

Synthesis and Photophysical Properties of Novel Highly Stable Zero/Bis-Zero Methine Cyanine Dyes Based on N-Bridgehead Heterocycles

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Abstract

Cyanine dyes of zero/bis-zero methine incorporating imidazo(1,2-a)Pyridine (quinoline) or pyrazino(1,2-a)pyridine (quinoline) with stable C-N bond were synthesized using keto-oxime methylene C-link heterocyclic quaternary salts [1-phenyl-3-methyl-pyrazolino-4-keto-oxime- α -methylene-bis-pyridin-(quinoin)-1(4)-di-ium-iodide(ethiodide) salts and 1-phenyl-3-methyl-pyrazolino-4-ketooxime- α -methylene-N-2-methyl-bis pyridin (quinoin)-1(4)-di-ium-iodide(ethiodide) salts]. Such heterocyclic precursors and related dyes were identified by elemental and spectral analyses. The absorption spectra properties of such dyes were investigated in 95% Ethanol to attempt and throw some light on the influence of such new heterocyclic nuclei and to compare or evaluate spectral behaviors. The absorption spectra of dyes in different pure solvents were examined in the visible region showing solvatochromism and the colour changes of dyes with solvents having different polarities. This permits a selection of the optimal solvent (fractional solvent) when such dyes are applied as photosensitizers. The spectral behavior of some selected newly synthesized cyanine dyes is observed in mixed solvents of different polarities and progressively increasing quantities of one solvent over the other were studied and showed an increase in the absorbance of CT band with increasing proportion of that solvent. Evidence for hydrogen bond formation between the solute molecules and solvent molecules allows measurement of certain energies such as hydrogen bonding, orientation, and free energies.

Keywords

N-Bridgehead Heterocycles, Cyanine Dyes, Zero/Bis-Zero Methine,

1. Introduction

Special attention is given to the implementation, preparations, and applications of heterocyclic cyanine dyes to show the various aspects in order to satisfy the great demand in industrial, physiology, biochemistry and various biological fields. Cyanine dyes are colorant compounds used in staining of internal limiting membrane (ILM) [1] [2] [3], as fluorescent dyes in DNA detection [4] [5] [6] [7], optical sensors [8] [9], organic photoconductors [10], vulcanizing accelerator agents, photographic sensitizers [11], solar cell [12]. This multi-property and numerous applications of cyanine dyes push the scientist to design and improve synthetic procedure of new cyanine dyes based on N-bridgehead heterocycles [13] [14], which are characterized by outstanding chemical stability, absorb at long wavelength [15] [16], high solubility and change their optical, thermal or electronic properties to meet the requirements for opto-electronic or biological products.

N-Bridgehead heterocyclic cyanine dyes are an important class of dyes which are characterized by the presence of nitrogen atom inside the ring. N-bridge head heterocyclic compounds used as precursors possess high site reactivity susceptible to be attacked by either Electrophile/Nucleophile in the substitution/addition reactions which give high stability nature for the dyes [17]. These dyes have many vital general applications back to their higher stability which can be used as bioactive compounds such as the N-methyl-D aspartate antagonists [18]. Furthermore, N-Bridgehead heterocyclic cyanine dyes have a wide range of potential applications in fluorescent compounds, DNA-binding dyes [19] and organic materials [20]. According to their bioactivity and structural planarity, it is a reasonable idea to develop functional dyes based on these N-Bridgehead heterocycles. A variety of cyanine dyes incorporating different N-bridgehead heterocyclic moieties have been reported [21] [22] [23] [24].

In this paper, we designed and synthesized novel highly stable cyanine dyes. Keto-oxime methylene C-link heterocyclic quaternary salts were used in the synthesis of N-bridge head heterocyclic incorporating imidazolo(1,2-a)pyridine(quinoline) or pyrazino(1,2-a)pyridine(quinoline) as main entities for zero and bis-zero methine cyanine dyes synthesis. The spectral, solvatochromic behavior and mixed solvent effect are described.

2. Experimental

2.1. Physical and Chemical Properties Determinations

All melting points are uncorrected Elemental and spectral analysis was carried out at the microanalytical center (Cairo University). The IR (ν KBr) spectra were determined with Perkin Elmer Infrared 127B spectrophotometer (Cai-

ro-University). $^1\text{H-NMR}$ spectra were recorded with a Bruker AMX-250 spectrometer (Cairo-University). Mass spectra were recorded on an HpMs 6988 spectrometer (Cairo University). The absorption spectra were recorded immediately after preparation of the solutions within the wavelength range (350 - 700) on 6405 UV/Visible recording spectrophotometers, Faculty of Science, Aswan University.

2.2. Synthesis

Analytical data and molecular Properties for all the starting N-bridge head heterocycles and the target dyes involved in this study was obtained and summarized in (Table 1).

Table 1. Characterization data for (1; 2a, b; 3a, b; 4a, b; 5a, b and 6a-f).

Comp. No.	M.P °C	Yield %	Color	Mol. Formula (Mol. Wt.)	Calcd. (Found)%			Absorption spectra in EtOH	
					C	H	N	λ_{max} (nm)	ϵ_{max} ($\text{M}^{-1} \text{cm}^{-1}$)
1	125	78	Pale brown	$\text{C}_{23}\text{H}_{24}\text{IN}_5\text{O}$ (513)	53.81	4.71	13.64	350	1778
					53.82	4.70	13.66		
2a	129	60	Brown	$\text{C}_{28}\text{H}_{28}\text{I}_2\text{N}_6\text{O}$ (718)	46.81	3.93	11.70	365	1785
					46.80	3.95	11.71		
2b	135	58	Red	$\text{C}_{32}\text{H}_{30}\text{I}_2\text{N}_6\text{O}$ (768)	50.02	3.94	10.94	365 440	1795, 797
					50.09	3.94	10.95		
3a	140	75	Dark red	$\text{C}_{29}\text{H}_{30}\text{I}_2\text{N}_6\text{O}$ (732)	47.56	4.13	11.47	365 490	1667, 923
					47.54	4.14	11.48		
3b	145	82	Brown	$\text{C}_{19}\text{H}_{16}\text{N}_6\text{O}_2$ (360)	63.26	4.43	23.30	365 495	1789, 1100
					63.29	4.47	23.32		
4a	165	71	Brown	$\text{C}_{28}\text{H}_{25}\text{IN}_6$ (572)	58.75	4.40	14.68	470	1092
					58.73	4.41	14.69		
4b	190	66	Brown	$\text{C}_{32}\text{H}_{27}\text{IN}_6$ (622)	61.74	4.37	13.50	485	1397
					61.76	4.35	13.52		
5a	127	61	Red	$\text{C}_{21}\text{H}_{18}\text{N}_6\text{O}_3\text{S}$ (434)	58.00	4.14	19.33	460	698
					58.09	4.15	19.30		
5b	170	65	Reddish	$\text{C}_{21}\text{H}_{18}\text{ClN}_5\text{OS}$ (423)	59.446	4.24	16.51	498	1010
					59.445	4.27	16.55		
6a	155	74	Red	$\text{C}_{21}\text{H}_{18}\text{N}_6\text{O}_3\text{S}$ (434)	58.001	4.14	19.33	390, 520	2700, 2443
					58.000	4.13	19.36		
6b	150	59	Red	$\text{C}_{40}\text{H}_{37}\text{I}_2\text{N}_7$ (869)	55.25	4.29	11.28	480	670
					55.25	4.30	11.30		
6c	130	59	Pale brown	$\text{C}_{21}\text{H}_{17}\text{Cl}_2\text{N}_5\text{O}$ (426)	59.11	3.987	16.420	500	1780
					59.10	3.89	16.41		
6d	185	68	Brown	$\text{C}_{40}\text{H}_{39}\text{I}_2\text{N}_7$ (871)	55.12	4.51	11.25	475	612
					55.14	4.5	11.23		
6e	185	75	Red	$\text{C}_{44}\text{H}_{39}\text{I}_2\text{N}_7$ (919)	57.47	4.27	10.66	478	1593
					57.45	4.28	10.69		
6f	160	61	Red	$\text{C}_{44}\text{H}_{39}\text{I}_2\text{N}_7$ (919)	57.47	4.27	10.66	474	1012
					57.48	4.28	10.65		

2.2.1. 3-Methyl-1-phenyl-pyrazolin-4,4-ketooxime-methylene-pyridine (quinoline)-1-ium Ethiodide Salt (1)

A mixture of 3-methyl-1-phenyl-pyrazolino-5-imino-4-(N-acetyl-quinolin-1-ium iodide, 1 mole), hydroxylamine hydrochloride (2 moles) and sodium acetate (3 moles) was dissolved in ethanol (30 ml) and heated in a water bath for an hour. The reaction mixtures were filtrated from unreacted materials. The reaction mixture quenched by water and extracted by chloroform (3 × 50 ml). The combined organic layers were washed with water, dried over MgSO₄ and evaporated under reduced pressure. The product was purified via recrystallization from ethanol.

2.2.2. 1-Phenyl-3-methyl-pyrazolin-4-ketooxime- α -methylen-bis-pyridine (quinoline)-4(1)-di-ium-iodide(ethiodide) Salts (2a, b & 3a, b)

Ethanolic solution of compound 1 (1 mol) with pyridine (quinoline) or 2methyl pyridine (2-methyl quinoline) (1 mol) and iodine (1mol). The mixture was stirred and refluxed for 3 - 5 hrs. The reaction mixtures were filtrated from unreacted materials. The filtrate was concentrated to one third of its volume, cooled. The precipitated products after dilution with water were separated, filtrated, recrystallized from diethyl ether.

2.2.3. Synthesis of 2-[3-Methyl-1-phenyl-pyrazolin-5-imine]imidazo(1,2-a) Pyridine (quinoline)-zero-3[4(1)] Methine Cyanine Dyes (4a, b)

Fusion of **2a, b** with piperidine for about an hour then dissolved the reaction mixture in anhydrous ethanol and reflux for 3 hours. The reaction mixture quenched by water and extracted by methylene chloride (50 ml). The combined organic layers were washed with water, dried over MgSO₄ and evaporated. The product was purified via recrystallization from petroleum ether.

2.2.4. 3-[3-Methyl-1-phenyl-pyrazolin-5-imine]pyrazino(1,2-a) Pyridine (quinoline)-zero-4-[4(1)] Methine Cyanine Dyes (5a, b)

Fusion of **3a, b** with piperidine for about an hour then dissolved the reaction mixture in ethanol and reflux for 3 hours. The reaction mixture concentrated to half of its volume, cooled and precipitated with ice water then recrystallized from petroleum ether.

2.2.5. 2-[H]-3-[3-Methyl-1-phenyl-pyrazolin-5-imine]pyrazino(1,2-a) Pyridine (Quinoline)-bis-zero-1,4[4(1)] Methine Cyanine Dyes (6a-f)

Ethanolic solution of dye **5a, b** (1 mol) and pyridin [quinolin]-2(4)-ium-1-ethiodide salts (1 mol) in the presence of few drops of piperidine were stirred and refluxed for 5 - 7 hrs. The reaction mixtures were filtrated from unreacted materials. The filtrate concentrated to one third of its volume, cooled and acidified with acetic acid. The precipitated products after dilution with water were separated, filtrated, recrystallized from petroleum ether.

2.3. UV-Vis Spectra Absorption

UV-Vis spectra for all dyes in pure and mixed solvents were recorded at 25°C in

a 1 cm path length quartz cell on a Cary 3 Spectrophotometer. Ethanolic solution of 1×10^{-5} M was prepared, and the absorbance was measured and the extinction coefficient was calculated in each case.

2.4. Solvatochromic Studies

The organic solvents were used of spectroscopic grade which purified according to the recommended methods [25]. The electronic absorption spectra of the studied dyes in different organic solvents were recorded within the wavelength (350 - 700 nm) on 6405 UV/Visible recording spectrophotometers using 1 cm cell. The stock solution of the dye was of the order 10^{-3} M. Solutions of low molarities used in spectral measurements were obtained by accurate dilution.

Preparation of Working Dye Solutions

For studying the effect of pure solvents in the UV and visible range: An accurate volume of the stock solution (10^{-3} M in ethanol) 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. A range of organic solvents was investigated, including water, dimethylformamide (DMF), ethanol, acetone, carbon tetrachloride, chloroform and benzene. Moreover, to study the spectral behavior in mixed solvents in the visible region: An accurate volume of stock solution (10^{-3} M in ethanol) of the dyes were placed in 10 ml measuring flask containing the required volume of ethanol, then completed to the mark with the other solvent.

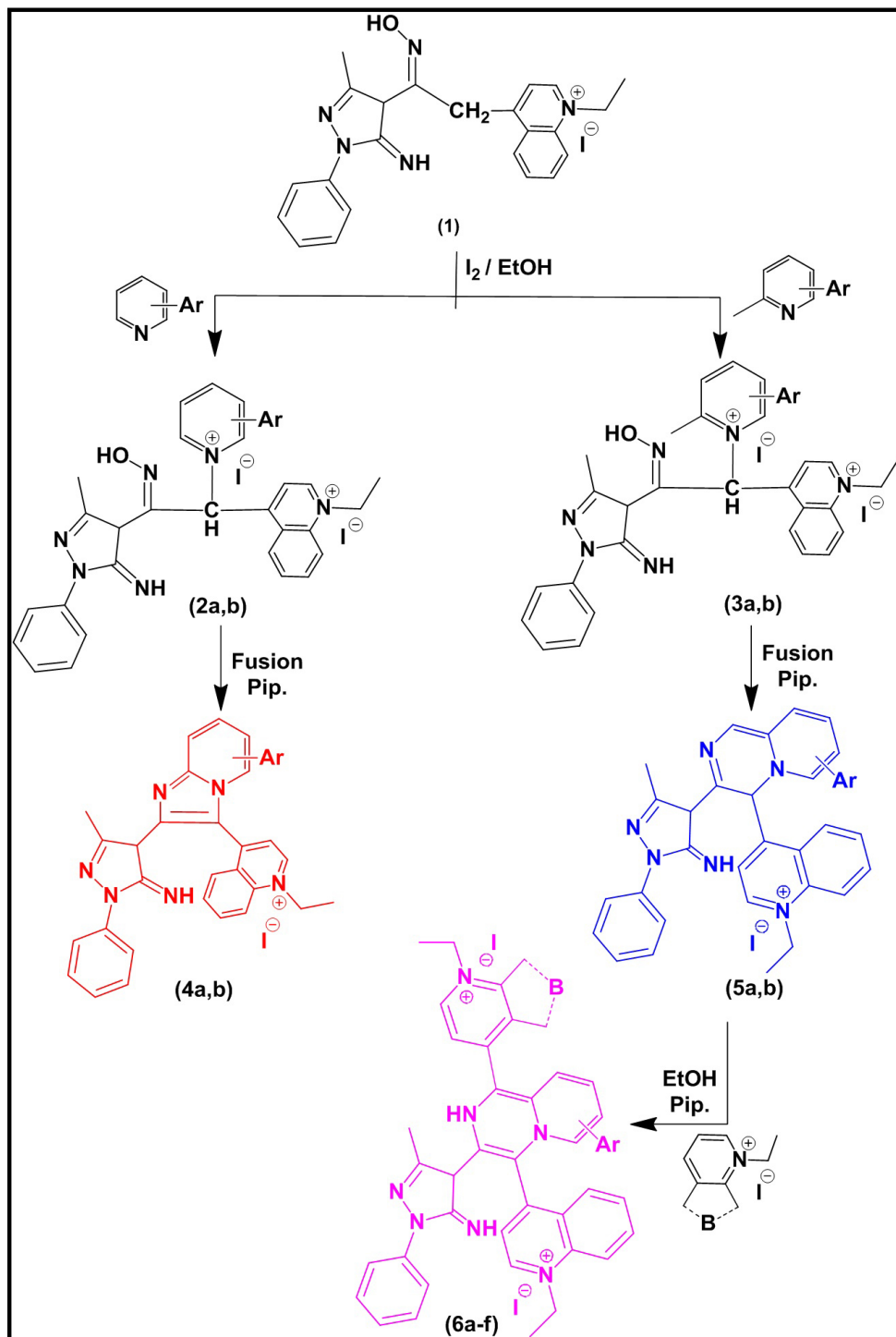
3. Results and Discussions

3.1. Synthesis and Structural Characterization of Dyes

3.1.1. Dye Synthesis

The synthesis of zero methine (**4a, b** & **5a, b**) and bis-zero methine (**6a-f**) cyanine dyes was started by preparation of 3-methyl-1-phenyl-pyrazolin-4,4-keto-methylene-quinolin-1-ium ethiodide salts (**1**) according to reference [26] followed by the reaction of an ethanolic solution of (**1**) with hydroxyl amine in the presence of sodium acetate to afford 3-methyl-1-phenyl-pyrazolin-4,4-ketooxime-methylene-pyridine (quinoline)-1-ium ethiodide salt (**2**). The reaction of an ethanolic solution of (**2**) with I_2 and pyridine (quinoline) and/or 2-methyl-quinoline afforded 1-phenyl-3-methyl-pyrazolin-4-ketooxime- α -methylene-bis pyridin (quino)in)-1(4)-di-ium-iodide(ethiodide) salts (**2a, b**) & 1-phenyl-3-methyl-pyrazolino-4-ketooxime- α -methylene-N-2-methyl-bis-pyridine (quinoline)-1(4)-di-ium-iodide(ethiodide) salts (**3a, b**) respectively. Compounds (**2a, b**) and (**3a, b**) undergo ring closure involving dehydration reaction in piperidine catalyst to afford 2-[3-methyl-1-phenyl-pyrazolin-5-imine] imidazo(1,2-a)Pyridine (quinoline)-zero-3[4(1)] methine cyanine dyes (**4a, b**) & 3-[3-Methyl-1-phenyl-pyrazolin-5-imine]pyrazino(1,2-a)Pyridin (quinolin)-zero-4-[4(1)] methine cyanine dyes (**5a, b**) respectively. Finally, dyes (**5a, b**) reacted with pyridin [quinolin]-4(1)-ium-1-ethiodide salts in presence of piperidine catalyst to afford 2-[H]-3-

[3-methyl-1-phenyl-pyrazolin-5-imine]pyrazino(1,2-a)pyridin(quinolin)-bis-zer o-1,4 [4(1)] methine cyanine dyes (**6a-f**), **Scheme 1**.



Scheme 1. Synthetic routes of dyes (**4a, b**), (**5a, b**) and (**6a-f**). Where, (**2, 3, 4, 5a, b**): Ar = 2, 3 di[H] (a); A = 2, 3-C₄H₄ (b); (**6a-f**): Ar = 2, 3 di[H], B = 1-ethyl pyridin-4-ium salt (a); A = 2, 3 di[H], B = 1-ethyl-quinolin-4-ium salt (b); A = 2, 3 di[H], B = 2-ethyl-quinolin-1-ium salt (c); A = 2, 3-C₄H₄, B = 1-ethyl pyridin-4-ium salt (d); A = 2, 3-C₄H₄, B = 1-ethyl-quinolin-4-ium salt (e); A = 2, 3-C₄H₄, B = 1-ethyl-quinolin-1-ium salt (f).

3.1.2. Structural Characterization

The structures of **1**, **2b**, **3b**, **4b**, **5b** & **6e** was characterized & identified by elemental analysis (Table 1), IR, ¹H-NMR and Mass spectral data. Thus, IR (ν^{KBr} cm^{-1}) showed general absorption bands at 3426.89 cm^{-1} (OH of oxime), 2963.09 cm^{-1} (heterocyclic quaternary salt), 1601.59 cm^{-1} (C=C) conjugated, 1501.31 cm^{-1} (C=N), 750.174 cm^{-1} (Aromatic compound) for **1**; 3427.85 cm^{-1} (OH of oxime), 2926.45 cm^{-1} (heterocyclic quaternary salt), 1598.7 cm^{-1} (C=C) conjugated, 1494.56 cm^{-1} (C=N), 755.959 cm^{-1} (Aromatic compound) for **2b**; 3423.99 cm^{-1} (OH of oxime), 2966.95 cm^{-1} (heterocyclic quaternary salt), 1597.73 cm^{-1} (C=C) conjugated, 1493.6 cm^{-1} (C=N), 756.923 cm^{-1} (Aromatic compound) for **3b**. Mass spectra of **1**, **2a**, **3b**, **4a**, **5a** and **5b** confirmed a molecular formula agree with a molecular ion peaks at $m/z = 515$, and base peak at $m/z = 69$ for compound **1**, a molecular ion peaks at $m/z = 719$, and base peak at $m/z = 77$ for dye **2a**, a molecular ion peaks at $m/z = 362$, and base peak at $m/z = 77$ for dye **3b**, a molecular ion peaks at $m/z = 574$, and base peak at $m/z = 69$ for dye **4a**, a molecular ion peaks at $m/z = 435$, and base peak at $m/z = 77$ for compound **5a** and a molecular ion peaks at $m/z = 635$, and base peaks at $m/z = 158$ & 377 for **5b**. ¹H-NMR (DMSO, 300 MHz) spectra of showed signals at δ 1.01 - 1.113 (s, 3H, CH₃) and (t, 3H, CH₃), 1.89 (s, H, CH), 2.5 (s, 2H, CH₂), 2.28 (s, 1H, OH), 3.16 - 3.76 (q, 2H, CH₂), 6.65 - 7.199 (m, 9H, Ar-H), 7.4 - 8.2 (m, 6H, heterocyclic quaternary salt); δ 1.3 (t, 3H, CH₃), 1.45 (s, 1H), 2.02 (s, 3H, CH₃), 2.1 (s, 1H, CH), 2.67 (s, 1H, OH), 2.8 (s, 1H, NH), 4.3 (q, 2H, CH₂), 6.6 - 8.4 (m, 16H, Ar) for **2a**; δ 1.43 (t, 3H, CH₃), 1.6 (s, 1H, CH), 1.92 (s, 3H, CH₃), 2.9 (s, 1H, NH), 4.02 (q, 2H, CH₂), 6.6 - 8.8 (m, 16H, Ar) for **5a** and δ 1.45 (t, 6H, 2CH₃), 1.6 (s, 3H, CH₃), 2.27 (s, 1H, CH), 4.52 (q, 4H, 2CH₂), 6.7 - 8.9 (m, 19H, Ar), 12.6 (s, 1H, =NH), for **6a**.

3.2. Color, Spectral and Solvatochromic Behaviour

3.2.1. Spectral Behavior in EtOH

2-[3-Methyl-1-phenyl-pyrazolin-5-imine] imidazo(1, 2-a)Pyridin (quinolin)-zero-3[4(1)] methine cyanine dyes (**4a**, **b**) & 3-[3-Methyl-1-phenyl-pyrazolin-5-imine] pyrazino(1,2-a)Pyridin (quinolin)-zero-4-[4(1)] methine (**5a**, **b**) and 2-[H]-3-[3-methyl-1-phenyl-pyrazolin-5-imine] pyrazino (1, 2-a)Pyridine (quinoline)-bis-zero-1,4[4(1)] methine cyanine dyes (**6a-f**) are highly colored compounds. Their color ranging from (reddish-red), easily (partially) soluble in polar (non) organic solvents exhibiting colored solutions concomitant with slight or intense greenish-red fluorescence depending upon the solvent used. They are soluble in concentrated H₂SO₄ acid liberating iodine vapour on warming. Their ethanolic solutions gave permanent colours in basic media which reversibly discharged on acidification. Thus, the visible absorb-maximum of dye **4a** [A = pyridin-4-ium salt] showed ($\lambda_{\text{max}} = 470$ nm; $\epsilon_{\text{max}} = 1092$ M⁻¹ cm⁻¹). Substitution of [A = pyridin-4-ium salt] in dye **4a** by [A = quinolin-4-ium salt] in **4b** exhibit ($\lambda_{\text{max}} = 492$ nm; $\epsilon_{\text{max}} = 1397$ M⁻¹ cm⁻¹) resulted in bathochromic shift of $\Delta\lambda_{\text{max}} = 22$ nm. This is due to the more extensive π -delocalization and extra conjugation in

the quinoline ring. Moreover, the visible absorb-maximum of **5a** [A = pyridin-4-ium salt] showed ($\lambda_{\max} = 460$ nm; $\epsilon_{\max} = 698$ M⁻¹ cm⁻¹). Substitution of [A = pyridin-4-ium salt] in dye **5a** by [A = quinolin-4-ium salt] in dye **5b** exhibit ($\lambda_{\max} = 498$ nm; $\epsilon_{\max} = 1010$ M⁻¹ cm⁻¹) resulted in bathochromic shift of $\Delta\lambda_{\max} = 38$ nm. This is due to the more extensive π -delocalization and extra conjugation in the quinoline ring. Finally, dye **6a** [A = 2, 3 di[H], B = 1-ethyl pyridin-4-ium salt] showed ($\lambda_{\max} = 390$ & 520 nm; $\epsilon_{\max} = 2700$ & 2443 M⁻¹ cm⁻¹). Substitution of [A = A = 2, 3 di[H], B = 1-ethyl pyridin-4-ium salt] in dye **6a** by [A = 2, 3 di[H], B = 1-ethyl-quinolin-4-ium salt] in dye **6b** exhibit ($\lambda_{\max} = 480$ nm; $\epsilon_{\max} = 670$ M⁻¹ cm⁻¹) resulted in bathochromic shift of $\Delta\lambda_{\max} = 40$ nm. This is due to the more extensive π -delocalization and extra conjugation in the quinoline ring. Substitution of [A = 2, 3 di[H], B = 1-ethyl pyridin-4-ium salt] in dye **6a** by [A = 2, 3 di[H], B = 1-ethyl-quinolin-4-ium salt] in dye **6c** exhibit ($\lambda_{\max} = 500$ nm; $\epsilon_{\max} = 1780$ M⁻¹ cm⁻¹). Substitution of [A = 2, 3 di[H], B = 1-ethyl-quinolin-4-ium salt] in dye **6c** by [A = 2, 3-C₄H₄, B = 1-ethyl pyridin-4-ium salt] in dye **6d** exhibit ($\lambda_{\max} = 475$ nm; $\epsilon_{\max} = 612$ M⁻¹ cm⁻¹) resulted in hypsochromic shift of $\Delta\lambda_{\max} = 25$ nm. This is due to the less extensive π -delocalization and less conjugation in the quinoline ring. Substitution of [A = 2, 3-C₄H₄, B = 1-ethyl pyridin-4-ium salt] in dye **6d** by [A = 2, 3-C₄H₄, B = 1-ethyl-quinolin-4-ium salt] in dye **6e** exhibit ($\lambda_{\max} = 478$ nm; $\epsilon_{\max} = 1593$ M⁻¹ cm⁻¹) resulted in hypsochromic shift of $\Delta\lambda_{\max} = 3$ nm. This is due to the more extensive π -delocalization and extensive conjugation in the quinoline ring. Substitution of [A = 2, 3-C₄H₄, B = 1-ethyl-quinolin-4-ium salt] in dye **6e** by [A = 2, 3-C₄H₄, B = -ethyl-quinolin-1-ium salt] in dye **6f** exhibit ($\lambda_{\max} = 474$ nm; $\epsilon_{\max} = 1012$ M⁻¹ cm⁻¹) resulted in hypsochromic shift of $\Delta\lambda_{\max} = 4$ nm. This is due to the less extensive π -delocalization and less conjugation in the isoquinoline ring. Comparison of dyes (**4a, b**) and (**5a, b**), Observed that dyes (**4a, b**) giving higher values of λ_{\max} than dyes (**5a, b**) this can be explained from the extending of π -delocalization through three rings in case of dyes (**4a, b**). Moreover 3-Methyl-1-phenyl-pyrazolin-5-imine-4-pyrazino(1,2-a) Pyridine (quinoline)-bis-zero-2,5[4(1)]methine cyanine dyes (**6a-f**) are bathochromic shift to 3-Methyl-1-phenyl-pyrazolin-5-imine-4-pyrazino(1,2-a) Pyridine (quinoline)-zero-2[4(1)] methine cyanine dyes (**5a, b**) this back to extend of π -delocalization in case of bis zero methine cyanine dyes (**6a-f**).

3.2.2. Solvatochromism

The color changes of cyanine dyes with solvents (solvatochromism) was previously discussed by [27] and extended [28] 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. The visible absorption spectra of dyes **5b** and **6e** in the wavelength range 400 - 700 nm have been studied in different organic solvents (H₂O, DMF, EtOH, acetone, CCl₄, CHCl₃, & C₆H₆) respectively [29] as shown in (Figure 1). This is constructed with the intention to illustrate the solvatochromic behavior of these dyes, (λ_{\max} and ϵ_{\max}) values of the intramolecular charge transfer bands are given in (Table 2). These

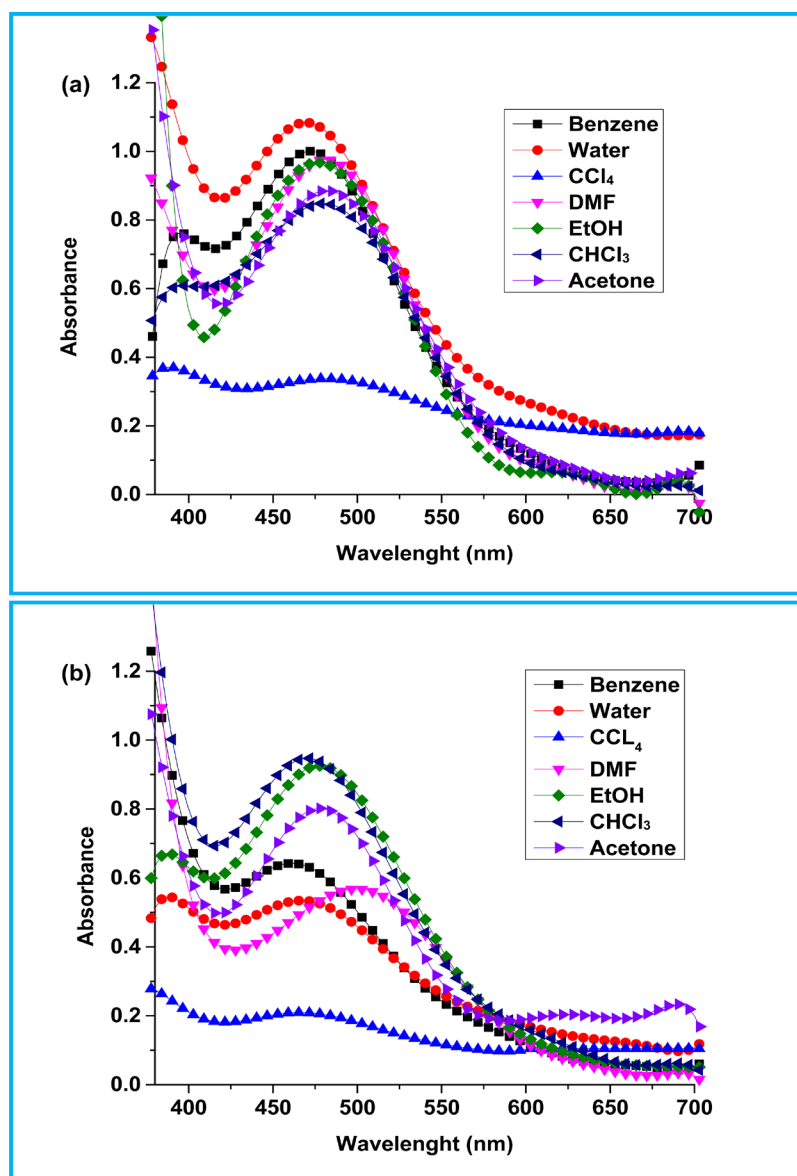


Figure 1. (a) (b) Vis. spectra of (5b) and (6e) respectively in pure organic solvents.

Table 2. Values of absorption (nm) and extinction coefficients ($M^{-1} cm^{-1}$) of dyes (5b) and (6e) in pure organic solvents.

Solvent	5b		6e	
	λ_{max}	ϵ_{max}	λ_{max}	ϵ_{max}
C_6H_6	470	984.7	462	642.03
Water	474	669.9	469	534.2
CCl_4	449	647.9	465	220
DMF	501	869.49	500	568
EtOH	498	918.86	478	925.5
$CHCl_3$	470	977.42	472	947
Acetone	492	771.46	478	802

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 behaviour occurs as a result of electrostatic interactions of the distributed cationic charges with the dipoles of the solvated molecules which lead to formation of specific solvated forms of dyes. The absorption spectra of the dyes in ethanol are characterized by the presence of one or two essential bands which reflects the presence of intermolecular charge transfer. This intermolecular charge transfer had arisen from transferring the electron lone pair of the nitrogen atoms of the heterocyclic ring system towards the positively charged residue along the conjugated chain between both. The representing graphs disclosed that these electronic charge transfer bands exhibit a hypsochromic shifts in ethanol relative to DMF, CHCl_3 , and CCl_4 . This shift can be attributed to the following factors: The bathochromic shift occurred in DMF relative to ethanol is mainly a result of the increase in solvent polarity due to increasing the dielectric constant of the former. The hypsochromic shifts appeared in ethanol relative to CHCl_3 & CCl_4 is generated from the solute-solvent interaction through intermolecular hydrogen bonding between ethanol and the lone pair of electrons within the heterocyclic ring system. Otherwise, this decreases the mobility of the electron cloud over the conjugated pathway towards the positively charged center. It was worth mentioning that the intermolecular hydrogen bonding between CHCl_3 molecules and the lone pair of electrons of nitrogen atoms of the heterocyclic ring system is difficult due to the steric hindrance of the three bulk chlorines. Moreover, the solute solvent interactions in cases of CHCl_3 & CCl_4 generated a residual negative charge on the nitrogen atoms of the heterocyclic ring system which intern facilitated the electronic charge transfer to the positively charged center and this explain the bathochromic shifts in these solvents relative to ethanol. The unexpected hypsochromic shifts in the absorption spectral maxima in water relative to ethanol and its lower extinction coefficients were mainly ascribed to the ease of interactions of water molecules, through intermolecular hydrogen bonding, with the lone pair of electrons of the nitrogen atoms of the heterocyclic ring system, through intermolecular hydrogen bonding, which intern preclude the charge transfer from the heterocyclic ring system to the positively charged residue along the conjugated bridge.

3.2.3. Absorption Spectra in Mixed Solvent

The absorption spectra of dye (**6e**) in 1×10^{-4} M DMF in the presence of different concentrations of benzene are shown in (Figure 2).

It was obvious that in presence of 12.97 M of DMF, the spectrum exhibits a band located at 500 nm. In the presence of 1.16 M of DMF, the band is shifted to 463 nm concomitant with a gradual blue shift. Also, an increase in band intensity at fixed wavelength (500 nm) is observed on increasing of C_6H_6 concentration as depicted in (Figure 3(a)). The increase in absorbance as well as the gradual

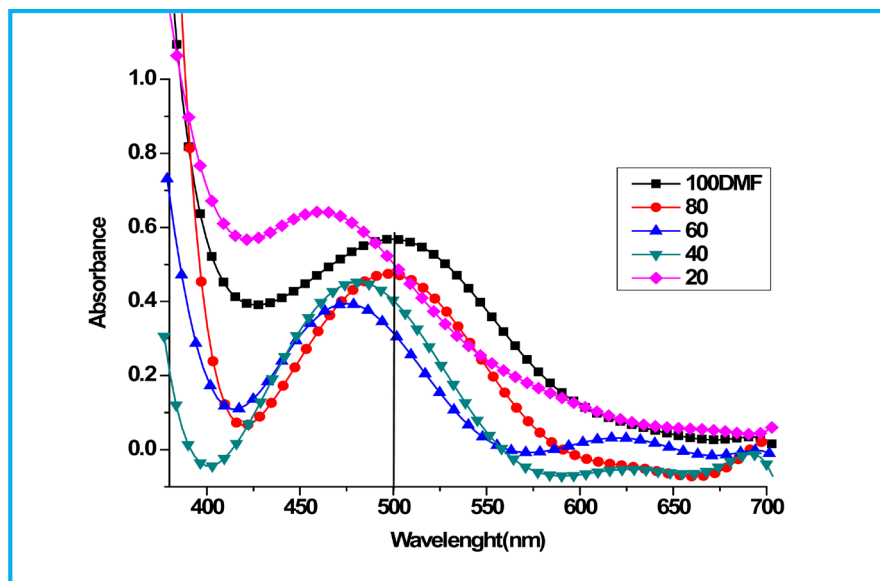


Figure 2. Absorption spectra of dye **6e** in DMF- C_6H_6 mixed solvents.

blue shift in the maximum absorption wavelength on increasing the C_6H_6 , content can be described to the gradual formation of the complex species through intermolecular hydrogen-bond. The graphical representation of absorbance at 500 nm against the mole fraction of DMF (**Figure 3(b)**), reveals that the absorbance increases gradually with increasing mole fraction. on plotting versus $(D-1/D+1)$ (D is dielectric constant of the solvent added) versus the band shift ($\Delta\nu$), a straight line is obtained which at 5.19 M DMF give another straight-line (**Figure 3(d)**). Furthermore, a broken line is obtained on plotting the absorbance against the dielectric constant of the medium (**Figure 3(c)**). Such behaviour indicates that factors other than the change in the dielectric constant of the medium are responsible for the shift of λ_{max} at lower and higher percentage of DMF. These factors mainly include the solute-solvent interaction through intermolecular hydrogen bond which leads to the formation of some molecular complex. On plotting the excitation energy (E) versus the mole fraction of ethanol (**Figure 3(e)**), a broken line with three segments is obtained. The first segment represents the orientation energy of the solvent molecules around the solute. The second segment corresponds to the molecule complex formation, where the third one represents the steady state of energy attained after complete formation of the molecular complex. From the above relations, it is clear that the position of the bands and consequently the excitation energy depends not only on the mole fraction of ethanol, but also on the following: 1) Solvation energy. 2) Orientation of solvent molecules around the solute molecule in the ground states. 3) Dipole moment of the solute in both ground and excited states. 4) Dipole-dipole interaction between solute and solvents. 5) The strength of H-bond between solute and solvent in both ground and excited states. In pure DMF solution, the dye molecule form solvent cage, which is affected on adding C_6H_6 . At lower C_6H_6 content, DMF molecules will distribute themselves uniformly on all

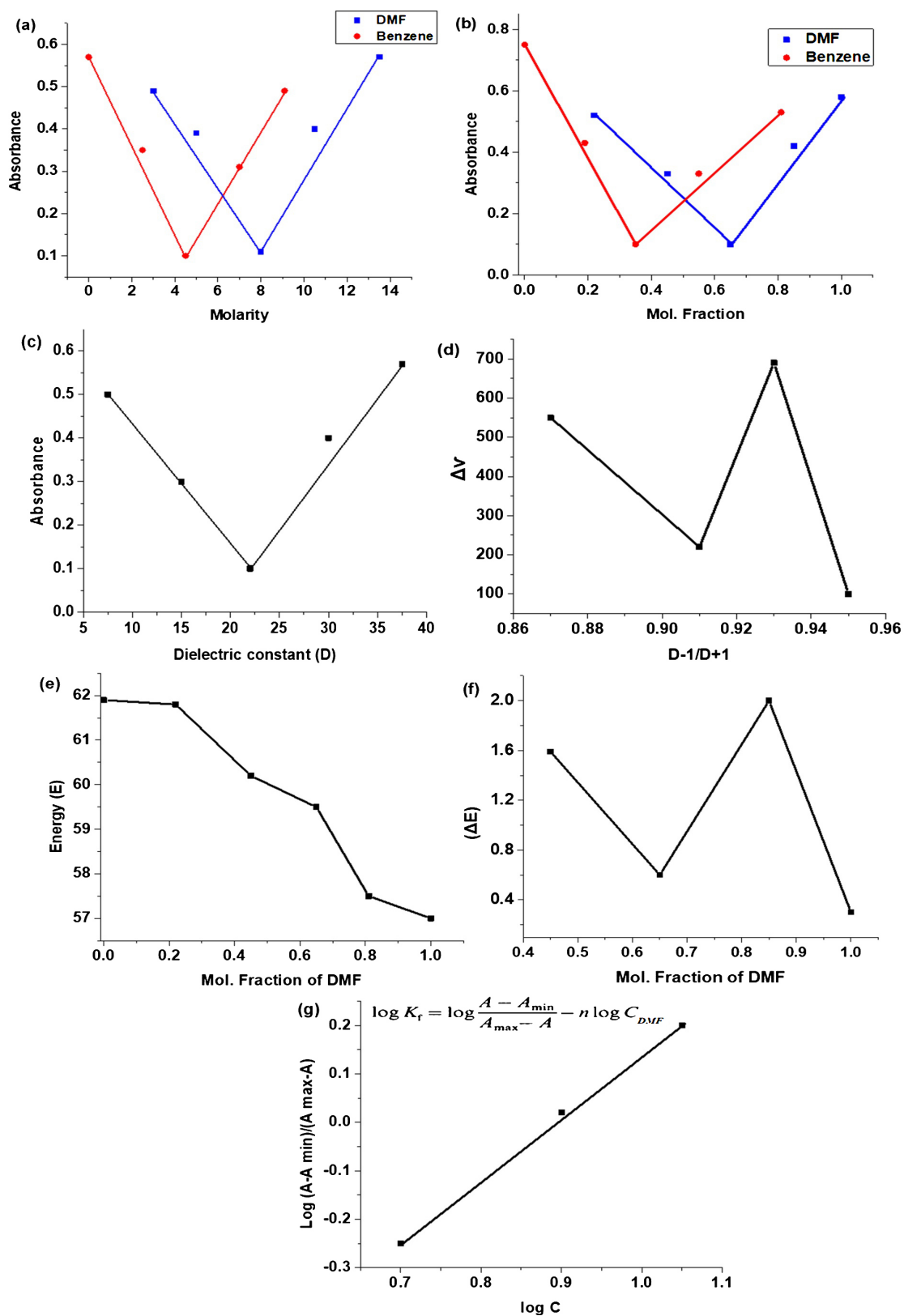


Figure 3. Relation between (a) Absorbance and molarity; (b) mole fraction (b) for dye **6e** in DMF-C₆H₆ mixed solvents; Relation between (c) absorbance and D of the medium; (d) $\Delta\nu$ and $D-1/D+1$; Relation between (e) the mole fraction of DMF and E; (f) the mole fraction and ΔE ; (g) Relation between $\log \left(\frac{A - A_{\min}}{A_{\max} - A} \right) / (A_{\max} - A)$ and $\log C$.

the solvation sheaths around the molecules. The added molecules may first enter the outer solvation sheaths and then will introduce themselves in the first sheaths as their proportions are increased. This is probably due to the fact that addition of DMF permits the formation of a solvent cage around the solute molecules, through intermolecular hydrogen-bonding as shown in (Table 3) it is possible to evaluate the excitation energy of the solute in pure C₆H₆ is equal to 61.9 K Cal mol⁻¹ whereas the value in pure DMF amounts to 57.2 K Cal mol⁻¹. The difference between the excitation energy in pure DMF (Figure 3(f)) and the first inflection point is called orientation energy of the solvent molecules around the solute molecules and equal to 3 K Cal mol⁻¹. While, the difference between the excitation energy in pure DMF and the second inflection point is called H-bond energy and equal to 2.3 K Cal mol⁻¹. The value of the stability constant (K_f) of the complex with C₆H₆ was determined from the spectral behaviour in mixed solvents at fixed λ_{max} = 500 nm using the relations described in (Figure 3(g)) From this figure, it is observed that log K_f is 1.464, and thus K_f is equal to 29.1. Finally, the values of ΔG (free energy change of formation) can be calculated from Gibbs Equation (1)

$$-\Delta G = RT \ln K_f \quad (1)$$

where *R* is the constant of ideal gas, *T* is the absolute temperature and ln*K_f* calculated from log *K_f* (log *K_f* = 1.464; *K_f* = 29.1), and the calculation gives -Δ*G* = 0.345 K cal mol⁻¹. The number of C₆H₆ molecules (*n*) complexed with the solute is computed from (Figure 3(g)); the value of *n* was found to be 1 indicate that 1:1 complex is formed. The value of *K_f* is dependent on both solute and solvent used.

4. Conclusion

Highly stable series of novel zero/Bis zero methine cyanine dyes stabilized by C-N bond were synthesized based on N-Bridge head heterocyclic compounds. The stability of dye formation is due to that N-bridge head heterocyclic compounds used as precursors possess high site reactivity susceptible to be attacked by either Electrophile/Nucleophile in the substitution/addition reactions. The absorption spectra of the synthesized dyes were investigated in different organic solvents and a mixed solvent system. The results indicated that the colour of these dyes depends on the length of conjugation within the structure. Dyes having unsaturated terminal groups are more bathochromic than those with saturated terminal groups. The absorption spectra of these dyes in different organic

Table 3. Commutative data obtained for dye **6e** in mixed solvents. Where **N**: Number of hydrogen bonding.

Dye	Solvent System	Excitation energy K Cal mol ⁻¹ Pure Solvents		Orient energy K Cal mol ⁻¹	H-bond energy K Cal mol ⁻¹	Total energy K Cal mol ⁻¹	N	Log K _f (-)	K _f (-)	ΔG K Cal mol ⁻¹ (±)
6e	(DMF-Benzene)	57.2 (DMF)	61.9 (Benzene)	3	2.3	5.2	2	1.464	29.1	0.3454

solvents undergo bathochromic or hypsochromic shift depending on the structure of dye and the type of solvent. The results of spectral behaviour in a mixed solvent system indicate the formation of a hydrogen bonding between the solute and solvent molecules and allow the measurement of certain energies, such as hydrogen-bonding, orientation and free energy.

Conflicts of Interest

The authors declare no conflicts of interest regarding the publication of this paper.

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