Spectrophotometric studies on some Schiff bases derived from benzidine

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Abstract—The effect of substituents, solvent polarities and hydrogen ion concentrations on the electronic structure and spectrum of the Schiff bases (X-benzylidene-4-benzidine) have been investigated. In ethanol, the longer wavelength absorption band appeared in all the compounds studied (348–387 nm), due to the electronic transitions within the whole molecule of such compounds as an intramolecular charge transfer interaction, and the red shift of this band can be assigned to the presence of the electron-withdrawing character of the substituent X. The spectral shifts in various organic solvents were discussed on the basis of the complexed solute–solvent interaction through the formation of hydrogen bonds of the different species. Furthermore, the acidity constant values of the compounds have been determined and related to the geometric flexibility of the substituent X.

INTRODUCTION

A LARGE number [1-7] of interesting observations and theories have been reported to elucidate the effect of substituents on the electronic absorption spectra of aliphatic and/ or aromatic Schiff bases. Scanning the literature reveals that no similar studies have been carried out on such investigated compounds in the present note. Accordingly, in this paper we intend to deal with the spectra of the azomethines derived from benzidine and certain aromatic aldehydes. In addition, the pK_a of the synthesized compounds for the present work has been determined and its values were in accordance with the Schiff base molecular structures.

EXPERIMENTAL

Materials

All chemicals used in this work were of AnalaR or extrapure grade. The organic solvents used were spectroscopic grade products.

Solid Schiff bases

Equimolecular proportions (0.01 mol), of benzidine and aromatic aldehyde were dissolved in ethanol (100 ml), to which piperidine (0.5 ml) was added. The reaction mixture was refluxed for about 3-5 h. The precipitated product was filtered off, washed more than once with ethanol and recrystallized from methanol. The structure of the different synthesized compounds was confirmed by microchemical analysis and i.r. spectroscopy techniques. The following Schiff base models were synthesized:



X = p-H (I); p-OH (II); p-OH (III); $m-OCH_3$, p-OH (IV); $p-N(CH_3)_2$ (V) and $p-NO_2$ (VI).

Solutions

Stock solutions $(1 \times 10^{-3} \text{ mol dm}^{-3})$, of each of the Schiff bases studied (I-VI), were prepared in the appropriate volume of the required pure organic solvent. Aqueous buffer solutions used components of the modified universal series of BRITTON and ROBINSON [8].

The electronic absorption spectra were recorded very rapidly after preparing the solutions to avoid the rapid hydrolysis of these compounds. All measurements were carried out at 25°C.



Fig. 1. Electronic absorption spectra of Schiff bases in ethanol at 25°C. $4 \times 10^{-5} \text{ mol dm}^{-3}$ for compound II (X = o-OH), $2 \times 10^{-5} \text{ mol dm}^{-3}$ for compounds I, III-VI.

Apparatus

The electronic absorption spectra were carried out on a Shimadzu u.v.-vis. recording spectrophotometer UV-240, using a 1 cm matched silica cell. pH measurements were made with a MV-87 digital pH meter, accurate to ± 0.05 units. Infrared spectra were recorded in the region 4000-200 cm⁻¹ on a Pye Unicam SP 1100 infrared recording spectrophotometer using the KBr disc technique.

RESULTS AND DISCUSSION

Figure 1 shows the variations in the experimental spectra of our Schiff bases (I–VI), in ethanol. The values of λ_{max} and ε_{max} , of the different absorption bands of these compounds in ethanol and in the organic solvents of different polarities are evaluated and shown in Table 1.

Absorption spectra in ethanol medium

On the light of the recorded electronic spectra as shown in Fig. 1, it is clear that all the Schiff bases investigated have three main absorption bands, except the Schiff base V $[X = p-N(CH_3)_2]$ which exhibits two main absorption bands. The first u.v. band (226-233 nm) observed in the electronic absorption spectra of all the studied compounds can be assigned to the excitation of the π -electrons of the aromatic system. It is worthy to note that the position of this band is not nearly shifted with changing the Schiff base substituents, this is good support for the above assignment.

The main visible band observed in all the studied compounds, at longer wavelength range, 348–387 nm, can be assigned to the electron transitions within the whole molecule of such compounds. This transition can be represented schematically as below, where the azomethine group is considered as an acceptor centre.



X = p-H; o-OH; p-OH; m-OCH₃, p-OH and p-N(CH₃)₂.

Table 1. Electronic spectral characteristics of (X-benzylidene-4-benzidine) I-VI in pure organic solvents at 25°C

	Ĭ	MSO	ם	MF	H	lanol		HG	ر	ਰੁੱ	ā	oxan	
Compound	$\lambda_{\rm max}$	Emax	λ_{max}	Emax	Amax	Emax	λ _{max}	Emar	λ _{max}	Emax	λ _{max}	Emax	Assignment
					226	145.000	243	44.000	255	28.000	245	42.500	л−л*
$\mathbf{X} = \mathbf{p} \cdot \mathbf{H}$	282	28.500	281	24.000	272	27.000	275	26.500	278	26.000	278	29.000	$\pi - \pi^*$
- -	353	38.000	352	32.500	348	33.000	353	31.750	353	30.000	353	35.000	Intra CT trans
Ш	255	16.000	I	I	233	148.000	248	84.500	258	49.000	249	75.000	<i>π</i> −π*
X = 0.0H	280	9.000	280	8.500	275	9.500	275	9.500	280sh	10.000	275	9.200	<i>n</i> - <i>n</i> *
	367	25.000	364	23.000	363	24.500	368	20.000	368	19.500	364	24.000	Intra CT trans
Ш	١	ļ	I	1	233	164.000	248	95.000	258	61.000	250	97.000	л-л [*]
$\mathbf{X} = \mathbf{p} \cdot \mathbf{OH}$	295	40.000	297	39.000	292	41.500	292	41.300	290	44.500	292	44.300	$\pi - \pi^*$
•	357	59.000	355	57.500	350	60.000	350	53.000	253	55.000	352	56.500	Intra CT trans
N	I	1	I	ļ	233	153.000	248	90.00	257	51.000	250	94.000	$\pi - \pi^*$
$X = m - OCH_3$	290	16.000	290	15.250	285	17.000	286	19.000	287	20.000	288	21.000	<i>π</i> л*
HO-d	367	45.000	364	45.000	355	45.000	355	41.500	356	40.500	356	45.000	Intra CT trans
^	1	I	ł	ł	232	152.000	248	85.000	258	46.500	250	93.500	<i>п</i> -л*
$\mathbf{X} = \mathbf{p} \cdot \mathbf{N}$	355sh	32.000	355sh	31.300	355sh	42.000	350	33.600	335	30.500	340sh	33.550	<i>n</i> - <i>n</i> *
(ĊH ₃),	387	40.000	383	39.000	372	45.000	375	37.500	375	38.000	375	44.000	Intra CT trans
М	1	I	1	ł	232	164.000	249	95.000	258	62.000	251	97.500	<i>n</i> - <i>n</i> *
$\mathbf{X} = p - \mathbf{NO}_2$	290	32.000	290	31.500	280	36.500	285	35.000	282	33.250	285	34.000	л−л*
•	391	27.000	390	27.000	387	30.000	390	27.000	389	28.000	389	29.500	Intra CT trans

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The above behaviour strongly supports the concept that the transition of this visible band is influenced by an intramolecular charge transfer (CT) interaction within the solute molecule. In addition, a satisfactory straight line which passes through the origin is constructed on plotting the absorbance of this band against the molar concentration of each of the investigated compounds. This is more convincing evidence for the CT nature of this band. It is worthwhile to note that the position of the CT band is quite sensitive to the nature of the substituent X, attached to the aldehydic moiety. From the data shown in Table 1, it is observed that the visible band of compound VI (X = p-NO₂), is red shifted by approximately 15–40 nm relative to the visible band of the other studied compounds. This red shift is most likely attributed to the electron-withdrawing substituent [10–12]. Whereas the high electron-withdrawing power of the -NO₂ group makes it behave as a CT acceptor centre, accordingly, the CT interaction is expected to be easier in the *p*-NO₂ derivative relative to the other ones, this behaviour confirms the CT nature of this band.

$$H_2 N \longrightarrow V \longrightarrow N \longrightarrow CH \longrightarrow NO_2 \longrightarrow H_2 N \longrightarrow CH \longrightarrow NO_2$$

The former assignments can be confirmed by considering the spectral behaviour of the studied compounds in a series of aqueous buffer solutions of various pHs (Fig. 2). However, it has been found that the intensity of the CT band of compounds II-IV gradually decreases as the pH of the medium is lowered. This is pronounced in the spectra of all the compounds. On the other hand, the CT band of compounds III (X = p-OH) and IV $(X = m-OCH_3, p-OH)$, exhibit a relatively gradual blue shift with lowering the pH values of the medium, i.e. a relatively high excitation energy is observed. In the case of compound II (X = o-OH), the CT band (λ = 375 nm) submerges in the solutions of pH less than 8.70, and appears again ($\lambda = 325$ nm) with a high extinction coefficient. This means a great blue shift is observed with lowering the pH of the medium. This behaviour of the compounds in a solution of low pH value was expected to occur and can be interpreted on the basis that decreasing the pH of the medium will result in lowering the degree of ionization of the -OH group belonging to these compounds and thus, protonation of the nitrogen atom of both the azomethine group and the amino benzidine takes place. This makes CT interaction difficult, i.e. blue shift is observed. Accordingly, it seems reasonable that the intramolecular CT inter-



Fig. 2. Electronic absorption spectra of 2×10^{-5} mol dm⁻³ of compound III (X = p-OH) in pure organic solvents at 25°C.

action occurs more easily within the solute molecule of these compounds under basic conditions than it occurs under acidic conditions. This is good evidence for the CT nature of the visible band.

Absorption spectra in different organic solvents

It is noticed that the visible band influenced by intramolecular CT within the solute molecule as assigned above is also red shifted with changing the solvent nature, according to the following order:

EtOH < DMF < DMSO.

The blue shift observed in the case of ethanol can be ascribed to the protonation of the nitrogen atom attached to the benzidine ring by ethanol, whereas ethanol acts as a proton donor solvent.



It seems reasonable to say that such protonation will result in blocking the *n*-electrons of the nitrogen atom, so that the electron charge transfer through the solute molecule is hard, accordingly high excitation energy is required and blue shift is observed in ethanol medium. DMF and DMSO do not have protic characters, consequently, they cannot interact as a proton donor since red shift of the CT band is observed for them.

On the other hand, it is also observed that the CT band is red shifted as the solvent polarity decreases from ethanol to dioxane. This can be assigned to the high ability of ethanol to form an intermolecular hydrogen bond with the solute molecule rather than with the non-polar solvents, $CHCl_3$, CCl_4 and dioxane as represented below:



The *n*-electrons of the nitrogen benzidine ring are blocked by an ethanol molecule through an intermolecular hydrogen bond leading to the electron charge transfer being difficult, i.e. high excitation energy is observed for this band in ethanol medium.

Determination of acid dissociation constants

The acidity constant values of the studied compounds were determined taking into consideration the spectral shifts of these compounds in aqueous universal buffer solutions (pH range 1.29–11.36). Clear isosbestic points at different positions were observed in the recorded spectra of the examined compounds (Fig. 3), this indicates that a chemical equilibria exist between different species of these compounds, two equilibria between the protonated and the neutral forms and other one between the neutral and the ionic forms as shown below:





Fig. 3. Electronic absorption spectra of 2×10^{-5} mol dm⁻³ of compound III (X=p-OH) in aqueous universal buffer solutions at 25°C.

The pK_a values of compounds I, V and VI (X = p-H, p-N(CH₃)₂ and p-NO₂, respectively), cannot be determined. This is attributed to the low soluble character of compound I, in the aqueous solutions. In the case of compound V, this is presumably due to the hydrolysis of this compound in such media being too fast. The spectra of compound VI, in different pHs do not show any order in the absorbance of the CT band and the other bands, this makes the evaluation of pK values inaccurate.

According to the compiled pK_a values of the studied compounds, in Table 2, it is noticed that these compounds give three pK values. pK_1 and pK_2 may be assigned to deprotonation of both the nitrogen azomethine group and the nitrogen of the benzidine ring, respectively, and pK_3 can be ascribed to ionization of the phenolic *o*-OH or *p*-OH groups, as represented schematically above. In the light of this scheme, deprotonation of both nitrogen atoms referred to above does not take place simultaneously. This may be attributed to the geometric flexibility and non-planarity of such Schiff bases [13, 14] and thus to the presence of some steric factors.

Moreover, the pK_3 value of ionization of the *o*-OH group is higher than that of the *p*-OH, this is most likely due to the strong intramolecular hydrogen bonding between the

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Compound	λ (nm)		pK _a Half-height method	Limiting- absorbance method	Mean value
II (X = o-OH)	375	p <i>K</i> ₁	4.70	4.80	4.75±0.05
	375	pK_2	7.70	7.66	7.68 ± 0.02
	375	pK_3	11.05	11.10	11.07 ± 0.02
III $(X = p - OH)$	275	pK_1	5.00	5.10	5.05 ± 0.05
	275	pK_2	6.80	6.92	6.86 ± 0.06
	275, 360	pK_3	9.40	9.60	9.50 ± 0.10
$IV (X = m - OCH_3; p - CH)$	380	pK_1	5.30	5.22	5.26 ± 0.04
	380	pK_{2}	8.20	8.00	8.10 ± 0.10
	380	р <i>К</i> 3	9.10	9.25	9.17 ± 0.08

Table 2. The pK, values of the compounds II-IV at 25°C

The accuracy of the pK_a values was checked by using the standard deviation method.

o-OH group and the nitrogen azomethine group. This behaviour will result in an increase of the stability of the o-OH group, so its ionization is difficult, i.e. a high pK_a value is observed for it. This account is typical of that previously induced [9].



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