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Electronic Absorption Spectra of New γ -Keto-dimethine Cyanine Dyes and Apocyanines

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New asymmetrical γ -keto-dimethine cyanines (2_{a-f}) were prepared through the condensation of phenyl glycosal derivatives (1_{a-e}) with 2-methyl pyridinium (quinolinium)-2yl salts. Such dyes were converted into the corresponding dyes (3_{a-g} and 4_{a-d}) by cyclocondensation with hydrazines or hydroxylamine hydrochloride under suitable conditions. The new synthesized cyanines were identified by elemental and spectral analyses. The UV-visible absorption spectra of some selected dyes were investigated in pure and mixed solvents as well as in aqueous buffer solutions. Molecular complex formation with ethanol was verified by mixed solvent studies. Electronic transitions were attributed to either locally excited or predominantly charge transfer states. The spectral shifts were discussed in relation to molecular structure and in terms of medium effects. The variation of absorbance with pH was utilized for the determination of the pK_a value for a selected compound (2_e). The photostability of some selected dyes (2_e, 3_g and 4_d) was investigated.

INTRODUCTION

Dimethine cyanine dyes have various applications as photosensitizers in photographic processes¹ and as corrosion inhibitors.² Apocyanine dyes possess, also, various bactericidal activities.³ In the present investigation, new γ -keto-dimethine cyanines (2_{a-f}) and their converted apocyanines (3_{a-g} and 4_{a-d}) were prepared to study their spectral behaviour for their possible photosensitization and to study their sol-

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vatochromic-, acid-base behaviour. Photostability of some selected dyes (2_e, 3_g and 4_d) was also studied to help appropriate selection for their application as photosensitizers.

EXPERIMENTAL

All melting points are uncorrected. The IR spectra were determined with a Perkin Elmer Infrared 127 B spectrophotometer. The UV-visible absorption spectra were recorded on a Shimadzu UV-Vis recording spectrophotometer UV-240. The ¹H NMR spectra were recorded with a KEM-390 90 MHz NMR spectrometer.

Phenyl glycosal derivatives (1_{a-e}) were prepared in a way similar to that described earlier.⁴

Solutions

The stock solutions of the dyes were of the order 10⁻³ M. Solutions of low molarities used in spectral measurements were obtained by accurate dilution.

An accurate volume of 10⁻³ M ethanolic solution of the dye was placed in a 10 ml measuring flask containing the required volume of ethanol, then completed to the mark with the other solvent (CHCl₃ or H₂O) to study the spectral behaviour in mixed solvents.

An accurate volume of 10⁻³ M ethanolic solution of the dye was added to 5 ml of buffer solution in a 10 ml measuring flask and then completed to the mark with redistilled water. The pH of this solution was checked before spectral measurements. A modified buffer series derived from that of Britton²² was prepared.

A fresh ethanolic solution (10⁻³ M) of the dye was prepared, then diluted to (1.0x10⁻⁴ M) in a 10 ml measuring flask and exposed to the light source (white lamp 100 W). The solution used in spectrophotometric measurements was kept at (27.0±0.5)°C and measured at time intervals.

1. Synthesis of γ -Keto-dimethine Cyanine Dyes (2_{a-f})

To a warm solution of dissolved equimolar amounts of phenyl glycosal (1_{a-e}) and methyl quaternary salts (α -picoline- or quinaldine ethiodide), 0.01 mol in ethanol (30 ml), aqueous alcoholic NaOH solution (50% (v/v)) was added dropwise with stirring. After complete addition, the solution was stirred for 3 hrs. Then the products were filtered and recrystallized from ethanol to give (2_{a-f}). The results are listed in Table I-I. IR($\nu_{\text{max}}^{\text{KBr}}$ cm⁻¹) for 2_b, 3000-2970 cm⁻¹ (ν EtI), 1670 cm⁻¹ (ν C=O), 1600 cm⁻¹ (ν C=C) and 3500 cm⁻¹ (ν OH enol). ¹H NMR (CDCl₃) for (2_e), δ 6.9-6.1 ppm (m, 12 H, arom. + heter. + olefinic protons), δ 5.2 ppm (s, 1 H, enolic OH), δ 2.7 ppm (q, 2H, CH₂I), δ 5.7 ppm (s, 1 H, C=CH) and δ 1.7 ppm (t, 3H, CH₃).

2. Apocyanine Dyes (3_{a-g} and 4_{a-d}):

a) *Synthesis of saturated N-ethyl-2-azolyquinolinium salts (3_{a-g}).* - Equimolar amounts of (2_{a-e}) and hydrazine, phenyl hydrazine and/or hydroxylamine hydrochloride (0.01 mol) were dissolved in AcOH (30 ml) and refluxed for 8-10 hrs. The reaction mixture was filtered hot, the filtrate was concentrated and then cooled. The precipitated products after dilution with water were collected and recrystallized from the appropriate solvent, yields 19-31%. The results are summarized in Table (I-II). IR($\nu_{\text{max}}^{\text{KBr}}$ cm⁻¹) for (3_b) is 2990-2800 cm⁻¹ (ν EtI):

b) *Synthesis of unsaturated N-ethyl-2-azolyquinolinium salts (4_{a-d}).* - 1. To a mixture of (2_a or 2_e) (0.04 mol) and hydrazine, phenyl hydrazine and/or hydroxylamine hydrochloride (0.02

mol) in ethanol (50 ml), and alcoholic KOH (0.05 mol/50 ml ethanol)⁸ was added. The reaction mixture was refluxed on a steam bath for 8 hrs. The precipitated products which were formed after concentration were thoroughly washed with water to remove inorganic salts and recrystallized from absolute ethanol to give greenish crystals of (4_{a-d}), yield 34-58%. The results are summarized in Table I-III.

2. Equimolar amounts of (3_a and 3_{e-g}, 0.01 mol) and the corresponding γ -keto-dimethine cyanine (2_a or 2_e, 0.01 mol) were dissolved in ethanol (50 ml), to which an alcoholic KOH solution (0.02 mol/50 ml ethanol) was added. The reaction mixture was refluxed for 6 hrs. The precipitated products were collected, washed with warm water and recrystallized from absolute ethanol to give the same products (4_{a-d}) having the same m.p's and the other physical properties. The results are given in Table I-III. IR($\nu_{\text{max}}^{\text{KBr}}$ cm⁻¹) for (4_d) is 1600 cm⁻¹ ($\nu_{\text{C}=\text{C}}$).

RESULTS AND DISCUSSION

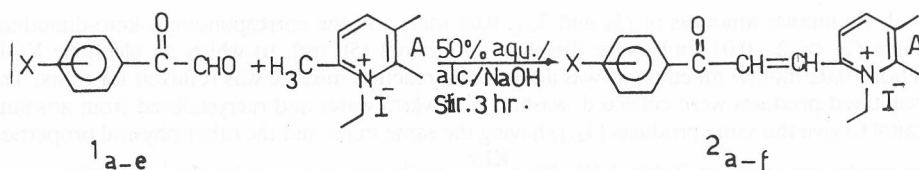
Interaction of phenyl glycosal derivatives (1_{a-e})⁴ with 2-methyl quaternary ammonium salts in 50% aqueous alcoholic NaOH⁵ afforded the corresponding γ -keto-dimethine cyanine dyes (2_{a-f}), Scheme (1). Their structures were confirmed by elemental analysis (Table I-I) IR and ¹H NMR spectral data.⁶ These compounds are coloured, soluble in non-polar and polar solvents, exhibiting slight green fluorescence and release iodine on warming with conc. H₂SO₄. The colour of their ethanolic solutions is discharged on acidification.

γ -Keto-dimethine cyanines (2_{a-f}) when cyclocondensed with hydrazines or hydroxylamine hydrochloride afforded the corresponding apocyanines (3_{a-g} and 4_{a-d}). The cyclocondensation reaction products depend upon the molarity of γ -keto-dimethine cyanines and on the nature of the catalyst used. Thus, the interaction of equimolar of γ -keto-dimethine cyanines and hydrazines or hydroxylamine hydrochloride in the presence of AcOH⁷ gave the corresponding saturated N-ethyl-2-azolyquinolinium salts (3_{a-g}), Table I-II, while the interaction of γ -keto-dimethine cyanines with hydrazines or hydroxylamine hydrochloride (2:1 molar ratios) in the presence of KOH⁸ afforded the corresponding unsaturated N-ethyl-2-azolyquinolinium salts (4_{a-d}), Table I-III. This reaction appears to proceed via dehydrogenation process of dihydro azolyl group.⁹ This suggestion was confirmed by the interaction of (3_a and 3_{e-g}) with excess of the corresponding γ -keto-dimethine cyanine (2_a or 2_e) to give the same isolated compounds (4_{a-d}), Scheme 1. The structures of these compounds (2_{a-g}, 4_{a-d}) were confirmed by elemental analyses (Table I) and IR spectra. The compounds (3_{a-g}) are fairly soluble in most polar and non-polar organic solvents with no fluorescence while the corresponding apocyanine derivatives (4_{a-d}) are coloured in solutions, exhibiting intense green to blue fluorescence depending upon the organic solvent used. They are soluble in conc. H₂SO₄, releasing iodine vapour on heating.

Relation Between Molecular Structure and Spectral Behaviour of the Synthesized Cyanines

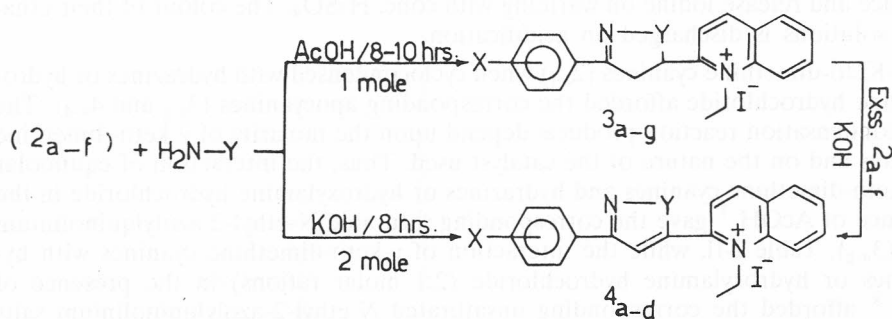
The visible absorption spectra of γ -keto-dimethine cyanines (2_{a-f}) in ethanol possess different absorption bands. The λ_{max} and ϵ_{max} values of these bands are collected in Table II-I. Substituting A=H in (2_f) by A= C₆H₄-2yl salt moiety in (2_e) causes a red shift of 13 nm with intensification of the longer wavelength band at

542 nm. This can be attributed to the higher coplanarity of (2_e) resulting from the greater bulk of the quaternary heterocyclic moiety attached to the -CH=CH- centre. This leads to a strong interaction of the electrons within the molecule and hence a lower excitation energy is required. On the other hand, the shoulder located at



(1_{a-e}): X=H(a), p-CH₃(b), p-OCH₃(c), p-NO₂(d) and p-Cl(e).

(2_{a-f}): A=C₆H₄-2yl-salt; X=H(a), p-CH₃(b), p-OCH₃(c), p-NO₂(d), p-Cl(e) and A=H-2yl-salt; X=p-Cl(f).



(3_{a-g}): Y=NH; ; X=H(a), p-CH₃(b), p-OCH₃(c), p-NO₂(d), p-Cl(e),
Y=N-ph; X=p-Cl(f) and
Y=O ; X=p-Cl(g).

(4_{a-d}): Y=NH ; X=H(a), p-Cl(b),
Y=N-ph; X=p-Cl(c) and
Y=O ; X=p-Cl(d).

Scheme 1.

TABLE I

Characterization of γ -keto-dimethine cyanine dyes (2_{a-t}) and their derived apocyanines (3_{a-g} and 4_{a-d}).

Compound No.	M.P. (°C)	Yield %	Molecular formula (Mol. Wt.)	Elemental analysis		
				Calculated	Found	
			C	H	N	
I. γ -Keto-dimethine cyanines (2 _{a-f})						
2 _a	165	70	C ₂₀ H ₁₈ NOI (415)	57.83 (57.80)	4.34 (4.37)	3.37 (3.35)
2 _b	140	58	C ₂₁ H ₂₀ NOI (429)	58.74 (58.75)	4.66 (4.61)	3.26 (3.30)
2 _c	135	43	C ₂₁ H ₂₀ NO ₂ I (445)	56.63 (56.70)	4.49 (4.46)	3.15 (3.16)
2 _d	140	48	C ₂₀ H ₁₇ N ₂ O ₃ I (460)	52.17 (52.20)	3.70 (3.75)	6.09 (6.13)
2 _e	175	60	C ₂₀ H ₁₇ NOCII (449.5)	53.39 (53.38)	3.78 (3.80)	3.11 (3.09)
2 _f	160	18	C ₁₆ H ₁₅ NOCII (399.5)	48.06 (48.10)	3.75 (3.70)	3.50 (3.55)
II. Apocyanines (3 _{a-d})						
3 _a	210	31	C ₂₀ H ₂₀ N ₃ I (429)	55.94 (55.96)	4.66 (4.70)	9.79 (9.80)
3 _b	215	21	C ₂₁ H ₂₂ N ₃ I (443)	56.88 (56.88)	4.97 (4.92)	9.48 (9.51)
3 _c	212	19	C ₂₁ H ₂₂ N ₃ OI (459)	54.90 (54.92)	4.79 (4.82)	9.15 (9.13)
3 _d	205	21	C ₂₀ H ₁₉ N ₃ O ₂ I (474)	50.63 (50.60)	4.01 (4.08)	11.81 (11.80)
3 _e	192	25	C ₂₀ H ₁₉ N ₃ ClII (463.5)	51.78 (51.80)	4.10 (4.11)	9.06 (9.05)
3 _f	171	30	C ₂₆ H ₂₃ N ₃ ClII (539.5)	57.83 (57.85)	4.26 (4.33)	7.78 (7.70)
3 _g	185	29	C ₂₀ H ₁₈ N ₂ OClII (464.5)	51.67 (51.70)	3.88 (3.92)	6.03 (6.01)
III. Apocyanines (4 _{a-d})						
4 _a	188	34	C ₂₀ H ₁₈ N ₃ I (427)	56.21 (56.26)	4.22 (4.21)	9.84 (9.85)
4 _b	185	44	C ₂₀ H ₁₇ N ₃ ClII (461.5)	52.00 (52.03)	3.68 (3.73)	9.10 (9.11)
4 _c	212	58	C ₂₆ H ₂₁ N ₃ ClII (537.5)	58.05 (58.10)	3.91 (3.88)	7.81 (7.80)
4 _d	195	50	C ₂₀ H ₁₆ N ₂ OClII (462.5)	51.89 (51.93)	3.46 (3.49)	6.05 (6.08)

TABLE II
 Visible absorption spectra characteristics of γ -keto-dimethine cyanine dyes (2-a-f) and their derived apocyanines (3-a-g and 4-a-d) in ethanol at 27°C.

I. γ -Keto-dimethine cyanines (2 a-f)					
2 a	2 b	2 c	2 d	2 e	2 f
$\lambda_{\max} (\epsilon_{\max} \times 10^{-3})$	$\lambda_{\max} (\epsilon_{\max} \times 10^{-3})$	$\lambda_{\max} (\epsilon_{\max} \times 10^{-3})$	$\lambda_{\max} (\epsilon_{\max} \times 10^{-3})$	$\lambda_{\max} (\epsilon_{\max} \times 10^{-3})$	$\lambda_{\max} (\epsilon_{\max} \times 10^{-3})$
nm (cm ² mol ⁻¹)	nm (cm ² mol ⁻¹)	nm (cm ² mol ⁻¹)	nm (cm ² mol ⁻¹)	nm (cm ² mol ⁻¹)	nm (cm ² mol ⁻¹)
400sh(2.9)	400sh(2.9)	400sh(9.3)	400(2.9)	-	400sh(2.4)
-	-	425sh(8.8)	-	-	-
498sh(8.1)	498sh(12.4)	498sh(10.3)	-	-	-
520(12.3)	519sh(13.5)	518(13.1)	525(9.7)	521sh(11.9)	520sh(6.3)
555(19.4)	555(21.1)	558(15.9)	556(15.5)	555(19.1)	542(10.1)
640sh(2.7)	640sh(2.1)	640sh(3.4)	640sh(1.7)	-	-

Table II to be continued

Table II continued

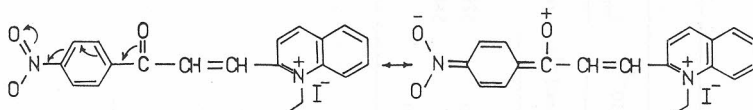
II. Apocyanine dyes (3_{a-g})

3 _a	3 _b	3 _c	3 _d	3 _e	3 _f	3 _g
$\lambda_{\max} (\epsilon_{\max} \times 10^{-3})$	$\lambda_{\max} (\epsilon_{\max} \times 10^{-3})$	$\lambda_{\max} (\epsilon_{\max} \times 10^{-3})$	$\lambda_{\max} (\epsilon_{\max} \times 10^{-3})$	$\lambda_{\max} (\epsilon_{\max} \times 10^{-3})$	$\lambda_{\max} (\epsilon_{\max} \times 10^{-3})$	$\lambda_{\max} (\epsilon_{\max} \times 10^{-3})$
nm (cm ² mol ⁻¹)	nm (cm ² mol ⁻¹)	nm (cm ² mol ⁻¹)	nm (cm ² mol ⁻¹)	nm (cm ² mol ⁻¹)	nm (cm ² mol ⁻¹)	nm (cm ² mol ⁻¹)
-	492sh(6.6)	-	492sh(5.4)	-	-	-
522sh(5.4)	522(8.4)	528sh(6.6)	528sh(6.4)	522sh(5.0)	528sh(4.6)	528sh(5.0)
564(7.9)	552sh(7.0)	565(8.6)	561(8.4)	563(7.8)	560(6.9)	560(7.1)
578(7.9)	-	-	-	578(7.8)	578sh(6.0)	-

III. Apocyanine dyes (4_{a-d})

4 _a	4 _b	4 _c	4 _d
$\lambda_{\max} (\epsilon_{\max} \times 10^{-3})$	$\lambda_{\max} (\epsilon_{\max} \times 10^{-3})$	$\lambda_{\max} (\epsilon_{\max} \times 10^{-3})$	$\lambda_{\max} (\epsilon_{\max} \times 10^{-3})$
nm (cm ² mol ⁻¹)	nm (cm ² mol ⁻¹)	nm (cm ² mol ⁻¹)	nm (cm ² mol ⁻¹)
367(9.6)	366sh(6.5)	-	366(9.7)
419(12.8)	418(9.2)	416sh(9.6)	418(11.2)
435(13.9)	434(9.3)	433(9.4)	435(12.4)
560sh(1.4)	560sh(2.3)	565(6.4)	565(3.2)

518-525 nm is influenced by the nature of the aryl substituents (X) (Table II-I), as well as the solvent nature, which can be attributed to an electronic transition originating from the carbonyl group as a source to the strong electron withdrawing nitro group as a sink (2_d , X=*p*-NO₂). The other substituents (X) have minor effects. The CT that takes place can be represented as follows:



A good linear relationship is obtained on plotting $1/\lambda_{\max}$ (intramolecular CT band) vs the Hammett constant¹⁰ ($-\sigma$) of the substituent X (Figure 1a) supporting the CT nature of this band.

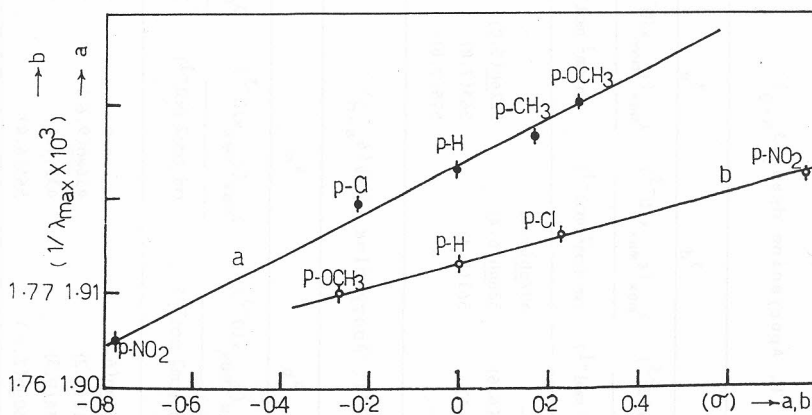


Figure 1. (a) The $1/\lambda_{\max}$ versus $-\text{Hammett constant } (-\sigma)$ plot for the CT bands of compounds (2a-e) in EtOH at 27°C.

(b) The $1/\lambda_{\max}$ versus Hammett constant (σ) plot for the CT bands of compounds (3a-e) in EtOH at 27°C.

The band located at 542-558 nm is largely affected by the solvent polarity and its position is slightly affected by the nature of the aryl substituents (X) (Table II-I). It can be assigned to an intramolecular CT transition originating from carbonyl group as a source to the positively charged heterocyclic quaternary (N) atom as a sink. This intramolecular CT transition can be represented as follows:

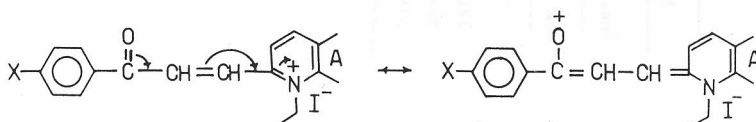
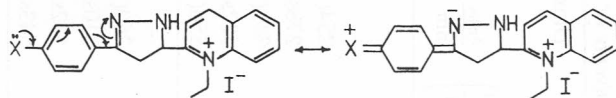


TABLE III
Electronic absorption spectra characteristics of γ -keto-dimethine cyanine dyes (2e and 2f) in pure solvents at 27°C

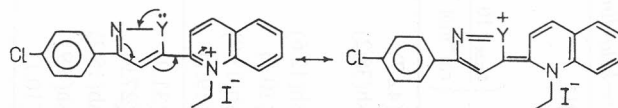
Compound No.	Water	DMF	EtOH	CHCl ₃	CCl ₄	Dioxane
	$\frac{\lambda_{\max}}{\text{nm}} \left(\frac{\epsilon_{\max} \times 10^{-3}}{\text{cm}^2 \text{ mol}^{-1}} \right)$	$\frac{\lambda_{\max}}{\text{nm}} \left(\frac{\epsilon_{\max} \times 10^{-3}}{\text{cm}^2 \text{ mol}^{-1}} \right)$	$\frac{\lambda_{\max}}{\text{nm}} \left(\frac{\epsilon_{\max} \times 10^{-3}}{\text{cm}^2 \text{ mol}^{-1}} \right)$	$\frac{\lambda_{\max}}{\text{nm}} \left(\frac{\epsilon_{\max} \times 10^{-3}}{\text{cm}^2 \text{ mol}^{-1}} \right)$	$\frac{\lambda_{\max}}{\text{nm}} \left(\frac{\epsilon_{\max} \times 10^{-3}}{\text{cm}^2 \text{ mol}^{-1}} \right)$	$\frac{\lambda_{\max}}{\text{nm}} \left(\frac{\epsilon_{\max} \times 10^{-3}}{\text{cm}^2 \text{ mol}^{-1}} \right)$
2e	198(27.7)	—	209(42.7)	—	—	—
	228(22.9)	—	228sh(38.2)	—	—	—
	—	—	—	266(12.6)	261(39.0)	254(27.4)
	275sh(6.1)	—	227sh(12.6)	278sh(11.2)	277sh(31.9)	278sh(20.7)
	318(7.5)	315sh(8.5)	315(10.1)	315sh(8.5)	316(23.0)	315(14.8)
	518sh(3.0)	524sh(10.1)	521sh(11.9)	525sh(10.1)	527sh(7.0)	522sh(8.6)
552(4.3)	559(17.3)	555(19.1)	560(20.2)	563(88.5)	556(12.8)	
2f	206(36.6)	—	210(31.9)	—	—	—
	261(27.6)	—	255(27.9)	270(18.0)	260(16.8)	260(27.5)
	310sh(9.6)	310sh(11.6)	312sh(15.2)	312sh(15.2)	310sh(12.4)	310sh(14.8)
	510sh(1.9)	524sh(6.7)	520sh(8.9)	520sh(7.8)	530sh(4.0)	522sh(1.3)
	538(2.2)	544(9.0)	542(10.1)	550(9.3)	556(4.4)	543sh(0.8)

The visible absorption band of compounds (3_{a-e}) located at 552-565 nm is greatly influenced by the substituent (X) (Table II-II) which can be attributed to an electronic transition from the 4-aryl residue as a source to the N-heteroatom of pyrazoline as a sink. The CT takes place can be represented schematically as follows:



A good linear relationship is obtained on plotting $1/\lambda_{\max}$ (intramolecular CT band) vs the Hammett constant¹⁰ (σ) of the substituent (X) (Figure 1b), supporting the CT nature of this band. Substituting (Y=NH) 3_e by (Y=N-ph) 3_f or (Y=O) 3_g results in a slight blue shift by 3 nm. This can be attributed to the retardation of this type of transition as a result of increasing the electron donating character of the heterocyclic moiety (N-ph or (O) > NH).

The longer wavelength band of apocyanine dyes (4_{a-d}), located at 560-565 nm, is influenced by the type of azolyl group (Table II-III). Thus, substituting (Y=NH) 4_b by (Y=N-ph) 4_c intensifies the absorption band accompanied with a red shift by 5 nm. This may be attributed to the increasing of the mesomeric effect of N-phenyl pyrazolo moiety. Similar behaviour was also noticed for 4_d (Y=O) due to the greater electron density of oxygen atom in isoxazoline moiety. The CT that transition takes place can be represented as follows:



Solvatochromic Behaviour of γ -Keto-dimethine Cyanine Dyes (2_e and 2_f) in Pure Solvents

The λ_{\max} and ϵ_{\max} values of the absorption bands due to different electronic transitions within the solute molecules (2_e and 2_f), obtained in pure solvents of different dielectric constants¹¹ (viz. H₂O, DMF, EtOH, CHCl₃, CCl₄ and dioxane), are represented in Table III.

The spectra of compounds (2_e and 2_f) in ethanol consist of six and five essential absorption bands, respectively. The UV-bands lying up to 315 nm can be assigned to $\pi-\pi^*$ transitions within the benzenoid and heterocyclic rings. These bands are little influenced by changing the polarity of the medium. As reported above, the pronounced shoulder located at 521 and 520 nm in compound (2_e and 2_f), respectively, was attributed to an electronic transition originating from the carbonyl group as a source to the (Cl) atom as a sink. While the visible band located at 555 and 542 nm in 2_e and 2_f , respectively, was attributed to an intramolecular CT transition originating from the carbonyl group as a source to the positively charged heterocyclic quaternary (N) atom as a sink.

Careful examination of the results reported in Table III reveals that the bands corresponding to CT transitions show a red shift on changing the organic solvent from EtOH to dioxane, DMF, CHCl₃ and CCl₄. The unexpected blue shift observed

TABLE IV
 Cumulative data obtained for γ -keto-dimethine cyanine dyes (2e and 2f) in mixed solvents at 27°C.

Compound No.	System	Excit. energy		n	K_f
		Pure solvent	Pure EtOH		
2e	CHCl ₃ —EtOH	213(CHCl ₃)	215	1	0.015
	H ₂ O—EtOH	216(H ₂ O)	215	2	0.042
2f	CHCl ₃ —EtOH	218(CHCl ₃)	221	1	0.196
	H ₂ O—EtOH	224(H ₂ O)	221	2	0.052

in the λ_{\max} of the two CT bands for the two compounds (2_e and 2_f) in ethanol can be mainly explained as a result of intermolecular H-bond formation between ethanol and the lone pair of electrons of the oxygen of the γ -keto group. Thus, the ability of electron releasing power of the γ -keto oxygen is decreased and consequently the observed high excitation energy needed in ethanolic medium relative to the other organic solvents used. The stronger blue shift observed in λ_{\max} of the two CT bands of compounds (2_e and 2_f) in water (dielectric constant = 78.54)¹¹ relative to ethanol (24.3)¹¹, as well as the lower extinction, can be ascribed to the stronger interaction of water molecule with the lone pair of the electrons on the oxygen of the γ -keto group.

Spectral behaviour of 4-chlorophenyl-2-keto-dimethine quinolinium (pyridinium) ethiodide (2_e and 2_f) in mixed solvents

This study was done to test the possibility of formation of H-bonded solvated complex between the solute molecules and ethanol/or water. The visible spectra of compounds (2_e and 2_f) in CHCl₃ and H₂O each containing successively increased quantities of EtOH were studied.

The stability constant (K_f) of the complex can be determined from a consideration of the behaviour¹²⁻¹⁶ in the mixed solvents applied using the previously applied relation (1).^{15,16}

$$\log K_f = \log \frac{A - A_{\min}}{A_{\max} - A} - n \log C_{\text{EtOH}}$$

The values of K_f of the H-bonded molecular complex liable to form in solution between the molecules of compounds (2_e and 2_f) and EtOH/or H₂O are given in Table IV. The values of K_f and n (the number of EtOH/or H₂O molecules which are complexed with the solute molecule) indicate that a 1:1 complex is formed in solution between the molecule and ethanol whereas a 1:2 complex is formed between the solute and water molecules.

Examination of the results reported in Table IV indicates that the ability of EtOH/or H₂O to form solvated complexes depends on the nature of the solute used.

The plots of $\Delta\tilde{\nu}$ of the longer wavelength band as a function of $(D-1)/(D+1)$ ¹⁷ for compounds (2_e and 2_f) are nonlinear. Therefore, the CT band shift is governed by other factors in addition to the dielectric constant of the medium.¹⁸ These factors include solute-solvent interaction.

On drawing the excitation energy (E) of the CT band in the mixed solvent vs the ethanol mole fractions, for compounds 2_e and 2_f, broken lines with three segments are obtained for each. The first segment indicates the orientation of the solvent molecules around the solute molecule. The second one represents the molecular complex formation while the third segment represents the steady state of the energy attained after the complete formation of the molecular complex.

Acid-Base Properties of 2[4-Chlorophenyl]- γ -keto-quinolinium-2-yl-salt Dimethine Cyanine (2_e) in Aqueous Universal Buffers

The solution of some selected γ -keto-dimethine cyanines give a permanent colour in the basic medium discharged on acidification. This prompted us to study the spectral behaviour of one of these compounds in aqueous buffer solution in order to ensure the optimal pH in the application of these dyes. The effectiveness of the compounds as photosensitizers increases when they are present in the ionic form, which has a higher planarity.

The electronic absorption spectra of dye (2_e) in aqueous buffer solutions of varying pHs (1.80-11.58) show regular changes with increasing pH of the medium, especially the CT bands. Increasing the pH of the medium results in increased absorbance of the CT bands. As the pH of the medium decreases, the extinction of these bands becomes lower and disappears at $\text{pH} \leq 3.29$. This behaviour can be interpreted on the principle that the carbonyl group becomes protonated in solution of low pH values and, therefore, the CT interaction within the protonated form is expected to be difficult, i.e. the protonated form does not absorb energy in the visible region. On the other hand, as the pH of the medium increases ($\text{pH} \geq 5.60$), the carbonyl group becomes deprotonated and, therefore, its mesomeric interaction with the rest of the molecule is intensified. Consequently, the CT interaction within the free base is facilitated, i.e. the free base absorbs energy in the visible region.

The recorded visible absorption spectra of compound (2_e) in aqueous buffer solutions of varying pH's were applied to the spectrophotometric determination of the pK_a value. The absorbance-pH curve is a typical dissociation curve, supporting the acid-base equilibrium. The acid dissociation constant (pK_a) was determined from the variation of absorbance with pH using the spectrophotometric half-height, limiting absorbance and Colleter methods.¹⁹⁻²¹ The mean pK_a value is 6.1.

Photostability of Some Selected Synthesized Cyanine Dyes

The photochemical stability of some selected cyanine dyes has been examined to shed some light on the relation between the chemical structure and their photostability. An ethanolic solution ($1.0 \times 10^{-4} \text{M}$) of γ -keto-dimethine cyanine (2_e) and its derived compounds (3_g and 4_d) were irradiated by a white lamp (100 W) for 0-12 hrs for 1-5 days. The photostability was found to be in the order $2_e > 3_g > 4_d$.

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SAŽETAK

Elektronski apsorpcijski spektri novih γ -keto-dimetin-cijaninskih bojila i odgovarajućih apocijanina

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Kondenzacijom derivata fenil-glikosala (1_{a-e}) s 2-metilpiridinijevim ili 2-metilkinolinijevim solima pripremljeni su novi asimetrični γ -keto-dimetin-cijanini (2_{a-f}), a iz njih (ciklokondenzacijom s hidrazin-hidrokloridom ili s hidroksilamin-hidrokloridom) odgovarajuća bojila (3_{a-g}, 4_{a-d}). Snimljeni su UV/VIS spektri odabranih bojila u različitim čistim i miješanim otapalima te u vodenim (puferskim) otopinama. Utvrđeno je nastajanje molekulskih kompleksa u etanolnim otopinama. Opaženi elektronski prijelazi pripisani su dijelom lokalnim ekscitacijama, a dijelom prijenosu naboja. Spektralni pomaci objašnjeni su molekulskom strukturom i (ili) utjecajem medija. Istraživana je i fotostabilnost odabranih bojila (2_e, 3_g, 4_d).