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The use of oxonium salts in the synthesis of mono-, β-substituted dimethine and styryl cyanine dyes

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Abstract

Pyrazolopyrylium perchlorate salt derivatives were obtained from the reaction of 5-chloro-4-formyl-1-phenyl pyrazole with phenylpyrazolone, [4(2-propenyl)-1,6-ene-2-cyclohexanone] and cyclohexanone give pyrazolopyrylium perchlorate salt derivatives. Reaction of the latter compounds with 2(4)-methyl substituted heterocyclic quaternary salts gave the pyrazolopyrylium 4[2(4)]-monomethine cyanine dyes. Meanwhile, reaction with amide compounds gives an intermediate compounds which when reacted with 2(4)-methyl substituted heterocyclic quaternary salts gave the pyrazolopyrylium 4[2(4)]-β-substituted dimethine. Reaction of the intermediate compounds with various aromatic aldehydes followed by the reaction with 2-methyl quinolinium ethiodide salt give bis styryl cyanine dyes. Elemental analyses, visible absorption, IR, ^{1}H NMR spectroscopy and mass spectra established the structures of these compounds. The relationship between the structure and properties of these dyes is discussed.

Keywords: β-Substituted dimethine; Styryl cyanine; Pyrylium salts; Carvon; Electronic absorption spectra

1. Introduction

There is increasing interest in the synthesis of pyrylium and related heterocycles cyanine dyes because of their wide application such as application as laser dyes for the near-IR region [1,2], for optical recording materials [3–6] and for laser-beam addressed displays with liquid crystal cells doped with IR dyes [7]. They were applied as fluorescent probes for ion detection, improve dyes for solar collectors [8–10]. Also, they are useful as light-sensitive photographic elements [11], laser disc media [12] and optical recording material [13]. These compounds improve the spectral sensitizers and provide photographic materials with good sharpness; good colour and reduce colour stain after development.

This paper reports the synthesis of new tri-heterocyclic and bi-heterocyclic compounds incorporating a pyrylium moiety condensed to different cycles used in the synthesis of monomethine, β-substituted dimethine and bis styryl cyanine dyes. The structure-property relationships of these dyes were studied from their visible absorption spectra.

2. Experimental

Melting points were recorded on a Galenkanp melting point apparatus and are uncorrected. Microanalyses were carried out at the Microanalytical center at Cairo University. Infrared spectra were recorded in potassium bromide on a Perkin–Elmer 127B Infrared spectrophotometer. ^{1}H NMR spectra were recorded in

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deuterated DMSO-d_6 on a Varian Gemini 200 NMR spectrometer using tetramethylsilane as an internal reference. Mass spectra were recorded on HpMs 6988 spectrometer and electron-ionization (EI). Visible spectra (300–700 nm) were recorded on a Shimadzu UV/visible 160-A spectrophotometer at the Aswan-Faculty of Science. All reagents and solvents were obtained from Aldrich Chemical Company (Mil-Waukee, WI, USA). Synthesis of 5-chloro-4-formyl-3-methyl-1-phenyl pyrazole was carried out according to reference [14].

3. Synthesis of 3,5-dimethyl-1,7-diphenyl bispyrazolo [2,3-b;2′,3′-b′]pyrylium salt, 3,8-dimethyl-1-phenyl-5(2-propenyl)-5,7-enylpyrazolo[2,3-b]di(tetra) hydrochromylium perchlorate salts 1a–c

A mixture of 5-chloro-4-formyl-3-methyl-1-phenyl pyrazole (8.860 g, 0.04 mol) and 3-methyl-1-phenyl-pyrazolin-5-one (**a**) (6.96 g, 0.04 mol), 1-methyl-4(2-propenyl)-2-oxo-cyclohex-1,5-diene (**b**) (6.00 g, 0.04 mol), or cyclohexanone (**c**) (3.92 g, 0.04 mol), were dissolved in acetic acid (143 ml for **a**, 123 ml for **b** and 70 ml for **c**) and perchloric acid (12 ml). The reaction mixture was refluxed for 1 h. The precipitated products on cooling were collected, washed with ether, air-dried and recrystallised from ethanol.

(**1a**): Yield 79%; m.p 160–162 °C, Anal. cald for $C_{21}H_{17}N_4O_5Cl$ (440.50): C, 57.21; H, 3.86; N, 12.71. Found: C, 57.10; H, 3.96; N, 12.91. Ms: $m/z=442$. IR (ν^{KBr}, cm^{-1}), at 1650 cm^{-1} (υ pyrylium salts), 1590 cm^{-1} (υ C=C) 1560 cm^{-1} (υ C=N) and 2890 cm^{-1} (υ ylide perchlorate salt). ^{1}H NMR (DMSO-200 MHz) 1.15 ppm (s, 6H, CH_3-pyrazole), 6.45 ppm (s, 1H, CH-pyrylium), 7.10–7.95 ppm (m, 10H, Ar-H).

(**1b**): Yield 77%; m.p °C 230–232, Anal. cald for $C_{21}H_{21}N_2O_5Cl$ (416.50): C, 60.50; H, 5.04; N, 6.72. Found: C, 60.73; H, 5.15; N, 6.57. Ms: $m/z=418$. IR (ν^{KBr}, cm^{-1}), at 1640 cm^{-1} (υ dihydrochromylium salts), 1585 cm^{-1} (υ C=C) 1565 cm^{-1} (υ C=N) and 2875 cm^{-1} (υ ylide perchlorate salt). ^{1}H NMR (DMSO-200 MHz), 1.03 ppm (s, 3H, CH_3–), 1.15 ppm (s, 3H, CH_3-pyrazole), 2.11 ppm (s, 3H, CH_3–), 2.41 ppm (t, 2H, CH_2–), 2.85 ppm (t, 1H, CH–), 3.11 ppm (s, 2H, CH_2=C–), 6.21 ppm (t, 1H, CH=C), 6.45 ppm (s, 1H, CH-pyrylium), 7.13–7.95 ppm (m, 5H, Ar-H).

(**1c**) Yield 68%; m.p °C 215–217, Anal. cald $C_{17}H_{17}N_2O_5Cl$ (364.50): C, 55.96; H, 4.66; N, 7.68. Found: C, 56.15; H, 4.35; N, 7.47. Ms: $m/z=366$. IR (ν^{KBr}, cm^{-1}), at 1640 cm^{-1} (υ tetrahydrochromylium salts), 1585 cm^{-1} (υ C=C) 1565 cm^{-1} (υ C=N) and 2875 cm^{-1} (υ ylide perchlorate salt). ^{1}H NMR (DMSO-200 MHz), 1.15 ppm (s, 3H, CH_3-pyrazole), 2.35 ppm (m, 4H, two CH_2–), 2.75 ppm (t, 2H, CH_2–), 2.85 ppm (t, 2H, CH_2–), 6.45 ppm (s, 1H, CH-pyrylium), 7.11–8.01 ppm (m, 5H, Ar-H).

4. Synthesis of unsymmetrical 3,5-dimethyl-1,7-diphenyl bispyrazolo[2,3-b;2′,3′-b′] pyrylium,-3, 8-dimethyl-3-methyl-1-phenyl-5(2-propenyl)-5,7-enylpyrazolo[2,3-b] di(tetra)hydrochromylium salt mono methine-4[2(4)] cyanine dyes 2a–e

A mixture of compounds **1a–c** (0.01 mol) and 2(4)-methyl quaternary salts ($\alpha(\gamma)$-picoline and/or quinaldine ethiodide) (0.01 mol) were dissolved in ethanol (30 ml) and piperidine (3–5 drops) was added. The reaction mixture was refluxed for 8 h, filtered hot, concentrated and cooled. The precipitated products **2a–e** after dilution with water were collected and crystallized from ethanol.

(**2a**) Yield 73%; m.p °C 180–182, Anal. cald $C_{29}H_{26}N_5O_5Cl$ (559.50): C, 62.20; H, 4.65; N, 12.51. Found: C, 62.35; H, 4.77; N, 12.81. Ms: $m/z=561$. IR (ν^{KBr}, cm^{-1}), at 1650 cm^{-1} (pyrylium salts), 1590 cm^{-1} (υ C=C) 1560 cm^{-1} (υ C=N) and 2890 cm^{-1} (υ ylide perchlorate salt). ^{1}H NMR (DMSO-200 MHz) 1.15 ppm (s, 6H, CH_3-pyrazole), 1.25 ppm (t, 3H, CH_3–), 1.79 ppm (q, 2H, CH_2–), 6.45–7.95 ppm (m, 15H, Ar-H + Het-H + CH=).

(**2b**) Yield 82%; m.p °C 175–177, Anal. cald $C_{33}H_{28}N_5O_5Cl$ (609.50): C, 64.97; H, 4.59; N, 11.49. Found: C, 65.15; H, 4.67; N, 11.59. Ms: $m/z=611$. ^{1}H NMR (DMSO-200 MHz) 1.15 ppm (s, 6H, CH_3-pyrazole), 1.25 ppm (t, 3H, CH_3–), 1.79 ppm (q, 2H, CH_2–), 6.45–7.95 ppm (m, 17H, Ar-H + Het-H + CH=).

(**2c**) Yield 75%; m.p °C 150–152, Anal. cald $C_{29}H_{26}N_5O_5Cl$ (559.50): C, 62.20; H, 4.65; N, 12.51. Found: C, 62.35; H, 4.77; N, 12.81. Ms: $m/z=561$. ^{1}H NMR (DMSO-200 MHz) 1.15 ppm (s, 6H, CH_3-pyrazole), 1.25 ppm (t, 3H, CH_3–), 1.79 ppm (q, 2H, CH_2–), 6.45–7.95 ppm (m, 15H, Ar-H + Het-H + CH=).

(**2d**) Yield 87%; m.p °C 130–132, Anal. cald $C_{33}H_{32}N_3O_5Cl$ (585.50): C, 67.60; H, 5.46; N, 7.17. Found: C, 67.35; H, 5.51; N, 7.37. Ms: $m/z=587$. IR (ν^{KBr}, cm^{-1}), at 1640 cm^{-1} (υ dihydrochromylium salts), 1585 cm^{-1} (υ C=C) 1565 cm^{-1} (υ C=N) and 2875 cm^{-1} (υ ylide perchlorate salt). ^{1}H NMR (DMSO-200 MHz), 1.03 ppm (s, 3H, CH_3–), 1.15 ppm (s, 3H, CH_3-pyrazole), 1.21 ppm (t, 3H, CH_3–), 1.73 ppm (q, 2H, CH_2–), 2.11 ppm (s, 3H, CH_3–), 2.41 ppm (t, 2H, CH_2–), 2.85 ppm (t, 1H, CH–), 3.11 ppm (s, 2H, CH_2=C–), 6.21 ppm (t, 1H, CH=C), 6.65–8.13 ppm (m, 12H, Ar-H + Het-H + CH=).

(**2e**) Yield 76%; m.p °C 190–192, Anal. cald $C_{29}H_{28}N_3O_5Cl$ (535.50): C, 65.22; H, 5.62; N, 7.87. Found: C, 65.05; H, 5.45; N, 7.67. Ms: $m/z=537$. IR (ν^{KBr}, cm^{-1}), at 1640 cm^{-1} (υ tetrahydrochromylium salts), 1585 cm^{-1} (υ C=C) 1565 cm^{-1} (υ C=N) and 2875 cm^{-1} (υ ylide perchlorate salt). ^{1}H NMR (DMSO-200 MHz), 1.15 ppm (s, 3H, CH_3-pyrazole), 1.21 ppm (t, 3H, CH_3–), 1.73 ppm (q, 2H, CH_2–), 2.35 ppm (m, 4H, two

CH_2–), 2.75 ppm (t, 2H, CH_2–), 2.85 ppm (t, 2H, CH_2–), 6.55–8.01 ppm (m, 12H, Ar-H + Het-H + CH=).

5. Synthesis of unsymmetrical 4-formyl (acetyl/benzoyl) bispyrazolo[2,3-b;2′,3′-b′] pyridine,-5 (2-propenyl)-5,7-enylpyrazolo[2,3-b]di(tetra) hydroquinoline derivatives 3a–e

A mixture of compounds **1a–c** (0.01 mol) and formamide, acetamide and/or benzamide (0.01 mol) were fused under reflux for 1 h. The reaction mixture was extracted by ethanol, and then filtered hot; the filtrate was concentrated and cooled, where the products were precipitated after dilution with water. They were collected and crystallized from methanol.

(**3a**): Yield 45%; m.p 230–232 °C, Anal. cald for $C_{22}H_{17}N_5O$ (367): C, 71.93; H, 4.63; N, 19.07. Found: C, 71.77; H, 4.85; N, 18.81. Ms: $m/z = 367$. IR (ν^{KBr}, cm^{-1}), at 1610 cm^{-1} (υ hydroquinoline ring stretching), 820 cm^{-1} (υ 4-substituted incorporated pyridine), 1675 cm^{-1} (υ conjugated C=O). ^{1}H NMR (DMSO-200 MHz), 1.15 ppm (s, 6H, CH_3-pyrazole), 7.10–7.95 ppm (m, 10H, Ar-H), 9.85 ppm (s, 1H, CH=O–).

(**3b**): Yield 49%; m.p 210–212 °C, Anal. cald for $C_{23}H_{19}N_5O$ (381): C, 72.44; H, 4.99; N, 18.37. Found: C, 72.29; H, 5.15; N, 18.57. Ms: $m/z = 382$. ^{1}H NMR (DMSO-200 MHz), 1.15 ppm (s, 6H, CH_3-pyrazole), 2.90 ppm (s, 3H, CH_3–C=O), 7.10–7.95 ppm (m, 10H, Ar-H).

(**3c**): Yield 63%; m.p 160–162 °C, Anal. cald for $C_{28}H_{21}N_5O$ (443): C, 75.85; H, 4.74; N, 15.80. Found: C, 76.05; H, 4.83; N, 15.67. Ms: $m/z = 444$. ^{1}H NMR (DMSO-200 MHz), 1.15 ppm (s, 6H, CH_3-pyrazole), 7.10–7.95 ppm (m, 15H, Ar-H).

(**3d**): Yield 61%; m.p 165–167 °C, Anal. cald for $C_{23}H_{23}N_3O$ (357): C, 77.31; H, 6.44; N, 11.77. Found: C, 77.15; H, 6.63; N, 11.59. Ms: $m/z = 358$. IR (ν^{KBr}, cm^{-1}), at 1595 cm^{-1} (υ hydroquinoline ring stretching), 794 cm^{-1} (υ 4-substituted incorporated pyridine), 1650 cm^{-1} (υ conjugated C=O). ^{1}H NMR (DMSO-200 MHz), 1.03 ppm (s, 3H, CH_3–), 1.15 ppm (s, 3H, CH_3-pyrazole), 2.11 ppm (s, 3H, CH_3–), 2.41 ppm (t, 2H, CH_2–), 2.85 ppm (t, 1H, CH–), 2.95 ppm (s, 3H, CH_3–C=O), 3.11 ppm (s, 2H, CH_2=C–), 6.21 ppm (t, 1H, CH=C), 7.13–7.95 ppm (m, 5H, Ar-H).

(**3e**): Yield 51%; m.p 110–112 °C, Anal. cald for $C_{19}H_{19}N_3O$ (305): C, 74.75; H, 6.23; N, 13.77. Found: C, 74.59; H, 6.43; N, 13.91. Ms: $m/z = 305$. IR (ν^{KBr}, cm^{-1}), at 1595 cm^{-1} (υ hydroquinoline ring stretching), 794 cm^{-1} (υ 4-substituted incorporated pyridine), 1650 cm^{-1} (υ conjugated C=O). ^{1}H NMR (DMSO-200 MHz), 1.15 ppm (s, 3H, CH_3-pyrazole), 2.35 ppm (m, 4H, two CH_2–), 2.75 ppm (t, 2H, CH_2–), 2.85 ppm (t, 2H, CH_2–), 2.95 ppm (s, 3H, CH_3–C=O), 7.11–8.01 ppm (m, 5H, Ar-H).

6. Synthesis of 4[α,β-unsaturated carbonyl] bis pyrazolo[2,3-b;2′,3′-b′]pyridine, 5(2-propenyl)-5, 7-enyl pyrazolo[2,3-b]di(tetra)-hydroquinoline 4a–e

A mixture of compounds **3b, 3d, 3e** (0.01 mol) and aromatic aldehydes (benzaldehyde, p-hydroxybenzaldehyde and p-nitrobenzaldehyde) (0.01 mol) was dissolved in ethanol (30 ml) and piperidine (5 drops) was added. The reaction mixture was refluxed for 5 hrs, filtered hot, and cooled. The products **4a–e** were precipitated after dilution with water, collected and crystallized from ethanol.

(**4a**): Yield 55%; m.p 145–147 °C, Anal. cald for $C_{30}H_{23}N_5O$ (469): C, 76.76; H, 4.90; N, 14.93. Found: C, 76.49; H, 5.13; N, 15.07. Ms: $m/z = 470$. IR (ν^{KBr}, cm^{-1}), at 1675 cm^{-1} (υ conjugated C=O), 1350 cm^{-1} (υ CH=). ^{1}H NMR (DMSO-200 MHz), 1.15 ppm (s, 6H, CH_3-pyrazole), 6.65–7.95 ppm (m, 17H, Ar-H + Het-H + CH=).

(**4b**):Yield 65%; m.p 130–132 °C, Anal. cald for $C_{30}H_{23}N_5O_2$ (485): C, 74.23; H, 4.74; N, 14.43. Found: C, 74.47; H, 4.33; N, 14.17. Ms: $m/z = 486$. ^{1}H NMR (DMSO-200 MHz), 1.19 ppm (s, 6H, CH_3-pyrazole), 6.55–7.95 ppm (m, 17H, Ar-H + Het-H + CH=), 9.25 ppm (s, 1H, OH).

(**4c**): Yield 52%; m.p 160–162 °C, Anal. cald for $C_{30}H_{22}N_6O_3$ (514): C, 70.04; H, 4.28; N, 16.34. Found: C, 69.89; H, 4.45; N, 16.23. Ms: $m/z = 515$. ^{1}H NMR (DMSO-200 MHz), 1.15 ppm (s, 6H, CH_3-pyrazole), 6.65–7.95 ppm (m, 16H, Ar-H + Het-H + CH=).

(**4d**): Yield 68%; m.p 170–172 °C, Anal. cald for $C_{30}H_{27}N_3O_2$ (461): C, 78.09; H, 5.86; N, 9.11. Found: C, 77.85; H, 6.03; N, 9.39. Ms: $m/z = 462$. IR (ν^{KBr}, cm^{-1}), at 1650 cm^{-1} (υ conjugated C=O), 1380 cm^{-1} (υ CH=). ^{1}H NMR (DMSO-200 MHz), 1.03 ppm (s, 3H, CH_3–), 1.15 ppm (s, 3H, CH_3-pyrazole), 2.11 ppm (s, 3H, CH_3–), 2.41 ppm (t, 2H, CH_2–), 2.85 ppm (t, 1H, CH–), 3.11 ppm (s, 2H, CH_2=C–), 6.21 ppm (t, 1H, CH=C), 6.65–7.95 ppm (m, 11H, Ar-H + CH=CH), 9.15 ppm (s, 1H, OH).

(**4e**): Yield 66%; m.p 155–157 °C, Anal. cald for $C_{26}H_{23}N_3O_2$ (409): C, 76.28; H, 5.62; N, 10.27. Found: C, 76.55; H, 5.43; N, 9.97. Ms: $m/z = 409$. IR (ν^{KBr} cm^{-1}), at 1650 cm^{-1} (υ conjugated C=O), 1380 cm^{-1} (υ CH=). ^{1}H NMR (DMSO-200 MHz), 1.15 ppm (s, 3H, CH_3-pyrazole), 2.35 ppm (m, 4H, two CH_2–), 2.75 ppm (t, 2H, CH_2–), 2.85 ppm (t, 2H, CH_2–), 6.55–8.01 ppm (m, 11H, Ar-H + CH=CH), 9.17 ppm (s, 1H, OH).

7. Synthesis of unsymmetrical bis pyrazolo[2,3-b;2′, 3′-b′]pyridine; 5(2-propenyl)-5,7-enylpyrazolo [2,3-b]di(tetra) hydroquinoline-4-[2(4)]-β-substituted dimethine cyanine dyes 5a–g

A mixture of compounds **3a–e** (0.01 mol) and 2(4)-methyl quaternary salts (α(γ)-picoline and quinaldine)

ethiodide (0.01 mol) were dissolved in ethanol (30 ml) and piperidine (3–5 drops) was added. The reaction mixture was refluxed for 10 hrs; filtered hot, concentrated and cooled. The products **5a–g** were precipitated on dilution with water and crystallized from ethanol.

(**5a**): Yield 69%; m.p 195–197 °C, Anal. cald for $C_{34}H_{29}N_6I$ (648): C, 62.96; H, 4.48; N, 12.96. Found: C, 63.23; H, 4.15; N, 13.11. Ms: $m/z=649$. IR (ν^{KBr}, cm^{-1}), at 1610 cm^{-1} (υ hydroquinoline ring stretching), 820 cm^{-1} (υ 4-substituted pyridine), 2960 cm^{-1} (υ ethyl iodide). ^1H NMR (DMSO-200 MHz), 1.15 ppm (s, 6H, CH_3-pyrazole), 1.27 ppm (t, 3H, CH_3–), 3.95 ppm (q, 2H, CH_2–), 6.50–8.05 ppm (m, 18H, Ar-H + Het-H + CH=CH).

(**5b**): Yield 83%; m.p 200–202 °C, Anal. cald for $C_{35}H_{31}N_6I$ (662): C, 63.44; H, 4.68; N, 12.69. Found: C, 63.29; H, 4.25; N, 12.37. Ms: $m/z=662$. ^1H NMR (DMSO-200 MHz), 1.15 ppm (s, 6H, CH_3-pyrazole), 1.23 ppm (t, 3H, CH_3–), 1.76 ppm (s, 3H, CH_3–), 3.97 ppm (q, 2H, CH_2–), 6.55–7.97 ppm (m, 17H, Ar-H + Het-H + CH=CH).

(**5c**): Yield 83%; m.p 200–202 °C, Anal. cald for $C_{40}H_{33}N_6I$ (724): C, 66.30; H, 4.56; N, 11.60. Found: C, 63.51; H, 4.75; N, 11.87. Ms: $m/z=725$. ^1H NMR (DMSO-200 MHz), 1.15 ppm (s, 6H, CH_3-pyrazole), 1.23 ppm (t, 3H, CH_3–), 3.97 ppm (q, 2H, CH_2–), 6.65–7.97 ppm (m, 22H, Ar-H + Het-H + CH=CH).

(**5d**): Yield 74%; m.p 235–237 °C, Anal. cald for $C_{31}H_{33}N_4I$ (588): C, 63.27; H, 5.61; N, 9.52. Found: C, 63.39; H, 5.43; N, 9.17. Ms: $m/z=589$. IR (ν^{KBr}, cm^{-1}), at 1595 cm^{-1} (υ hydroquinoline ring stretching), 794 cm^{-1} (υ 4-substituted pyridine), 2975 cm^{-1} (υ ethyl iodide). ^1H NMR (DMSO-200 MHz), 1.03 ppm (s, 3H, CH_3–), 1.15 ppm (s, 3H, CH_3-pyrazole), 1.95 ppm (s, 6H, CH_3–), 2.41 ppm (t, 2H, CH_2–), 2.85 ppm (t, 1H, CH–), 1.25 ppm (t, 3H, CH_3–), 4.07 ppm (q, 2H, CH_2–), 3.11 ppm (s, 2H, CH_2=C–), 6.21 ppm (t, 1H, CH=C), 6.55–7.95 ppm (m, 10H, Ar-H + Het-H + CH=C–CH_3).

(**5e**): Yield 87%; m.p 185–187 °C, Anal. cald for $C_{35}H_{35}N_4I$ (638): C, 65.83; H, 5.49; N, 8.78. Found: C, 66.05; H, 5.33; N, 8.69. Ms: $m/z=639$. ^1H NMR (DMSO-200 MHz), 1.03 ppm (s, 3H, CH_3–), 1.15 ppm (s, 3H, CH_3-pyrazole), 1.95 ppm (s, 6H, CH_3–), 2.41 ppm (t, 2H, CH_2–), 2.85 ppm (t, 1H, CH–), 1.25 ppm (t, 3H, CH_3–), 4.07 ppm (q, 2H, CH_2–), 3.11 ppm (s, 2H, CH_2=C–), 6.21 ppm (t, 1H, CH=C), 6.55–7.95 ppm (m, 12H, Ar-H + Het-H + CH=).

(**5f**): Yield 77%; m.p 190–192 °C, Anal. cald for $C_{31}H_{33}N_4I$ (588): C, 63.27; H, 5.61; N, 9.52. Found: C, 63.49; H, 5.39; N, 9.25. Ms: $m/z=589$. ^1H NMR (DMSO-200 MHz), 1.03 ppm (s, 3H, CH_3–), 1.17 ppm (s, 3H, CH_3-pyrazole), 1.90 ppm (s, 6H, CH_3–), 2.45 ppm (t, 2H, CH_2–), 2.85 ppm (t, 1H, CH–), 1.25 ppm (t, 3H, CH_3–), 4.07 ppm (q, 2H, CH_2–), 3.15 ppm (s, 2H, CH_2=C–), 6.21 ppm (t, 1H, CH=C), 6.55–7.95 ppm (m, 10H, Ar-H + Het-H + CH=C–CH_3).

(**5g**): Yield 82%; m.p 150–152 °C, Anal. cald for $C_{31}H_{31}N_4I$ (586): C, 63.48; H, 5.29; N, 9.56. Found: C, 63.67; H, 5.43; N, 9.71. Ms: $m/z=587$. IR (ν^{KBr}, cm^{-1}), at 1595 cm^{-1} (υ hydroquinoline ring stretching), 794 cm^{-1} (υ 4-substituted pyridine), 2975 cm^{-1} (υ ethyl iodide). ^1H NMR (DMSO-200 MHz), 1.15 ppm (s, 3H, CH_3-pyrazole), 2.35 ppm (m, 4H, two CH_2–), 2.75 ppm (t, 2H, CH_2–), 2.85 ppm (t, 2H, CH_2–), 1.25 ppm (t, 3H, CH_3–), 4.07 ppm (q, 2H, CH_2–), 1.75 ppm (s, 3H, CH_3–), 6.65–8.01 ppm (m, 12H, Ar-H Het-H + CH=).

8. Synthesis of unsymmetrical bispyrazolo[2,3-b; 2′,3′-b′]pyridine-5(2-propenyl)-5,7-enylpyrazolo [2,3-b]di(tetra) hydroquinoline bis styryl-4(2)cyanine dyes 6a–e

A mixture of compounds **4a–e** (0.01 mol) and 2-methyl quinoline ethiodide (0.01 mol) were dissolved in ethanol (30 ml) and piperidine (3–5 drops) was added. The reaction mixture was refluxed for 8 hrs, filtered hot, concentrated and cooled. The products **6a–e** was precipitate by dilution with water, and recrystalized from ethanol.

(**6a**): Yield 60%; m.p 195–197 °C, Anal. cald for $C_{42}H_{35}N_6I$ (750): C, 67.20; H, 4.67; N, 11.20. Found: C, 67.49; H, 4.53; N, 11.37. Ms: $m/z=751$. IR (ν^{KBr}, cm^{-1}), 1350 cm^{-1} (υ CH=), 2965 cm^{-1} (υ ethyl iodide). ^1H NMR (DMSO-200 MHz), 1.15 ppm (s, 6H, CH_3-pyrazole), 1.21 ppm (t, 3H, CH_3–), 3.98 ppm (q, 2H, CH_2–), 6.65–7.95 ppm (m, 24H, Ar-H + Het-H + CH=).

(**6b**): Yield 68%; m.p 200–202 °C, Anal. cald for $C_{42}H_{35}N_6OI$ (766): C, 65.80; H, 4.57; N, 10.97. Found: C, 65.47; H, 4.33; N, 11.17. Ms: $m/z=767$. ^1H NMR (DMSO-200 MHz), 1.15 ppm (s, 6H, CH_3-pyrazole), 1.21 ppm (t, 3H, CH_3–), 3.98 ppm (q, 2H, CH_2–), 6.65–7.95 ppm (m, 24H, Ar-H + Het-H + CH=), 9.15 ppm (s, 1H, OH).

(**6c**): Yield 52%; m.p 160–162 °C, Anal. cald for $C_{42}H_{34}N_7O_2I$ (795): C, 63.70; H, 4.28; N, 12.33. Found: C, 63.99; H, 4.13; N, 12.23. Ms: $m/z=796$. ^1H NMR (DMSO-200 MHz), 1.15 ppm (s, 6H, CH_3-pyrazole), 1.23 ppm (t, 3H, CH_3–), 3.95 ppm (q, 2H, CH_2–), 6.65–7.95 ppm (m, 23H, Ar-H + Het-H + CH=).

(**6d**): Yield 73%; m.p 215–217 °C, Anal. cald for $C_{42}H_{39}N_4OI$ (742): C, 67.93; H, 5.26; N, 7.55. Found: C, 68.15; H, 5.09; N, 7.31. Ms: $m/z=743$. IR (ν^{KBr}, cm^{-1}), at 2950 cm^{-1} (υ ethyl iodide), 1380 cm^{-1} (υ CH=). ^1H NMR (DMSO-200 MHz), 1.03 ppm (s, 3H, CH_3–), 1.15 ppm (s, 3H, CH_3-pyrazole), 2.11 ppm (s, 3H, CH_3–), 2.41 ppm (t, 2H, CH_2–), 1.23 ppm (t, 3H, CH_3–), 3.95 ppm (q, 2H, CH_2–), 2.85 ppm (t, 1H, CH–), 3.11 ppm (s, 2H, CH_2=C–), 6.21 ppm (t, 1H, CH=C), 6.65–7.95 ppm (m, 18H, Ar-H + CH=CH), 9.15 ppm (s, 1H, OH).

(**6e**): Yield 72%; m.p 220–222 °C, Anal. cald for $C_{38}H_{35}N_4OI$ (690): C, 66.09; H, 5.07; N, 8.12. Found: C, 66.33; H, 5.23; N, 8.27. Ms: $m/z=691$. IR (υ^{KBr}, cm^{-1}), at 2975 cm^{-1} (υ ethyl iodide), 1380 cm^{-1} (υ CH=). ^1H NMR (DMSO-200 MHz), 1.15 ppm (s, 3H, CH_3-pyrazole), 1.23 ppm (t, 3H, CH_3–), 3.95 ppm (q, 2H, CH_2–), 2.35 ppm (m, 4H, two CH_2–), 2.75 ppm (t, 2H, CH_2–), 2.85 ppm (t, 2H, CH_2–), 6.55–8.01 ppm (m, 18H, Ar-H+CH=CH), 9.17 ppm (s, 1H, OH).

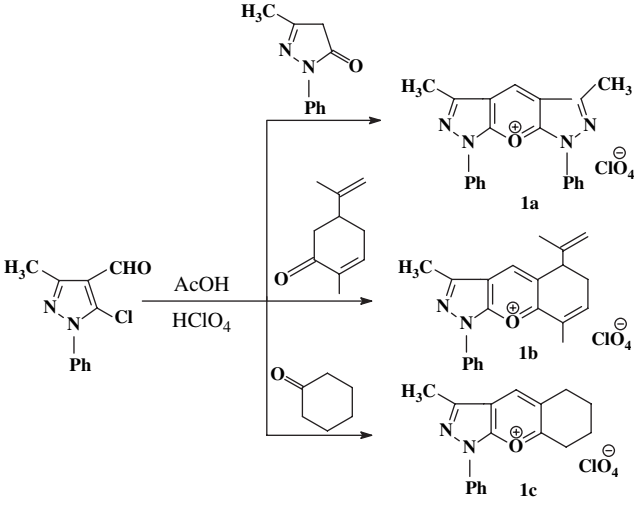
9. Results and discussion

9.1. Synthesis

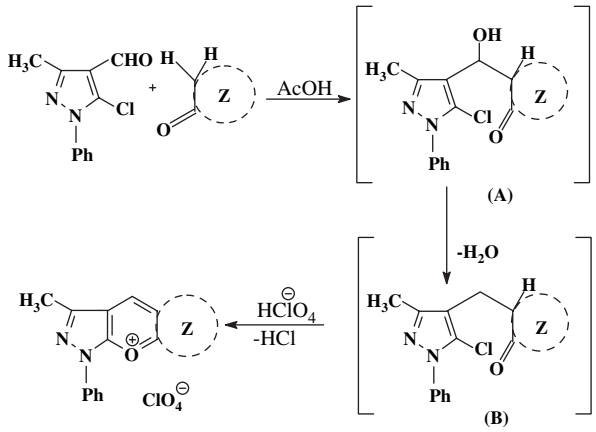
The newly synthesized bi- and tri-heterocyclic condensed salts **1a–c** were prepared via reaction of 5-chloro-4-formyl-3-methyl-1-phenylpyrazoline [14] and equimolar quantity of cyclic α-active methylene compounds in a glacial acetic and perchloric acids mixture (Scheme 1) [15,16].

The formation of heterocyclic derivatives **1a–c** is suggested to proceed through the nucleophilic addition/elimination reaction of the active methylene compounds to a carboxaldehyde group to give intermediates A, B. The latter intermediate B undergoes ring closer in the presence of acid mixture medium to form the hetero bi (tri) cyclic pyrylium salts. The mechanistic pathway is represented in Scheme 2.

The structure of compounds **1a–c** was established by elemental analysis, IR and ^1H NMR. Thus IR, spectra of compounds **1a–c** showed, in addition to the absence of absorption band at 1715–1730 cm^{-1} (υ acyclic C=O), the appearance of skeleton vibrations of pyrylium and/or di (tetra) hydrochromylium salts



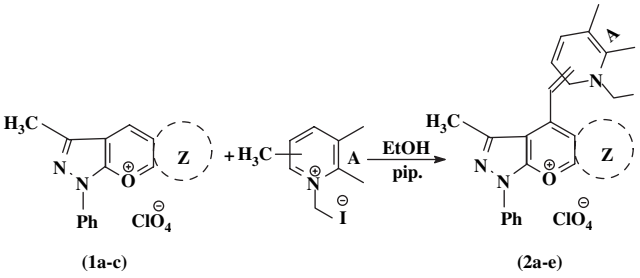
Scheme 1.



Scheme 2.

moieties at 1650–1640 cm^{-1}, at 1590 cm^{-1} (υ C=C) 1560–1800 cm^{-1} (υ C=N) and well defined absorption band at 2890 cm^{-1} (υ ylide per chlorate salt). ^1H NMR spectra of compounds **1a**, taken as an example, 1.15 ppm (s, 6H, CH_3-pyrazole), 6.45ppm (s, 1H, CH-pyrylium), 7.10–7.95 ppm (m, 10H, Ar-H).

The reaction of equimolar amounts of **1a–c** and 2(4)-methyl substituted heterocyclic quaternary salts such as 2(4)-methyl pyridine (quinoline)-2(4)-ium ethiodide salts in the presence of a basic catalyst afforded the corresponding monomethine cyanine dyes **2a–e**, Scheme 3.



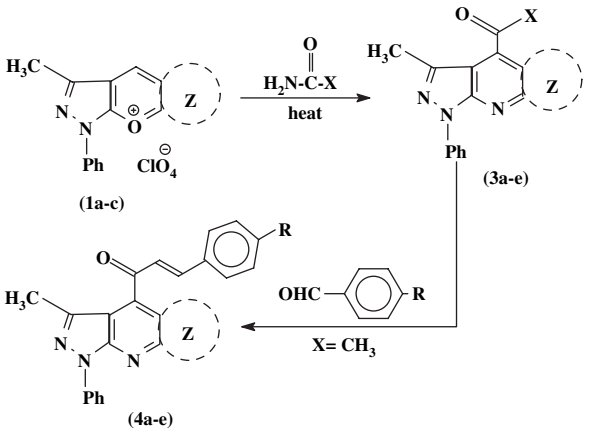
Scheme 3.

(2a–e):
Z = 3-methyl-1-phenylpyrazolo.
A = 1-ethyl pyridine-2-ium **(a)**
Z = 3-methyl-1-phenylpyrazolo.
A = 1-ethylquinoline-2-ium **(b)**
Z = 3-methyl-1-phenylpyrazolo.
A = 1-ethyl pyridine-4-ium **(c)**
Z = 1-methyl-4(2-propenyl)cyclohexen-1,5-diene.
A = 1-ethylquinoline-2-ium **(d)**
Z = cyclohexene.
A = 1-ethylquinoline-2-ium **(e)**

The structure of the compounds **2a–e** was confirmed by elemental analysis, IR and ^1H NMR spectral data.

Thus, IR (ν^{KBr}, cm^{-1}) spectrum of compound **2c**, taken as an example reveals absorption bands, at 1650 cm^{-1} (pyrylium salts), 1590 cm^{-1} (υ C=C) 1560 cm^{-1} (υ C=N) and 2890 cm^{-1} (υ ylide perchlorate salt). ^1H NMR (DMSO-200 MHz) spectra of compounds **2c** showed signals 1.15 ppm (s, 6H, CH_3-pyrazole), 1.25 ppm (t, 3H, CH_3–), 1.79 ppm (q, 2H, CH_2–), 6.45–7.95 ppm (m, 15H, Ar-H + Het-H + CH=).

The reaction of equimolar amounts of compounds **1a–c** and formamide, acetamide and/or benzamide under heating and basic condition afforded the corresponding 4-formyl (acetyl, benzoyl) bis pyrazolo[2,3-b; 2′,3′-b′]pyridine, pyrazolo[2,3-b]di (tetra) hydroquinoline derivatives **3a–e**. The intermediate compounds **3b** and **3e** were selected for condensation reactions with different aromatic aldehydes under piperidine catalysis to produce the corresponding 4[α,β-unsaturated carbonyl] derivatives **4a–e**, Scheme 4.



Scheme 4.

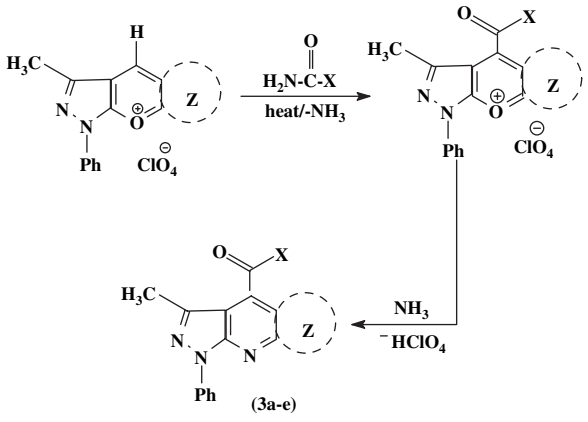
(3a–e):
Z = 3-methyl-1-phenylpyrazolo,
X = H **(a)**
Z = 3-methyl-1-phenylpyrazolo,
X = CH_3 **(b)**
Z = 3-methyl-1-phenylpyrazolo,
X = Ph **(c)**
Z = 1-methyl-4(2-propenyl)cyclohexen-1,5-diene,
X = CH_3 **(d)**
Z = cyclohexene,
X = CH_3 **(e)**

(4a–e):
A = 3-methyl-1-phenylpyrazolo,
R = H **(a)**
A = 3-methyl-1-phenylpyrazolo,
R = OH **(b)**
A = 3-methyl-1-phenylpyrazolo,
R = NO_2 **(c)**
A = 1-methyl-4(2-propenyl)cyclohexen-1,5-diene,
R = OH **(d)**
A = cyclohexene,
R = OH **(e)**

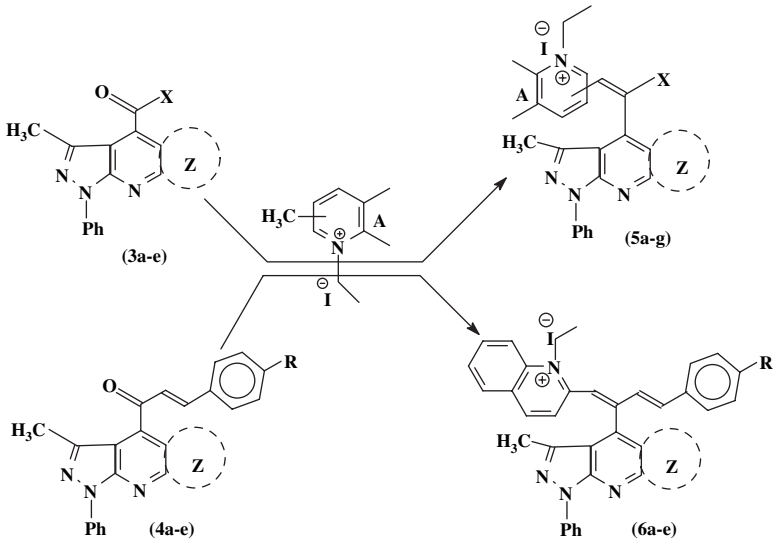
The conversion of pyrylium moiety in pyridine (quinoline) system is depicted in Scheme 5. The intial acylic substitution determines the evolution of ammonia [15]. The nucleophile attacks the pyrylium salt with formation of a like Meisenheimer intermediate, which open and closes to pyridine ring by elimination of a water molecule [17].

The structure of compounds **3a–e** and **4a–e** was confirmed by elemental analysis, IR and ^1H NMR spectral data. Thus, IR(ν^{KBr}, cm^{-1}) spectra of compound **3b** and **4a** taken as example, showed the hydroquinoline skeleton vibration at 1610–1595 cm^{-1} (υ ring stretching), 820–794 cm^{-1} (υ 4-substituted pyridine), and the disappearance of absorption bands of pyrylium, di(tetra)hydrochromylium salts skeleton vibrations at (υ 1650–1640) cm^{-1}, 1675 cm^{-1} (υ conjugated C=O). ^1H NMR ($CDCl_3$) spectra of compounds **3b** and **4a** showed 1.15 ppm (s, 6H, CH_3-pyrazole), 2.90 ppm (s, 3H, CH_3–C=O), 7.10–7.95 ppm (m, 10H, Ar-H) for compound **3b** and 1.15 ppm (s, 6H, CH_3-pyrazole), 6.65–7.95 ppm (m, 17H, Ar-H + Het-H + CH=) for compound **4a**.

The reaction of equimolar amounts of the both key intermediate compounds **3a–e** and **4a–e** with 2(4)-methyl substituted heterocyclic quaternary salts [α(γ)-picoline and quinaldine] ethiodide in presence of basic catalyst gave the corresponding 4[2(4)]-β-substituted dimethine **5a–g** and 4(2)-bis styryl cyanine dyes **6a–e** respectively Scheme 6.



Scheme 5.



Scheme 6.

(5a–g):
Z = 3-methyl-1-phenylpyrazolo,
X = H, A = 1-ethylquinolin-2-ium **(a)**
Z = 3-methyl-1-phenylpyrazolo,
X = CH_3, A = 1-ethylquinolin-2-ium **(b)**
Z = 3-methyl-1-phenylpyrazolo,
X = Ph, A = 1-ethylquinolin-2-ium **(c)**
Z = 1-methyl-4(2-propenyl)cyclohexen-1,5-diene,
X = CH_3, A = 1-ethylpyridin-2-ium **(d)**
Z = 1-methyl-4(2-propenyl)cyclohexen-1,5-diene,
X = CH_3, A = 1-ethylquinolin-2-ium **(e)**
Z = 1-methyl-4(2-propenyl)cyclohexen-1,5-diene,
X = CH_3, A = 1-ethylpyridin-4-ium **(f)**
Z = 5-cyclohexene,
X = CH_3, A = 1-ethylquinolin-2-ium **(g)**

(6a–e):
Z = 3-methyl-1-phenylpyrazolo,
R = H; **(a)**
Z = 3-methyl-1-phenylpyrazolo,
R = OH **(b)**
Z = 3-methyl-1-phenylpyrazolo,
R = NO_2 **(c)**
Z = 1-methyl-4(2-propenyl)cyclohexen-1,5-diene,
R = OH **(d)**
Z = cyclohexene,
R = OH **(e)**

The structure of compounds (**5a–g**) and (**6a–e**) was confirmed by elemental analysis; IR and ^{1}H NMR spectral data. Thus, of compounds **5c** and **6a**, taken as example, showed well defined absorption bands, at 2960 cm^{-1} (υ ethyl iodide), 1610 cm^{-1} (υ hydroquinoline ring stretching), 820 cm^{-1} (υ 4-substituted pyridine) and disappearance of the absorption band at 1675 cm^{-1} (υ cyclic C=O). ^{1}H NMR (DMSO-200 MHz), of compounds **5c** and **6a** showed signals at δ 1.15 ppm (s, 6H, CH_3-pyrazole), 1.23 ppm (t, 3H, CH_3–), 3.97 ppm (q, 2H, CH_2–), 6.65–7.97 ppm (m, 22H, Ar-H + Het-H + CH=CH) for compound **5c** and at δ 1.15 ppm (s, 6H, CH_3-pyrazole), 1.21 ppm (t, 3H, CH_3–), 3.98 ppm (q, 2H, CH_2–), 6.65–7.95 ppm (m, 24H, Ar-H + Het-H + CH=) for compound **6a**.

9.2. Electronic absorption spectra in ethanol

The new synthesized cyanine compound are highly coloured ranging from brownish-violet to intense violet. They are soluble (partially) in polar (non-polar) solvents with pale (strong) green-yellow fluorescence. They are soluble in concentrated H_2SO_4 with liberating of iodine vapour on warming. They show reversible alochromic appearing violet and colourless in basic and acidic media respectively.

The electronic absorption spectra of monomethine cyanine dyes **2a–e** in 95% ethanol showed absorption bands, whose intensities and locations in the visible region depend mainly upon the nature of both N-ethyl heterocyclic ring A and tri-heterocyclic or/bi-heterocyclic rigid moieties Z (Table 1). Thus, the absorption spectra of **2a**, Z = 3-methyl-1-phenylpyrazole, A = pyridine-2-ium showed absorption bands located at λ_{max} 410, 510 nm. Substituting A = pyridine-2-ium in compound **2a** by A = quinoline-2-ium in compound **2b** causes strong bathochromic shift 20–60 nm accompanied with appearance of two new absorption bands located at λ_{max} 600 and 670 nm respectively. This is attributable to the more extensive π-electron delocalization within benzo conjugation condensed to pyridine nuclei.

Changing the linkage position from pyridine-2-ium in compound **2a** to pyridine-4-ium in compound **2c** resulted in a bathochromic shift 10–15 nm. This is

Table 1
Electronic absorption spectra of monomethine (**2a–e**), β-substituted dimethine (**5a–g**) and bis styryl (**6a–e**) cyanine dyes

λ_{max} (nm)/log ϵ_{max} mol^{-1} cm^{-1}						
Monomethine cyanine dyes **(2a–e)**						
2a	**2b**	**2c**	**2d**	**2e**		
410 (3.94)	470 (3.92)	420 (3.00)	420 (3.98)	410 (3.86)		
510 (3.68)	530 (3.94)	525 (3.93)	520 (3.72)	520 (3.69)		
–	–	–	565 (3.85)	560 (4.55)		
–	600 (3.78)	–	–	605 (3.76)		
–	670 (3.59)	–	665 (3.82)	657 (3.71)		
β-Substituted dimethine cyanine dyes **(5a–g)**						
5a	**5b**	**5c**	**5d**	**5e**	**5f**	**5g**
380 (3.68)	380 (4.59)	390 (4.69)	–	375 (4.57)	380 (4.65)	370 (4.67)
500 (4.70)	515 (4.91)	515 (4.97)	515 (4.71)	520 (4.89)	–	515 (4.91)
–	600 (4.78)	–	–	602 (4.82)	–	600 (4.81)
–	665 (4.10)	660 (4.12)	–	655 (3.79)	–	650 (3.91)
Bis styryl cyanine dyes **(6a-e)**						
6a	**6b**	**6c**	**6d**	**6e**		
410 (4.13)	415 (4.45)	–	420 (4.05)	–		
–	–	–	465 (4.97)	460 (4.87)		
510 (4.95)	535 (4.97)	500 (4.89)	520 (4.82)	518 (4.78)		
–	–	–	560 (4.77)	555 (4.65)		
–	–	–	605 (3.63)	600 (3.51)		
660 (3.31)	680 (3.80)	650 (4.08)	655 (3.47)	650 (3.42)		

due to the increase of conjugation of the pyridine moiety at 4-linkage position rather than 2-linkage analogous.

On comparing the electronic absorption spectra of 4[2(4)]-monomethine cyanine dyes **2b**, **2d**, **2e** incorporating bis pyrazolo[2,3-b;2′,3′-b′]pyrylium and/or pyrazolo di(tetra) hydrochromylium perchlorate salts moities, it was obvious that pyrazolo[2,3-b,2′,3′-b′]di (tetra) hydrochromylium perchlorate 4[2(4)]-monomethine cyanine dyes **2d**, **2e** have absorption bands hypsochromiclly shifted than those of bispyrazolo[2,3-b;2′,3′-b′]pyrylium monomethine analogous **2b**.

The electronic absorption spectra of β-substitued dimethine cyanine dyes (**5a–g**) in 95% ethanol resulted in a batho (hypso) chromic shifted depending on the nature of the heterocyclic quaternary residue A, the substituents R or X as well as the heterocyclic (alicyclyl) residue Z (Table 1). Thus, the absorption spectra of **5d** (A = pyridin-2-ium) showed absorption bands located at λ_{max} 515 nm. Substituting A of pyridine-2-ium in compound **5d** by quinoline-2-ium in compound **5e** causes a bathochromic shift by 5 nm accompanied by the appearance of three new absorption bands at λ_{max} 375, 602 and 655 nm, respectively. This due to more extensive π-delocalization within the benzo conjugation attached to pyridine nuclei.

In addition, substituting of X = H in compound **5a** (λ_{max} 380, 500 nm) by R = CH_3 in compound **5b** resulted in a bathochromic shift of 10–15 nm accompanied with the appearance of two new absorption bands at λ_{max} 600 and 665 nm. This is due to the presence of the methyl group due to hyperconjugative effect causes an easier charge transfer from this group as an electron source towards positive nitrogen of the quaternary salt.

Substituting Z = 3-methyl-1-phenylpyrazole in compound **5b** by Z = 1-methyl-4(2-propenyl) cyclohexene-1,5-diene in compound **5e** resulted in slight hypsochromic shift. This is due to the additional strength of the rigidized moieties in conjunction with pyridine nuclei. They act mainly as perturbing influences on the chromogen itself.

The electronic absorption spectra of unsymmetrical 4(2)-bis styryl cyanine dyes **(6a–e)** in 95% ethanol showed absorption bands in the visible region (350–700 nm) which undergoes batho (hypso) chromic shifts depending on the extent of conjugation of aryl substituents (R) and the heterocycle (alicyclyle) moieties Z (Table 1). Thus, the absorption spectra of compound **6a**, Z = 3-methyl-1-phenyl pyrazolo, R = H showed absorption bands at λ_{max} 410, 510, 660 nm. Substituting R = H in compound **6a** by R = p–OH in compound **6b** causes a bathochromic shift by 5–25 nm. This is due to increasing the conjugation through the releasing character of hydroxyl group.

10. Conclusion

It has been shown the synthesis of new tri-heterocyclic and bi-heterocyclic compounds incorporating a pyrylium moiety condensed to different cycles used in the synthesis of monomethine, β-substituted dimethine and bis styryl cyanine dyes. The structure-property

relationships of these dyes were studied from their visible absorption spectra. This observation show that the synthesized cyanine dyes were influenced by N-ethyl heterocyclic ring A and tri-heterocyclic or/bi-heterocyclic rigid moieties Z, in all synthesized compounds.

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