(**5a**): Yield 45%; m.p. 133–135 °C, Anal. cald for $C_{16}H_{13}N_4OI$ (404): C, 57.53; H, 3.22; N, 13.86. Found: C, 57.67; H, 3.37; N, 14.01. MS: $m/z = 405$.
(**5b**): Yield 49%; m.p. 148–150 °C, Anal. cald for $C_{20}H_{15}N_4OI$ (454): C, 52.86; H, 3.30; N, 12.33. Found: C, 52.87; H, 3.15; N, 12.13. MS: $m/z = 456$. IR (ν^{KBr} cm^{-1}) at 1487 cm^{-1} (cyclic C=N), 1595 cm^{-1} (conjugated C=C), 3062 cm^{-1} (N–OH), 2922–2924 cm^{-1} (quaternary ylide iodide). The ^1H NMR (MeOH, 250 MHz) at δ 1.15 ppm (s, 3H, CH_3 of pyrazol), 7.10–7.94 ppm (m, 11H, Ar–H + Het–H), 8.85 ppm (s, 1H, N–OH).

2.4. Synthesis of 2-methyl-4-phenyl pyrazolo[4,5-d]Indolizine (benzoindolizine)-5[2(4)]-aza-monomethine cyanine dyes (**6a–d**)

A mixture of compounds **5a**,**b** (0.01 mol) and 2(4)-methyl quaternary salts [α (γ)-picoline and quinaldine] methyl iodide (0.01 mol) was dissolved in ethanol (20 ml) and 3–5 drops of piperidine was added. The reaction mixture was refluxed for 12 h, filtered hot, concentrated and cooled. The precipitated product was collected and crystallized from ethanol to give (**6a–d**).

(**6a**): Yield 47%; m.p 118–120 °C, Anal. cald for $C_{23}H_{20}N_5I$ (493): C, 55.98; H, 4.06; N, 14.20. Found: C, 56.67; H, 3.87; N, 13.91. MS: $m/z = 494$.
(**6b**): Yield 65%; m.p. 132–134 °C, Anal. cald for $C_{27}H_{22}N_5I$ (543): C, 59.67; H, 4.05; N, 12.89. Found: C, 59.55; H, 4.23; N, 13.01. MS: $m/z = 544$. IR (ν^{KBr} cm^{-1}) at 1487 cm^{-1} (cyclic C=N), 1595 cm^{-1} (conjugated C=C), 2921–2925 cm^{-1} (methiodide of heterocyclic salt). The ^1H NMR (MeOH, 250 MHz) at 1.17 ppm (s, 3H, CH_3 of pyrazol), 3.97 ppm (s, 3H, CH_3–N^+), 6.45–7.83 (m, 16H, Ar–H + Het–H + CH=).
(**6c**): Yield 51%; m.p. 120–122 °C, Anal. cald for $C_{23}H_{20}N_5I$ (493): C, 55.98; H, 4.06; N, 14.20. Found: C, 56.57; H, 3.87; N, 13.91. MS: $m/z = 494$.
(**6d**): Yield 75%; m.p. 143–145 °C, Anal. cald for $C_{31}H_{24}N_5I$ (593): C, 59.67; H, 4.05; N, 12.89. Found: C, 59.55; H, 4.23; N, 13.01. MS: $m/z = 594$. IR (ν^{KBr} cm^{-1}) at 1487 cm^{-1} (cyclic C=N), 1595 cm^{-1} (conjugated C=C), 2921–2925 cm^{-1} (methiodide of heterocyclic salt). The ^1H NMR (MeOH, 250 MHz) at 1.17 ppm (s, 3H, CH_3 of pyrazol), 3.97 ppm (s, 3H, CH_3–N^+), 6.45–7.83 (m, 18H, Ar–H + Het–H + CH=).

2.5. Synthesis of 2-methyl-4-phenyl pyrazolo[4,5-d]Indolizine (benzoindolizine)-β-substituted-5(2)-aza-trimethine cyanine dyes (**8a–d**)

A mixture of compounds **5a**,**b** (0.01 mol) and carbonyl compounds such as (acetaldehyde, acetone and/or acetophenone) (0.01 mol) was heated on sand

bath without solvent in presence of piperidine (3–5 ml), for 15 min, and cooled. The product was dissolved in ethanol and refluxed for 30 min, filtered hot, concentrated and cooled. The product was recrystallized from methanol to give well-formed crystals of compounds (**7a–d**).

(**7a**): Yield 45%; m.p. 228–230 °C, Anal. cald for $C_{18}H_{15}N_4OI$ (430): C, 50.23; H, 3.49; N, 13.02. Found: C, 50.35; H, 3.67; N, 13.31. (ν^{KBr} cm^{-1}) at 1487 cm^{-1} (cyclic C=N), 1595 cm^{-1} (conjugated C=C), 1717 cm^{-1} (C=O), 2921–2925 cm^{-1} (methiodide of heterocyclic salt), 2922–2924 cm^{-1} (quaternary ylide iodide). The ^{1}H NMR (MeOH, 250 MHz) at 1.15 ppm (s, 3H, CH_3 of pyrazol), 2.85 ppm (s, 2H, CH_2), 7.25–7.94 (m, 9H, Ar–H + Het–H), 9.97 ppm (s, 1H, CHO).
(**7b**): Yield 48%; m.p. 218–220 °C, Anal. cald for $C_{19}H_{17}N_4OI$ (444): C, 51.35; H, 3.83; N, 12.61. Found: C, 51.05; H, 3.59; N, 12.87. (ν^{KBr} cm^{-1}) at 1487 cm^{-1} (cyclic C=N), 1595 cm^{-1} (conjugated C=C), 1717 cm^{-1} (C=O), 2922–2924 cm^{-1} (quaternary ylide iodide). ^{1}H NMR (MeOH, 250 MHz) at 1.15 ppm (s, 3H, CH_3 of pyrazol), 2.85 ppm (s, 2H, CH_2), 3.15 ppm (s, 3H, CH_3), 7.15–7.94 ppm (m, 9H, Ar–H + Het–H).
(**7c**): Yield 50%; m.p. 215–217 °C, Anal. cald for $C_{24}H_{19}N_4OI$ (506): C, 56.92; H, 3.75; N, 11.07. Found: C, 56.73; H, 3.69; N, 10.87. MS: $m/z = 507$.
(**7d**): Yield 43%; m.p. 241–243 °C, Anal. cald for $C_{28}H_{21}N_4OI$ (556): C, 60.43; H, 3.78; N, 10.07. Found: C, 60.73; H, 3.89; N, 10.23. MS: $m/z = 557$. ^{1}H NMR (MeOH, 250 MHz) at 1.15 ppm (s, 3H, CH_3 of pyrazol), 2.85 ppm (s, 2H, CH_2), 7.25–7.94 (m, 16H, Ar–H + Het–H).

A mixture of compounds (**7a–d**) (0.01 mol) and 2-methylquinolinium methyl iodide (0.01 mol) was dissolved in ethanol and piperidine (3–5 drops) was added. The reaction mixture was refluxed for 8 h, filtered hot, concentrated and cooled. The solid was triturated with cold, dilute acetic acid and the solid product, was collected and recrystallized from ethanol to give the corresponding products (**8a–d**).

(**8a**): Yield 50%; m.p. 220–222 °C, Anal. cald for $C_{29}H_{24}N_5I$ (569): C, 61.16; H, 4.22; N, 12.30. Found: C, 61.33; H, 4.43; N, 12.11. (ν^{KBr} cm^{-1}) at 1487 cm^{-1} (cyclic C=N), 1595 cm^{-1} (conjugated C=C), 2921–2925 cm^{-1} (methiodide of heterocyclic salt). The ^{1}H NMR (MeOH, 250 MHz) at 1.15 ppm (s, 3H, CH_3 of pyrazol), 3.97 ppm (s, 3H, CH_3–N^+), 6.55–7.94 ppm (m, 18H, Ar–H + Het–H + CH=).
(**8b**): Yield 65%; m.p. 200–202 °C, Anal. cald for $C_{30}H_{26}N_5I$ (583): C, 61.75; H, 4.46; N, 12.01. Found: C, 61.89; H, 4.23; N, 12.19. MS: $m/z = 584$. ^{1}H NMR (MeOH, 250 MHz) at 1.15 ppm (s, 3H, CH_3 of pyrazol), 2.35 ppm (s, 3H, CH_3), 4.05 ppm (s, 3H, CH_3–N^+), 6.55–7.94 ppm (m, 17H, Ar–H + Het–H + CH=).
(**8c**): Yield 69%; m.p. 220–222 °C, Anal. cald for $C_{35}H_{28}N_5I$ (645): C, 65.12; H, 4.65; N, 10.85. Found: C, 64.85; H, 4.35; N, 10.61. MS: $m/z = 646$.
(**8d**): Yield 62%; m.p. 217–219 °C, Anal. cald for $C_{39}H_{30}N_5I$ (695): C, 67.24; H, 5.32; N, 10.06. Found: C, 67.45; H, 5.57; N, 10.21. ^{1}H NMR (MeOH, 250 MHz) at 1.17 ppm (s, 3H, CH_3 of pyrazol), 3.95 (s, 3H, CH_3–N^+) and 6.55–7.95 (m, 24H, Ar–H + Het–H + CH=).

*2.6. Synthesis of 2-methyl-4-phenylpyrazolo[4,5-d]indolizine-5[4(1)]-aza-dimethine cyanine dyes (**12a–c**)*

A mixture of compound **9** (0.01 mol) and hydroxylamine hydrochloride was dissolved in ethanol and plates of sodium hydroxide were added. The reaction mixture was refluxed for 8 h, filtered hot, concentrated and cooled. The solid was triturated with cold, conc. HCl acid and the product was collected and recrystallized from ethanol to give the corresponding product **10**.

(**10**): Yield 46%; m.p. 119–121 °C, Anal. cald for $C_{17}H_{16}N_4OI$ (419): C, 48.69; H, 3.82; N, 13.37. Found: C, 48.85; H, 3.69; N, 13.19. MS: $m/z = 420$.

A mixture of compound **10** (0.01 mol) and *N*-methyl heterocyclic quaternary salts (pyridine, quinoline, isoquinoline) methyl iodide (0.01 mol) were dissolved in acetic acid (30 ml). The reaction mixture was refluxed for 5 h, filtered hot, concentrated and cooled. The solid was diluted with cold water. The product was collected and recrystallized from ethanol to give the corresponding products (**11a–c**).

(**11a**): Yield 43%; m.p. 130–132 °C, Anal. cald for $C_{24}H_{21}N_5I_2$ (633): C, 45.50; H, 3.32; N, 11.06. Found: C, 45.55; H, 3.49; N, 10.89. MS: $m/z = 634$.
(**11b**): Yield 55%; m.p. 158–160 °C, Anal. cald for $C_{28}H_{23}N_5I_2$ (683): C, 49.20; H, 3.37; N, 10.25. Found: C, 49.43; H, 3.19; N, 10.39. ^{1}H NMR (MeOH, 250 MHz) at δ 1.17 ppm (s, 3H, CH_3–pyrazol), 3.97 ppm (s, 3H, CH_3–N^+), 6.65–7.97 ppm (m, 17H, Ar–H + Het–H + CH=).
(**11c**): Yield 41%; m.p. 133–135 °C, Anal. cald for $C_{28}H_{23}N_5I_2$ (683): C, 49.20; H, 3.37; N, 10.25. Found: C, 49.45; H, 3.17; N, 10.31. MS: $m/z = 684$.

A mixture of compounds (**11a–c**) was dissolved in ethanol (30 ml) and piperidine (3–5 drops) was added. The reaction mixture was refluxed for 5 h, filtered hot,

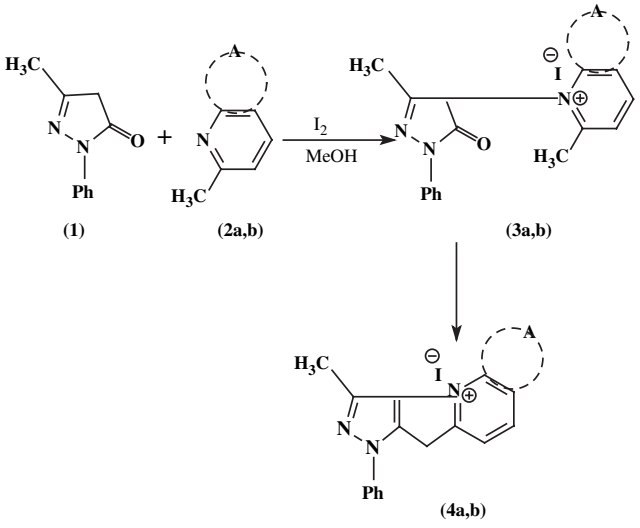
concentrated, cooled and acidified with acetic acid. The precipitated solid after dilution with water was collected and crystallized from aqueous ethanol to give the corresponding products (**12a–c**).

(**12a**): Yield 53%; m.p. 120–122 °C, Anal. cald for $C_{24}H_{20}N_5I$ (507): C, 56.81; H, 4.34; N, 13.81. Found: C, 57.03; H, 4.45; N, 13.67. MS: $m/z = 508$.
(**12b**): Yield 53%; m.p. 120–122 °C, Anal. cald for $C_{28}H_{22}N_5I$ (557): C, 60.32; H, 4.31; N, 12.57. Found: C, 60.55; H, 4.15; N, 12.75. IR (ν^{KBr} cm^{-1}) 1497 (C=N), 1595 (C=C) 2925 (MeI of heterocyclic salt). ^1H NMR (DMSO, 400 MHz) at δ 1.24 ppm (s, 3H, CH_3 of pyrazol), 2.53 (s, 3H, N^+-CH_3), 7.10–7.92 (m, 16H, Ar + Het + =CH).
(**12c**): Yield 53%; m.p. 120–122 °C, Anal. cald for $C_{28}H_{22}N_5I$ (557): C, 60.32; H, 4.31; N, 12.57. Found: C, 60.51; H, 4.19; N, 12.73.

3. Synthesis

The reaction of equimolar amounts of 3-methyl-1-phenylpyrazol-5-one **1**, with iodine, 2-methylpyridine and/or (2-methylquinoline), **2a**,**b** in absolute methanol gives the intermediate compounds 3-methyl-1-phenyl-4-(2-methyl-*N*-pyridin/quinolin-1-ium iodide) pyrazol-5-one **3a**,**b** which under piperidine catalysis and ethanol as solvent achieved *N*-bridgehead heterobicyclic 2-methyl-4-phenylpyrazolo[4,5-*d*]indolizinium (benzoindolizinium) ylide iodide **4a**,**b** [16] (Scheme 1).

The formation of 2-methyl-4-phenylpyrazolo[4,5-*d*] indolizinium (benzoindolizinium) ylide iodide **4a**,**b** was suggested to proceed either through the nucleophilic substitution reaction of 3-methyl-1-phenylpyrazol-5-one **1** and iodine involving dehydrohalogenation (–HI) followed by selective quaternization processes for 2-methyl pyridine (quinoline) **2a**,**b** to form the intermediate compounds **3a**,**b** or via direct selective intermolecular quaternization of 2-methyl pyridine (quinoline) using 3-methyl-1-phenylpyrazol-5-one **1**. The separated intermediate compounds undergo ring closer involving dehydration process to give compounds **4a**,**b** through the intermediate compound **A**. The reaction mechanistic pathway is represented in Scheme 2.



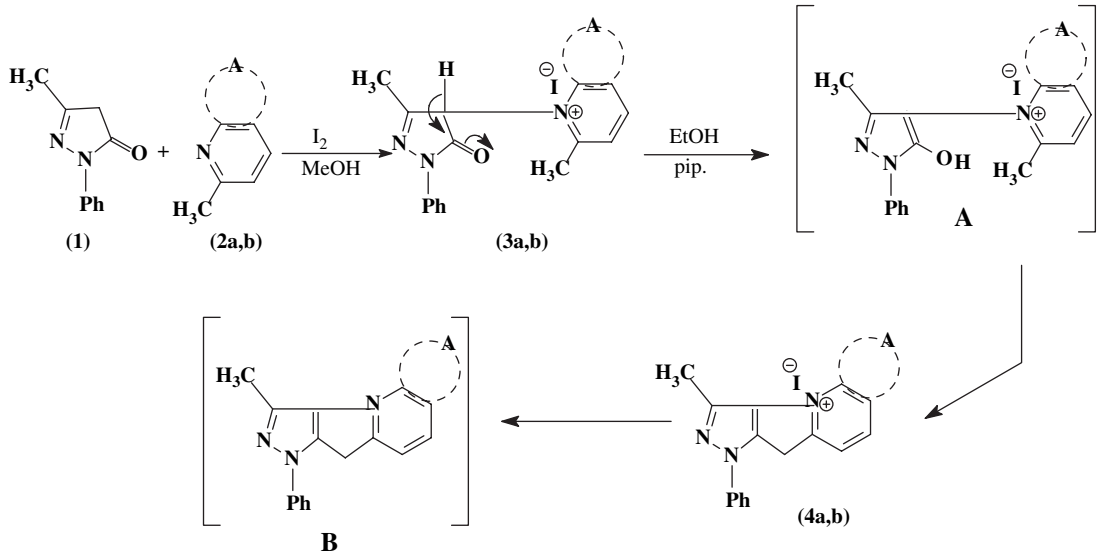
Scheme 1. **4a**,**b**: A = H (a); A = C_4H_4– (b).

The anhydro base of the bridgehead heterobicyclic ylide iodide moieties **B** was produced on treatment of compounds **4a**,**b** with ethyl alcohol and triethylamine, which on warming with conc. sulphuric acid liberated no iodine vapour (Scheme 2).

The structure of compounds **2**, **4a** and **4b** was confirmed by elemental analysis IR, ^1H NMR, mass spectra and ^{13}C NMR spectral data. Thus, the IR (ν^{KBr} cm^{-1}) of **2**, **4a** showed in addition to general absorption bands at 1497 cm^{-1} (C=N), 1594 cm^{-1} (C=C), 2919–2921 cm^{-1} (quaternary ylide iodide), well define absorption band at 1710 cm^{-1} (C=O), characteristic absorption band at 3557 cm^{-1} (CH-stretching) for compound **2**, 3457 cm^{-1} (spreading CH_2) for compound **4a**. ^1H NMR (CD_3OD, 250 MHz) spectra of **2** and **4a**,**b** showed in addition to the general single and multiple signals at δ 1.15–1.29 ppm (s, 3H, CH_3 of pyrazol), 6.8–8.77 ppm (m, 9H, Ar + Het), well define signals at 2.6 ppm (s, 1H, H mesomeric α,β-unsaturated), 2.2 ppm (s, 3H, CH_3 of pyridine) for compound **2**, 3.27 ppm (s, 2H, CH_2) for compounds **4a**,**b** 7.23–8.77 ppm (m, 11H, Ar + Het–H) for compound **4b**. ^{13}C NMR with the aid of carbon DEPT (MeOH, 250 MHz) spectra of **2** and **4a** showed in addition to the general single and multiple signals at δ 118.6–146.2 (d, 9 CH=, Ar + Het), 12.1–12.4 (q, CH_3), well defined signals at 16.4 (q, CH_3), 19.9 (d, CH= of pyrazol), 188.05 (s, C=O), 161.7, 153.45 (s, 2C=N), 135.29 (s, Ar + Cq) for compound **2**, 147.2, 152, 153.1, 161.6, 163.8 (s, 5q carbons) and 22.1 (t, CH_2) for compound **4a**.

The mass spectrum of compound **2** showed the molecular ion at m/z 394 (M + 1), m/z 250 (base peak), compound **4a** showed the molecular ion at m/z 375 (M^+), m/z 146 (base peak).

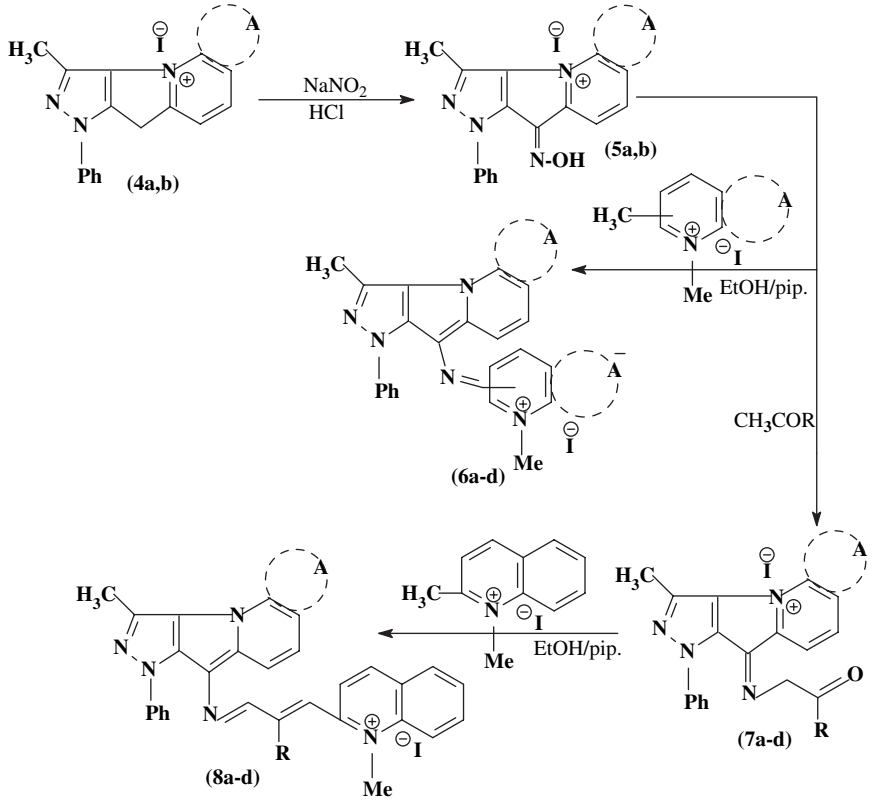
The reaction of compounds **4a**,**b** with nitrous acid afforded the intermediate compounds 2-methyl-5-oximel-phenylpyrazolo[4,5-d] indolizinium (benzoindolizinium) iodide **5a**,**b**. Reaction of equimolar amounts of compounds **5a**,**b** with 2(4)-methyl heterocyclic quaternary salts [α (γ)-picoline and quinaldine] methiodide in a basic catalyst afforded the corresponding *N*-bridgehead 2-methyl-4-phenylpyrazolo[4,5-d] indolizine (benzoindolizine)-5[2(4)]aza-monomethine (**6a–d**) (Scheme 3). The reaction of equimolar amounts of compounds **5a**,**b** with carbonyl compounds such as acetaldehyde, acetone and/or acetophenone in equimolar ratios under thermal conditions and a basic catalyst producing the



Scheme 2.

intermediate compounds (**7a–d**), which reacted with 2-methylquinolinium methiodide in presence of piperidine afforded the corresponding *N*-bridgehead 2-methyl-4-phenylpyrazolo[4,5-*d*] indolizine (benzoindolizine)-β-substituted-5(2)-aza-trimethine cyanine dyes (**8a–d**) (Scheme 3).

The reaction takes place through nucleophilic addition of active methyl of 2(4)-methyl heterocyclic



Scheme 3. **5a**,**b**: A = indolizinium iodide (a); A = benzoindolizinium iodide (b). (**6a–d**): A = indolizinium iodide; A′ = 1-methylpyridine-2-ium (a); A = indolizinium iodide; A′ = 1-methylquinoline-2-ium (b); A = indolizinium iodide; A′ = 1-methylpyridine-4-ium (c); A = benzoindolizinium iodide; A′ = 1-methylquinoline-2-ium (d). (**7a–d**): A = indolizinium iodide; R = H (a); A = indolizinium iodide; R = CH_3 (b); A = indolizinium iodide; R = C_6H_5 (c); A = benzoindolizinium iodide; R = C_6H_5 (d). (**8a–d**): A = indolizine; R = H (a); A = indolizine; R = CH_3 (b); A = indolizine; R = C_6H_5 (c); A = benzoindolizine; R = C_6H_5 (d).

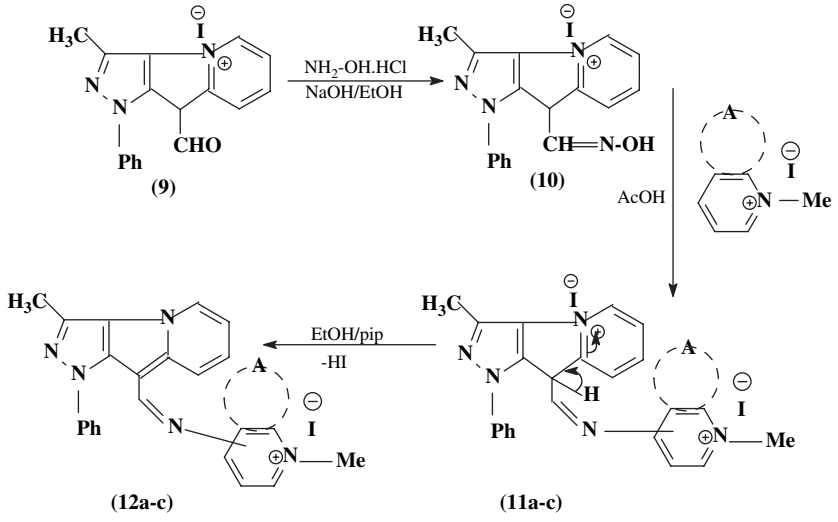
quaternary salts to carbonyl group of the compounds (**7a–d)** involving elimination of water followed by dehyhydrohalogenation of HI to give the corresponding aza-β-substituted trimethine cyanine dyes.

The structures of compounds **5a**, **6a**, **7c**, and **8c** were confirmed by elemental analysis IR, ^{1}H NMR, ^{13}C NMR and mass spectral data. Thus, the IR (ν^{KBr} cm^{-1}) of compounds **5a**, **6a**, **7c**, and **8c** showed in addition to general absorption bands at 1487 cm^{-1} (cyclic C=N), 1595 cm^{-1} (conjugated C=C), 1717 cm^{-1} (C=O), well defined absorption band at 3062 cm^{-1} (N–OH), 2922–2924 cm^{-1} (quaternary ylide iodide) for compounds **5a**, **7c** and 2921–2925 cm^{-1} (methiodide of heterocyclic salt) for **6a**, **8c**. The ^{1}H NMR (MeOH, 250 MHz) spectra of compounds **5a**, **6a**, **7c**, and **8c**, showed signals at δ 1.15 ppm (s, 3H, CH_3 of pyrazol), 7.10–7.94 ppm (m, 9H, Ar–H + Het–H), 8.85 ppm (s, 1H, N–OH) for compound **5a**, 1.17 ppm (s, 3H, CH_3 of pyrazol), 3.97 ppm (s, 3H, CH_3–N^+), 6.45–7.83 (m, 14H, Ar–H + Het–H + CH=) for compound **6a**, and 1.15 ppm (s, 3H, CH_3 of pyrazol), 2.85 ppm (s, 2H, CH_2), 7.25–7.94 (m, 14H, Ar–H + Het–H), for compound **7c**, and 1.17 ppm (s, 3H, CH_3 of pyrazol), 3.95 ppm (s, 3H, CH_3–N^+) and 6.55–7.95 ppm (m, 22H, Ar–H + Het–H + CH=) for compound **8c**. The ^{13}C NMR with the aid of carbon DEPT (MeOH, 250 MHz) spectra of **5a** reveals signals at δ 10.85 (s, CH_3), 52.62 (s, CH, N–OH) and 118.09–128.1 (14 carbons of Ar + Het).

Reaction of compound 5-formyl-2-methyl-4-phenyl-pyrazolo[4,5-*d*]indolizinium iodide **9** [3] with hydroxyl-amine hydrochloride in equimolar amounts under basic condition gave the corresponding 5-formyloxime-2-methyl-4-phenylpyrazolo [4,5-*d*] indolizinium iodide **10**. The reaction of compound **10** with the *N*-methyl heterocyclic quaternary (pyridine-4-ium, quinolin-4-ium, and isoquinolin-1-ium) methiodide salts, in equimolar amounts under acidic condition give compounds (**11a–c**). Further refluxing of the latter compounds (**11a–c**) in the presence of ethanol/piperidine condition afforded the corresponding 3-methyl-4-phenylpyrazolo[4,5-*d*] indolizine-5[4(1)]-aza-dimethine cyanine (**12a–c**) (Scheme 4).

The formation of the newly synthesized compound **10** was suggested to proceed through initial nucleophilic addition reaction of hydroxyl amine hydrochloride to acyclic carbonyl group in compound **9** to give formyloxime compound. Additionally, the formation of novel *N*-bridgehead 2-methyl-4-phenyl pyrazolo[4,5-*d*]indolizine-8[4(1)]-aza-dimethine cyanine dyes **12a–c** was suggested to proceed through water elimination process under acidic condition from hydroxyl group of formyloxime of compound **10** and active hydrogen of heterocyclic residue to give compounds (**11a–c**), which undergo dehydrohalogenation of HI under basic condition to produce the corresponding 5[4(1)]-aza-dimethine cyanine dyes (**12a–c**).

The structure of compounds **10**, **11a**, and **12a** was confirmed by elemental analysis IR, ^{1}H NMR and mass spectral data. Thus, the IR (ν^{KBr} cm^{-1}) of compounds **10**, **11a**, **12a** showed in addition to general absorption bands at 1487 cm^{-1} (cyclic C=N), 1595 cm^{-1} (conjugated C=C), well defined absorption band at 3062 cm^{-1} (N–OH), 2922–2924 cm^{-1} (quaternary ylide iodide) for compounds **10**, **11a** 2941–2965 cm^{-1} (methiodide of heterocyclic salt) for **11a**, **12a**. The ^{1}H NMR (MeOH, 250 MHz) spectra was showed signals at δ 1.19 ppm (s, 3H, CH_3–pyrazol), 6.55–7.95 ppm (m, 11H, Ar–H + Het–H + CH=), 8.93 ppm (s, 1H, N–OH), for compound **10**, δ 1.17 ppm (s, 3H, CH_3–pyrazol), 3.97 ppm (s, 3H, CH_3–N^+), 6.65–7.97 ppm (m, 15H, Ar–H + Het–H + CH=), for compound **11a**, δ 1.17 ppm (s, 3H, CH_3–pyrazol), 3.95 ppm (s, 3H,



Scheme 4. Compounds (**11a–c**) and (**12a–c**): A = pyridin-4-ium salt (a); A = quinolin-4-ium salt (b); A = isoquinolin-1-ium salt (c).

CH_3-N^+), 6.65–7.97 ppm (m, 14H, Ar–H + Het–H + CH=), for compound **12a**.

The condensed *N*-bridgehead 2-methyl-4-phenylpyrazolo[4,5-*d*] Indolizine (benzoindolizine)-5[2(4)]-aza-monomethine (**6a–d**), ß-substituted-5(2)-aza-trimethine cyanine dyes (**8a–d**), 2-methyl-4-phenylpyrazolo[4,5-d] indolizine-5[4(1)]-aza-dimethine cyanine dye (**12a–c**) are highly coloured compounds. Their colour in ethanol is ranging from brownish-violet to intense reddish-violet. They are soluble in concentrated H_2SO_4 acid liberating iodine vapour on warming. Their ethanolic solutions give permanent colours (brownish-violet/intense violet) in basic media, which reversibly discharged (yellow) on acidification.

4. Visible absorption spectra of the new cyanine dyes in ethanol

The electronic absorption spectra of 2-methyl-4-phenylpyrazolo[4,5-*d*] Indolizinium (benzoindolizine)-5[2(4)]-aza-monomethine (**6a–c**), and/or β-substituted-5(2)-aza-trimethine cyanine dyes (**8a–d**) in 95% ethanol showed absorption bands batho (hypso)-chromically shifted depending upon the nature of heterocyclic A, heterocyclic quaternary residue A′, their linkage position and the substituents R in the ß-substituted-8(2)-tri azamethine cyanine dyes (**8a–d**). Thus, the visible absorption maxim of dye **6a** [A = indolizine, A′ = pyridine-2-ium] showed λ_{max} = 505 (sh), 540 nm. Substitution of [A′ = pyridine-2-ium] in dye **6a** by of [A′ = quinoline-2-ium] in dye **6b** resulted in bathochromic shift of the shorter (longer) wavelength of $\Delta\lambda_{max}$ = 5 (10) nm. This can be attributed to the more extensive π-delocalization within quinoline-2-ium salt, Table 1.

Changing the linkage position of the pyridinium residue from 2-ium in dye **6a** to 4-ium in dye **6c** causes bathochromic shift of absorption band $\Delta\lambda_{max}$ = 10 nm. This is due to the increase in the conjugation of the pyridinium in the 4-ium linkage relative to 2-ium analogue (Fig. 1).

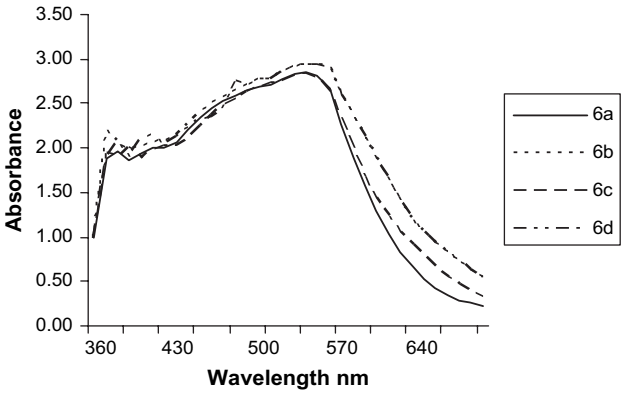


Fig. 1. The visible absorption spectra of compounds (**6a–d**) in EtOH.

The visible absorption maxima of phenylpyrazolo-[4,5-*d*]-indolizine (benzoindolizine)-ß-substituted-5(2)-aza-trimethine cyanine dyes (**8a–d**) are influenced by the substituents R and heterocyclic A (Table 1). Thus, the visible absorption spectra of dye **8a** [A = quinoline-2-ium, R = H] exhibited λ_{max} = 490, 600, 660 (sh) nm. Substitution of [R = H] in dye **8a** by [R = CH_3] in dye **8b** causes hypsochromic shift of the longer wavelength of $\Delta\lambda_{max}$ = 70 nm concomitant with the decreasing number of absorption bands. This is due to the decrease in the charge transfer with the antagonistic effect of CH_3 group. Also, substitution of [R = CH_3] in dye **8b** by [R = $-C_6H_5$] in dye **8c** caused bathochromic shift $\Delta\lambda_{max}$ = 25 nm concomitant with the appearance of two new absorption bands, located at λ_{max} = 600 and 660 nm. This is due to the increase of conjugation via the accepting ability of electron withdrawing phenyl group [17] (Fig. 2).

The electronic absorption spectra of 2-methyl-4-phenylpyrazolo[4,5-*d*] indolizine-5[4(1)]-aza-dimethine cyanine dye (**12a–c**) in 95% ethanol showed absorption bands batho (hypso)-chromically shifted depending upon the nature of heterocyclic quaternary residue A,

Table 1
Visible absorption spectra of mono-(tri)-azamethine (**6a–d**), (**8a–d**) and (**12a–c**) cyanine dyes in ethanol

λ_{max} (nm)/log ε_{max} mol^{-1} cm^{-1}			
*Aza-monomethine cyanine dyes (**6a–d**)*			
6a	**6b**	**6c**	**6d**
505 (3.43)	510 (3.44)	510 (3.44)	515 (3.75)
525 (2.46)	550 (3.47)	530 (3.45)	555 (3.83)
*Aza-trimethine cyanine dyes (**8a–d**)*			
8a	**8b**	**8c**	**8d**
490 (2.28)	530 (3.45)	555 (3.47)	610 (3.41)
600 (2.69)	–	600 (3.40)	675 (2.95)
sh 666 (2.87)	–	sh 660 (2.95)	–
*Aza-dimethine cyanine dyes (**12a–c**)*			
12a	**12b**	**12c**	
500 (3.42)	510 (3.43)	500 (3.41)	
–	560 (3.48)	–	

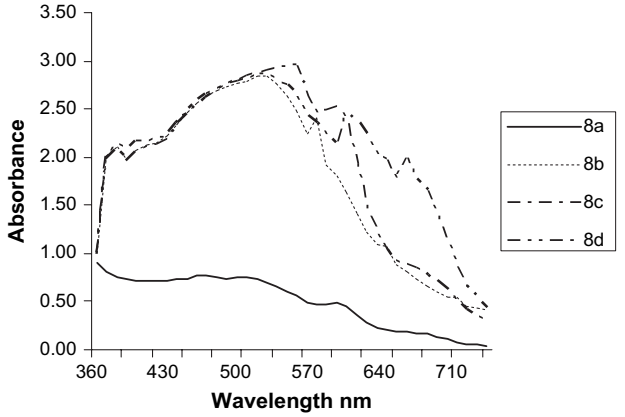


Fig. 2. The visible absorption spectra of compounds (**8a–d**) in EtOH.

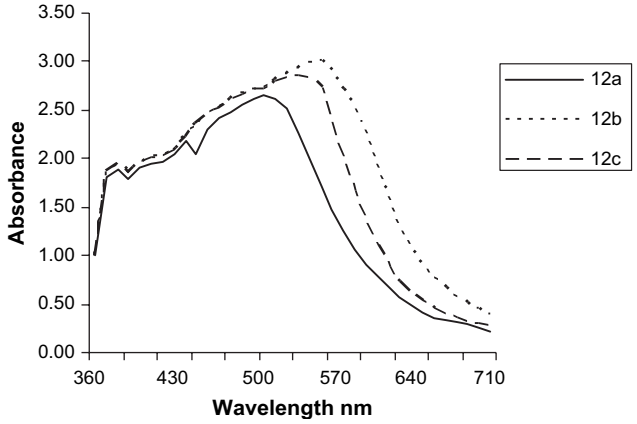


Fig. 3. The visible absorption spectra of compounds (**12a–c**) in EtOH.

their linkage position. Thus, the visible absorption maxima of dye **12a** [A = pyridine-4-ium] showed $\lambda_{max} = 500$ nm. Substitution of [A = pyridine-4-ium methiodide] in dye **12a** by [A = quinoline-4-ium] in dye **12b** resulted in bathochromic shift of $\Delta\lambda_{max} = 10$ nm. This can be attributed to the more extensive π-delocalization within quinoline-4-ium salt.

Changing the linkage position of the quinolinium residue from 1-ium in dye **12c** to 4-ium in dye **12b** causes bathochromic shift of absorption band $\Delta\lambda_{max} = 10$ nm. This is due to the increase in the conjugation of the quinolinium in the 4-ium linkage relative to 1-ium analogue (Fig. 3, Table 1).

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