

ULTRAVIOLET AND VISIBLE ABSORPTION AND SPECTRAL SHIFTS OF SOME SCHIFF BASES DERIVED FROM N,N -ETHYLENEDIAMINE

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(Received June 3, 1990; revised November 14, 1993)

The electronic absorption spectra of the Schiff bases, in the present not $[N,N$ -di(X -benzylidenes) ethylenediamine], have been investigated in organic solvents of different polarities. The main visible band observed in all of the compounds examined, in ethanol, is assigned to the electronic transitions within the whole molecule of such compounds as an intramolecular charge transfer (CT) interaction. The position of this band is quite sensitive to nature of substituent X . On the other hand, an additional visible band appeared in each of compound II ($X=O-OH$) and compound IV ($X=N(CH_3)_2$). This can be attributed to an intermolecular CT transition in case of the former compound and to high stabilization of the polar excited state of later compound by an ethanol molecule. Furthermore, the pK_a values of the substituent X , have been determined and related to the geometric flexibility of such compounds.

Key words: Electronic absorption spectra, Schiff bases, N,N -Ethylenediamine.

Introduction

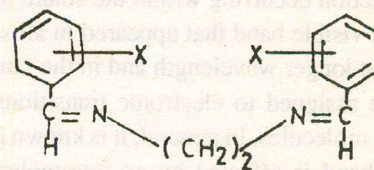
In general, the effect of substituents on the electronic absorption spectra of aliphatic and/or aromatic Schiff bases has been the focus of considerable study [1-15]. Recently there has been renewed interest in this subject [16]. In spite of this, little attention has been devoted to similar studies of the title compounds and this is addressed in the present note. This investigation sheds light on nature of the different absorption bands exhibited in spectra of the azomethines derived from N,N -ethylenediamine and selected aromatic aldehydes. In addition, the acidity constants of these compounds have been determined and discussed in terms of the molecular structures.

Experimental

The electronic absorption spectra were measured using a Shimadzu UV-Visible Recording Spectrophotometer UV-240, using 1 cm matched silica cells. pH-measurements for the determination of acid dissociation constant were made a MV-87 digital pH-messgerat PRACITRONIC, accurate to ± 0.05 units. Infrared spectra were recorded, in the region 4000-200 cm^{-1} , on Pye Unicam SP 1100 infrared recording spectrophotometer, using the KBr-disc technique. All measurements were carried out at 25°.

Materials. All chemicals used in this work were of Analar or extrapure grade. The organic solvents used were spectroscopic grade products. The dibasic Schiff bases employed in the present work were prepared in a way similar to that previously described [17], using N,N -ethylenediamine and certain aromatic aldehydes. The melting point and purity of the synthesised compounds were checked from microanalytical data as well as by infrared spectroscopy which were in good agreement with that compounds formerly prepared [17]. The

general formula of the synthesised Schiff bases can be cited as follows:



$X = p\text{-H(I)}; = o\text{-OH(II)}; = p\text{-OH(III)}; = p\text{-N(CH}_3)_2\text{(IV)}; = p\text{-NO}_2\text{(V)}; = p\text{-Cl(VI)}$.

Solutions. Stock solutions (1×10^{-3} mol dm^{-3}) of each of the Schiff bases (I-VI) were prepared in the various pure organic solvents used by conventional means.

Aqueous universal buffer solutions (H_3PO_4 , CH_3COOH , H_3BO_4 and $NaOH$) [18], in the pH range 1.89-11.98, were prepared and checked, at 25°.

The electronic absorption spectra (200-500 nm) were recorded immediately after preparing the solutions to avoid the rapid hydrolysis of these compounds.

Results and Discussion

Molecular structure and solvent effects. The results obtained from studying the electronic absorption spectra of the compounds investigated in various organic solvents of different polarities (methanol, ethanol, chloroform, acetonitrile and dimethylformamide) are collected in Table 1 and Figs. 1 and 2. In light of the results from measurements in ethanol the following assignments can be deduced.

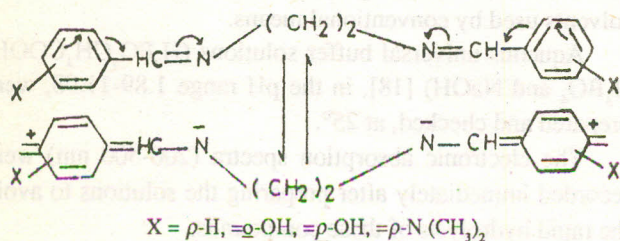
The recorded electronic absorption spectra of the compounds II ($X=O-OH$) and III ($X=p-OH$) show three main absorption bands while those of the compounds I ($X=p-H$), IV ($X=p-N(CH_3)_2$), V ($X=p-NO_2$) and VI ($X=p-Cl$) exhibit only two main absorptions. In addition, the spectra of the com-

pounds II and IV show an additional visible band at longer wavelength (Fig. 1).

The first UV band is located within the range 210-228 nm for all compounds examined and can be assigned to excitation of the π -electrons of the aromatic system [15-16]. It is noteworthy that the position of this band shows little sensitivity to the changing nature of the Schiff base substituents. In addition, this band is also observed with methanol as solvent but it does not appear in the other solvents used due to perturbation effect of them in this spectral region.

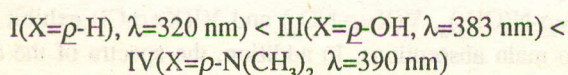
The second UV band observed in spectra of all compounds under investigation is within the wavelength range 245-298 nm (except in case of compound V ($X=p\text{-NO}_2$) and it can be ascribed to the transition between the π -orbital electrons largely localised on the central $\text{C}=\text{N}$ bonds [16]. The absence of this band in case of compound V is presumably due to its overlap within the strong visible band of this compound [16] as a result of a high electron-withdrawing of $-\text{NO}_2$ group. Generally, the second UV band is influenced by the charge transfer interaction occurring within the solute molecules.

The main visible band that appeared in all studied compounds were at longer wavelength and in the range, 273-383 nm. It can be assigned to electronic transitions within the whole of such molecules. In general, it is known [16], that the main visible band is affected by an intramolecular charge transfer (CT) interaction which occurs within the solute molecules. This can be represented as below, where the azomethine groups are considered as acceptor centers.



The good linear relations passing through the origin obtained on plotting the absorbance of main visible and versus the molar concentration of each of the studied compounds support the conception that this transition is intramolecular [15,16].

An examination of Table 1 reveals that the position of CT band is quite sensitive to nature of the aryl substituent X. In the case of the compounds I, III and IV, it is clear that the excitation energy of this band decreases as the electron-donor power of substituent X is increased [16], whereas CT band is red-shifted according to the following sequence:



The high excitation energy of the intramolecular CT band observed in case of compound V ($X=p\text{-NO}_2$, $\lambda=273 \text{ nm}$) and compound VI ($X=p\text{-Cl}$, $\lambda=290 \text{ nm}$) relative to that observed in case of compound III ($X=p\text{-OH}$, $\lambda=383 \text{ nm}$), can be presumably attributed to the high CT interaction that liable to occur in each of the two former compounds (V,VI). This is due to the high electron-withdrawing character [15] of each of the substituents $-\text{NO}_2$ and $-\text{Cl}$, which are likely to act as CT acceptor centers. The intramolecular CT transition within such derivatives can be represented as below:

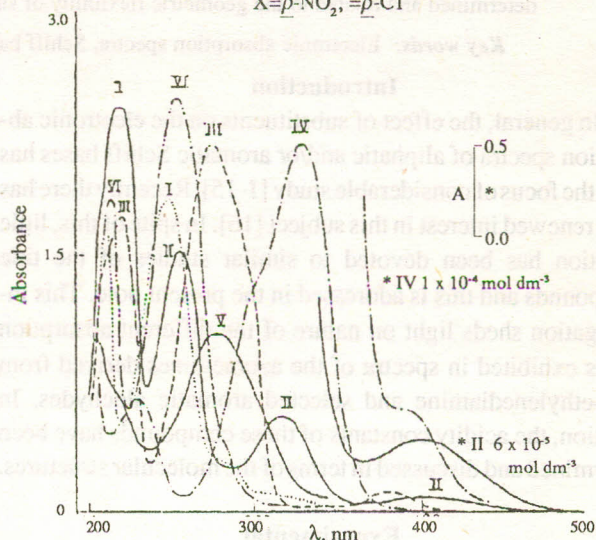
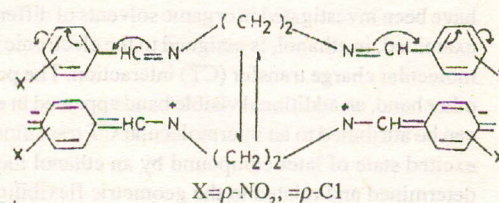


Fig. 1. Electronic absorption spectra of N,N-bis(x-benzylidene) ethylenediamine compounds I-VI, in ethanol at 25°. $6 \times 10^{-5} \text{ mol dm}^{-3}$ for the compounds, I, II, III, V and VI. $4 \times 10^{-5} \text{ mol dm}^{-3}$ for the compound IV.

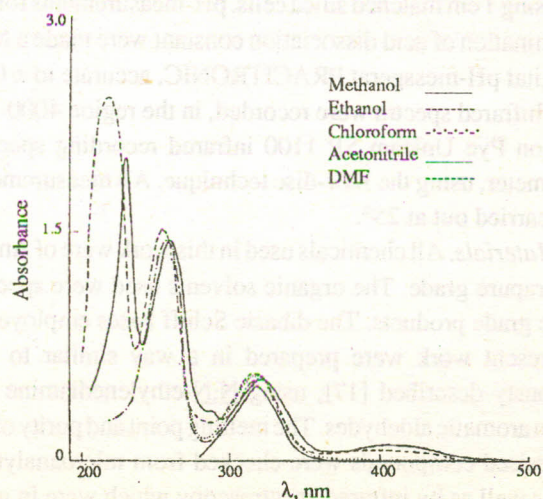


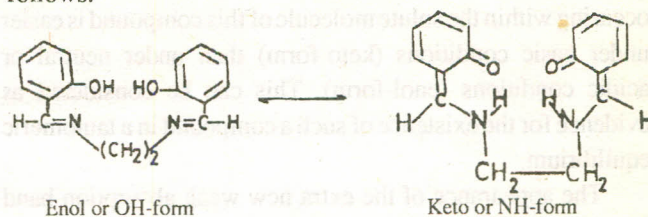
Fig. 2. Electronic absorption spectra of $6 \times 10^{-5} \text{ mol dm}^{-3}$ of the compound II (Salen), in pure organic solvents at 25°.

This behaviour strongly supports the CT nature of this band.

Moreover, it is evident that in the case of dipolar aprotic solvents, *viz.* acetonitrile and dimethylformamide, the CT band exhibits relatively low excitation energy relative to that in the other dipolar protic solvents, *viz.* methanol and ethanol and also in the non-polar solvents *viz.* chloroform (Table 1). This is likely due to the high stabilization of the polar excited state by the high polar solvent molecules through dipole-dipole interactions leading to lowering the excitation energy of this band.

The extra new weak absorption band that appears at longer wavelength in spectra of compound II ($X=p\text{-OH}$) in protic solvents can be attributed to the existence of such compound in a tautomeric equilibrium [16] of the OH-form \rightleftharpoons NH-form. Such a type of tautomeric equilibrium

originates from the *ortho*-position of hydroxyl group with respect to the azomethine unit which can be represented as follows:



This behaviour is confirmed by the results obtained on studying the spectral behaviour of this compound in a series of aqueous solutions of different pH's as illustrated in Fig. 3. From this study, it is observed that upon decreasing the pH to a values $\text{pH} \leq 3.93$, the longer wavelength band is blue-shifted and its intensity is decreased. This behaviour can be inter-

TABLE 1. ELECTRONIC SPECTRAL CHARACTERISTICS OF N, N' -BIS (X-BENZYLIDENES) ETHYLENEDIAMINE, I-VI, IN PURE ORGANIC SOLVENTS, AT 25°C.

Compound	Methanol		Ethanol		Chloroform		Acetonitrile		DMF		Assign-ment
	λ_{max} nm	$10^{-3} \epsilon_{\text{max}}$ $\text{mol}^{-1} \text{cm}^2$	λ_{max} nm	$10^{-3} \epsilon_{\text{max}}$ $\text{mol}^{-1} \text{cm}^2$	λ_{max} nm	$10^{-3} \epsilon_{\text{max}}$ $\text{mol}^{-1} \text{cm}^2$	λ_{max} nm	$10^{-3} \epsilon_{\text{max}}$ $\text{mol}^{-1} \text{cm}^2$	λ_{max} nm	$10^{-3} \epsilon_{\text{max}}$ $\text{mol}^{-1} \text{cm}^2$	
I ($X=p\text{-H}$)	212	9.667	210	27.667	—	—	—	—	—	—	$\pi - \pi^*$
	245	30.333	245	30.833	247	30.667	—	—	—	—	$\pi - \pi^*$
	320sh	0.333	320sh	1.000	320sh	0.833	—	—	—	—	Intramol. CT trans.
II ($X=p\text{-OH}$)	230	34.000	220	40.000	—	—	—	—	—	—	$\pi - \pi^*$
	260	24.500	254	25.667	255	24.166	—	—	—	—	$\pi - \pi^*$
	320	9.000	315	9.500	315	8.667	320	8.500	320	9.500	Intramol. CT trans.
	400	1.500	400	1.000	—	—	—	—	—	—	Intramol. CT trans.
III ($X=p\text{-OH}$)	223	29.000	218	29.083	—	—	—	—	—	—	$\pi - \pi^*$
	273	34.667	273	36.333	273	36.333	278	24.333	275	36.333	$\pi - \pi^*$
	375	5.416	383	1.750	—	—	—	—	—	—	Intramol. CT trans.
IV ($X=p\text{-N}$ (CH_3) ₂)	228	15.750	228	16.500	—	—	—	—	—	—	$\pi - \pi^*$
	298sh	25.500	298sh	33.000	298sh	33.500	298sh	38.000	298sh	37.500	$\pi - \pi^*$
	328	45.500	328	54.500	328	53.250	323	52.500	323	51.250	Intramol. CT trans.
	390	20.250	390	1.000	—	—	390	0.300	—	—	$n - \sigma^*$
V ($X=p\text{-NO}_2$)	220	9.500	218	12.000	—	—	—	—	—	—	$\pi - \pi^*$
	275	19.500	273	17.750	280	18.000	285	15.333	285	15.000	Intramol. CT trans.
VI ($X=p\text{-Cl}$)	226	32.167	210	31.000	—	—	—	—	—	—	$\pi - \pi^*$
	252	40.333	255	41.000	256	40.500	273	3.6670	265	16.000	$\pi - \pi^*$
	290sh	3.667	290sh	3.833	290sh	4.000	292sh	2.000	292sh	2.833	Intramol. CT trans.

sh = shoulder.

preted on the basis that CT interaction within the enol-form is expected to be more difficult than that from the keto-form. Accordingly, it is logically to say that the CT interaction occurring within the solute molecule of this compound is easier under basic conditions (keto-form) than under neutral or acidic conditions (enol-form). This can be considered as evidence for the existence of such a compound in a tautomeric equilibrium.

The appearance of the extra new weak absorption band ($\lambda=4.00$ nm) in spectra of compound II in the protic solvents than that is the other aprotic solvents studied can be assigned to an intermolecular CT transition through the formation of hydrogen bonding as electron transfer from the lone pair of electrons of the oxygen atom of ethanol molecules to the antibonding orbital of the substituent -OH group (-OH...O). The nonlinear relation obtained on plotting the absorbance of this band vs. the concentration of the compound supports the intermolecular CT nature of this band. Similar assignment was induced by Mahmoud and others [15,16].

The longer wavelength band observed in spectra of compound IV ($X=p\text{-N(CH}_3)_2$, at 390 nm in ethanol, can be assigned to a complexed solute-solvent. Formation of hydrogen bonding by donation of the lone pair of electrons of the substituent -N(CH₃)₂ to the antibonding orbital of the hydrogen atom of ethanol molecule allows for a $n\rightarrow\sigma^*$ transition. The location of this band at longer wavelength than that of the usual $n\rightarrow\sigma^*$ transition is presumably due to high stabilization of the polar excited state of this transition, (-OH...N(CH₃)₂) by the polar solvent. The low molar extinction coefficient of this band (1000 mol⁻¹ cm²) is in accordance with its assignment. This assignment is typical of those induced by Hires [20], Charette [3] and Mahmoud [14].

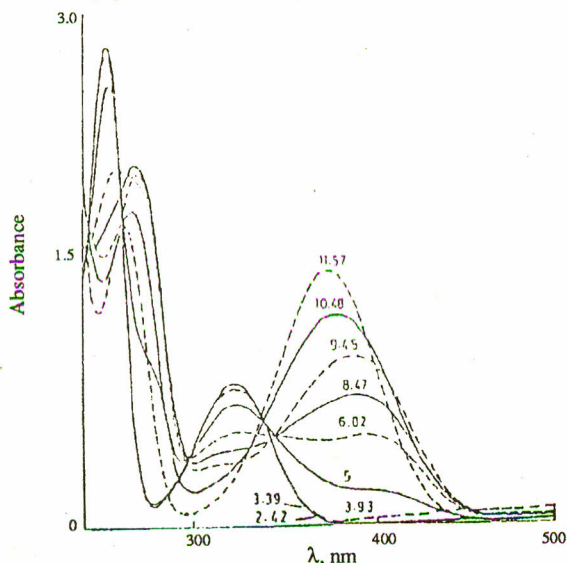
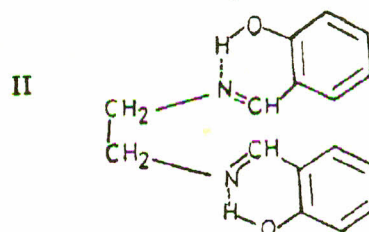


Fig. 3. Electronic absorption spectra of 1×10^{-4} mol dm⁻³ of the compound II, in aqueous universal buffer solutions at 25°.

Determination of acidity constants. The electronic absorption spectra of the studied compound in aqueous universal buffer solutions of varying pH's were applied to determine the pK_a values of these compounds spectrophotometrically. The recorded spectra of the compounds II, III, IV and VI, exhibit clear isosbestic points, as shown in Fig. 3 for compound II. This indicates that chemical equilibria exist among different species of studied compounds. The absorbance-pH relationships of these compounds are typical [15] dissociation curves and support the establishment of acid-base equilibria within the pH range examined. The pK_a values are compiled in Table 2. Measurement of the pK_a data for compounds I and V was not achieved in this work due to overlap of their absorption spectra at the different pH's. In light of the results listed in Table 2, we can deduce that compounds II and III, having hydroxy groups, give two pK_a values, one of which may be assigned to the deprotonation of an azomethine group, C=NH-, and the other to the ionization of the phenolic *o*-OH or *p*-OH group. On the other hand, compounds IV and VI give only one pK_a value due to the deprotonation of an azomethine group. Moreover, the pK_a value of the hydroxy group at the *ortho*-position is higher than that at *para*-position. This is presumably due to strong intramolecular hydrogen bonding between the hydrogen of *o*-OH group and the central azomethine nitrogen [16] as represented below. This behaviour will result in a more difficult ionization and thus a high pK_a value as is observed.



N, N-bis (salicylidene)s ethylenediamine (Salen)

TABLE 2. THE pK_a VALUES OF THE COMPOUNDS II, III, IV AND VI, AT 25°C.

Compound	λ , nm	pK _a		Mean value
		Half-height method	Limiting absorbance method	
II (X= <i>o</i> -OH)	380	8.55	8.50	8.53±0.03
	325	6.85	6.82	6.84±0.02
III (X= <i>p</i> -OH)	330	7.80	7.75	7.78±0.03
	280	7.75	8.10	7.93±0.18
IV (X= <i>p</i> -N(CH ₃) ₂)	410	7.00	7.10	7.05±0.05
VI (X= <i>p</i> -Cl)	255	7.80	8.0	7.90±0.1

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

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