Asian Journal of Chemistry Vol. 2, No. 4 (1990), 389-398

Spectral Properties and Acidity Constants of Some Schiff Bases Derived from Salicylaldehyde and Phenylenediamine

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The electronic spectral properties of two bifunctional Schiff bases were studied in organic solvents. The assignment of spectral bands was investigated according to the influence of the solvent's polarity. The possibility of π–π^* CT complex formation between the studied compounds as electron donors and some acceptors have been examined. The pK_α values of *o*-OH group and the effect of different proportions of organic solvents (EtOH, $(CH_3)_2CO$ and DMF) on the pK_a values were also determined and discussed.

INTRODUCTION

Although much work has been published on the electronic spectra and acid-base equilibrium of Schiff bases containing one azomethine group, little information is reported concerning similar studies on those containing two azomethine groups.[1–5] Accordingly the present investigation was aimed to study the effect of organic solvents and π-acceptors organic compounds (*o*-chloronitrobenzene, CHNB, 3,5-dinitrobenzoic acid, DNBA, picric acid, PA, and chloranil, CHL) on the spectral behaviour of bifunctional Schiff bases derived from salicylaldehyde with *m*-phenylenediamine (H_2A) and *p*-phenylenediamine (H_2B). Moreover, the acidity constants of these compounds were determined in pure aqueous buffer solutions and in those containing different proportions of organic solvents (ethanol, acetone, DMF). The results are discussed in terms of molecular structure and the nature of the organic co-solvent used. Salicylaldehyde with *m*-phenylenediamine (H_2A) and *p*-phenylenediamine (H_2B). Moreover, the acidity constants of these compounds were determined in pure aqueous buffer solutions and in those containing different proportions of organic solvents (ethanol, acetone, DMF). The results are discussed in terms of molecular structure and the nature of the organic co-solvent used.

EXPERIMENTAL

Chemicals of purest grade (B.D.H. products) were used. The bifunctional Schiff bases H_2A and H_2B were prepared according to procedure given in literature[6]. The structure and purity of the compounds were checked by IR spectra and microanalysis. Organic solvents used were all of spectral grade B.D.H. or Merk products. Stock solutions were prepared by dissolving the accurately weighed amount of each compound in the appropriate volume of the solvent. The modified universal buffer series of Britton and

Robinson were prepared[7]. The pH values were checked by Digital MV-pH meter accurate to ±0.005 pH units. The pH values for partially aqueous solutions were corrected making use of the procedure described by Douheret.[8] The pH meter reading pH(R) obtained in partially aqueous medium differs by an amount (δ) from the corrected reading pH*, where $pH^* = pH(R) - \delta$. The δ values of the aqueous buffer solutions containing varying proportions of each organic solvent used were determined as reported earlier.[8, 9] The electronic spectra were recorded on a Shimadzo recording 240 spectrophotometer at 25°C using 1 cm matched silica cell.

RESULTS AND DISCUSSION

The electronic absorption spectra of compounds H_2A and H_2B in EtOH, $CHCl_3$, CCl_4, DMF and dioxan are recorded (Fig. 1 for H_2B). The λ_{max} and ϵ_{max} values in these media are collected in Table 1. The spectra of H_2A and H_2B in ethanol exhibit mainly three and four bands respectively. The first UV band (215 – 230 nm) is ascribed to π–π^* transition within the aromatic system[10]. This assignment is confirmed by little influence of its position by changing the solvent polarity. The second band located within the range 250–272 nm is due to transitions between π-orbitals

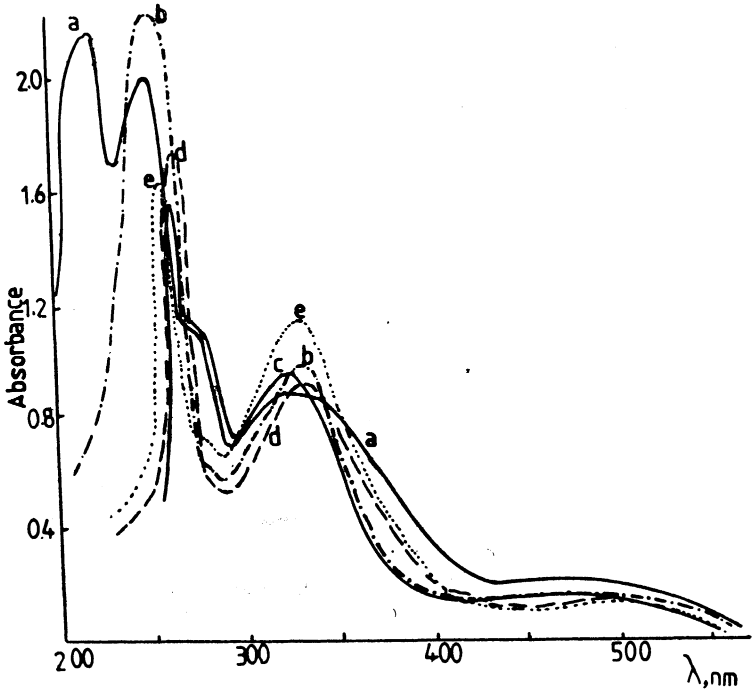


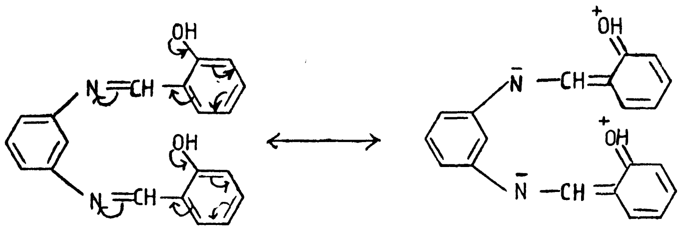
Fig. 1 Electronic absorption spectra of 1×10^{-4}M H_2B in different solvents: EtOH (a), $CHCl_3$ (b), CCl_4 (c), DMF (d), and dioxane (e)

TABLE 1

ELECTRONIC ABSORPTION SPECTRAL DATA OF COMPOUND H_2A AND H_2B IN ORGANIC SOLVENTS

Solvent	Compound H_2A		Compound H_2B	
	λ_{max}	ϵ_{max}	λ_{max}	ϵ_{max}
EtOH	230	27000	215	22000
	268	21200	248	20000
	339	13800	330	8800
	—	—	504*sh*	2600
$CHCl_3$	242	23000	—	—
	258	25200	250	22800
	338	16500	328	9700
	—	—	502*sh*	1700
CCl_4	266	29800	258	16500
	338	15000	328	9500
	—	—	500*sh*	1500
DMF	272	24800	262	14300
	342	17500	320	8800
	—	—	500*sh*	1700
Dioxan	260	21000	258	16400
	330	13800	335	11400
	—	—	496	1420

localized on the central C=N bond[11]. It is suggested that this band is influenced by CT interaction occurring in the solute molecules as shown below. The third band observed at 320–342 nm. can be ascribed to intramolecular CT transition within the whole molecule[12]. Since it is known that in similar compounds, the N-phenyl is twisted out of plane[13], the intramolecular CT seems to originate from the aldehydic moiety to the C=N groups as acceptor centre as represented below:



The high molar extinction coefficient of this band as well as the linear relationship passing through the origin between the absorbance of the intramolecular CT band and the molar concentration of the compound are in accordance with this assignment. The broad band observed at $\simeq$ 500 nm in the spectra of H_2B in all solvents used can be explained on the base of the presence of this compound in a keto-enol tautomeric equilibrium as represented before. Therefore, this band can be assigned to intramolecular CT transition of the keto imine tautomer and, thus, for the third band of the same compound can be attributed to the same transition but within the enol form. This is confirmed from the solvent effect on the two longer wavelength bands of H_2B (Table 1). The shorter wavelength CT band shows a relatively high intensity in nonpolar solvents and blue shifted with increasing solvent polarity. The opposite phenomenon is observed for the longer wavelength CT one. This is expected, since the enol imine predominates in nonpolar solvents where strong intramolecular H-bond has been presented[14]. Therefore the CT of enol imine tautomer is expected to be blue shifted in ethanol as a result of weakening the intramolecular H-bond as a result of solute-solvent interaction. Similar changes have been observed for other salicylidene-imines.[5, 15, 16]

Moreover, a convincing evidence for the CT nature of the above described bands as well as the suggestion that the presence of the neutral form of compound H_2B in a tautomeric equilibrium is substantiated by considering the spectral behaviour of the two studied compounds in aqueous solutions of varying pH's (Fig. 3). Thus in acidic solutions ($pH \leqslant 3.82$), the second UV band acquires a blue shift in its λ_{max} and the third band is greatly lowered. This behaviour can be discussed on the basis that in acidic solutions, the H_2B exists mainly in OH-form and, therefore, the CT interaction within this form is difficult compared to what takes place in the NH-form. By increasing the pH of the medium, the second and the third band acquire a red shift in their λ_{max} and the extinction coefficient of the OH-form band decreases, due to the increase in the proportion of the NH-form as the pH of the medium is increased. Furthermore, as the pH of the medium increases above 7.36, the extinction coefficient of the NH-form band becomes lower, meanwhile a new band is formed at longer wavelength. This behaviour can be explained on the principle that in alkaline medium the OH groups of the compounds become ionised and therefore their mesomeric interaction with the rest of the molecule becomes high. Consequently the CT interaction within the free base is facilitated.

Effect of organic acceptor compounds

The electronic absorption spectra of mixed solution of each of H_2A and H_2B with each of the acceptor *o*-chloronitrobenzene (CHNB), 3,5-dinitrobenzoic acid (DNBA), picric acid (PA) and chloranil (CHL) are investigated in methylene chloride solution. The extra new absorption broad band observed in the visible region can be attributed to the donor-acceptor molecular complex formation[17], since neither free electron donors nor electron acceptors under investigation absorbs in this region. Except in case of the acceptor DNBA with H_2A, the electronic spectra of the donor with all acceptors studied are characterized by one main broad absorption band. This band can be assigned to π–π^* CT from the HOMO of the donor which has π-bonding character to the LUMO of the acceptor. The CT nature of the band is substantiated by calculating the CT energy (E_{CT}) using Bregelb relation[18]. Also, the π-ionization potentials of the donors (I_P) were determined from the electronic absorption spectra applying the relation $I_P = a + b\nu_0$ in which a and b are constants (4.39 and 0.857[19] or 5.11 and 0.701[20]) and ν_0 is the energy of HOMO-LUMO π–π^* transition. The values are in reasonable with the transition energies of CT complexes (Table 2).

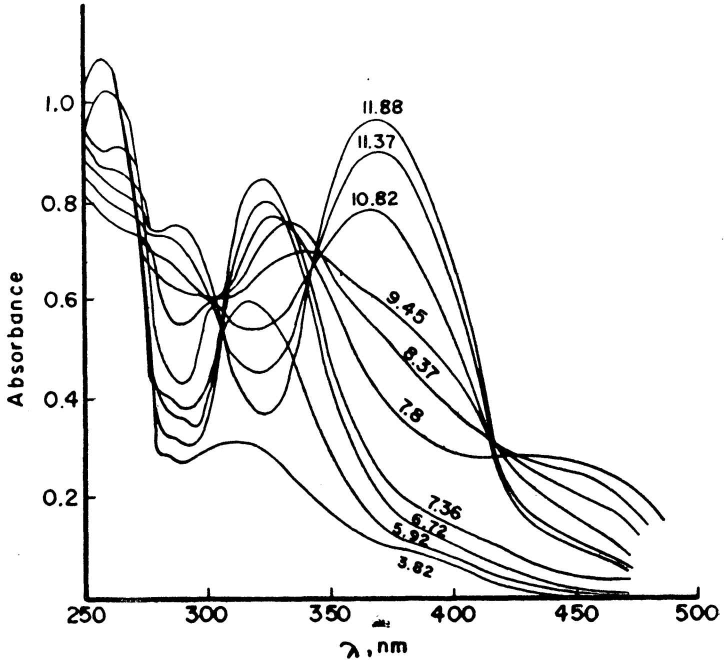


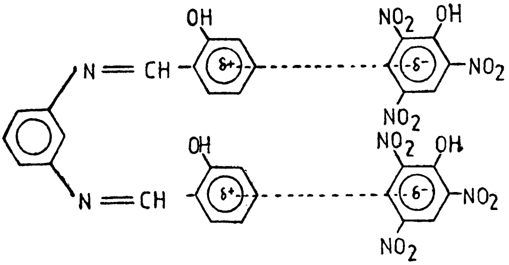
Fig. 2 Electronic absorption spectra of 8.2×10^{-5}M compound H_2B in universal buffer solutions

TABLE 2

λ_{max} (nm), ϵ_{max} (mol^{-1} cm^{-1}), CT ENERGY (E_{CT}, ev) AND IONIZATION POTENTIAL (I_P, ev) DATA OBTAINED FROM DONOR-ACCEPTOR COMPLEXES STUDIED

Acceptor	H_2A complexes				H_2B complexes			
	λ_{max}	ϵ_{max}	E_{CT}	I_P	λ_{max}	ϵ_{max}	E_{CT}	I_P
CHNB	510	50	2.44	8.76	414	386	3.00	8.20
DNBA	550*sh*	128.5	2.56	8.25	430	285	2.89	8.60
	428	471	2.91	8.56	—	—	—	—
PA	454	585	2.20	8.62	435	531	2.86	8.70
ChL	685*sh*	357	1.82	8.22	600	271	2.07	7.80

It is worth mentioning that the appearance of only one broad band in spectra of compound H_2B denotes that n–π^* interaction has low contribution to occur. This behaviour can be interpreted if compound H_2B exist in keto-enol structure as suggested above. Thus the keto form leads to blocking the C = N nitrogen lone pair through intramolecular proton transfer. This will result in a difficult transfer of n-electron from C=N to π^* of the acceptor. Moreover, in case of H_2A with DNBA, the data shows the existence of a second CT band which can be explained in terms of transitions from more than one occupied orbitals of the electron donor to the same unoccupied orbitals of the π-acceptors.[21] The stoichiometry of the π–π^* CT complexes studied was determined by the spectrophotometric Job's method[22] which revealed 1 : 2 stoichiometric ratio of all systems studied. Hence based on the above results the CT interaction can be represented as follows:



Acidity constants and medium effect

The acidity constants (pK_α) for the two compounds under study (H_2A and H_2B) were determined from their spectral behaviour in unversal buffer solutions of pH* ranging from 3.8 to 12.4. Effects of medium on the pK_α values were studied in the same series of buffer solutions, but each containing varying proportions of organic solvents of different polarities (ethanol, acetone, and DMF). Representative results are given in Fig. 3.

Generally, for the two compounds, the band observed at pH $\leqslant$ 7.36 can be ascribed to the absorption of the nonionic form. Increasing the pH of the medium results in red shift of λ_{max} (H_2B) or decreasing the intensity (H_2A) of this band, whereby a new band is developed at longer wavelength representing the ionic form of the compounds. This is due to the increased negative charge density on the phenolate ions in the high pH range which, in turn, facilitate the CT which takes place within the free base.

The recorded spectra of the two compounds show isobestic points in acidic (pH $\leqslant$ 7.36) and in alkaline (pH $\geqslant$ 9.3) medium, denoting the existence of an acid-base equilibium among different species in solution. The

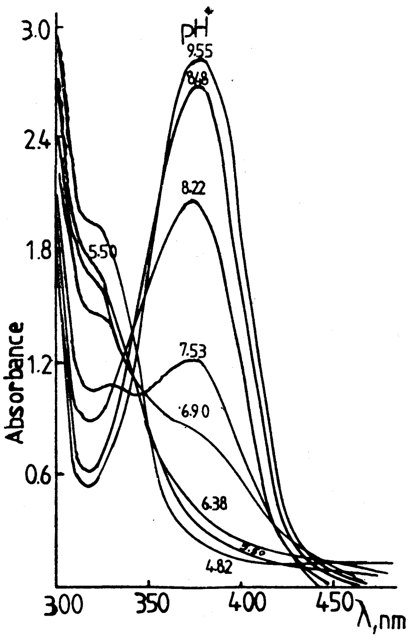
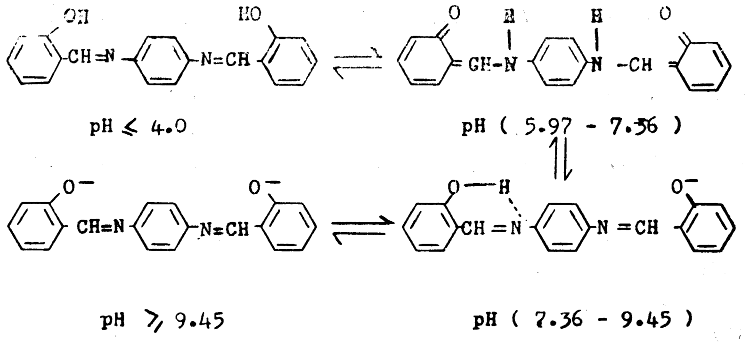


Fig. 3 Spectra of 2×10^{-4}M of compound H_2A in aqueous buffer solutions containing (% w/w) 16.49 acetone

possible species for H_2B can be represented as follows:



This is confirmed by the typical dissociation curves obtained from the absorbance-pH* relations. The pK_α values in aqueous and in partially aqueous medium were determined from the different spectrophotometric methods previously described[23]. Moreover, the simultaneous ionizations of the two –OH groups were confirmed by pH-metric titration method. The titration graphs of H_2A and H_2B compounds give two steep inflection points of values of C_{OH}/C_A of 1 and 2 around pH = 7.2, 7.7 and 8.4, 10.5 respectively. The pK_α values obtained using this method are in accordance with those obtained spectrophotometrically. The limit accuracy was checked by making use of the least-squares method. The results are collected in Table 3. It is worth mentioning that the presence of two different pK_α values for the two *o*-OH groups indicate that one of them is in a position that facilitates the formation of intramolecular hydrogen bond with the azomethine nitrogen. The presence of such H-bonding causes a forced planarity of this compound[24]. This facilitates the ionization of one of the *o*-OH groups.

Examination of the results cited in Table 3 reveal that the ionization constant decreases (*i.e.* increase in pK_α values) with increasing the amount of organic co-solvent in the medium. This behaviour can be explained on the basis of the relation between the acidity constant in aqueous medium (K_1) and that in a partially aqueous medium (K_2) with the activity coefficient (γ) of the species in equilibrium as represented below:[25]

TABLE 3

MEAN pK_α VALUES FOR H_2A AND H_2B IN AQUEOUS-ORGANIC SOLVENT BUFFER MIXTURES

% (w/w) organic solvent	*D*	Compound H_2A		Compound H_2B	
		$pK_{\alpha 1}$	$pK_{\alpha 2}$	$pK_{\alpha 1}$	$pK_{\alpha 2}$
0.00	78.4	7.46±0.02	8.38±0.04	7.62±0.04	10.62±0.01
		Aqueous-Acetone mixtures			
16.50	75.05	7.08±0.01	7.98±0.03	7.15±0.05	10.00±0.05
25.29	72.07	7.22±0.03	8.15±0.02	7.29±0.01	10.28±0.03
34.49	69.15	7.30±0.01	8.32±0.04	7.40±0.02	10.55±0.01
		Aqueous-Ethanol mixtures			
16.49	74.52	6.92±0.03	7.85±0.02	7.11±0.04	9.92±0.02
25.29	72.05	7.17±0.02	7.96±0.04	7.27±0.02	10.17±0.06
34.49	69.15	7.25±0.04	8.24±0.02	7.13±0.05	10.22±0.03
		Aqueous-DMF mixtures			
19.17	76.09	6.86±0.01	7.82±0.02	7.04±0.04	9.87±0.01
28.91	74.60	6.92±0.04	8.15±0.05	7.10±0.04	9.90±0.02
34.50	72.77	7.14±0.05	8.22±0.02	7.25±0.03	10.18±0.05

$$HA \leftrightarrow A^{-} + H^{+}$$

$$K_1 = K_2 \frac{\gamma_{H^+} \cdot \gamma_{A^-}}{\gamma_{HA}}$$

Since the electrostatic effects resulting from the change in dielectric constant of the medium (D) will operate on the activity coefficient of the charged species only, where its magnitude is inversely proportional to the ionic radius[26]. Thus, it is expected that the ionization constant is decreased as the proportion of the organic co-solvent increases in the medium. This means that the decrease in pK_α values is influenced by other solvent effects beside the change in the dielectric constant of the medium. These effects can be interpreted in the light of the obtained results (Table 3) as follows: the high pK_α values in pure aqueous medium relative to that in presence of organic solvents can be ascribed to the high stabilization of the ionic form (A^-) by hydrogen bond donor in pure aqueous medium. This is due to the tendency of water molecules to donate hydrogen bond as compared with the other solvent molecules[25]. The results also indicate that, in the media containing the same percentage of organic solvents studied, the variation of pK_α values follows the sequence DMF $<$ EtOH $<$ acetone. This behaviour can be attributed to the high basicity of DMF relative to other solvents. This reflects itself in formation of H-bond acceptor from the hydroxy groups of the compound. This facilitates the ionization process (i.e. low pK_α). Moreover, the low tendency of acetone to donate hydrogen bond to the free base A^- relative to ethanol reflects itself in a relatively high pK_α value in acetone relative to ethanol.[27]

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[*Received*: 12 October 1989; *Accepted*: 2 January 1990] AJC–127