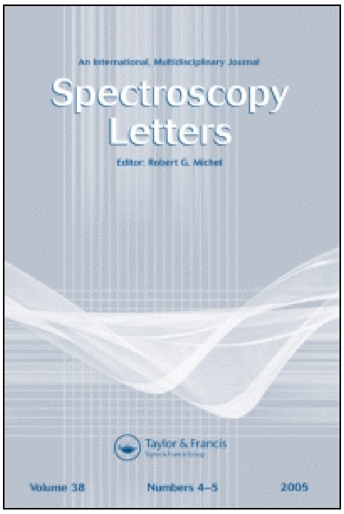

Spectroscopy Letters
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597299

Spectrophotometric Studies of the Influence of Organic Solvents and Substituents on Some Schiff Bases

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To cite this Article Sovilj, S. P. , Vasić, V. M. , Stojić, D. Lj. , Stojčeva-Radovanović, B. and Petkovska, Ljubica T.(1998) 'Spectrophotometric Studies of the Influence of Organic Solvents and Substituents on Some Schiff Bases', Spectroscopy Letters, 31: 5, 1107 — 1122

To link to this Article: DOI: 10.1080/00387019808003288

URL: http://dx.doi.org/10.1080/00387019808003288

SPECTROSCOPY LETTERS, 31(5), 1107-1122 (1998)

SPECTROPHOTOMETRIC STUDIES OF THE INFLUENCE OF ORGANIC SOLVENTS AND SUBSTITUENTS ON SOME SCHIFF BASES

Keywords: Schiff bases, organic solvents, spectrophotometric studies

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ABSTRACT

The effect of the substituents, solvent polarities and hydrogen ion concentration on the electronic structure and UV/VIS absorption spectra of some Schiff bases, derivatives of N-(R-benzylidene)benzidine (R = o-NO_2 and o-OH, p-OH) and N-(R-furfurylidene)benzidine (R = H and 5 - NO_2), have been studied. The

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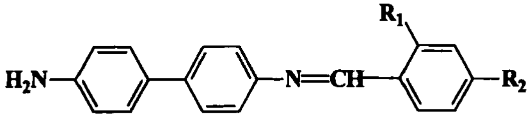
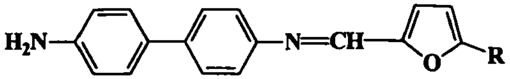
spectral shifts obtained in various organic solvents were discussed on the basis of the specific solute - solvent interactions through the formation of hydrogen bonds between hydrogen-bond donor (HBD) solvents and the benzidine nitrogen atom of the Schiff bases. Some interpretations of the electronic aspects of this type of hydrogen bonding were discussed as well as the stabilization effects due to the solvation. Finally, the pK values of the compounds were determined.

INTRODUCTION

Although solvent effects on the UV-VIS spectral behavior of aromatic[1-9] and of some nitrogen heterocyclic[10-17] Schiff bases have been extensively investigated in recent years, only spare information is available on the other heterocyclic Schiff bases, in spite of their importance in the biological field[18-20]. Accordingly, the present paper deals with solvent and substituent effects on the UV-VIS absorption spectra of some newly synthesized Schiff bases N-(R-benzylidene)benzidine and N-(R-furfurylidene) benzidine having the general structures (1) - (4):



compound (1): $R_1=NO_2$; $R_2=H$
compound (2): $R_1=OH$; $R_2=OH$



compound (3): R=H
compound (4): $R=NO_2$

Further, the acidity constants of these derivatives were determined and discussed in the terms of their molecular structure.

As far as we know, it is the first time that Schiff bases with oxygen-containing heterocyclic rings are investigated.

EXPERIMENTAL

All chemicals used in the present work were p.a. Merck products. The organic solvents used were spectroscopic grade products. The solid Schiff bases were prepared according to the literature procedure[9], by condensation of benzidine with the corresponding heterocyclic and aromatic aldehyde, using the requisite amount in an ethanolic medium. The crude products were purified by repeated crystallization from methanol. The structure and purity of the compounds were checked by IR spectra and elemental microanalysis.

Stock solutions (1×10^{-3} mol dm^{-3}) of each of Schiff bases studied **(1)**-**(4)**, were prepared in the appropriate volume of the required pure organic solvent. The electronic absorption spectra were recorded immediately after preparing the solutions to avoid hydrolysis of these compounds. In some cases the spectra of Schiff bases change with time. As the changes occur immediately after preparing the solution, spectra were recorded rapidly at least twice to prove they refer to the same species. The electronic absorption spectra of the solutions (concentration 1×10^{-5} mol dm^{-3} - 1×10^{-6} mol dm^{-3}) were investigated in various organic solvents of different polarities: dimethylsulfoxide (DMSO), N,N'-dimethylformamide (DMF), chloroform ($CHCl_3$), methanol (MeOH) and ethanol (EtOH). The protolytic constants were examined in water solutions within pH range from pH 0 to pH 14. The universal buffer solutions were prepared according to Britton[21]. The pH values were checked using Beckman expandomatic digital pH-meter, accurate to ± 0.05 units. The electronic spectra were recorded on a GBC UV VIS 911A spectrophotometer using 1cm quartz cell. All measurements were carried out at 25 °C.

RESULTS AND DISCUSSION

The UV-VIS absorption spectra

The electronic spectra of compounds **(1)**-**(4)** in DMSO, DMF, $CHCl_3$, MeOH and EtOH were recorded in wavelength range from 200 nm to 400 nm. The absorption spectra of compound **(1)**, which belongs to a group of Schiff bases derived from benzidine and aromatic aldehydes, studied in different organic solvents, are shown in Fig.1. For comparison, the absorption spectra of compound **(3)**, derived from a benzidine and heterocyclic aldehyde, are presented in Fig.2. The corresponding λ_{max} and ϵ_{max} values of the characteristic absorption bands for all investigated compounds are summarized in Table 1.

The results show that the absorption spectra of both groups of compounds are similar to those of the other azomethines[6,9].

It can be seen in Figs. 1 and 2 that three main absorption bands of different intensities appear in the 200 - 400 nm region. Those bands indicate that different electronic transitions are involved. We presume that the same transitions are included in the spectra of all the Schiff bases studied. The first UV band located in the range 220 - 260 nm could be assigned to the π-π^* transition within the aromatic system[6,14]. The position of the second UV band in 270 - 300 nm range could be ascribed to a transition between π- orbitals mainly localized in the central C = N bond[15,22]. The long-wavelength visible band in 350 - 400 nm region is the effect of an intramolecular charge transfer (CT) transition within the whole azomethine molecule[9].

Solvent effects on the UV/VIS absorption spectra

The results presented in Table 1 show that the wavelengths of the first two UV bands at about 220 - 260 nm and 270 - 300 nm vary with the solvent change ($\Delta\lambda$= 10-30 nm), possible as a consequence of different polarities of the solvents supporting their π-π^* character[15], although there are known π-π^* absorptions which are solvent-independent[23]. It can also be seen that a visible band at about 350 - 390 nm influenced by intramolecular CT within the solute molecule is dependent on the solvent nature[3].

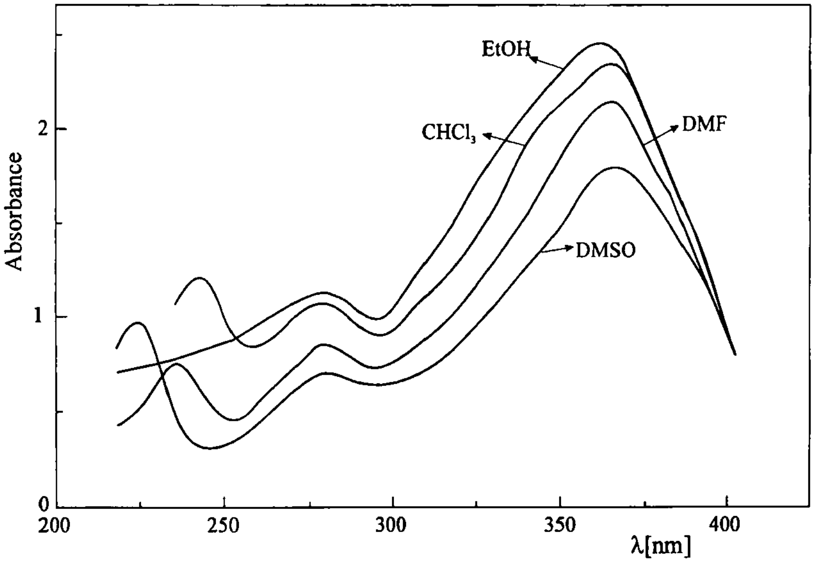


Fig. 1. The influence of solvents on the UV/VIS absorption spectra of compound (1), c = 1.00 x 10^{-5} mol dm^{-3}.

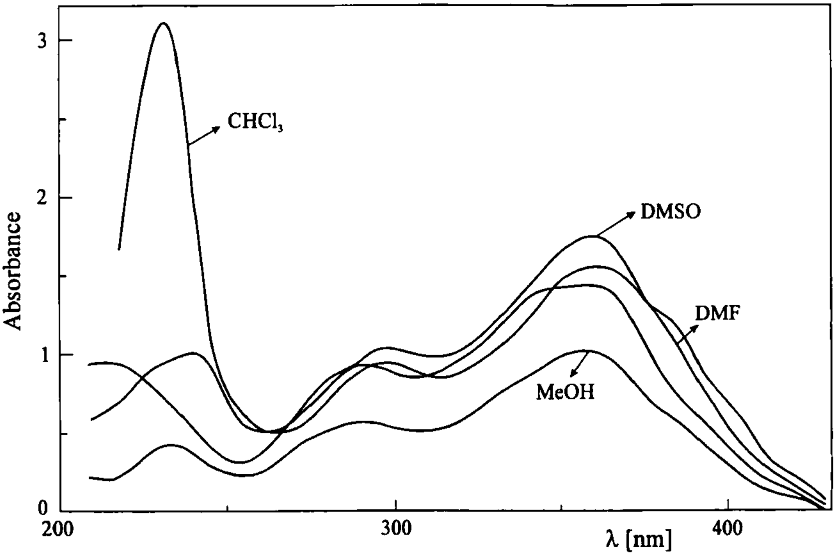


Fig. 2. UV/VIS absorption spectra of compound (3) in DMSO, DMF and MeOH (c = 0.25 x 10^{-5} mol dm^{-3}) as well as in CHCl$_3$ (c = 1.00 x 10^{-5} mol dm^{-3}).

TABLE 1
UV/VIS absorption maxima and molar extinction coefficients of the Schiff bases (1) - (4) in pure organic solvents measured at 25°C

	DMSO		DMF		$CHCl_3$		MeOH		EtOH	
	λ_{max}	ϵ_{max} x10^{-5}	λ_{max}	ϵ_{max} x10^{-5}	λ_{max}	ϵ_{max} x10^{-5}	λ_{max}	ϵ_{max} x10^{-5}	λ_{max}	ϵ_{max} x10^{-5}
1	229	0.89	261	0.75	240	1.26	*		-	-
	276	0.66	280	0.78	276	1.03			270	1.11
	368	1.67	366	2.11	364	2.33			360	2.38
2	252	1.02	256	1.24	236	1.10	248	0.47	220	1.08
	296	3.92	296	4.12	284	3.06	288	2.50	288	3.12
	364	4.20	356	6.11	352	2.20	350	1.10	345	4.20
3	221	2.01	238	0.90	240	2.78	232	0.81	-	-
	296	2.29	296	1.94	292	0.88	288	1.35	291	1.08
	365	4.04	362	3.44	360	1.40	356	2.95	352	1.91
4	249	0.21	246	1.20	*		229	1.50	228	1.39
	300	3.28	296	3.03			292	2.98	290	2.80
	384	0.24	392	0.27			383	0.31	382	0.38

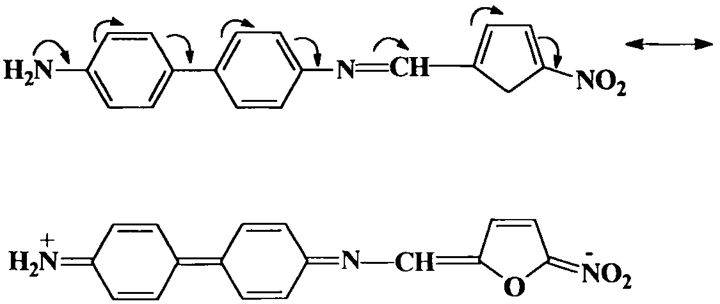
* insoluble
λ_{max} (nm) ϵ_{max} x 10^{-5} (mol^{-1} dm^3 cm^{-1})

The wavelength of this band produced by association in solvation, is slightly red-shifted with changing the solvent physical parameters, according to the following order:

EtOH < MeOH< $CHCl_3$ < DMF < DMSO except for compound (4) in DMSO. The positive solvatochromic effect can be properly explained with the help of CT interactions between the solute and solvent molecules, assuming strong donating activity by the solute[3]. Thus, the solute molecules play the role of donor component forcing an accepting function upon the solvent molecules.

In ethanol and methanol, as hydrogen-bond donor solvents, the blue shift (~ 10 nm) is observed for all compounds, compared to the other solvents (DMSO, DMF). It could be ascribed to the hydrogen-bonding of the nitrogen atom attached to the benzidine ring by a hydrogen-bond donor (HBD) solvents (EtOH and MeOH). The effect of hydrogen bonding in general is not negligible. Similar modifications occur in other solvents with known hydrogen bonding ability[24] (Table 1). In the HBD solvents the electron charge transfer through the solute molecule is difficult[8,25], because an intermolecular hydrogen bond formed with the solute molecule results in blocking the *n*-electrons of the benzidine nitrogen atom. It is worth mentioning that the effect of a protonated nitrogen benzidine atom is not caused only in a slightly acidic medium (as it is seen later) but in the presence of HBD solvents as well. The behavior can be interpreted on a principle that the absorption of energy in the visible range is difficult as a result of reduced CT interaction within the whole molecule, and a small shift is occurring. DMSO and DMF do not have a hydrogen-bond donating character[23]. Consequently, they cannot interact as a hydrogen-bond donor since a red shift of the CT band is observed for them (Table 1).

The present observation is important in two aspects. First, the presence of the heterocyclic oxygen atom in compounds **(3)** and **(4)** decreases the charge density on the azomethine nitrogen. Secondly, in the case of compounds **(1)** and **(4)**, the high electron-withdrawing power of the -NO_2 group makes it possible to become an electron-acceptor center. The azomethine group is primary the center contributing to the intramolecular CT interaction[10], but in the compounds **(1)** and **(4)** the -NO_2 group takes part in the decreasing of electron density[7], represented schematically, as below for compound **(4)**:



This conclusion suggests that the molecules are planar and the CT transition can be realized through the whole molecule. The increase in intensity of the CT band as a result of the deprotonation of the benzidine ring in the high pH range, can be considered as evidence for the coplanarity of the benzidine ring and the rest of the Schiff base molecule, as well. In the case of compound **(2)**, the position of this band depends on the position of the - OH groups relative to the azomethine linkage and on their number as well[10].

Substituent effects on the UV/VIS absorption spectra

It is well known that the position of the intramolecular CT band is strongly influenced by the nature of substituent R, attached to the aldehydic moiety[8,13,14].

The results presented in Table 1 show that the change of substituents in the benzene ring for compounds **(1)** and **(2)** and the number of -OH groups in o- and p-positions as in compound **(2)**, slightly influence the position of the UV/VIS absorption maximum at about 360 nm (for about 10 nm) in different solutions. Even the replacement of a benzene ring by furfurylidene moiety did not influence the remarkable difference in the position of π-π_1 and CT bands compared to compounds **(1)** and **(2)** in different solvents. The position and molar extinction coefficient of the CT band is quite sensitive to the nature of the substituent, especially to the presence of $-NO_2$ group in compound **(4)**.The introduction of $-NO_2$ group in the position 5 of the furfurylidene moiety affects strongly the absorption spectra in DMSO, $\Delta\lambda = 24$ nm, as shown in Fig. 3. The substituent effect in the other investigated solvents is shown in Table 1 and it is very similar to that in DMSO, supporting the CT nature of the third band[6,9].

It is also observed that the CT band of compound **(4)** is red-shifted in all solvents by approximately 15 - 20 nm relative to the CT band of the other compounds studied. This red-shift can be attributed to the electron-withdrawing $-NO_2$ substituent[26,27]. The high electron-withdrawing power of the $-NO_2$ group makes it behaving as a CT acceptor center. This donor function of a highly electron-releasing substituent of $-NO_2$ group is mainly attributed to the n_1 orbital of the azomethine

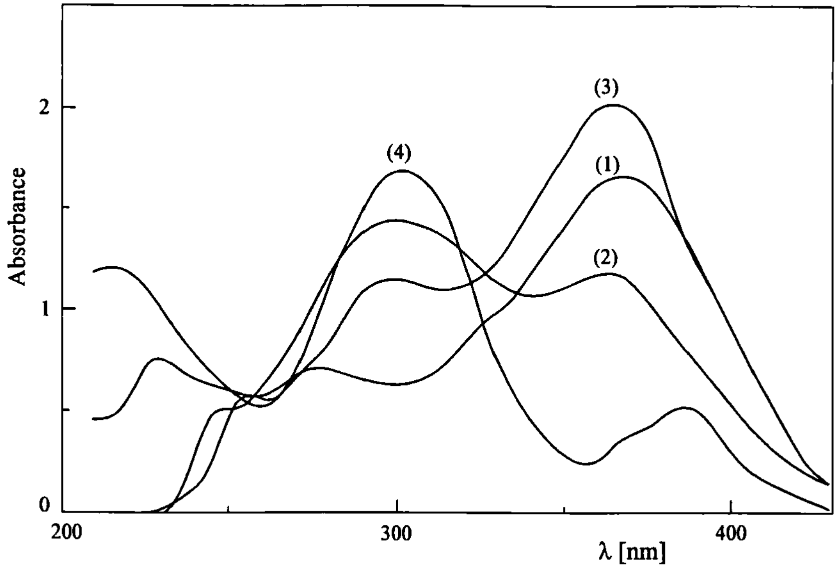


Fig. 3. UV/VIS absorption spectra of compounds **(1)-(4)** in DMSO, $c_1 = 1.00 \times 10^{-5}$ mol dm^{-3}, $c_2 = 0.25 \times 10^{-5}$ mol dm^{-3}, $c_3 = c_4 = 0.5 \times 10^{-5}$ mol dm^{-3}.

nitrogen atom. Participation of the π_1 orbital in acceptor-donor coupling is also possible but only to a very limited extent[3].

Determination of the acidity constants

The absorption spectra of the compounds **(1)** - **(4)** were recorded in water solutions of various acidity, from pH 0 to pH 14. The changes in the absorption spectra due to the variable media acidity are the consequence of the changed ionic forms of the compounds. The spectral behavior of all compounds in aqueous universal buffer solutions followed by the appearance of the clear isosbestic points at different positions undoubtedly confirm the presence at least two equilibria in the investigated acidity range.The absorbance vs. acidity curves were produced for the investigated acidity range. Table 2 summarizes the pH intervals where no change of the absorbance

TABLE 2

Spectral characteristics and optimal acidity range for ionic forms of the compounds (1)-(4)

Compound	Ionic form	Optimal pH range	λ_{max}	$\epsilon_{max} \times 10^{-4}$
1	BH_2^{2+} BH^+ B	< 2 5 - 7.5 >10	240 278 (365)* 285 (370)	6.74 4.80 (1.19) 5.00 (1.59)
2**	BH_2^{2+} BH^+ B	<3 5 - 6 9 - 11	253 (345) 271 (330) 269 (338)	1.16 (0.68) 0.82 (0.86) 0.92 (0.09)
3	BH_2^{2+} BH^+ B	< 2 6 - 8.5 > 11.5	262 267 270 (350)	1.77 2.74 1.77 (0.64)
4	BH_2^{2+} BH^+ B	< 2.5 5 - 9 > 12.5	247 282 284	5.87 6.03 6.83

λ_{max} (nm)

$\epsilon_{max} \times 10^{-4}$ ($mol^{-1} dm^3 cm^{-1}$)

*values in brackets relate to CT bands

** the optimal pH range and λ_{max} of monoanion and dianion forms, connected with dissociation of -OH groups, could not be determined because of overlapping equilibria

takes place (optimal pH for particular molecular species), together with wavelength and molar absorptivity of the peak absorption of the corresponding molecular species.

Taking into account that there are different basic sites, the multiple protonation equilibria in the acidity range from pH 0 to 14, occur:

$$BH_{n-1}^{(n-1)+} + nH^+ \rightleftharpoons BH_n^{n+}$$

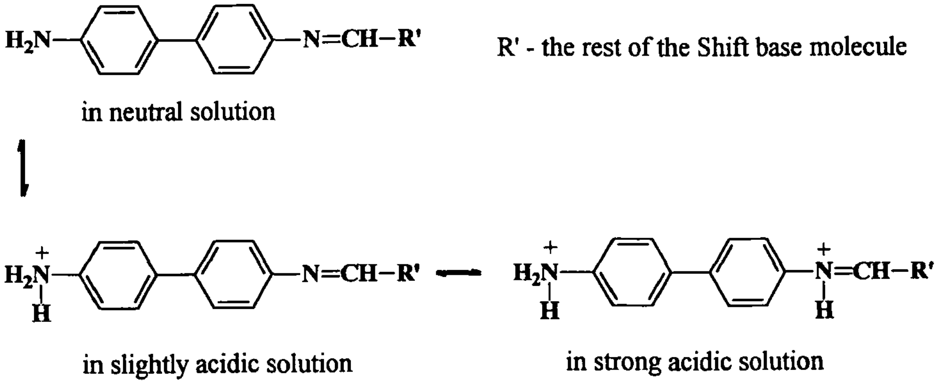
$$K_n = \frac{[BH_n^{n+}]}{[BH_{n-1}^{(n-1)+}]\,[H^+]^n}\ , \quad n = 1,2,3$$

The pK_a values of **(1)** to **(4)** were determined by linear least-square method, from variation of the absorbance with pH using the following equation:

$$pK = pH - \log \frac{[BH_n^{n+}]}{[BH_{n-1}^{(n-1)+}]}$$

The results obtained are listed in Table 3.

On the basis of the compound's structures and comparing the values of pK_a obtained with the literature data of similar compounds[9], it is clear that, by the compounds **(1)**, **(3)** and **(4)**, protonation of amino (pH~ 7) and azomethine (pH~ 4) groups occur, as represented below:



In the case of compound **(2)** equilibria include the ionic forms (pH~ 9 and pH > 11) due to ionization of two -OH groups. As shown on the following page.

The results in Table 2 indicate that the position of the CT band, at about 350 - 360 nm by all compounds is sensitive to the pH. Namely, in solutions with pH < 2, a weak broad band at about 350-360 nm with low intensity is present. From pH 0 to pH 7.50 and 8.50 for compounds **(1)** and **(3)**, respectively, well-defined bands at about 245 nm are red-shifted by approximately 30-70 nm and have higher molar absorption coefficients. It seems that these bands are covered by CT band, whose intensity increases as the pH is increased (pH = 10.00) (Figs. 4 and 5).

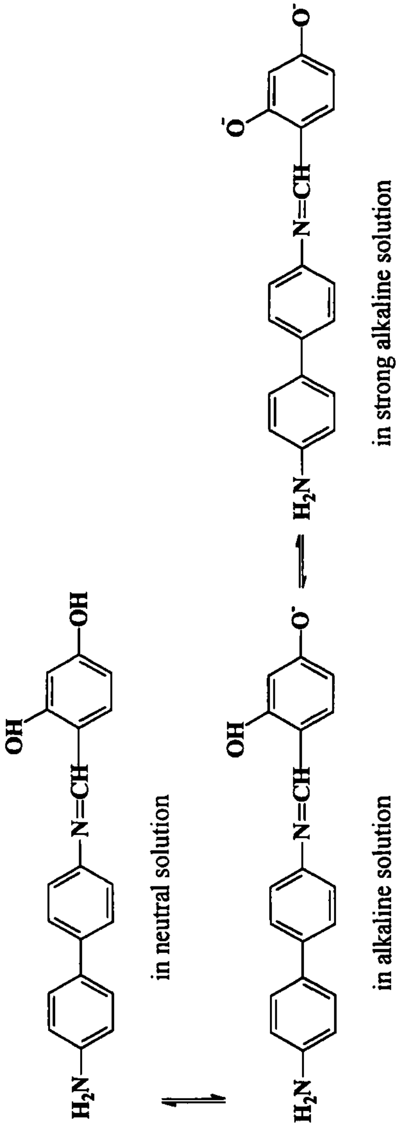

H2N
N=CH
OH
OH
in neutral solution
H2N
N=CH
OH
O⁻
in alkaline solution
H2N
N=CH
O⁻
O⁻
in strong alkaline solution

TABLE 3
pK_a values of the compounds (1)-(4)

Compound	Reaction site	pK_a	
1	azomethine group	pK_1	3.79 ± 0.37
	amino group	pK_2	7.71 ± 0.51
2	azomethine group	pK_1	4.75 ± 0.05
	amino group	pK_2	7.68 ± 0.02
	hydroxy group (o -OH)	pK_3	11.07 ± 0.02
	hydroxy group (p -OH)	pK_4	13.50 ± 0.10
3	azomethine group	pK_1	3.94 ± 0.09
	amino group	pK_2	10.51 ± 0.26
4	azomethine group	pK_1	3.75 ± 0.22
	amino group	pK_2	11.40 ± 0.07

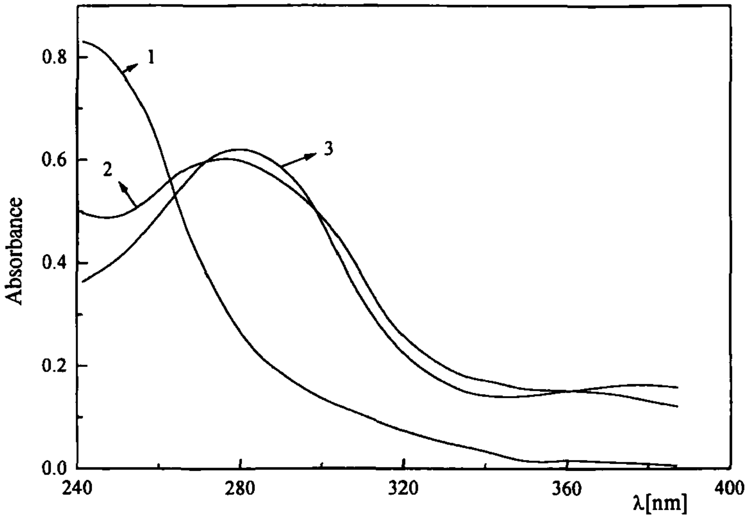


Fig. 4. UV/VIS absorption spectra of 1.26 x 10^{-5}moldm^{-3} of compound (1) in aqueous universal buffer solutions: 1- pH 0; 2 - pH 7.42; 3 - pH 10.10.

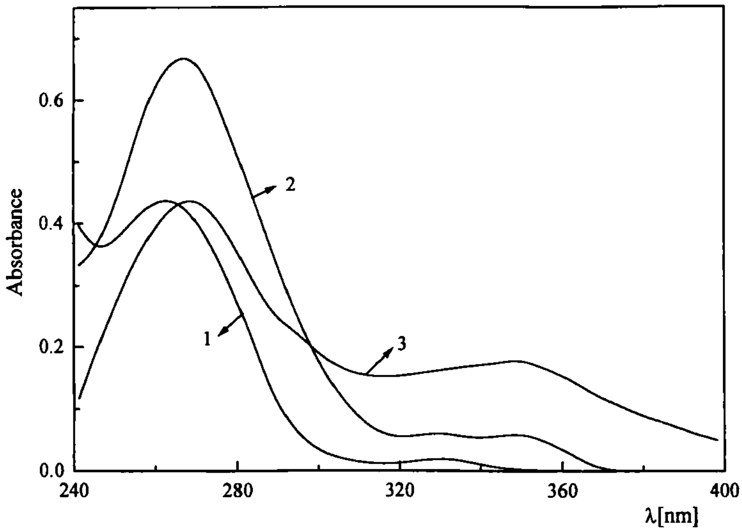


Fig. 5. UV/VIS absorption spectra of 2.48 x 10^{-5}mol dm^{-3} of compound **(3)** in aqueous universal buffer solutions: 1 - pH 0; 2 - pH 8.12; 3 - pH 10.00.

These observations can be explained as a consequence of both nitrogen atoms protonation in the solutions with law pH values and reduced CT interactions within the protonated forms. On the contrary, as the pH of the solution increases, the nitrogen atoms become deprotonated and therefore the CT interaction within the neutral form is of greater importance. By considering the increase in intensity of the CT band as a result of the deprotonation of the two nitrogens in the high pH range confirm the actual coplanarity of all the Schiff bases studied.

It is evident that two 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, while pK_3 and pK_4 can be dascribed to ionization of two -OH groups in compound **(2)**.

It can be seen (Table 3) that pK_1 values are very close for all Schiff bases. In the case of compounds **(1)** and **(4)** with -NO_2 substituent they are slightly lower, because the nitrogen protonation of the azomethine group is occurring at lower pH. The high electron-withdrawing strength of $-NO_2$ group results in a decreased density of charge on azomethine nitrogen and protonated form are expected to be reduced.

On the basis of the pK_2 values it can be concluded that the degree of protonation of the amino benzidine group belonging to furan compounds **(3)** and **(4)** increases with increasing the pH. The weak resonance effect of the furan compounds relates the high electron density on the benzidine nitrogen, resulting the protonation becomes facile. The corresponding pK_2 values are therefore higher.

In the case of compound **(2)** the pK_3 and pK_4 values of ionization of two -OH groups are expected, similar to those of the corresponding compounds with only one -OH group in the o- or p- position[6,9]. Convincing evidence for the higher pK_4 value (o-OH) than that of pK_3 (p-OH) is presumably due to an intramolecular hydrogen bond between the o-OH group and the nitrogen azomethine group. The interaction in the case of p-OH group is excluded and therefore its ionization is facilitated.

ACKNOWLEDGMENT

The authors are grateful to the Ministry of Science and Technology of the Republic Serbia for financial support.

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Date Received: February 27,1998
Date Accepted: April 6, 1998