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Syntheses and Electronic Absorption Spectra of Some New Penta- and Di-Methine Cyanine Dyes

Reda M. Abd El-Aal,* Hassan A. Shindy, and
Ahmed Ibrahim M. Koraiem

Chemistry Department, Aswan Faculty of Science, Aswan, Egypt

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ABSTRACT

*The reaction of a ratio of 1 mole of 5-chloro-3-methyl-1-phenyl pyrazolo-4[2(4)]-dimethine cyanine (***1a,b***) or (5-chloro-4-formyl-3-methyl-1-phenylpyrazole)* **2** *with 2 moles of an appropriate 2(4)-heterocyclic quaternary salt afforded the novel pentamethine cyanine dyes (***3a–3e***). Other reactions of* **2** *with heterocyclic nitrogen bases, followed by condensation of the newly formed quaternary nitrogen salts (***4a–4c***) with methoheterocyclic iodide salts provided the corresponding unsymmetrical dimethine cyanine dyes (***5a–5g***). The new pentamethine and dimethine cyanine dyes were identified by elemental analyses and IR and* ^{1}*H-NMR spectral data. The visible absorption spectra of some selected dyes were investigated in pure and mixed solvents as well as in universal buffer solutions. The measure of the variation of absorbance with pH was utilized for the determination of the* pK_a *values for compounds* **3b, 3d, 3e, 5e***, and* **5f***, and these data are discussed. © 1997 John Wiley & Sons, Inc. Heteroatom Chem* **8***: 259–266, 1997.*

INTRODUCTION

Varieties of methine cyanine dyes incorporating the pyrazole moiety have been reported [1–3]. Polymethine cyanine dyes have many vital applications, such as their use as photosensitizers in photographic processes [4], in optical recording media [5], in silver halide emulsions [6], and as laser sensitive electrophotographic lightograph printing plate materials [7]. The object of this investigation is to report the synthesis, electronic absorption spectra in ethanolic solution, solvatochromic, and acid-base behavior of new polymethine cyanine dyes, which have not been reported in the literature. We are comparing them with cyanine dyes previously reported [1–3], in the hope that we might discover new photosensitization effects. A correlation has been established between molecular structure and spectral behavior of the synthesized compounds. Solvatochromic and acid-base behavior were investigated in order to make suitable selections for their applications as photosensitizers.

RESULTS AND DISCUSSION

Reaction of a ratio of 1 mole amount 5-chloro-3-methyl-1-phenylpyrazolo-4[2(4)]-dimethine cyanine (**1a,b**) or 5-chloro-4-formyl-3-methyl-1-phenylpyrazole **2** [8] with 2 mole amounts of a 2(4)-methyl quaternary salt (ethylpyridinium or ethylquinolinium iodide) in the presence of acetic anhydride afforded the corresponding pentamethine cyanine dyes (**3a–3e**). The formation of **3a–3e** is assumed to take place by either of two routes, as shown in Scheme 1. The starting material **2** was also selected as a key intermediate for preparing pyridinium, quinolinium, and isoquinolinium chlorides (**4a–4c**). The formation of

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*To whom correspondence should be addressed.

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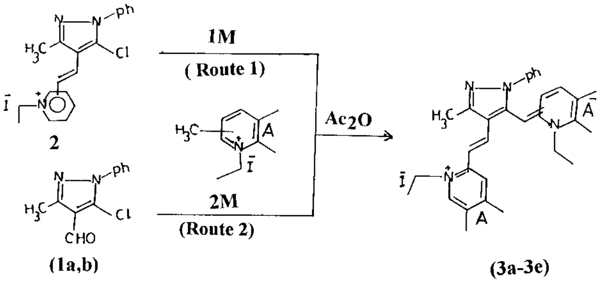
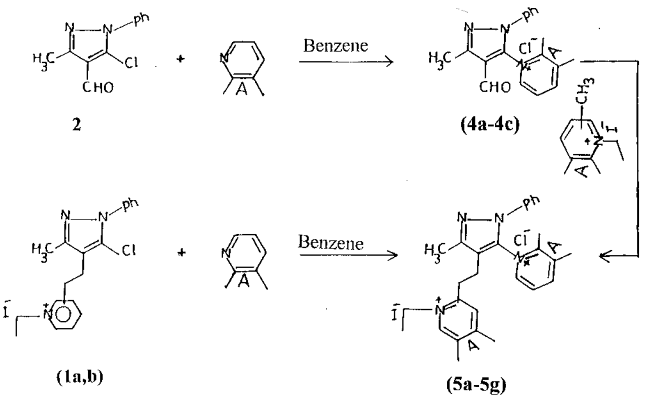


(3a-3e):-
A=Ā=1-ethylpyridinium-2-yl salt (a)
A=Ā=1-ethylquinolinium-2-yl salt (b)
A=Ā=1-ethylpyridinium-4-yl salt (c)
A=1-ethylpyridinium-2-yl salt, Ā=1-ethylquinolinium-2-yl salt (d)
A=1-ethylpyridinium-4-yl salt, Ā=1-ethylquinolinium-2-yl salt (e)

SCHEME 1



(4a-c):-
A=pyridinium-1-yl chloride salt(a), A=quinolinium-1-yl chloride salt(b)
A=isoquinolinium-2-yl chloride salt (c).

(5a-5g):-

4-position	5-position	
A=N-pyridinium chloride;	A=1-ethylpyridinium-2-yl salt	(a)
A=N-pyridinium chloride;	A=1-ethylquinolinium-2-yl salt	(b)
A=N-pyridinium chloride;	A=1-ethylpyridinium-4-yl salt	(c)
A=N-quinolinium chloride;	A=1-ethylpyridinium-2-ylsalt	(d)
A=N-quinolinium chloride;	A=1-ethylquinolinium-2ylsalt	(e)
A=N-quinolinium chloride;	A=1-ethylpyridinium-4-yl salt	(f)
A=N-isoquinolinium chloride;	A=1-ethylquinolinium-2-ylsalt	(g)

SCHEME 2

the new quaternary salts was confirmed by their fusion with potassium iodide to give the corresponding quaternary iodides or by warming in conc. H_2SO_4 to give iodine vapor. Reaction of equimolar amounts of the 4-formyl-3-methyl-1-phenylpyrazole-5(1)-quaternary salts (**4a–4c**) with ethylpyridinium or ethylquinolinium iodide in the presence of acetic anhydride afforded the corresponding 3-methyl-1-phenylpyrazole-5(1)-heterocyclidinium chloride salts 4[2(4)]-dimethine cyanine dyes (5a–5g) Scheme 2.

The structures of compounds **3a–3e**, **4a–4c**, and **5a–5g** were confirmed by elemental analyses (Table 4) and by IR and ^{1}H-NMR spectral data. The pentamethine and dimethine cyanine dyes were highly colored and fairly soluble in polar organic solvents giving a green fluorescence. The dyes were only sparingly soluble in nonpolar solvents. The cyanine dyes were readily soluble in conc. H_2SO_4, liberating iodine vapor on warming. Their ethanolic solutions gave a violet color in alkaline medium that was discharged on acidification.

Effect of Molecular Structure on the Electronic Spectra of the Synthesized Cyanine Dyes

The electronic absorption spectral features (λ_{max} and ε_{max} values) of pentamethine cyanines (**3a–3e**) and dimethine cyanine dyes (**5a–5g**) in ethanolic solutions are depicted in Table 1. Substitution of the A = Ā = 1-ethylpyridinium-2-yl salt moiety in compound **3a** by the A = Ā = 1-ethylquinolinium-2-yl salt moiety in compound **3b** resulted in bathochromic shifts of 10 and 140 nm in the bands at 515 and 645 nm, respectively, accompanied by the appearance of two new shoulders at 410 and 605 nm. This could be attributed to the more extensive π-conjugation in compound **3b**. On the other hand, substitution of the A = 1-ethyl pyridinium-2-yl salt moiety in compound **3a** by the 2-methylquinolinium-2-yl salt moiety in compound **3d** caused a slightly red shift of 7 nm. This may be attributed to the increase in the conjugation of the quinoline ethyl iodide moiety in compound **3d**. These bands are influenced by the type of heterocyclic quaternary salts A,Ā and can be attributed to an electronic transition within the whole molecule associated with intramolecular charge transfer.

The visible absorption spectra of the dimethine cyanines (**5a–5g**) in 95% ethanol undergo bathochromic or hypsochromic shifts depending on the nature of the quaternary residue A in both the 4 and 5 positions. Dyes derived from the quinolinium-2-yl salt either in the conjugated 4-linkage position or from the quinolinium-1-yl(isoquinolinium-2-yl) salts in the 5-linkage position showed bathochromic shifts with an increasing number of absorption bands relative to those from the pyridinium-2(1)-yl salts, at the same linkage position. Thus, substitution of the A = 1-ethyl pyridinium-2-yl salt moiety in compound **5a** by the A = 1-ethylquinolinium-2-yl salt moiety in compound **5b** in the conjugated 4-linkage position brought about a bathochromic shift of 10–25 nm, with an increasing number of absorption bands as the same substituting heterocyclic quaternary-1(2)-yl salts at the 5 position. On the other

TABLE 1 Visible Absorption Spectral[a] Characteristics of Pentamethine (**3a–3e**) and Dimethine (**5a–5g**) Cyanine Dyes in Ethanol at 27°C

*Pentamethine cyanine dyes **3a–3e***

3a	**3b**	**3c**	**3d**	**3e**
395(9.80)	393(12.04)	—	365(9.44)	375(10.40)
—	sh 410(10.64)	410(9.44)	—	—
505(7.72)	515(15.00)	510(3.40)	512(7.44)	515(12.30)
—	605(02.20)	—	—	—
—	645(01.72)	—	—	—

*Dimethine cyanine dyes **5a–5g***

5a	**5b**	**5c**	**5d**	**5e**	**5f**	**5g**
355(2.38)	380(3.60)	365(7.32)	—	—	360(5.14)	375(4.76)
400(0.60)	420(3.20)	405(3.60)	410(5.08)	410(5.20)	405(5.08)	—
—	530(2.40)	520(0.16)	520(1.76)	517(6.00)	522(1.70)	515(5.60)
—	570(2.16)	—	—	600(1.36)	—	600(1.40)
—	595(1.60)	—	—	640(0.48)	—	630(0.48)

[a]Data shown are $\mu_{\max}$ (nm) with $\varepsilon_{\max} = 1 \times 10^{-3}$ (mol^{-1} cm^{2}) in parentheses; sh = shoulder.

hand, changing the linkage position from the 2-yl salt in compound **5a** to the 4-yl salt in compound **5c** caused a bathochromic shift of 5–10 nm. This is due to the extended conjugation in both the heterocyclic quaternary salts and their linkage positions. Also, replacement of the 5-linkage position in compounds **5e** and **5g** by the 4 linkage brought about a bathochromic shift of 30–45 nm. This is due to the more extensive π-conjugation in both quinolinium (isoquinolinium)-1(2)-yl salts, respectively (Table 1). According to the MO interpretation, the excitation corresponds to promotion of an electron from the highest occupied molecular orbital (HOMO), best described by the lone pair of the N-heterocycle of the pyridinium (quinolinium) ring at the 5 position for cyanine dyes **3a**–**3e**, to the lowest unoccupied antibonding molecular orbital (LUMO), centered on the pyridinium (quinolinium) salt [9]. It can be concluded that the substituents are not part of the chromogen, but rather act mainly as perturbing influences in the context that the electron excitation does not extend to the substituents on the N-quaternary salts.

Solvatochromic Behavior of Pentamethine and Dimethine Cyanines 3a, 3b, *and* 3e *and* 5e, 5f, *and* 5g *in Pure Solvents at 27°C*

The electronic absorption spectra of the title cyanine dyes, in the wavelength range 340–700 nm, have been studied in different organic solvents (viz, H_2O, DMF, EtOH, $CHCl_3$, CCl_4, and dioxane) [10] and the results are presented in Table 2. This is constructed with the intention to illustrate the solvatochromic behavior of these compounds. $\lambda_{\max}$ and $\varepsilon_{\max}$ values of the intramolecular and intermolecular charge transfer bands are given in Table 2. It is clear from these data that $\lambda_{\max}$ of the intramolecular charge transfer band exhibits a marked red shift on transfer from nonpolar to polar solvents. This behavior indicates that the polar excited states of these cyanine dyes are stabilized by polarization interaction forces as the polarizability of the solvent is increased. The unexpected blue shift observed in the $\lambda_{\max}$ of these cyanine dyes in ethanol and water may be due to strong electrostatic interactions [H-bonding] of solvent that cause a hypsochromic shift of $\lambda_{\max}$.

Spectra in Mixed Organic Solvents

The visible spectra of compound (**3a**) were measured in DMF–CCl_4 mixtures. This was done in order to study possible H bonding between the solute molecules and an H-bond acceptor solvent. The visible spectrum of compound **3a** in pure CCl_4 displayed a band with $\lambda_{\max} = 385$ nm. On addition of DMF, a new band at ~450 nm appeared, its absorbance increasing as the molarity of DMF was increased. A fine isosbestic point was obtained, indicating the existence of an equilibrium between the solvated complex and the free solute molecules (Figure 1). It shows the solvent effect of one transition band in different solvents (DMF–CCl_4).

Evidence for hydrogen-bond formation between the solute molecules and the mixed solvents was obtained from data on the free-energy change of formation (ΔG) of the molecular complex, calculated by use of the following relationship:

$$\Delta G = -\mathrm{RT} \ln K_f \qquad (1)$$

TABLE 2 Electronic Absorption Spectral[a] Characteristics of pentamethine Cyanine (**3a**, **3b**, and **3e**) and Dimethine Cyanine Dyes (**5e**, **5f**, and **5g**) in Pure Organic Solvents at 27°C

Compd. No.	*Water*	*DMF*	*EtOH*	*CHCl$_3$*	*CCl$_4$*	*Dioxan*
	—	342(4.80)	—	—	—	375(6.70)
3a	sh 440(2.80)	444(7.40)	395(9.80)	395(6.00)	400(5.50)	—
	500(4.00)	530(2.60)	505(7.72)	520(1.60)	500(6.00)	515(2.30)
	—	—	393(12.04)	392(5.48)	—	370(6.24)
	—	420(6.20)	sh 410(10.64)	—	400(5.28)	—
3b	488(1.50)	520(5.00)	520(1.50)	518(6.62)	505(1.40)	510(2.96)
	—	620(1.20)	605(2.20)	600(1.00)	—	—
	—	655(0.64)	645(1.72)	645(0.62)	—	—
	355(8.60)	375(6.30)	375(20.8)	388(16.48)	—	398(4.60)
3e	—	—	—	—	520(3.20)	—
	485(3.10)	—	—	—	465(3.72)	—
	—	525(6.66)	515(24.64)	520(4.60)	510(4.60)	505(7.00)
	365(2.00)	385(6.60)	—	380(2.17)	387(7.56)	380(4.60)
	400(2.30)	405(6.66)	—	400(2.20)	—	—
	—	410(6.45)	410(5.20)	410(2.08)	410(6.60)	410(3.80)
5e	485(1.14)	530(7.22)	517(6.00)	425(2.68)	520(5.16)	515(3.00)
	—	—	600(1.36)	—	—	—
	—	650(1.26)	640(0.48)	650(0.35)	—	—
	—	670(1.14)	—	—	—	—
	375(6.76)	365(8.38)	360(5.14)	370(11.10)	385(14.10)	375(10.89)
5f	395(6.60)	410(7.00)	405(5.08)	382(11.22)	—	—
	—	535(2.60)	522(1.70)	520(03.48)	sh 510(1.80)	sh 510(1.20)
	395(2.40)	400(8.24)	375(4.76)	400(8.88)	395(1.08)	390(4.04)
	—	—	—	—	410(1.03)	—
	—	—	—	—	435(9.20)	—
5g	480(1.10)	—	—	—	465(0.80)	—
	—	530(7.68)	515(5.60)	520(8.32)	510(0.76)	510(3.40)
	—	610(2.72)	600(1.14)	610(2.76)	—	—
	—	655(1.52)	630(0.48)	650(0.80)	—	—

[a] Data shown are λ_{max} (nm) with ε_{max} 1×10^{-3} (mol^{-1} cm^2) in parentheses; sh = shoulder.

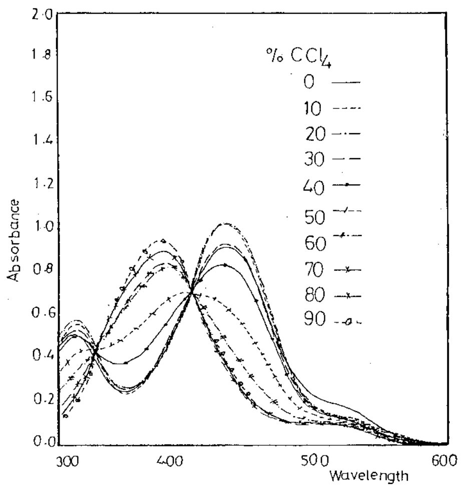


FIGURE 1

The stability constant (K_f) of the complex could be determined from a consideration of the behavior in mixed solvents [11,12] by use of the relationship (2) [13,14]:

$$\text{Log } K_f = \text{Log } [(\text{A} - \text{A}_{\text{min}})/(\text{A} - \text{A}_{\text{max}})] - n \text{ Log } \text{C}_{\text{DMF}} \qquad (2)$$

A least-squares fit was applied to the experimental data, and the values of K_f and ΔG ($K_f = 7.67$ and $\Delta G = 1.11$ Kcal.) and n (the number of solvent molecules that are complexed with the solute molecule) indicated that a 1:1 complex was formed (Figure 2).The plot of $\Delta\nu$ of the CT band as a function of $(D-1)/(D+1)$ for compound (**3a**) is nonlinear (Figure 3). Therefore, the CT band shift is governed by other factors in addition to the dielectric constant (D) of

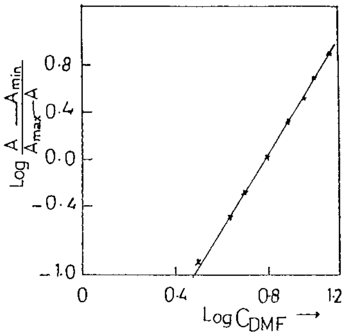


FIGURE 2

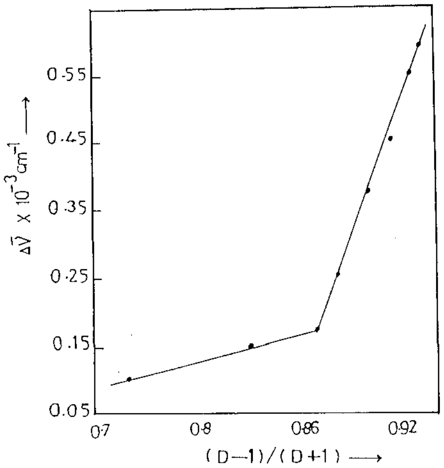


FIGURE 3

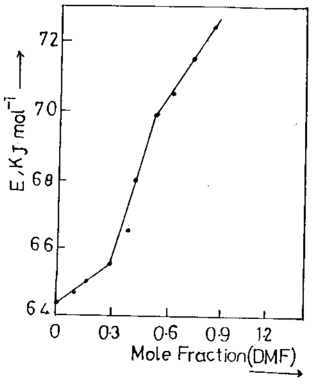


FIGURE 4

the medium. These factors include the solute–solvent interaction.

In a plot of the excitation energy (E) of the CT band in a mixed solvent versus the DMF mole fraction (Figure 4), a broken line with three segments was obtained. The first segment indicates the orientation of the solvent molecules around the solute molecules [14]. The second segment represents the molecular complex formation, while the third segment represents the steady state of the molecular complex [15]. The values of orientation and hydrogen-bond energies are given in Table 3.

TABLE 3 Data Obtained for the Cyanine Dyes **3a** in Mixed Solvents at 27°C

System	*DMF–CCL$_4$*
Excitation energy (KJ mol^{-1})	
Pure DMF	64.27 ± 0.12
Pure CCl$_4$	72.40 ± 0.05
Orientation energy (KJ mol^{-1})	2.65 ± 0.07
Hydrogen-bond energy (KJ mol^{-1})	4.25 ± 0.03
n	1.00 ± 0.01
K_f	7.76 ± 0.08
ΔG (KJ mol^{-1})	1.11 ± 0.06

Acid-Base Behaviors of Pentamethine Cyanines 3b, 3d, *and* 3e *and Dimethine Cyanines* 5e *and* 5f *in Aqueous Universal Buffers at 27°C*

The solutions of the new penta- and di-methine cyanines gave a permanent color in the basic medium that was discharged on acidification. This prompted us to study the spectral behavior of such dyes in aqueous universal buffer solution in order to ensure the optimal pH in the application of these dyes as photosensitizers. The effectiveness of the compounds as photosensitizers increases when they are present in ionic form, which has a higher planarity [16].

The electronic absorption spectra of 3-methyl-1-phenylpyrazole-4,5[2(4)]-pentamethine **3b**, **3d**, and **3e** and/or 4(2)-dimethine-5(1)-heterocylidinium chloride salts **5e** and **5f** in aqueous universal buffer solutions of varying pH values (1.00–12.00) show regular changes with increases in the pH of the medium (Figures 5a–5c). Increasing the pH resulted in an increase in the absorption of the n-π^* and the CT bands. As the pH of the medium was decreased, the extinction coefficient of these bands became lower, and the n-π^* bands showed a blue shift in $\lambda_{\max}$. This behavior can be interpreted on the basis that the hetero-nitrogen atom becomes protonated at lower pH, and therefore, the CT interaction is inhibited. The protonated form does not absorb in the visible region. On the other hand, as the pH is increased, the hetero-nitrogen atom becomes deprotonated. Therefore, mesomeric interaction with the rest of the molecule is enhanced, and consequently, the CT interaction within the free base is facilitated, and the free base absorbs in the visible region.

The spectrophotometric determination of the dissociation and protonation pK_a values of these

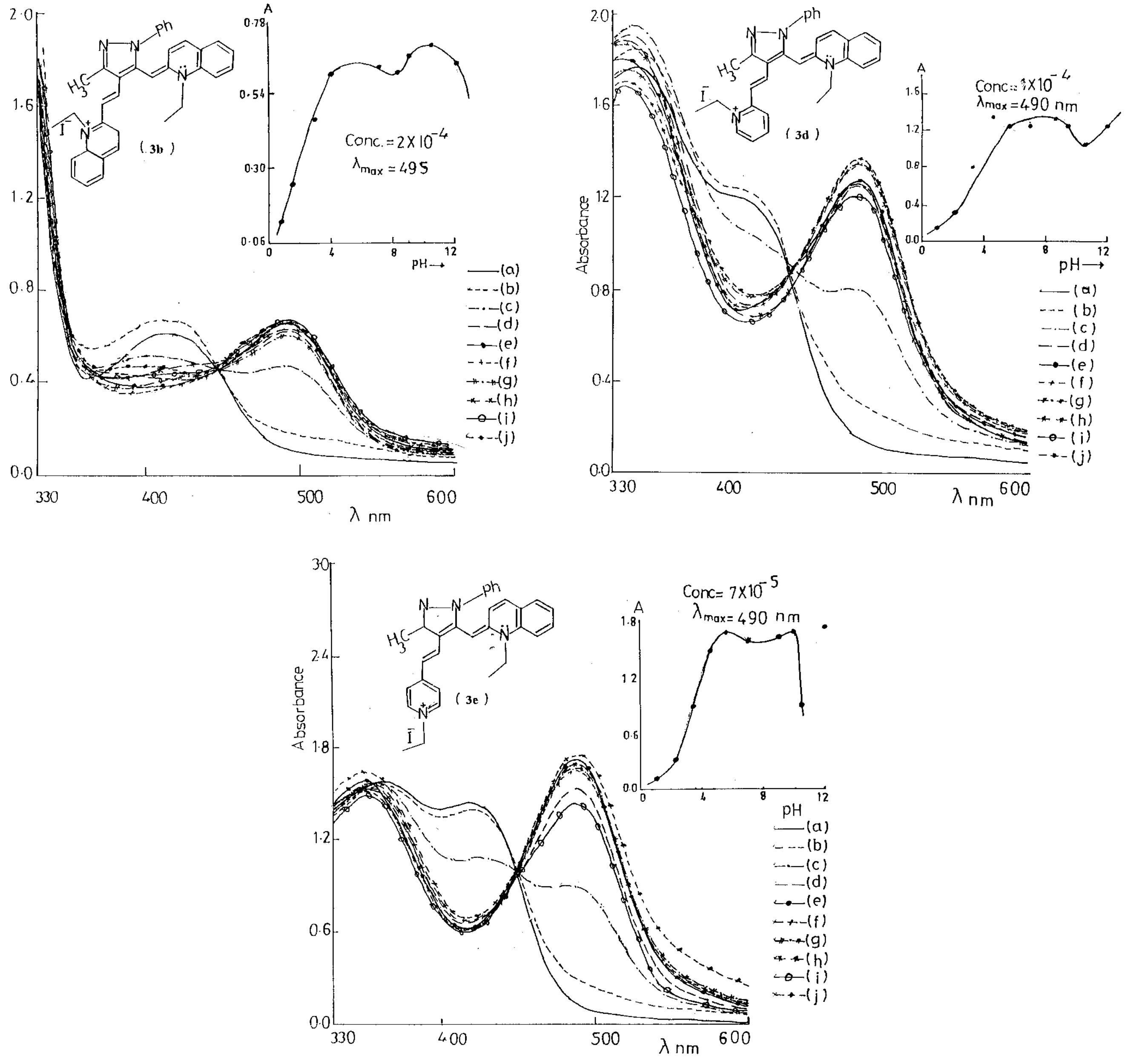


FIGURE 5

compounds can be utilized through the variation of the absorbance with pH values. Thus, the absorbance–pH curves are typical dissociation curves, supporting an acid-base equilibrium. The acid dissociation constants (pK_a) of the compounds were determined from variation of the absorbance with pH using the spectrophotometric half-light, limiting absorbance and Colleter methods [17–20]. In view of spectral behavior in aqueous universal buffer solution and the determination of pK_a values of the newly synthesized pentamethine and dimethine cyanines, the appearance of the ionic (nonprotonated) forms at lower pH indicates that the synthesized cyanine dyes are more basic in character (more photosensitive). Thus, the results of the absorption values of compounds (**3b**, **3d**, and **3e**) at pH > 3.43 represent the absorption of the ionic (nonprotonated) form of such dyes, and these dyes reveal pK_a = 5.40, 6.98, and 5.4, respectively. The results show that the pK_a values of the pentamethine dyes involving conjugated heterocyclic quaternary salts either as the quinolinium-2-yl salt (**3b**) or the pyridinium-4-yl salt

TABLE 4 Characterization Data for 3-Methyl-1-phenylpyrazolo-4,5[2(4)]-pentamethine Cyanines (**3a–3e**), 4-Formyl-3-methyl-1-phenylpyrazole-5-heterocyclidinium Chloride (**4a–4c**), and 3-Methyl-1-phenylpyrazole-4[2(4)]-dimethine Cyanine (**5a–5g**)

Compd. No.	*MP (°C)*	*Yield (%)*	*Molecular formula (mol. wt.)*	*Elemental analysis % Calculated (Found)*		
				C	*H*	*N*
3a	185	63	$C_{27}H_{29}N_4I$ (536)	60.45(60.38)	5.41(5.51)	10.45(10.55)
3b	219	81	$C_{35}H_{33}N_4I$ (636)	66.04(65.97)	5.19(5.11)	8.81(8.93)
3c	167	65	$C_{27}H_{29}N_4I$ (536)	60.45(60.31)	5.41(5.48)	10.45(10.50)
3d	155	69	$C_{31}H_{31}N_4I$ (586)	63.48(63.44)	5.29(5.31)	9.56(9.61)
3e	177	75	$C_{31}H_{31}N_4I$ (586)	63.48(63.37)	5.29(5.33)	9.56(9.58)
4a	223	72	$C_{16}H_{14}N_3O\ Cl$ (299.5)	64.11(63.98)	3.67(3.71)	14.02(13.95)
4b	245	85	$C_{20}H_{16}N_3O\ Cl$ (349.5)	68.67(68.59)	4.58(4.47)	12.02(12.10)
4c	215	77	$C_{20}H_{16}N_3O\ Cl$ (349.5)	68.67(68.61)	4.58(4.61)	12.02(12.09)
5a	160	58	$C_{24}H_{24}N_4Cl\ I$ (530.5)	54.29(54.33)	4.52(4.49)	10.56(10.51)
5b	180	68	$C_{28}H_{26}N_4\ Cl\ I$ (580.5)	55.88(55.91)	4.48(4.45)	9.65(9.62)
5c	125	66	$C_{24}H_{24}N_4\ Cl\ I$ (530.5)	54.29(54.26)	4.52(4.54)	10.56(10.53)
5d	165	62	$C_{28}H_{26}N_4\ Cl\ I$ (580.5)	55.88(55.86)	4.48(4.47)	9.65(9.69)
5e	170	75	$C_{32}H_{28}N_4\ Cl\ I$ (630.5)	60.90(60.84)	4.44(4.52)	8.88(8.91)
5f	195	65	$C_{28}H_{26}N_4\ Cl\ I$ (580.5)	55.88(55.83)	4.48(4.45)	9.65(9.71)
5g	189	72	$C_{32}H_{28}N_4\ Cl\ I$ (630.5)	60.90(60.93)	4.44(4.41)	8.88(9.01)

(**3e**) at the conjugated 4-linkage position of pyrazole are smaller than those involving the pyridinium-2-yl salt (**3d**). This behavior may be explained on the principle of the higher planarity of the former dyes that favors the intramolecular charge transfer from the nonquaternary nitrogen atom. This suggests that dyes **3b** and **3e** are more sensitive as photosensitizers in acidic medium than is dye **3d**. As was observed in the determination of the pK_a values of pentamethine cyanine dyes **3b**, **3d**, and **3e**, the pK_a values of the dimethine cyanine dyes are 5.8 and 7.4 for compounds **5e** and **5f**, respectively. The results show that the pK_a values of the dimethine cyanine dyes involving a more conjugated quaternary salt, such as quinolinium-2(1)-yl salt (**5e**), are smaller than those of the dyes involving the quinolinium-2(2)-yl salt (**5f**).

EXPERIMENTAL

All melting points are uncorrected. The IR spectra (KBr) were determined on a Perkin-Elmer 127B spectrophotometer. The electronic absorption spectra were recorded on a Shimadzu UV-VIS recording spectrophotometer UV-240 and the ^{1}H-NMR on a EM-390 90 MHZ NMR spectrometer.

Stock solutions of the dyes (1.0×10^{-3} M) were prepared. The solutions used in spectral measurements were obtained by appropriate dilution. For mixed-solvent studies, an accurate volume of a 1.0×10^{-3} M solution of the dye in DMF was added to the required volume of DMF, and the solution made up to 10 mL with the other solvent (CCl_4). For pH studies, an accurate volume of a 1.0×10^{-3} M ethanolic solution of the dye was added to 5 mL of the buffer solution in a 10 mL measuring flask. A modified buffer series derived from that of Britton was used [21].

Synthesis of 3-Methyl-1-phenylpyazole-4,5[2(4)]-pentamethine Cyanine Dyes (3a–3e)

A mixture of 1 mole amount of compounds **1a,b** or **2** [8] and 1 or 2 mole amounts of 2(4)-heterocyclic quaternary salts 0.01 mol (0.02 mol) were dissolved in acetic anhydride (20 mL). The reaction mixture was refluxed for 5–10 minutes, and the excess of acetic anhydride was distilled off. The cooled residue was triturated with ethanol. The mixture was then filtered hot, and the filtrate concentrated and cooled. The precipitated products, after dilution with water, were collected and crystallized from ethanol to give the corresponding compounds **3a**–**3e**. The data for these compounds are listed in Table 4.

IR for **3a.** Absence of νCHO-group at 1750–1700 cm^{-1}, 1625–1585 cm^{-1} [ν (CH = CH)], and 1380 cm^{-1} [ν(CH3)]. ^{1}H-NMR (CDCl$_3$) for **3a** δ = 7.2–6.6 (m, 16 H, arom. + heter. + olefinic protons), 2.8 (t, 3H, CH3), 3.7 (q, 2H, CH2 joined to immonium center), 1.8 (t, 3H, CH3), 2.2 (q, 2H, CH2 joined to nitrogen atom), and 1.4 ppm (s, 3H, CH3-pyrazole).

IR for **3b.** Absence of CHO group at 1750–1700 cm^{-1}, 1625–1580 cm^{-1} [ν (CH = CH)], and 1380 cm^{-1} [ν(CH3)]. ^{1}H-NMR (CDCl$_3$) for **3b** δ = 7.8–6.8 (m, 18H, arom. + heter. + olefinic protons), 2.7 (t, 3H, CH3), 3.7 (q, 2H, CH2 joined to immonium center), 1.9 (t, 3H, CH3), 2.3 (q, 2H, CH2 joined to nitrogen atom), and 1.4 ppm (s, 3H, CH3 pyrazole).

Synthesis of 4-Formyl-3-methyl-1-phenylpyrazole-5(1)-quaternary Salts (4a–4c)

Equimolar amounts of compound **2** and pyridine, quinoline, and/or isoquinoline (actually, 0.01 mol) were dissolved in benzene. The reaction mixture was refluxed for 30 minutes. The benzene was then evaporated, and the residual precipitates were crystallized from ethanol to give the corresponding compounds **4a**–**4c**. The results are listed in Table 4.

IR for **4a.** 1750–1700 cm^{-1} [ν(CHO)] and 1380 cm^{-1} [ν(CH3)]. ^{1}H-NMR (CDCl$_3$) for **4a** δ = 10.2(s, 1H, CHO-), 6.5–7.2 (m, 10 H, arom. + heter. protons) and 1.4 (s, 3H, CH3-pyrazole).

Synthesis of 3-Methyl-1-phenylpyrazole-5(1)-heterocyclidinium Chloride-4[2(4)]-dimethine Cyanine Dyes (5a–5g)

Equimolar amounts of compounds **4a**–**4c** and 2(4)-methyl quaternary salts (α (γ)-picoline and/or quinaldine ethiodide) (0.01 mol) were dissolved in acetic anhydride (20 mL) during 5–10 minutes, the excess of the acetic anhydride distilled off. The residue was triturated with ethanol, filtered hot, and the filtrate concentrated and cooled. The precipitated products obtained by dilution with water were collected and crystallized from ethanol to give the corresponding compounds **5a**–**5g**. The results are listed in Table 4.

IR for **5a.** Absence of CHO-group at 1750–1700 cm^{-1}, 2980–2940 cm^{-1} [ν(ethiodide)], 1625–1580 cm^{-1} [ν(CH = CH)], and 1380 cm^{-1} [ν(CH3)]. ^{1}H-NMR (CDCl$_3$) for **5a** δ = 6.5–7.4 (m, 16H, arom. + heter. + olefinic protons), 3.7 (q, 2H, CH2 joined to immonium center), 2.8 (t, 3H, CH3 of ethyl iodide), and 1.4 (s, 3H, CH3-pyrazole).

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