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Synthesis and physicochemical properties of novel zero methine cyanine dyes based on N-bridgehead indolizine (benzoindolizine) heterocycles

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ABSTRACT: Novel zero methine cyanine dyes were starts to synthesize using a highly stable N-bridgehead heterocycle precursors. Such Heterocyclic precursors and related dyes were identified by elemental & spectral analyses. The absorption spectra properties of such selected 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 solvatochromic behavior of some selected newly synthesized cyanine dyes is observed here. 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 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 has been studied and progressively increasing quantities of one of each solvent were taken and showed an increase in the absorbance of the CT band with increasing proportion of this solvent. Evidence for hydrogen bond formation between the solute molecules and solvent molecules and allow measurement of certain energies such as hydrogen bonding, orientation, and free energies.

KEYWORDS: Heterocyclic precursors, related dyes synthesis, spectral, solvatochromic behaviours.

I. INTRODUCTION

There is a rising interest toward the synthesis of N-bridgehead heterocyclic compounds in view of their use in the synthesis of cyanine dyes. Zero methine cyanine dyes are one of the most versatile functional dyes. Besides their use as colorants they have considerable potential application in energy conversion [1] as laser dyes [2], as optoelectronic devices, perovskite [3], nucleic acids labelling [4], fluorescence sensors [5, 6], electro-, chemo-, and photoluminescent devices [7]. A variety of heterocyclic cyanine dyes incorporating N-bridgehead heterocyclic moieties have been reported [8-10]. These dyes have many vital general applications this back to the high stability of this type of dyes [11]. This paper reported the synthesis of some novel N-bridgehead heterocycles based on indolizine (benzoindolizine) and pyrolo[3,4-c]indolizine (benzoindolizine) as a main entities for the synthesis of novel zero-1[4(1)] 1,3[4(1)], (3- β -methyl-di)-[2(4)] pyrolo[3,4-c]indolizine methine, indolizine (benzoindolizine) methine cyanine dyes (23a-d, 24a-d, 25a-c, 26a-c, 27, 28, 29a,b & 30) and evaluated the structure-properties relationship of the new dyes on the basis of their visible absorption spectra in ethanol. Also, photophysical studies in different organic solvents are discussed, which might be used as photosensitizer dyes in different optical applications.

II. SIGNIFICANCE OF THE SYSTEM

The paper mainly focuses on the synthesis of N-Bridgehead heterocyclic compounds as precursors for highly stable cyanine dyes and more focused on studying the spectral, solvatochromic behaviour of some selected dyes.

III. EXPERIMENTAL RESULTS**A. Physical and Chemical Properties Determinations:**

All melting points are uncorrected Elemental and spectral analysis was carried out at the microanalytical centre (Cairo University). The IR (ν KBr) spectra were determined with Perkin Elmer Infrared 127B spectrophotometer (Cairo-University). $^1\text{H-NMR}$ spectra were recorded with a Bruker AMX-250 spectrometer (Cairo-University). Mass spectra were recorded on a 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.

B. 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). The synthetic details are described below.

1) 3-Methyl-1-phenyl-pyrazolin-4,4-ketomethylene-pyridin (quinolin)-1-ium ethiodide salts (21a, b).

Such compounds were prepared in a way similar to that described in [12].

2) 3-Methyl-1-phenyl-pyrazolin-4-keto- α -methylene-N-2-methyl -bis-pyridin (quinoin)-1(4)-di-ium-iodide(ethiodide) salts (22a, b).

An Ethanolic solution of (21a, b, 0.01mol.) and 2-methyl-pyridin [quinoline]-bases (0.01mol) in iodine was refluxed for 3-5 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, crystallized from ethanol.

3) 2[3-Methyl-1-phenyl-pyrazolin-5-imine]-N-bridge-head indolizin (Benzoindolizin)-zero-1[4(1)]methine cyanine dyes (23a-d)

An Ethanolic solution of (22a-d, 0.01mol) in few drops of piperidine was refluxed for 3-5 hrs. The reaction mixture was 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, crystallized from ethanol.

4) 2[3-Methyl-1-phenyl-pyrazolin-5-N-acetyl-imino]-3-acetyl-N-bridge head indolizin (benz-indolizin)-zero-1[4(1)] methine cyanine dyes (24a-d):

Mixture of (22a-d or 23a-d, 0.005 mol.) and acetic anhydride (10 ml) was refluxed for 3 hours. The reaction mixture was filtrated from unreacted materials, concentrated and cooled; the solid product was collected and crystallized from ethanol to give (24a-d).

5) 2[3-Methyl-1-phenyl-pyrazolin-5-imine]-N-bridge head indolizin (benzindolizin)-biszero-1,3[4(1)]methine cyanine dyes (25a-c).

An Ethanolic of (23d, 0.01 mol) and pyridine [quinolin]-4(1)-ium-ethiodide salts were dissolved in ethanol (30 ml) in few drops of piperidine and refluxed for 3hrs. The reaction mixtures were filtrated from unreacted materials. The filtrate was concentrated, cooled and acidified with acetic acid. The precipitated products after dilution with water were separated, filtrated, washed with water several times and crystallized from ethanol.

6) 2[3-Methyl-1-phenyl-pyrazolin-5-N-acetyl-imine]-N-bridge head indolizin (benzindolizin)-zero-1[4(1)]-(3- β -methyl-di)-[2(4)] methine cyanine dyes (26a-c).

An Ethanolic solution of (24d, 0.01mol) and 2-methyl-pyridin [quinolin]-2(4)-ium-ethiodide salts (0.01mol) in few drops of piperidine were 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, crystallized from ethanol to afford cyanine dyes (26a-c).

7) 2[3-Methyl-1-phenyl-pyrazolin-5-N-acetyl-imino]-3-acetyl-oxime-N-bridgehead-indolizin (benzoindolizin)-zero-1[4(1)]methine cyanine dye (27)

An Ethanolic solution mixture of (24d, 1 mol.), hydroxylamine hydrochloride (2 moles) and sodium acetate (3 moles) in few drops of piperidine and heated on a water bath for one hour. The reaction mixtures were filtrated from unreacted materials. The filtrate was concentrated and cooled. The precipitated products after dilution with water were separated, filtrated, washed with water several times and crystallized from ethanol to give (27).

8) 2[3-Methyl-1-phenyl-pyrazolin-5-N-acetyl-imino]-3-[β -methyl -aza-methine-pyridin-1-ium-chloride salt-N-bridge head indolizin (benzoindolizin)-zero-1[4(1)]methine cyanine dye (28).

An Ethanolic solution mixture of (**27**, 0.01 mole), 2-methyl-pyridine [quinoline] (0.01mol) and few mls of conc. HCl was refluxed on a water bath for an hour. The reaction mixture was filtrated from unreacted materials. The filtrate was concentrated and cooled. The precipitated products after dilution with water were separated, filtrated, washed with water several times and crystallized from ethanol to give (**28**).

9) 2[3-Methyl-1-phenyl-pyrazolin-5-N-acetyl-imino]-3 [pyrazolo (3,2-a)pyridin]-1-ium-chloride salt-N-bridge head indolizin(benzoindolizin)-zero-1[4(1)]methine cyanine dyes (29a,b).

Fusion of (**28a, b**, 0.01 mol.) in piperidine for few minutes, then reflux for two hours in ethanol solution. The reaction mixture was concentrated to half of its volume, cooled and precipitated with ice water, filtrated and washing well with water then recrystallized from ethanol to give (**29a, b**).

C. Preparation of working solutions

1) Preparation of dyes solution in pure solvents

For studying the effect of pure solvents in the UV and visible range: An accurate volume of the stock solution of the dyes were diluted to appropriate volume in order to obtain the required concentration. The spectra were recorded immediately after mixing in order to eliminate as much as possible the effect of time.

2) Preparation of dyes solution in mixed solvents

For studying the spectral behaviour in mixed solvents in the visible region: An accurate volume of stock solution (10^{-3} mol-dm⁻³ 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.

IV.RESULTS AND DISCUSSIONS

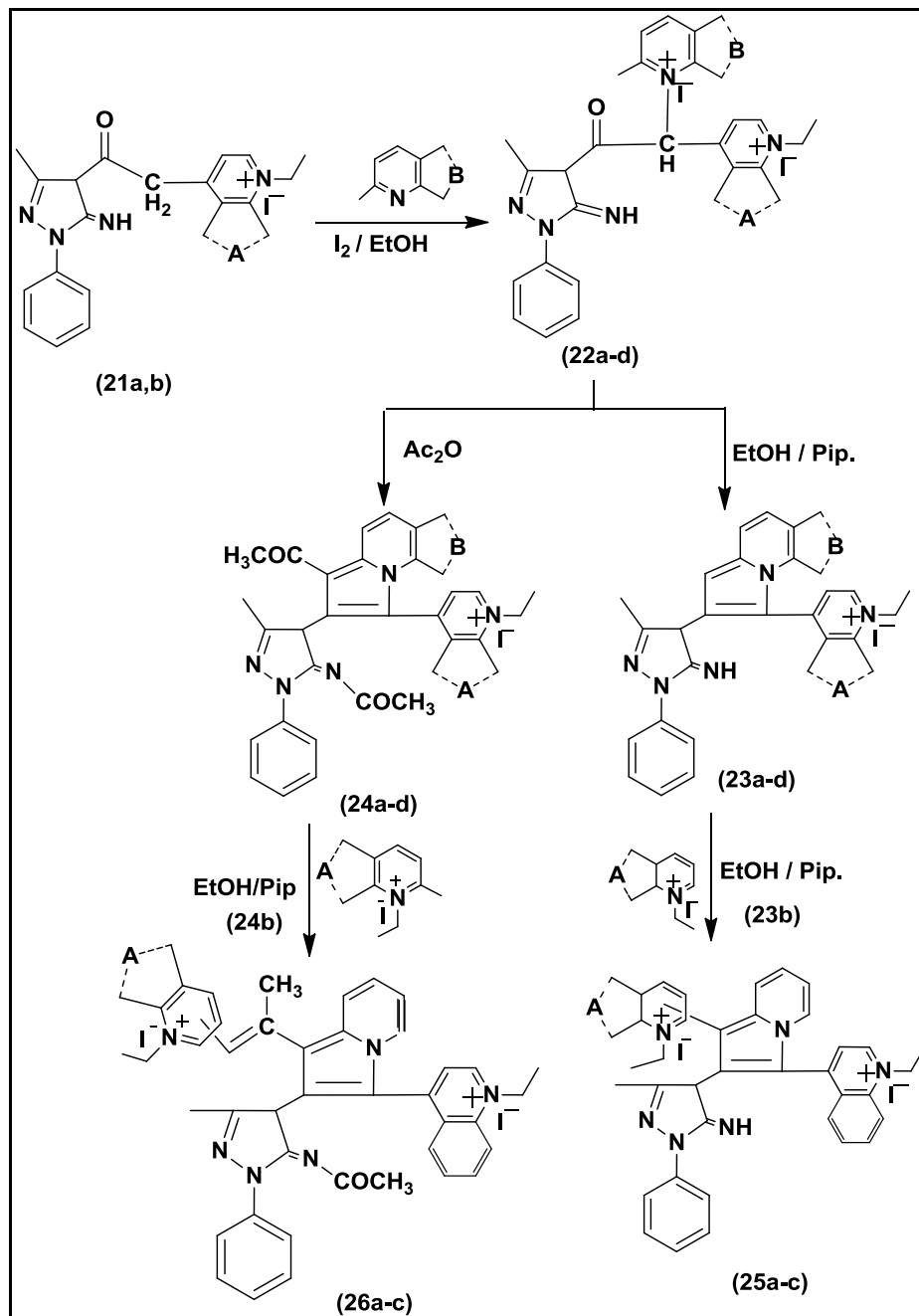
A. Synthesis and structural characterization of dyes

1) Dye synthesis

The reaction of 3-methyl-1-phenyl-pyrazolino-5-imino-4-(N-acetyl-pyridin (quinolin)-1-ium iodide) (**21a, b**) [12] with 2-methyl-pyridine[quinoline] bases in iodine in, equimolar amount, afforded 3-methyl-1-phenyl-pyrazolin-4-keto- α -methylene-N-2-methyl-bis-pyridin(quinolin)-1(4)-di-ium-iodide(ethiodide)salts **22a, b**. The later **22a, b** undergo Intramolecular heterocyclization ring closure in, equimolar amount, under (piperidine and/or acetic anhydride catalysis) to afford N-bridge head 2[3-methyl-1-phenyl-pyrazolin-5-imine]-indolizin(benzoindolizin)-zero-1[4(1)] methine cyanine dyes **23a-d** and N-bridge head 2[3-methyl-1-phenyl-pyrazolin-5-N-acetyl-imino]-3-acetyl-indolizin(benzoindolizin)-zero-1[4(1)] methine cyanine dyes **24a-d** which on their treatments with conc. sulphuric acid, liberating iodine vapors on warming. The reaction of N-bridge head 2[3-methyl-1-phenyl-pyrazolin-5-imine]-indolizin-zero-1[4(1)] methine cyanine dyes **23b** with N-ethyl-pyridin(quinolin)-4(1)-ium-ethyl iodide salts catalysis afforded N-bridge head-2[3-methyl-1-phenyl-pyrazolin-5-imine]- indolizin (benzoindolizin)-bis-zero-1,3[4(1)] methine cyanine dyes **25a-c**. The reaction of N-bridge head 2[3-methyl-1-phenyl-pyrazolin-5-N-acetyl-imino]-3-acetyl-indolizin-zero-1[4(1)] methine cyanine dye **24b** with 2 (4)-methyl-pyridin[quinolin]-2(4)-ium-1-ethiodide salts) in, equimolar amount, under piperidine catalysis afforded N-bridge head 2[3-methyl-1-phenyl-pyrazolin-5-N-acetyl-imine] indolizin (benzoindolizin)-zero-1[4(1)]-(3- β -methyl-di)-[2(4)]methine cyanine dyes **26a-c, Scheme (1)**.

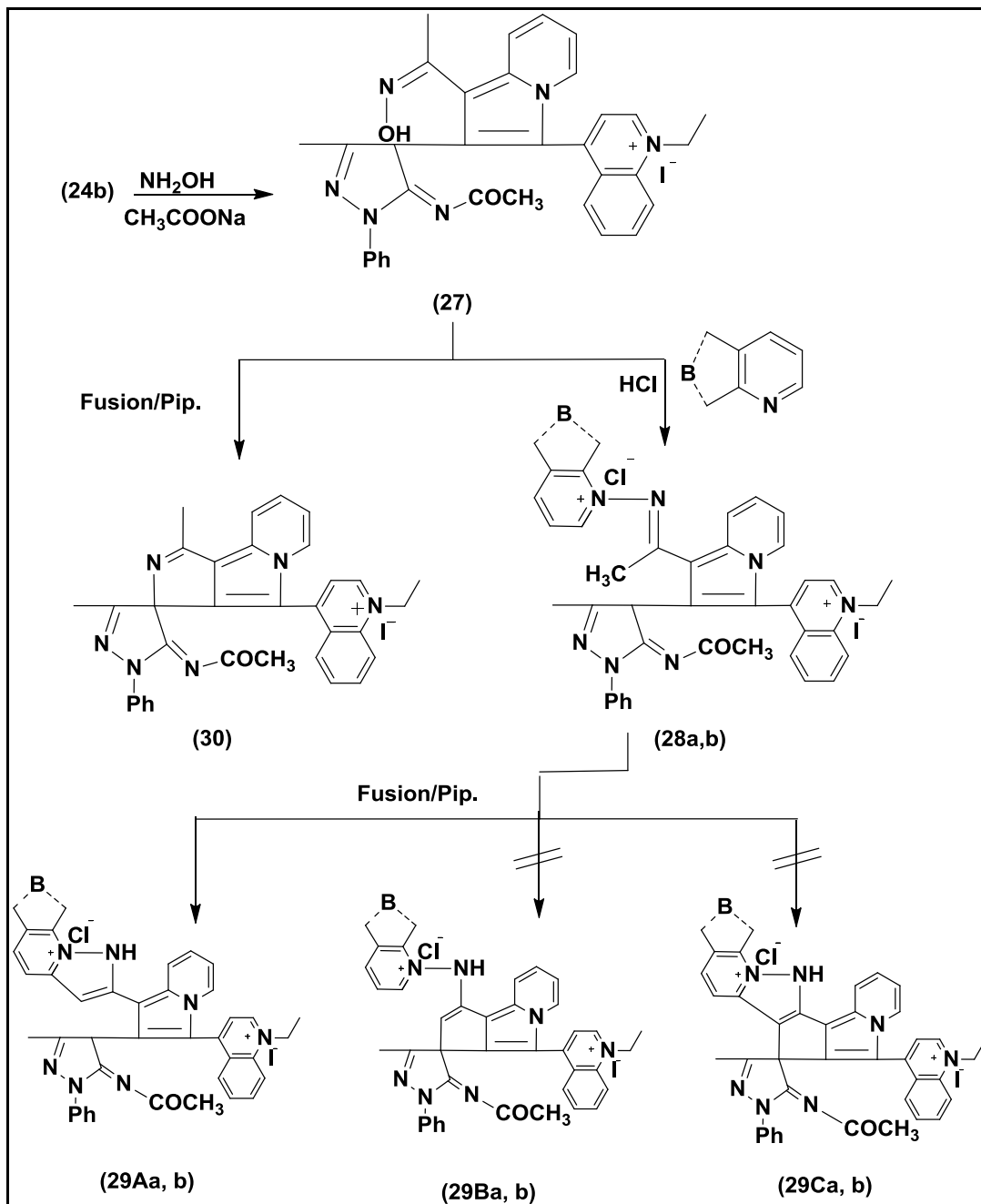
Condensation reaction of **24d** with hydroxyl amine hydrochloride in anhydrous sodium acetate in, equimolar amount, afforded 2[3-Methyl-1-phenyl-pyrazolin-5-N-acetyl-imino]-3-acetyl-oximino-N-bridge head indolizin (benzoindolizin)-zero-1[4(1)] methine cyanine dye **27**. Selective quaternization of **27** and pyridine (quinoline) in conc. HCl afforded 2[3-methyl-1-phenyl-pyrazolin-5-N-acetyl-imino]-3-[β -methyl-aza-methine-pyridin-1-ium-chloride salt-N-bridgehead indolizin (benzoindolizin)-zero-1[4(1)]methine cyanine dyes **28a, b** which under thermal piperidine catalysis undergoes cyclo-oxidative elimination to form 2[3-methyl-1-phenyl-pyrazolin-5-N-acetyl-imino]-N-bridgehead-3[pyrazolo(3,2-a)pyridin]-1-ium-chloride salt-indolizin(benzoindolizin)-zero-1[4(1)] methine cyanine dyes **29a, b**. On the other hand, N-bridgehead -2[3-methyl-1-phenyl-pyrazolin-5-N-acetyl-imino]-3-acetyl-oxime-indolizin(benzoindolizin)-zero-1[4(1)] methine cyanine dye (**27**) undergo cyclo-dehydration between hydroxyl oxime-group and pyrazoline methylene hydrogen in, equimolar amount, under piperidine catalysis to afford 4-methyl-2[3-

methyl-1-phenyl-5-N-acetyl-imino-Spiro-pyrazolin-4,2-pyrol[3,4-c] indolizine-zero-1[4(1)]methine cyanine 30,
 Scheme (2).



Scheme (1): Synthetic routes of dyes **23a-d**, **24a-d**, **25a-c** and **26a-c**. Where, (**21a, b**): A = 1-ethyl pyridin-4-ium salt (a); A = 1-ethyl-quinolin-4-ium salt (b), (**22a-d**): A = 1-ethyl pyridin-4-ium salt, B = 2-methyl pyridin-1-ium salt (a); A = 1-ethyl pyridin-4-ium salt, B = 2-methyl-quinolin-1-ium salt (b); A = 1-ethyl-quinolin-4-ium salt, B = 2-methyl pyridin-1-ium salt (d). (**23, 24 a-d**): A = 1-ethyl pyridin-4-ium salt, B = indolizine (a); A = 1-ethyl-quinolin-4-ium salt, B = indolizine (b); A = 1-ethyl-quinolin-4-ium salt, B = Benzoindolizine (c); A = 1-ethyl pyridin-4-ium salt, B = Benzoindolizine (d). (**25a-c**): A = 1-ethyl pyridin-4-ium salt

(a); 1-ethyl-quinolin-4-ium salt (b); 2-ethyl-quinolin-1-ium salt (c). (26a-c): A =1-ethyl pyridin-2-ium salt (a); 1-ethyl-quinolin-2-ium salt (b); 1-ethyl-pyridin-4-ium salt (c).



Scheme (2): Synthetic routes of (28, 29a, b). where, B = 1-ethyl pyridin-4-ium salt (a); 1-ethyl-quinolin-4-ium salt (b).

Table (1): Characterization data of the synthesized compounds and related dyes

Comp. No.	M.p. °C	Yield %	Colour	Mol. Formula (Mol.wt)	%Calcd. (Found)			Absorption spectra in EtOH	
					C	H	N	$\lambda_{\max}(\text{nm})$	$\epsilon_{\max}(\text{M}^{-1}\text{cm}^{-1})$
22a	130	67	Red	C ₂₉ H ₂₉ I ₂ N ₅ O (717)	48.55	4.07	9.76	395	2201
					48.54	4.11	9.767		
22b	139	70	Red	C ₂₅ H ₂₇ I ₂ N ₅ O (667)	45.00	4.08	10.49	390	2154
					44.97	4.10	10.50		
22c	158	79	Red	C ₃₃ H ₃₁ I ₂ N ₅ O (767)	51.65	4.07	9.13	495	2233
					51.66	4.10	9.13		
22d	134	73	Red	C ₂₉ H ₂₉ I ₂ N ₅ O (717)	48.55	4.07	9.76	445	1788
					48.59	4.09	9.79		
23a	125	65	Red	C ₂₉ H ₂₇ IN ₅ (572)	60.48	4.75	12.23	390	2251
					60.45	4.50	12.29		
23b	137	68	Red	C ₂₅ H ₂₄ IN ₅ (521)	57.59	4.64	13.43	365	2241
					57.57	4.63	13.41		
23c	145	74	Red	C ₃₃ H ₂₈ IN ₅ (621)	63.77	4.54	11.27	503	2261
					63.76	4.55	11.275		
23d	128	76	Dark red	C ₂₉ H ₂₇ IN ₅ (572)	60.48	4.75	12.23	488	1185
					60.47	4.76	12.21		
24a	109	62	brown	C ₃₃ H ₃₀ IN ₅ O ₂ (655)	60.46	4.61	10.68	390	1881
					60.46	4.60	10.68		
24b	132	60	Dark brown	C ₂₉ H ₂₈ IN ₅ O ₂ (605)	57.53	4.66	11.57	355	1721
					57.53	4.63	11.57		
24c	138	68	Brown	C ₃₇ H ₃₂ IN ₅ O ₂ (705)	62.98	4.57	9.93	425	2199
					62.93	4.55	9.94		
24d	113	63	Pale brown	C ₃₃ H ₃₀ IN ₅ O ₂ (655)	60.46	4.61	10.68	415	2105
					60.46	4.66	10.61		
25a	130	73	Red	C ₃₆ H ₃₅ I ₂ N ₆ (805)	53.68	4.38	10.43	500	2621
					53.67	4.39	10.42		
25b	135	80	Red crystals	C ₄₀ H ₃₇ I ₂ N ₆ (854)	56.15	4.36	9.82	525	2863
					56.4	4.36	9.83		
25c	142	77	Red	C ₄₀ H ₃₇ I ₂ N ₆ (854)	56.15	4.36	9.82	515	2789
					56.14	4.357	9.82		
26a	155	82	Pale violet	C ₄₁ H ₄₀ I ₂ N ₆ O (886)	55.54	4.55	9.48	480	1887
					55.58	4.53	9.49		
26b	180	77	Dark violet	C ₄₅ H ₄₂ I ₂ N ₆ O (936)	57.70	4.52	8.97	505	2520
					57.69	4.27	8.98		
26c	166	75	Violet	C ₄₁ H ₄₀ I ₂ N ₆ O (886)	55.54	4.55	9.48	495	2233
					55.58	4.58	9.49		
27	130	86	Dark brown	C ₃₃ H ₃₁ IN ₆ O ₂ (670)	59.11	4.66	12.53	455	1945
					59.10	4.65	12.58		
28a	160	68	Red	C ₃₈ H ₃₁ ClIN ₇ O (764)	59.68	4.05	12.82	490	1951
					59.66	4.04	12.83		
28b	170	75	Red	C ₄₂ H ₃₇ ClIN ₇ O (818)	61.57	4.52	11.97	530	2111
					61.49	4.47	12.01		
29a	195	74	brown	C ₃₈ H ₃₃ ClIN ₇ O (762)	59.84	4.33	12.86	454	1871
					59.83	4.33	12.87		
29b	210	76	dark brown	C ₄₂ H ₃₇ ClIN ₇ O (816)	61.72	4.51	12.00	460	1884
					61.79	4.53	12.01		
30	130	67	Dark red	C ₂₉ H ₂₇ IN ₆ O (602.468)	57.81	4.52	13.95	490	1781
					57.80	4.518	13.944		

2) Structural Characterization

The structure of the synthesized compounds was confirmed by spectral data IR, ¹H-NMR and mass analyses. Thus, IR(ν^{KBr} cm⁻¹) showed the general absorption bands at 1490.7 cm⁻¹ (C=N), 1617.98 cm⁻¹ (C=C) conjugated, 1711.51 cm⁻¹

(COCH₃) for **24d**; 1494.56 cm⁻¹ (C=N), 1597 cm⁻¹ (C=C) conjugated, 3058-3060 cm⁻¹ (stretching CH) and 2923 cm⁻¹ (heterocyclic quaternary salt) for **25b**; absorption bands at 1490.7 cm⁻¹ (C=N), 1617.9 cm⁻¹ (C=C) conjugated, 1711.51 cm⁻¹ (COCH₃), 3061 cm⁻¹ (stretching CH) and 2923 cm⁻¹ (heterocyclic quaternary salt); dyes **28b & 29b** showed, in addition to, the general absorption bands at 1494.56 cm⁻¹ (C=N), 1597.73 cm⁻¹ (C=C) conjugated, 1714.41 cm⁻¹ (COCH₃), well defined absorption band at 3061.44 cm⁻¹ (stretching CH) and 2923.56 cm⁻¹ (heterocyclic quaternary salt). Mass spectra reveals molecular ion peaks at m/z =571 and base peak at m/z =158 for **23d**; a molecular ion peaks at m/z =656 and base peak at m/z =60 for **24d**; a molecular ion peaks at m/z =854 and base peak at m/z=123 for **25b**; molecular ion peaks at m/z =884 and base peak at m/z=201 for **26a**; molecular ion peaks at m/z=819 and base peak at m/z =63 for **28b**, molecular ion peaks at m/z =817 and base peak at m/z=64 for **29b**, molecular ion peaks at m/z =667 and base peak at m/z=51 for **30**. ¹H-NMR (DMSO, 300 MHz) spectra of **23d & 24d** showed general single and multiple signals at δ 1.12 (t, 3H, CH₃), 1.23(q, 2H, CH₂), 2.3 (s, 3H, CH₃), 2.5 (s, 1H, CH), 3.5 (s, 1H, NH), 7.1-7.99 (m, 16H) three Aromatic systems for **23d** and at δ 1.5-1.8 (t, 3H, CH₃), 1.87 (q, 2H, CH₂), 2.46-2.47 (s, 3H, CH₃), 3.49 (s, 6H, 2CH₃) two acetyl groups, 7.8-8.8 (m, 15H) three Aromatic systems for **24d**.

B. Physicochemical studies

1) Colour and Spectral Behaviour

2[3-Methyl-1-phenyl-pyrazolin-5-imine]-N-bridge head indolizin (benzo-indolizin)-zero-1[4(1)] methine cyanine dyes (**23a-d**), 2[3-Methyl-1-phenyl-pyrazolin-5-N-acetyl-imino]-3-acetyl-N-bridge head indolizin (benz-indolizin)-zero-1[4(1)] methine cyanine dyes (**24a-d**), N-bridge head indolizin (benzoindolizin)-bis-zero-1,3[4(1)] methine cyanine dyes (**25a-c**), N-bridge head indolizin (benzoindolizin)-zero-1[4(1)]-(3-β-methyl-di)-[2(4)] methine cyanine dyes (**26a-c**), 2[3-Methyl-1-phenyl-pyrazolin-5-N-acetyl-imino]-3-[β-methyl-aza-methine-pyridin-1-ium-chloride salt-N-bridge head indolizin (benz-indolizin)-zero-1[4(1)] methine cyanine dye (**28a, b**) and 2[3-Methyl-1-phenyl-pyrazolin-5-N-acetyl-imino]-3[pyrazolo(3,2-a)pyridin]-1-ium-chloride salt-N-bridge head indolizin (benz-indolizin)-zero-1[4(1)] methine cyanine dyes (**29a, b**) are highly colored compounds their ethanolic solution ranging from red to violet, 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 conc. H₂SO₄ acid liberating iodine vapor on warming. Their Ethanolic solutions gave permanent colours in basic media which reversibly discharged on acidification. They possess interchangeable colours solution (brownish-red/intense red → yellow) in basic and acidic medium, **Table (1)**.

Moreover, the visible absorb-maximum of dye **23a** [A = 1-ethyl pyridin-4-ium salt, B = 1-ethyl-quinolin-4-ium salt] showed ($\lambda_{\max} = 390$ nm; $\epsilon_{\max} = 2251$ M⁻¹cm⁻¹). Substituting of [A = 1-ethyl pyridin-4-ium salt, B = 1-ethyl-quinolin-4-ium salt] in dye **23a** by [A = 1-ethyl pyridin-4-ium salt, B = 1-ethyl pyridin-4-ium salt] in dye **23b** exhibit ($\lambda_{\max} = 365$ nm; $\epsilon_{\max} = 2241$ M⁻¹cm⁻¹) resulted in hypsochromic shift of $\Delta\lambda_{\max} = 25$ nm. This is due to the decreasing π -delocalization and less conjugation in pyridine ring. Substituting of [A = 1-ethyl pyridin-4-ium salt, B = 1-ethyl pyridin-4-ium salt] in dye **23b** by [A = pyridin-4-ium salt, B = 1-ethyl-quinolin-4-ium salt] in dye **23c** exhibit ($\lambda_{\max} = 503$ nm; $\epsilon_{\max} = 2261$ M⁻¹cm⁻¹). This is due to the more extensive π -delocalization and extensive conjugation in the quinoline ring. Substituting of [A = pyridin-4-ium salt, B = 1-ethyl-quinolin-4-ium salt] in dye **23c** by [A = 1-ethyl-quinolin-4-ium salt, B = 1-ethyl pyridin-4-ium salt] in dye **23d** exhibit ($\lambda_{\max} = 488$ nm; $\epsilon_{\max} = 1185$ M⁻¹cm⁻¹) resulted in hypsochromic shift of $\Delta\lambda_{\max} = 15$ nm. This is due to the less extensive π -delocalization and less conjugation in the pyridine ring. The visible absorb-maximum of dye **24a** [A = 1-ethyl pyridin-4-ium salt, B = 1-ethyl-quinolin-4-ium salt] showed ($\lambda_{\max} = 390$ nm; $\epsilon_{\max} = 1881$ M⁻¹cm⁻¹). Substituting of [A = 1-ethyl pyridin-4-ium salt, B = 1-ethyl-quinolin-4-ium salt] in dye **24a** by [A = 1-ethyl pyridin-4-ium salt, B = 1-ethyl pyridin-4-ium salt] in dye **24b** exhibit ($\lambda_{\max} = 355$ nm; $\epsilon_{\max} = 1721$ M⁻¹cm⁻¹) resulted in hypsochromic shift of $\Delta\lambda_{\max} = 35$ nm. This is due to the decreasing π -delocalization and less conjugation in pyridine ring. Substituting of [A = 1-ethyl pyridin-4-ium salt, B = 1-ethyl pyridin-4-ium salt] in dye **24b** by [A = pyridin-4-ium salt, B = 1-ethyl-quinolin-4-ium salt] in dye **24c** exhibit ($\lambda_{\max} = 425$ nm; $\epsilon_{\max} = 2199$ M⁻¹cm⁻¹) resulted in bathochromic shift of $\Delta\lambda_{\max} = 35$ nm. This is due to the more extensive π -delocalization and extensive conjugation in the quinoline ring. Substituting of [A = pyridin-4-ium salt, B = 1-ethyl-quinolin-4-ium salt] in dye **24c** by [A = 1-ethyl-quinolin-4-ium salt, B = 1-ethyl pyridin-4-ium salt] in dye **24d** exhibit ($\lambda_{\max} = 415$ nm; $\epsilon_{\max} = 2105$ M⁻¹cm⁻¹) resulted in hypsochromic shift of $\Delta\lambda_{\max} = 25$ nm. This is due to both less extensive π -delocalization and conjugation in pyridine ring. On comparison of the absorption spectra of 2[3-Methyl-1-phenyl-pyrazolin-5-imine]-N-bridge head indolizin (benz-indolizin)-zero-1[4(1)] methine cyanine dyes (**23a-d**) and 2[3-Methyl-1-phenyl-pyrazolin-5-N-acetyl-imino]-3-

acetyl-N-bridge head indolizin (benzindolizin)-zero-1[4(1)] methine cyanine dyes **24a-d**. Observed that dyes **23a-d** giving higher values of λ_{\max} than dyes **24a-d**. This can be explained from the extending of π - delocalization through three rings in case of dyes **24a-d**. On comparison of the absorption spectra 2[3-Methyl-1-phenyl-pyrazolin-5-N-acetyl-imino]-3-acetyl-N-bridgehead indolizin (benz-indolizin)-zero-1[4(1)] methine **24a** and reported 3-methyl-1-phenyl-pyrazolin-5-imino-4(2)-indolizine (benzoindolizine)-zero-3(4)-methine cyanine dye **28** [13], it was obvious that the former dye (**24a**, $\lambda_{\max} = 390$ nm, $\epsilon_{\max} = 1881$ M⁻¹cm⁻¹) showed a hypsochromic shift of 80 nm than the reported dye (**28**, $\lambda_{\max} = 470$ nm, $\epsilon_{\max} = 11435$ M⁻¹cm⁻¹). This is due to the presence of an acetyl group in an pyrazolin-5-imine group in dye causes an antagonistic effect for CT absorption band for such former new dye. The absorption spectra of N-bridge head indolizin (benzoindolizin)-bis-zero-1,3 [4(1)]methine cyanine dyes **25a-c** in 95% ethanol showed absorption bands undergo batho(hypso)chromically shifted depending upon the nature of heterocyclic quaternary residue B and their linkage position. Thus, the visible absorb-maximum of dye **25a** [B = pyridin-4-ium ethiodide] showed $\lambda_{\max} = 500$ nm. Substitution of [B= pyridin-4-ium ethiodide] in dye **25a** by [B=quinolin-4-ium ethiodide] in dye **25b** resulted in bathochromic shift of absorption bands $\Delta\lambda_{\max} = 35$ nm concomitant with an increasing in their numbers in dye **25b**. This is due to the more extensive and extra conjugated π -delocalization in the quinoline ring. Additionally, changing the linkage position of pyridin-4-ium salt in dye **25a** to quinolin-4-ium salt in dye **25c** causes bathochromic shift of $\Delta\lambda_{\max} = 15$ nm. This is due to the extended of π -delocalization within quinolin-4-ium salt in dye **25c**. There is great relation between color and changing structure of the synthesized dyes **21b**, **23d** & **25b**, from faint red to red then dark red for bis-zero-methine cyanine dyes and synthesized dyes **21b**, **24d** & **26b** changing of the structure from faint red to pale brown then violet for (**26b**) dye. The absorption spectra of N-bridge head indolizin (benz-indolizin)-zero-1[4(1)]-(3- β -methyl-di)-[2(4)] methine cyanine dyes **26a-c** in 95% ethanol showed absorption bands undergo batho (hypso) chromically shifted depending upon the nature of heterocyclic quaternary residue A and their linkage position. Thus, the visible absorb-maximum of dye **26a** [A = pyridin-2-ium ethiodide] showed $\lambda_{\max} = 480$ nm. Substitution of [A= pyridin-2-ium ethiodide] in dye **26a** by [A= quinolin-2-ium ethiodide] in dye **26b** resulted in bathochromic shift of $\Delta\lambda_{\max} = 25$ nm concomitant with an increasing number of absorption bands in dye **26b**. This is due to the more extensive and extra conjugated π -delocalization in quinoline ring. Changing the linkage position of pyridin-2-ium salt in dye **26a** to pyridin-4-ium analogue salt in dye **26c** causes bathochromic shift of $\Delta\lambda_{\max} = 15$ nm. This is due to the extended of π -delocalization within pyridine-4-ium ethiodide in dye **26c**. On comparison between the absorption spectra of N-bridgehead indolizin (benzoindolizin)-bis-zero-1,3 [4(1)]methine **25a-c** & N-bridge head indolizin (benz-indolizin)-zero-1[4(1)]-(3- β -methyl-di)-[2(4)] methine cyanine dyes **26a-c**, it was obvious that the latter dyes (**26a-c**) showed absorption band more bathochromic shift relative to that band of dyes **25a-c**. This is due to the long chain chromophore in dyes **26a-c**.

The visible absorb-maximum of dye **28a** [B = 1-ethyl pyridin-4-ium salt] showed ($\lambda_{\max} = 490$ nm; $\epsilon_{\max} = 1951$ M⁻¹cm⁻¹). Substituting of [B = 1-ethyl pyridin-4-ium salt] in dye **28a** by [B= 1-ethyl pyridin-4-ium salt 1-ethyl-quinolin-4-ium salt] in dye **28b** exhibit ($\lambda_{\max} = 530$ nm; $\epsilon_{\max} = 2111$ M⁻¹cm⁻¹) resulted in bathochromic shift of $\Delta\lambda_{\max} = 40$ nm. This is due to the increasing π -delocalization and extensive conjugation in quinoline ring. The visible absorb-maximum of dye **29a** [B = 1-ethyl pyridin-4-ium salt] showed ($\lambda_{\max} = 454$ nm; $\epsilon_{\max} = 1871$ M⁻¹cm⁻¹). Substituting of [B = 1-ethyl pyridin-4-ium salt] in dye **29a** by [B= 1-ethyl pyridin-4-ium salt 1-ethyl-quinolin-4-ium salt] in dye **29b** exhibit ($\lambda_{\max} = 460$ nm; $\epsilon_{\max} = 1884$ M⁻¹cm⁻¹) resulted in bathochromic shift of $\Delta\lambda_{\max} = 6$ nm. This is due to the increasing π - delocalization and extensive conjugation in quinoline ring. 4-Methyl-2[3-methyl-1-phenyl-5-N-acetyl-imino-Spiro-pyrazolin-4, 2- pyrolo [3,4-c] indolizine-zero-1[4(1)]methine cyanine **30** showed ($\lambda_{\max} = 490$ nm; $\epsilon_{\max} = 1781$ M⁻¹cm⁻¹). On comparison of the absorption spectra of 2[3-Methyl-1-phenyl-pyrazolin-5-N-acetyl-imino]-3-acetyl-oxime-N-bridge head indolizin (benz-indolizin)-zero-1[4(1)]methine (**27**), 2[3-Methyl-1-phenyl-pyrazolin-5-N-acetyl-imino]-3-[β -methyl-aza-methine-pyridin-1-ium-chloride salt-N-bridge head indolizin (benz-indolizin)-zero-1[4(1)]methane **28**, 2[3-Methyl-1-phenyl-pyrazolin-5-N-acetyl-imino]-3 [pyrazolo(3,2-a)pyridin]-1-ium-chloride salt-N-bridge head indolizin (benz-indolizin)-zero-1[4(1)] methine **29a,b**, 4-Methyl-2[3-methyl-1-phenyl-5-N-acetyl-imino-Spiro-pyrazolin-4, 2-pyrolo [3,4-c] indolizine-zero-1[4(1)]methine cyanine dye **30** & 2[3-Methyl-1-phenyl-pyrazolin-5-imine]-N-bridge head indolizin (benzoindolizin)-zero-1[4(1)] methine cyanine dyes **23a-d**, 2[3-Methyl-1-phenyl-pyrazolin-5-N-acetyl-imino]-3-acetyl-N-bridge head indolizin (benz-indolizin)-zero-1[4(1)] methine cyanine dyes **24a-d** Observed that dyes (**27**, **28** , **29a,b** & **30**) giving higher values of λ_{\max} than dyes (**23a-d**, **24a-d**). This can be explained from the extending of π - delocalization through three rings in case of dyes **24a-d**.

**2) Solvatochromic behavior (solvatochromism)**

The colour changes of cyanine dyes with solvents (solvatochromism) was previously discussed by [14, 15] to correlate the effect of structure on molecular orbital energy levels. It is clear that the type of substituents and the solvent polarity change the electron densities of cyanine dyes. Solvatochromic dyes generally exhibit steady bathochromic (positive solvatochromism) or hypsochromic (negative solvatochromism) shifts in solvents of various polarities. Cyanine dyes are also ascribed a large change in dipole moment upon excitation due to the relative contribution of both dipolar zwitterionic benzenoid and neutral quinoid forms [16- 19]. Therefore, these dyes have been used by various workers to establish empirical relationships of solvent polarity. The solvatochromism is caused by differential solvation of the ground and Franck-Condon excited state, due to the absorption of electromagnetic radiation in the UV-vis region. If the ground state is more stabilized than the excited state due to solvation by solvents of increasing polarity, negative solvatochromism is exhibited and vice versa. According to the Franck-Condon principle, [20] the time required for molecules to be excited is much smaller than that required to execute vibration or rotation. Therefore, the first excited state of the molecule in solution, called the Franck-Condon excited state, has the same solvation pattern as in the corresponding ground state, called the equilibrium ground state. The first Franck-Condon excited state is much more dipolar than the ground state due to intramolecular charge transfer upon excitation. Stabilization of the Franck-Condon excited state before and after relaxation to the equilibrium excited state and the destabilization of the Franck-Condon ground state relative to the equilibrium ground state by differential solvation leads to the positive solvatochromism. Positive solvatochromism is more sensitive to changes in solvent polarity than the corresponding absorption band in suitable cases. The visible absorption spectra of some selected of newly synthesized cyanine dyes is discussed. Such dyes are **25b** and **26b**. The absorption spectra of the cited cyanine dyes **25b** and **26b** in the wavelength range 400-700 nm have been studied in different organic solvents (H₂O, DMF, EtOH, acetone, CCl₄, CHCl₃ & C₆H₆) respectively. The colour changes of these dyes with solvents having different polarities. This is constructed with the intention to illustrate the solvatochromic behaviour of these dyes (λ_{max} and ϵ_{max}) values of the intramolecular charge transfer bands are given in [Table 2]. These dyes are showed positive solvatochromism with increased solvent polarity, which depend on the structure and the type of dye. This indicates that the polar excited states of these cyanine dyes are stabilized by polarization interaction forces as the polarizability of the solvent is increased. This 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, CHCl₃, & CCl₄. 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 CHCl₃, & CCl₄ 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 CHCl₃ 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 CHCl₃ & CCl₄ 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, **Figs.1 a, b**.

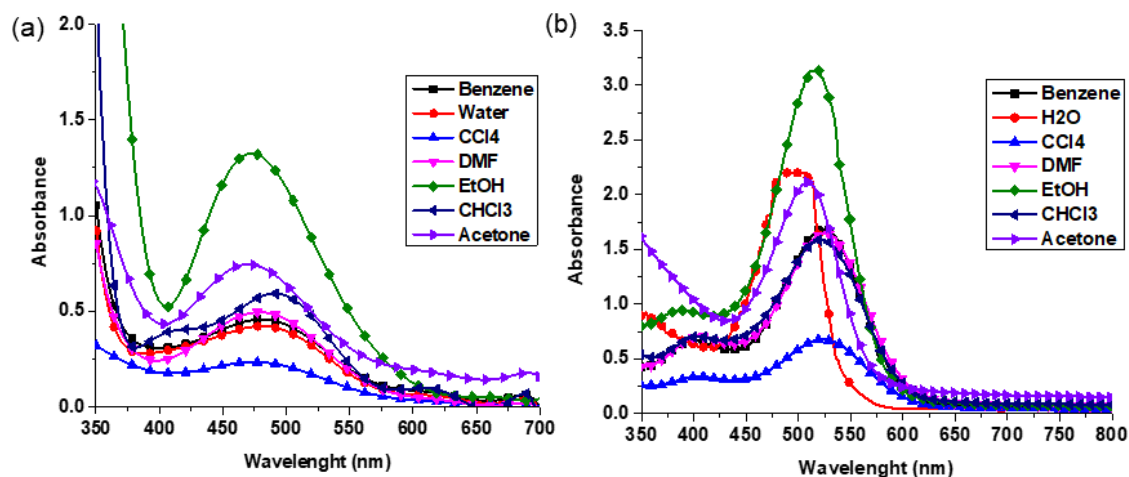


Fig. 1 a, b: Vis. spectra of dyes 25b and 26b in pure organic solvents

 Table 2: Values of absorption (nm) and extinction coefficients ($M^{-1} cm^{-1}$) of dyes 25b and 26b in pure organic solvents

Solvent	25b		26b	
	λ_{max}	ϵ_{max}	λ_{max}	ϵ_{max}
C₆H₆	481	4580	527	6782
Water	481	4225	497	21894
CCl₄	474	2349	524	6782
DMF	478	4949	524	15845
EtOH	474	1324.8	513	31495
CHCl₃	492	5928	521	21193
Acetone	471	7456	508	21193

V. CONCLUSION

All the observations and analytical spectra in this paper support the synthesis of N-bridgehead heterocycles to use it as main entity for a highly stable cyanine dye. The absorption spectra of the synthesized dyes were investigated in different organic solvents. The results indicated that the colour of these dyes depends on the terminal groups and the length of conjugation within the structure. Also, the color of the fluorescence intensity of all dyes depend basically upon the type of dye and solvent used. the UV-Vis absorption spectra of the synthesized cyanine dyes give bathochromic or hypsochromic shifted bands depending on the following factors: a) Increasing and/or decreasing π -delocalization conjugation in the dye molecule b) Presence of electron pushing and/or electron pulling groups c) Higher and/or lower planarity of the dye molecule d) The intensity of the color of the synthesized cyanine dyes is due to two suggested mesomeric structures producing a delocalized positive charge over the conjugated system. The absorption spectra of these dyes in different organic solvents exhibit large solvent effects, which depend on the structure of dye and the type of solvent.

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