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Electronic absorption spectra of some new heterocyclic azomethines derived from nitroso and active methyl compounds

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Abstract—The electronic spectra of some new heterocyclic azomethines derived from nitroso compounds and active methyl heterocyclic quaternary salts were studied. The main visible band appearing in the spectra of dialkylamino derivatives is assigned to an intramolecular charge transfer (CT) transition. On the other hand the visible spectra of *o*-hydroxy compounds are interpreted on the principle of the possible existence of such compounds in a enol ⇌ keto tautomeric equilibrium. In addition the pK_a values of these compounds were determined and discussed in terms of molecular structure.

INTRODUCTION

Though much work has been carried out on the electronic spectra and dissociation constants of azomethines derived from aldehydes and aliphatic or aromatic amines [1–16], little attention has been paid to similar studies on azomethines containing heterocyclic aromatic rings [17–20]. To interpret the longer wavelength spectra of *o*-hydroxy azomethines, some authors declared that these compounds exist in a tautomeric equilibrium of the type NH/OH [3, 9, 10, 21, 22]. Others suggested that these derivatives have a tendency to form an intermolecular hydrogen bond solvated molecular complex with the solvent [1, 2, 6, 23]. Moreover, MOSKAL and MOSKAL [14] assigned the longer wavelength band to an n–π^* transition involving the lone pair of electrons on the nitrogen atom of the azomethine group.

Therefore, the present investigation was devoted to elucidating the nature of the different absorption bands observed in the spectra of azomethines derived from nitroso compounds and active methyl hetrocyclic

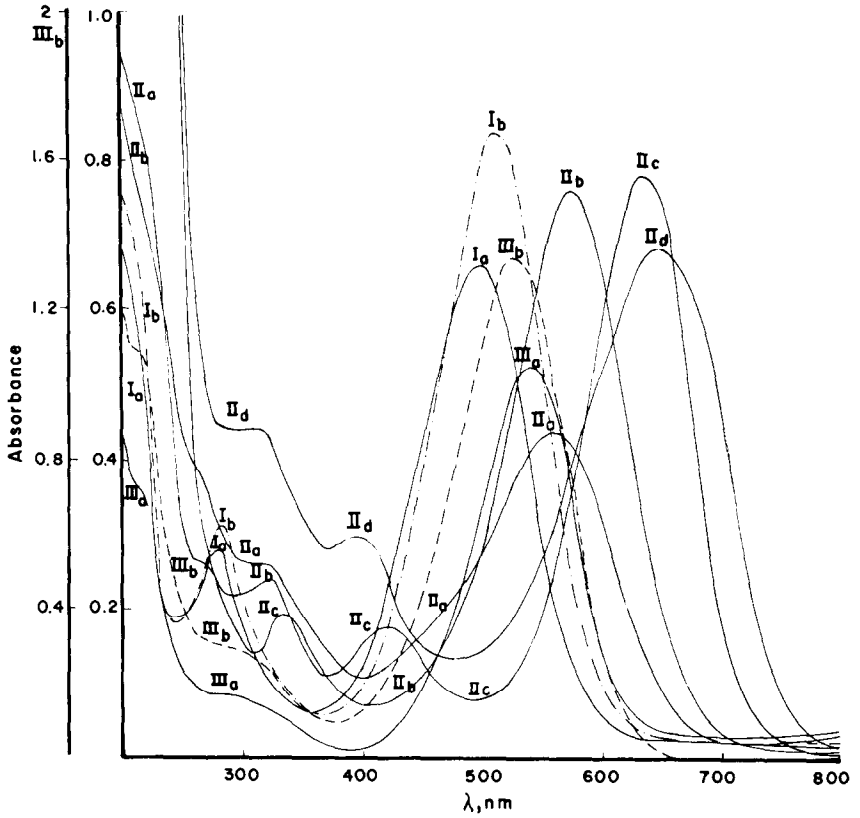

Fig. 1. Electronic absorption spectra of 2.5×10^{-5} M azomethines in ethanol, **Ia** (2.35×10^{-5} M).

quaternary salts. Moreover the acidity constant of these derivatives was determined and is discussed in terms of their molecular structure.

EXPERIMENTAL

Materials

Chemicals of the purest grade available (A. R. products) were used in all experiments. Active methyl heterocyclic quarternary salts were prepared according to methods described before [24, 25]. The azomethines studied were synthesized by condensation of the nitroso aromatic compound with the active methyl quarternary salt in the presence of one drop of piperidine as a base catalyst [26, 27]. The separated solid products were purified by trituration with ether several times. However, prolonged boiling of such compounds during crystallization from alcohol leads to their decomposition. Chemical analysis of the azomethines prepared was in accordance with their composition. Furthermore, i.r. spectra of the compounds exhibit a strong band at 1600 cm^{-1} which is ascribed to C=N stretching. The purity of the synthesized compounds was checked by thin layer chromatography using plates of silica gel. The hetrocyclic azomethines synthesized in this work are: 4-(*N,N*-dimethylamino)-*N*-(1-methylpyridinio-2-methylidene) aniline iodide, **Ia** (m. p. 207°C), 4-(*N,N*-diethylamino)-*N*-(1-methylpyridinio-2-methylidene) aniline iodide, **Ib** (m.p. 189°C), 4-(*N,N*-dimethylamino)-*N*-(1-methylquinolinio-2-methylidene) aniline iodide, **IIa** (m.p. 182°C), 4-(*N,N*-diethylamino)-*N*-(1-methylquinolinio-2-methylidene) aniline iodide **IIb** (m.p. 138°C), 2-hydroxy-*N*-(1-methylquinolinio-2-methylidene)-1-naphthylamine iodide, **IIc** (m. p. 224°C), 1-hydroxy-*N*-(1-methylquinolinio-2-methylidene)-2-naphthylamine iodide **IId** (m.p. 214°C), 4-(*N-N*-dimethylamino)-*N*-(3-methyl-4-phenylthiazolio-2-methylidene) aniline iodide **IIIa** (m.p. 246°C) and 4-(*N,N*-diethylamino)-*N*-(3-methyl-4-phenylthiazolio-2-methylidene) aniline iodide **IIIb** (m.p. 205°C). The above reported m.p. values are with decomposition. The structure of of the synthesized compounds can be represented as follows.

Several trials were made to isolate the azomethine products of 2-methylpyridinium and 4-phenylthiazolium with both 2-nitroso-1-naphthol and 1-nitroso-2-naphthol but all failed.

Solutions

2.5×10^{-2} M stock solutions of the azomethines under investigation were prepared by dissolving an accurately weighed amount of each compound in the appropriate pure solvent. Solutions for spectral measurements were obtained by accurate dilution of the stock solutions. Aqueous universal buffer solutions of pH range 2.40–12.04 were prepared [28]. The pH values of these solutions were checked at 25°C using an Orion pH-meter model (60/A) accurate to ± 0.005 pH units. The electronic spectra were recorded on Pye Unicam SP 8-100 UV/VIS spectrophotometer at 25°C using a 1 cm matched silica cell.

RESULTS AND DISCUSSION

Molecular structure and solvent effect

λ_{max} and ε_{max} values of the different absorption bands observed in the recorded spectra of the azomethines studied in various organic solvents of different polarities (cyclohexane, ethanol, DMF and chloroform) are collected in Table 1 (Figs 1, 2). Generally, except in the case of compounds **IIc** and **IId** the spectra of all compounds studied (**Ia, Ib, IIa, IIb, IIIa** and **IIIb**) in ethanol exhibit two bands in the u.v. region and one main band in the visible region while those of compounds **IIc, IId** exhibit one u.v. band and two visible bands. The first u.v. band, located within the range 213–218 nm in the spectra of compounds **Ia, Ib, IIa, IIb, IIIa** and **IIIb**, is ascribed to the excitation of π-electrons of the aromatic system, since the position of this band is little influenced by changing the polarity of the medium. The second u.v. band observed in the

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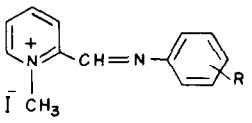
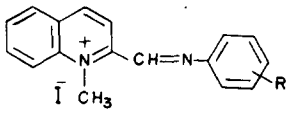
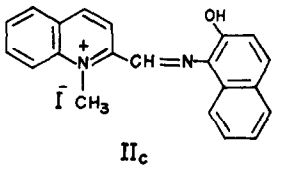


R = p-N(CH₃)₂ Ia
= p-N(C₂H₅)₂ Ib

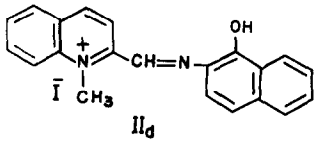
Series II



R = p-N(CH₃)₂ IIa
= p-N(C₂H₅)₂ IIb

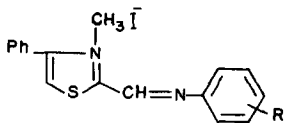


IIc



IId

Series III



R = p-N(CH₃)₂ IIIa
= p-N(C₂H₅)₂ IIIb

Table 1. Electronic spectral characteristics of the heterocyclic azomethines **I**, **II** and **III** in pure organic solvents

Compound	Cyclohexane		Ethanol		DME		Chloroform		Assignment
	λ_{max}	$\varepsilon_{max} \times 10^{-3}$	λ_{max}	$\varepsilon_{max} \times 10^{-3}$	λ_{max}	$\varepsilon_{max} \times 10^{-3}$	λ_{max}	$\varepsilon_{max} \times 10^{-3}$	
	210 sh	14.468	213	24.680	—	—	—	—	π–π^* within the aromatic system
Ia	280	8.085	286	10.000	280	10.638	287	11.489	π–π^* within the C=N centre
	486	17.446	502	27.234	488	24.787	525	31.170	Intramolecular CT
	211	31.600	215 sh	22.000	—	—	—	—	π–π^* within the aromatic system
Ib	280	10.600	286	9.600	282	10.000	288	10.500	π–π^* within the C=N centre
	498	24.400	518	28.000	502	26.800	538	33.600	Intramolecular CT
		—	215 sh	36.600	—	—	—	—	π-π^* within the aromatic system
IIa	*	—	320	10.800	320	10.400	320	10.900	π-π^* within the C=N centre
		—	560	18.100	552	15.300	592	19.200	Intramolecular CT
	215 sh	30.800	218 sh	31.000	—	—	—	—	π-π^* within the aromatic system
IIb	320	8.800	320	9.600	320	9.600	320	8.400	π-π^* within the C=N centre
	556	20.800	575	31.200	566	27.500	610	35.200	Intramolecular CT
	330	8.400	333	7.600	345	8.200	330	7.600	π–π^* within the C=N centre
IIc	455	6.600	420	7.800	420	6.000	445	6.000	Intramolecular CT within the enol form
	625	12.600	636	35.200	652	37.200	662	24.100	Intramolecular CT within the keto form
	320 sh	11.800	320 sh	10.400	320 sh	11.600	320 sh	11.200	π–π^* within the C=N centre
IId	415	7.400	400	8.600	395	8.100	415	7.800	Intramolecular CT within the enol form
	650	13.000	645	19.400	650	20.800	652	16.400	Intramolecular CT within the keto form
	215 sh	11.600	215 sh	14.200	—	—	—	—	π–π^* within the aromatic system
IIIa	285 sh	3.200	285 sh	3.600	295 sh	4.000	290 sh	4.000	π–π^* within the C=N centre
	510	11.200	530	18.000	525	17.200	557	19.200	Intramolecular CT
	216 sh	24.800	216 sh	28.400	—	—	—	—	π–π^* within the aromatic system
IIIb	280 sh	7.600	280 sh	7.200	280 sh	8.000	280 sh	3.600	π–π^* within the C=N centre
	526	31.500	544	38.100	536	36.600	572	44.000	Intramolecular CT

*Insoluble.
sh = Shoulder.
λ_{max}, nm.
ε_{max}, $mol^{-1} cm^2$.

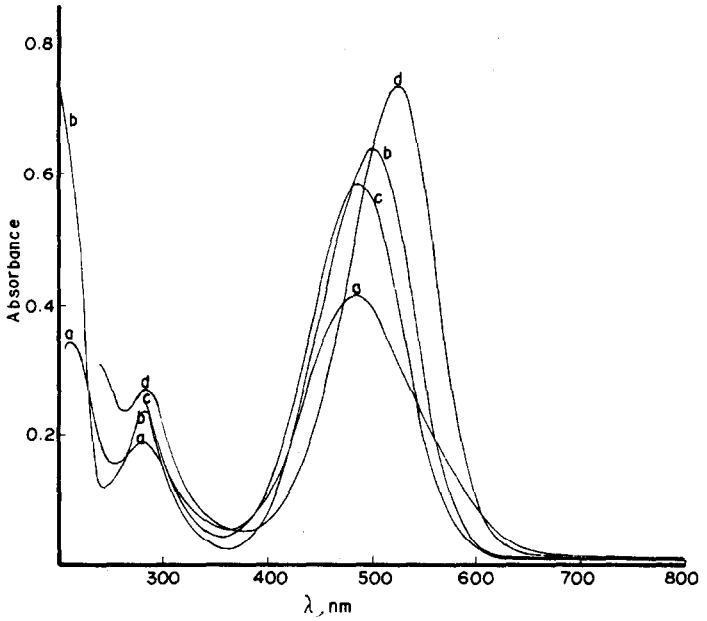
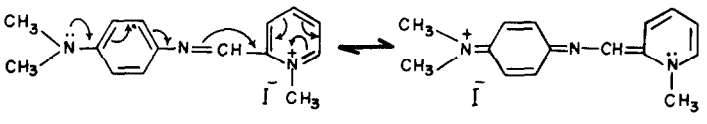


Fig. 2. Electronic absorption spectra of 2.35×10^{-5} M azomethine **Ia** in (a) cyclohexane, (b) ethanol, (c) DMF, (d) chloroform.

spectra of all compounds within the range 280–333 nm is due to the transition between π-orbitals largely localized on the central C=N bond. A similar assignment for this band was made by JAFFE *et al.* [29]. Moreover, it is suggested that this band is influenced by charge transfer interaction occurring in the solute molecule as shown below. The main visible band located in the wavelength range 502–575 nm in ethanol in the case of compounds **Ia, Ib, IIa, IIb, IIIa** and **IIIb** can be ascribed to an intramolecular CT transition within the whole azomethine molecule. This is based on the fact that the high electron withdrawing character of the heterocyclic moiety (pyridinium methiodide, quinolinium methiodide and 4-phenylthiazolium methiodide) as well as the high electron releasing character of the substituent R (dialkylamino group) causes a forced planarity of these azomethine molecules. This in turn facilitates the CT to take place within such molecules. The CT seems to originate from the amine moiety influenced by the substitutent R directly bonded to the phenyl ring; the acceptor centre is the positively charged hetrocyclic nitrogen atom as represented below.



The good linear relationship passing through the origin obtained on plotting the absorbance of this band vs the molar concentration of azomethine supports the idea that the transition of this band is intramolecular. Furthermore the very high molar extinction coefficient of this band (18000–38100 $mol^{-1} cm^2$) is in accordance with its CT nature.

Careful examination of the results reported in Table 1 reveals that the CT band acquires a lower excitation energy as the electron releasing power of the substituent dialkylamino group is increased or as the electron withdrawing power of the hetrocyclic moiety is increased (pyridinium methiodide < quinolinium methiodide). This behaviour supports the CT nature of this band. The unexpected high excitation energy of this band in the case of 4-phenylthiazolium methiodide (**IIIa, IIIb**) relative to that in the case of quinolinium methiodide (**IIa, IIb**) can be presumably attributed to the antagonizing effect of the phenyl group attached to the thiazole ring at position 4 when CT takes place within such derivatives (**IIIa, IIIb**). The increasing electron withdrawing character of the heterocyclic moiety on going from pyridinium methiodide →quinolinium methiodide→4-phenylthiazolium methiodide is supported by the observed decrease in pK_a of the dialkylamino group in the same direction (cf. Table 2).

Convincing evidence for the CT nature of this band, as well as the suggestion that the second u.v. band is influenced by CT interaction, is provided by studying the spectral behaviour of all compounds studied in aqueous buffer solutions of varying pHs (Fig. 3). It has

been found that in solutions of low pHs [pH = 3.40 (**Ia**), 2.40 (**Ib**), 2.67 (**IIa**, **IIb**), 2.57 (**IIIa**), 2.47 (**IIIb**)] the extinction coefficient of the longer wavelength visible bank is greatly lowered and the second u.v. band acquires a blue shift in its λ_{max} and in addition its extinction becomes lower. As the pH of the medium increases the extinction of these two bands becomes higher and the second u.v. band acquires a red shift in its λ_{max}. This behaviour can be interpreted on the principle that the dialkylamino group becomes protonated in solution of low pH 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 the dialkylamino group becomes deprotonated and therefore its mesomeric interaction with the rest of the molecule becomes high; consequently the CT interaction within the free base is facilitated, i.e. the free base absorbs energy in the visible region. Moreover, the CT band exhibits low excitation energy in protic solvents, *viz.* ethanol and $CHCL_3$, relative to that in aprotic solvents, *viz.* cyclohexane and DMF (Table 1 and Fig. 2). This is attributed to the difference in stabilization of both the ground and excited states through hydrogen bonding interactions with the protic solvents relative to that in aprotic solvents since there is no difference in the polarity of the ground and excited states of the compounds studied.

Table 2. pK_a values of the azomethines studied at 25°C

Compound	pK_a Method 1	Method 2	Mean value
Ia	4.00	4.05	4.025±0.3
Ib	4.80	5.00	4.90±0.10
IIa	3.60	3.57	3.59±0.02
IIb	4.50	4.55	4.53±0.03
IIc	6.90	6.92	6.91±0.00
IId	7.10	7.11	7.11±0.00
IIIa	3.38	3.40	3.39±0.01
IIIb	4.45	4.40	4.43±0.03

The two visible bands observed in the spectra of *o*-hydroxy compounds (**IIc** and **IId**) in ethanol within the range 400–420 and 636–645 nm, respectively (cf. Table 1, Fig. 1), can be interpreted on the principle of the possible existence of such compounds in a keto/enol tautomeric equilibrium. Thus, the shorter and longer wavelength bands can be ascribed to an intramolecular CT transition occuring within the enol and keto forms, respectively. This is confirmed by studing the solvent effect on the visible spectra of these compounds.

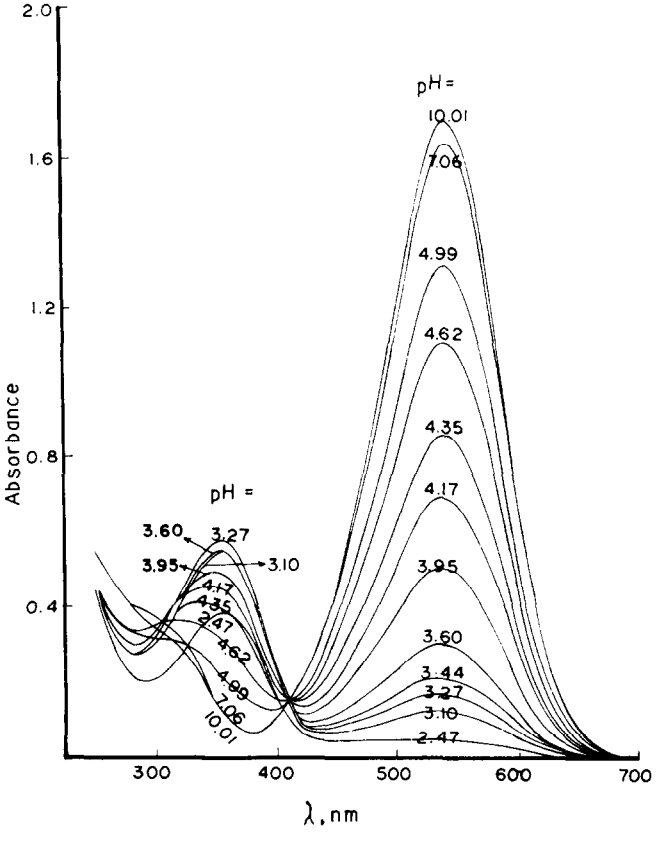
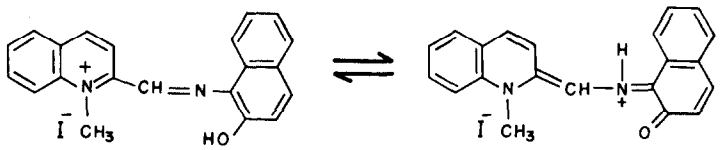


Fig. 3. Absorption spectra of 5×10^{-5} M azomethine **IIIb** in aqueous universal buffer solutions containing 3.94% (wt/wt) ethanol.

Generally, it is observed that increase of solvent polarity in the sequence cyclohexane → chloroform → ethanol → DMF results in increasing the extinction of the longer wavelength band (i.e. a high concentration of the keto form). Such tautomeric rearrangement can be represented as follows.



Enol form Keto form

Convincing evidence for the existence of these compounds in a tautomeric equilibrium is provided by the observed well-defined isosbestic point on studying the dependence of the visible spectra of these compounds in ethanol or DMF on the water content (cf. Fig. 4).

However, the unexpected blue shift observed in the λ_{max} of the longer wavelength visible band, as well as the lower extinction on increasing the water content in ethanol or in DMF, can be mainly ascribed to the possible interaction of water molecules with the lone pair of electrons of the central azomethine nitrogen through hydrogen bonding. This results in a difficult transfer of the proton from the OH group to the central azomethine nitrogen and consequently the concentration of the keto form in the medium is expected to diminish as the water content in the medium is increased.

Determination of acidity constant

The recorded visible absorption spectra of the compounds studied in aqueous buffer solutions of varying pHs (Fig. 3) were applied to the spectrophotometric determination of the pK_a values of these compounds. The recorded spectra of compounds **IIc**, **IId**, **IIIa** and **IIIb** exhibit a clear isosbestic point (Fig. 3) denoting the existence of an equilibrium essentially of

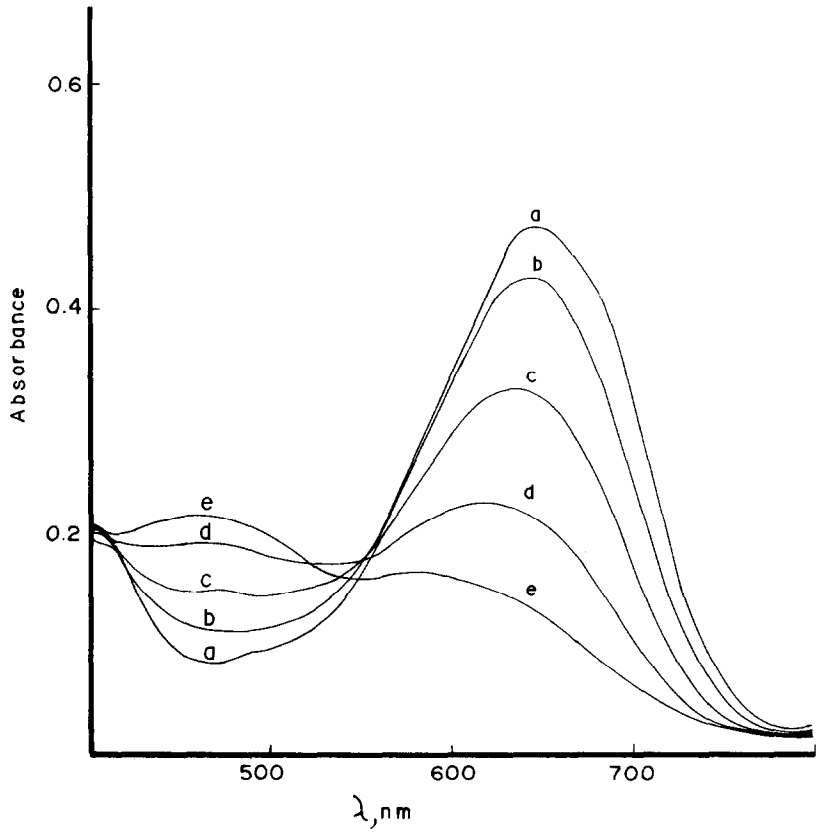


Fig. 4. Electronic absorption spectra of 2.5×10^{-5} M azomethine **IIa** in ethanol–water mixtures. (a) 0.0% water, (b) 20% water, (c) 40% water, (d) 60% water, (e) 80% water.

acid–base type between the two forms exists in solution.

The absorbance–pH curves are typical dissociation curves, supporting the acid–base equilibrium. The acid dissociation constants (pK_a) of the compounds were determined from the variation of absorbance with pH using the spectrophotometric half-height and limiting absorbance methods [30]. The limit of accuracy of the determined values was checked making use of the least squares method. The results obtained are listed in Table 2. It is evident that within each series of the hetrocyclic azomethines studied the pK_a value of the substituent $-\ddot{N}(C_2H_5)_2$ is higher than that for the substituent $-\ddot{N}-(CH_3)_2$. This is in accordance with the high basicity of the $-\ddot{N}(C_2H_5)_2$ group relative to that of the $-\ddot{N}-(CH_3)_2$ group. Moreover, the pK_a value of substituents $-\ddot{N}(CH_3)_2$ or $-\ddot{N}(C_2H_5)_2$ decreases as the heterocyclic moiety is changed from pyridinium methiodide → quinolinium methiodide → 4-phenylthiazolium methiodide (compounds **Ia, IIa, IIIa** or **Ib, IIb, IIIb**). This behaviour is in line with the expected increase in electron withdrawing power of the heterocyclic moiety in the same sequence.

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