Spectral Characterization and Charge – Transfer Complexes of Some Schiff Bases Derived from Aminopyridines and Hydroxyacetophenones

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Abstract

The molecular structures of acetophenonylidine-4-aminopyridine (I), 2, 6-dihydroxyacetophenonlidine-4-aminopyridine (II), 2, 4, 6- trihydroxyaceto phenonylidine-4-aminopyridine (III) and 2, 6-dihydroxyacetophenonylidine-2-aminopyridine (IV) have been investigated by IR and UV-visible spectrophotometry. The IR data indicate that the hydroxyl groups of these Schiff bases exist as tautomeric mixtures of free and bonded with the azomethine groups. The electronic spectra, effect of polar and nonpolar solvents, and the effect of acidity and basicity on the electronic spectra were studied and discussed. Their charge-transfer (CT) complexes with chloranil in chloroform solvent were also investigated; these complexes absorb light at 398-533 nm. The ionization potentials of Schiff bases, the equilibrium constants , molar extinction coefficients of CT complexes and the dissociation energies of the complexes excited states were estimated and discussed, the values are 8.38 – 8.98 eV , 138 – 560 mol^{-1} dm^3 , 530 – 1430 m^2 mol^{-1} and 4.68 – 4.75 eV , respectively .

Keywords: Charge–transfer complexes, acetophenone, aminopyridine, Schiff bases.

الخواص الطيفية ومعقدات انتقال– الشحنة لبعض قواعد شف المشتقة من أمينات البريدين وهيدروكسيلات الاسيتوفينون

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الخلاصة:

لقد فحصت التراكيب الجزيئية للاسي توفنليدين – 4–امينو بريدين (I) ، 6,2– ثنائي هيدروكسي اسيتوفينونيليدين –4–امينو بريدين (II) ، 6,4,2– ثلاثي هيدروكسي اسيتوفينونيليدين –4–امينو بريدين(III) و6,2– ثنائي هيدروكسي اسيتوفينونيليدين –2–امينو بريدين(VI) بأستخدام مطيافية الاشعة تحت الحمراء والفوق البنفسجية–المرئية بالإضافة الى تحليل العناصر الدقيق . دلت نتائج الأطياف تحت الحمراء على ان مجاميع الهيدروكسي بهذه القواعد تتواجد بهيئة خليط توتومري من HO الحر والمرتبط هيدروجينيا مع مجموعة الايزوميثين في القاعدة . درست ونوقشت أيضا الأطياف الالكترونية و تأثير المذيبات القطبية وغير القطبية و الحامضية والقاعدية على الأطياف الالكترونية . وكذلك فحصت معقدات انتقال – شحنتها مع مستقبل الكلورانيل بمذيب الكلوروفوم، وجد أن هذه المعقدات تمتص الضوء عند 398–533 نانومتر . لقد تم تقدير ومناقشة جهود تأين قواعد شف وثوابت التوازن وثوابت الامتصاص المولاري لمعقدات انتقال – الشحنة وكذلك طاقات تفكك حالات إثارة المعقدات، وان قيم هذه الثوابت الفيزيائية هي كالأتي : 8.38 – 8.98 إلكترون فولت و138–560 مول $^{-1}$.دسم ^{3} و 530–1430 متر^2 مول $^{-1}$ و 4.68–4.75 إلكترون فولت على التوالي.

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Introduction

The previous spectral studies on different kinds of Schiff bases have included the electronic, infrared, nuclear magnetic resonance, mass spectrometry and others[1-9], complexation with various metal ions in ethanolic solution [3-6,8], and charge – transfer (CT) complexes with various electron acceptors in chloroform and methanol solution [10,11]. The study of CT complexes between several Schiff bases as electron donors and different electron acceptors such as Iodine (I_2) ,DDQ(2,3-dichloro -5,6-dicyano-1,4-benzoquinone),p-CA(2,3,5,6-tetrachloro-1,4-benzoquinone), o-CA(3,4,5,6-tetrachloro-1,2-benzoquinone) and aromatic nitro compounds have been investigated and calculated the equilibrium constants , extinction coefficients of the CT complexes ,including the ionization potentials values of the Schiff base as electron donors [7,10-12] .

In this work different spectral properties, the effect of different solvents on the electronic spectra and charge – transfer complexes with the acceptor chloranil have been investigated on a new class of Schiff bases which were prepared with same the method ,previously [12], these bases are derived from 2-aminopyridine,4-aminopyridine and hydroxyacetophenones .

EXPERIMENTAL

Acetophenonylidine-4-aminopyridine (I) m.p = 94 °C (record. m.p = 95–6 °C) , 2,6-dihydroxyacetophenonlidine -4- amionpyridine (II) m.p = 117 °C (record. m.p = 116 – 8 °C), 2,4,6 – trihydroxyacetophenonylidine - 4-amionpyridine (III) m.p = 182 –3 °C (record. m.p = 183 – 5 C°) and 2,6 – dihydroxyacetophenonylidine – 2 –aminopyridine (IV) (Scheme 1) m.p= 114 – 6 °C (record. m.p = 114 – 7 °C) were prepared and purified as described previously [12] .

Chloranil CA (2,3,5,6-tetrachloro-1,4-benzoquinone) was of "Fluka" of purity greater than 96% . Sodium hydroxide (G.R) of "BDH" and hydrochloric acid (AnalaR) of "Ferak" .Cyclohexane , benzene , carbon tetrachloride , chloroform and n-butanol were (spectrosil) of "Fluka" . Ethanol dichloroethane and acetic acid were (AnalaR) of "BDH" . Dimethylsulfoxide DMSO and dimethylformamide DMF were (spectrosil) of "Merck".

Varian DMS 100 UV-Visible spectrophotometer was used to record the electronic spectra using (1 cm) quartz absorption cell . PyeUnicam SP3-300 IR spectrophotometer was used to record the IR spectra as KBr disks . Perkin Elmer 240 B Elemental Analyzer was used to record elemental analysis of the Schiff bases and the results obtained are shown in table-1.

Table 1- Molecular Formula, Molecular Weight (m.w), Melting point (m.p) and Elemental Analysis of the Schiff Bases.

Schiff base	**Molecular formula**	**m.w/g mol^{-1}**	**m.p / ^{o}c**	**Element analysis % calculated (found)**		
				C	H	N
I	$C_{13}H_{12}N_2$	196	95-96	79.59 (79.52)	6.12 (6.10)	14.26 (14.16)
II	$C_{13}H_{12}N_2O_2$	228	116-118	68.42 (68.33)	5.26 (5.29)	12.19 (12.08)
III	$C_{13}H_{12}N_2O_3$	244	183-185	63.93 (63.99)	4.92 (4.88)	11.48 (11.42)
IV	$C_{13}H_{12}N_2O_2$	228	114-117	68.42 (68.47)	5.26 (5.12)	12.19 (12.37)

Results and Discussion

Infrared spectra

Table-2 represent the major absorption peaks of the stretching and bending vibrations of compounds I –IV and some of their starting materials. The data confirm the molecular structures of compounds I-IV.The most important conclusion concerning the molecular structures can be outlined as follow: (i) the asymmetric and symmetric stretching vibrations of the free O-H bands in compounds II and IV located at 3460 and 3360 cm^{-1} and at 3380 and 3330 cm^{-1} respectively. These absorption peaks have

not observed in the spectrum of 2,6- dihydroxyacetophenon, although the bonded O-H was observed at 3300 cm^{-1}. This indicates that the O-H of 2,6- dihydroxyacetophenone is completely bonded with its carbonyl groups, whereas II and IV present as a tautomeric mixtures in which the O-H groups are free and bonded with the azomethine group of the molecule, this confirmed by the shift of $\upsilon_{C=O}$ absorption band of acetophenone from 1683 cm^{-1} [13] to 1620 cm^{-1}. In the case of 2,6- dihydroxyacetophenone, which means that C=O of 2,6- dihydroxyphenone is completely bonded with the O-H group. (ii) The asymmetric and symmetric stretching vibration of O-H at III are shifted to a lower frequencies by 140 and 120 cm^{-1} compared with that of 2,4,6- trihydroxyacetophenone, this provides another evidence for a greater hydrogen bonding of O-H with the azomethine .

Table 2- The most important peaks in the IR spectra of compounds I – IV and some of their starting materials, on KBr disks.

Compound	υ_{O-H} / cm^{-1}			$\upsilon_{C=N}$ / cm^{-1}	Skeletal bands phenol and / or pyridine ring/ cm^{-1}	υ_{C-N} /cm^{-1}	δ_{O-H} /cm^{-1}	υ_{C-O} /cm^{-1}
	Asym.	Sym.	Bounded					
2-Amino pyridine(*)	—	—	—	—	N = C ; 1480 s. C = C ; 1590, 1550, 1435 s.	1320 w	—	—
4- Amino pyridine(**)	—	—	—	—	N = C ; 1490 s C = C ; 1595 s, 1550 w, 1425 m	1320 m	—	—
2,6-Dihydroxy acetophenone(***)	—	—	3300 b.vs.		C = C ; 1580 s, 1510 w, 1450 s	—	1350 s	1040 vs
2,4,6trihydroxy acetophenone	3520 s	3450 s	3100 b.vs.		C = C ; 1550 m, 1520 m, 1445 w	—	1340 s	1030 vs
I	—	—	—	1625 s	N = C ; 1475 w. C = C ; 1535 m, 1580 s	1440 w	—	—
II	3460 s	3360 s	3200 m	1620 b,s	N = C ; 1485 m C = C ; 1510 m, 1560 s, 1590 s	1440 s	1330 m	1060 m
III	3380 s	3330 s	3200 s	1655 s	N = C ; 1495 s C = C ; 1520 s, 1550 w ,1600 s	1415 m	1360 s	1050 m
IV	3460 s	3360 s	3200 w	1620 s	N = C ; 1485 m. C = C ; 1590 s, 1560 s, 1510 m	1445 s	1360 m	1040 s

(*) υ NH 3430 cm^{-1} b.,w. δ NH, 1620 cm^{-1} s. (**) υ NH 3420 s, 33000 m cm^{-1} , δ NH 1640cm^{-1} s. (***) υ c=o 1620 cm^{-1} b.vs.
S, strong ; w. weak ; m, medium ; b, broad ; vs, very strong
υ, stretching vibration
δ, out of plane bending vibration

Electronic spectra and the effect of solvents

Figures 1 and 2 represent the electronic spectra of compounds I and II at different concentrations in ethanol as a typical examples. Table 3 shows the absorption bands in the electronic spectra of compounds I – IV and their starting materials in ethanol. The absorption bands at 203 and 205 nm of I – IV at 250 nm of I represent the local excitation $\pi \rightarrow \pi^*$ transitions of pyridine and acetophenone rings, which correspond the transition $^1A_{1g} \rightarrow {}^1B_{1U}$ at 203 nm in the spectrum of benzene molecule [14] . The electronic transition at 250 nm of I splits into two bands in spectra II and III , their positions at 224 , 247 nm and at 229 , 248 nm respectively; and concentrated at 228 nm in the spectrum of IV. The data of Table 3 indicate that the intensity of the band at 250 nm of I is greater than the total intensities of the bands at 224 and 247 nm of II equal to the total intensities of the bands at 229 and 246 nm of III , and approximately equal to the intensity of the band at 228 nm of IV , this confirms our suggestion mentioned just above .

The transitions at 267, 285 and 270 nm in the spectra of II , III and IV represent the local excitations $\pi \rightarrow \pi^*$ of pyridine and acetophenone rings which correspond the transition $^1A_{1g} \rightarrow {}^1B_{2u}$ at 256 nm in the spectrum of benzene molecule [14] . The absorption bands at 309 , 344 , 323 and 343 nm in the electronic spectra of I – IV respectively, represent $\pi \rightarrow \pi^*$ transitions which are originated from acetophenone rings and extended over the whole Schiff base molecules , the presence of more than hydroxyl group in the molecule enhances such transition [2,7,14,15] .

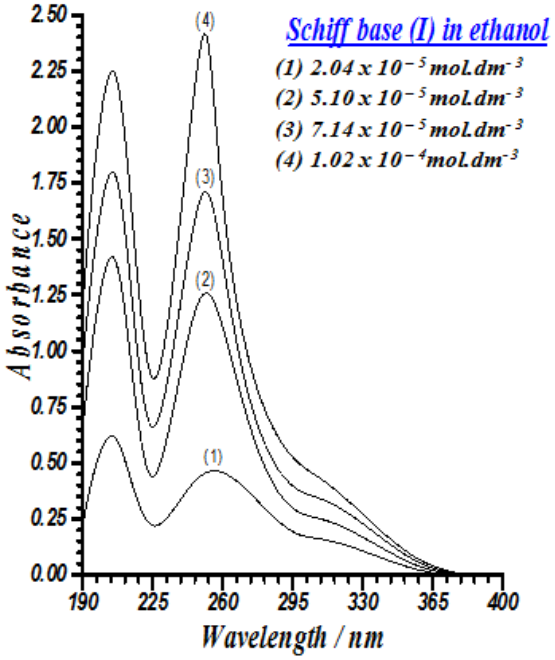


Figure 1-The electronic spectrum of Schiff base(1) In ethanol at different concentrations

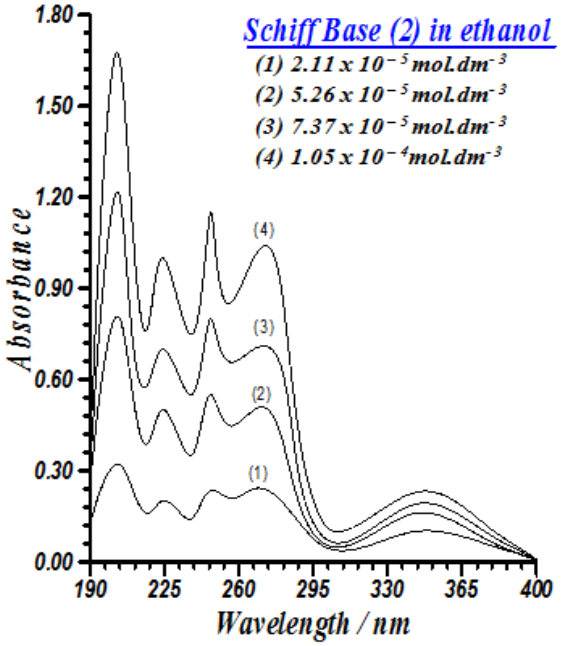


Figure 2-The electronic spectrum of Schiff base(2) in ethanol at different concentrations

Table 3 – The Electronic spectra of compounds I – IV and their starting materials in ethanol

Compound	$^{(*)}\lambda_{max}$**(nm)/Ɛ (m^2 mol^{-1})**
2-Aminopyridine	294(270±10) 233(800±20) 199(420±10)
4-Amino pyridine	sh.266(190±20) 254(840±10) 203(1020±150)
Acetophenone	277(80±5) 240(980±20) 202(1530±120)
2,6-Dihydroxy-acetophenone	269(660±10) 222(720±20) 202(830±50)
2,4,6-Trihydroxy-acetophenone	sh.322(310±10) 284(1710±60) 226(1500±70) , 200(2100±100)
I	sh.309(240±5) 250(2360±10) 205(2830±100)
II	344(200±10) 267(900±30) 247(1080±20), 224(920±20) 204(1600±50)
III	sh.323(310±5) 285(1550±20) 246(1300±10) 229(1490±20) 204(2610±30)
IV	343(340±30) sh.300(560±40) 270(1280±40) 228(2220±100) 203(1780±90)

$^{(*)}$Every reading is an average of four measurements.
sh. Shoulder

It seems that the polar and nonpolar solvents have no effect on the absorption bands at 203 – 285 nm in the electronic spectra of compounds I – IV, but there is a remarkable effect on the longer wavelength absorption bands , Table 4 shows such effects and Figure 3 summarizes the data of Table 4 . Figure 3 illustrates that the shift in $\lambda_{max}(\Delta\bar{\upsilon})$ increases rapidly with increasing dielectric constant of the solvent until the value 10, after that the increase became gradual to the value of water 76.5 . The increase of $\Delta\bar{\upsilon}$ with Ɛ may explained as follows: after absorption light , the excited state of Schiff base molecular becomes more polar than its ground state, therefore the polar solvent stabilizes the excited state by connection its dipole with positive and negative ends of the molecule . The more delocalization of the charge in the excited state, higher increase of $\Delta\bar{\upsilon}$ with Ɛ occurs. This effect is very clear in the case of compound III, figure-3. In this molecule there are three O-H groups, which increase the delocalization of the charge and so eventually leading to higher values of $\Delta\bar{\upsilon}$ compound with the other molecules. In DMSO, $\Delta\bar{\upsilon}$ is not uniform, this is because of some factors concerning this solvent such as its viscosity, basicity nature and ability to form charge transfer complexes with compounds containing two adjacent nitrogen atoms, the nitrogen act as electron donor and DMSO as electron acceptor [16,17]. The effect of 1.0 mol dm^{-3} hydrochloric acid and sodium hydroxide on the electronic spectra of compounds I – IV has also investigated, table-5 summarizes the results. Clearly, the data of Table 5 indicate that some absorption bands observed in alkaline medium only, some others observed only in the neutral and acidic media, and others observed in all media. The absorption bands in the electronic spectra in alkaline medium at 240 nm and 295 nm of II, at 240 and 315 nm of III, and at 289 nm of IV were not observed in the neutral and acidic media. It is reasonable to conclude that these absorption bands may represent the electronic structures of sodium salts of II – IV as shown in Scheme 1.

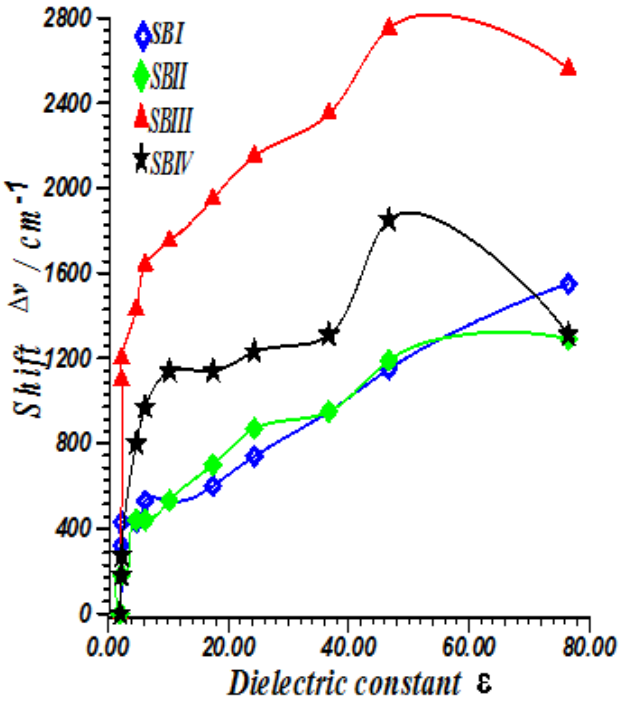


Figure 3- Variation of the dielectric constant of the solvent with the shift

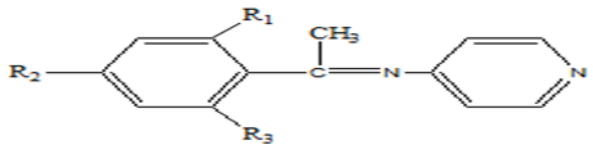
Table 4 – Variation of the red shift with the dielectric constant of the solvent on the longer wavelength absorption bands of compounds I – IV.

Solvent	Dielectric constant ε	Schiff base I			Schiff base II			Schiff base III			Schiff base IV		
		λ/nm	ν/cm^{-1}	Shift Δν	λ/nm	ν/cm^{-1}	Shift Δν	λ/nm	ν/cm^{-1}	Shift Δν	λ/nm	ν/cm^{-1}	Shift Δν
Cyclohexane	2.01	303	33000	-	334	29940	-	295	33900	-	330	30300	-
CCl_4	2.23	306	32680	320	336	29760	180	305	32790	1100	332	30120	180
C_6H_6	2.27	307	32570	430	336	29760	180	306	32680	1200	333	30030	270
$CHCl_3$	4.72	307	32570	430	339	29500	440	308	32470	1430	339	29500	800
CH_3COOH	6.19	308	32470	530	339	29500	440	310	32260	1640	341	29330	970
$(CH_2)_2Cl_4$	10.23	308	32470	530	340	29410	530	311	32150	1750	343	29160	1140
n-Butanol	17.45	309	32400	600	342	29240	700	311	31950	1950	343	29160	1140
Ethanol	24.33	310	32260	740	344	29070	870	315	31750	2150	344	29070	1230
DMF	36.71	312	32050	950	345	28990	950	317	31550	2350	345	28990	1310
DMSO	46.68	314	31850	1150	404	24750	5190	321	31150	2750	393	25450	4850
H_2O	76.54	316	31450	1550	349	28650	1290	320	31250	2650	345	28990	1310

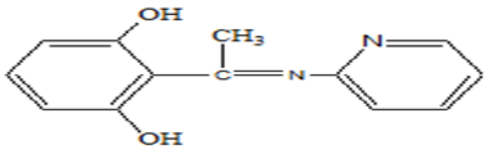
Table 5 – The electronic spectra of Schiff base I – IV in water, 1.0 mol.dm^{-3} hydrochloric acid, and 1.0 mol.dm^{-3} sodium hydroxide. The concentration of every Schiff base is constant 6.0 $*10^{-5}$ mol. dm^{-3} sh. , Shoulder

Schiff Base	λ_{max} / nm (ε / m^2.mol^{-1})		
	H_2O	HCl	NaOH
I	197(3250) 248(2040) sh.318(200)	199(2600) 353 (2580)	214(3240) 244(2480)
II	205(2590) sh.222(1250) 264(2400) 349(300)	198(2870) sh.208(1600) sh.221(870) 264(1880) 334(190)	211(3360) 240(1770) 295(380) sh.346(180)
III	205(440) sh.222(770) 265(1200) sh.285(850) sh.320(300)	200(2920) sh.206(2530) 224(1280) 266(2480) sh.291(1440) sh.325(270)	211(3300) 240(1770) 295(380) sh.346(180)
IV	199(2850) 225(1900) 270(1330) sh.297(700) 345(330)	198(2750) .223(1680) 269(1130) sh.299(690) sh.345(250)	213(3250) 289(780) sh.351(250)

On the other hand, the absorption bands in the electronic spectra in acidic medium at 253 nm of I and at 269 nm of IV not observed in the spectra in alkaline medium, but observed in their spectra in water with inconsistent intensities. Accordingly, these absorption bands can attributed to the protonated Schiff bases as shown in Scheme 2.



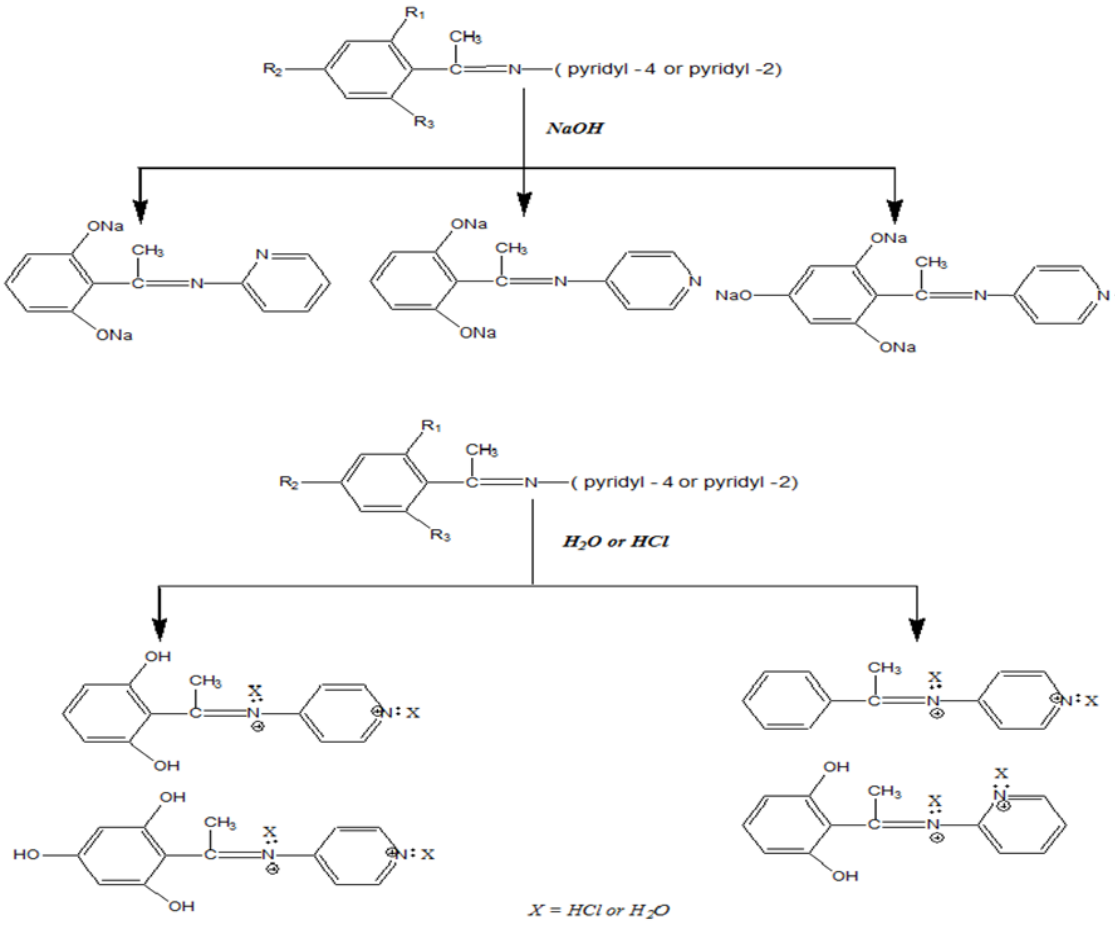
I; $R_1 = R_2 = R_3 = H$
II; $R_1 = R_3 = OH, R_2 = H$
III; $R_1 = R_2 = R_3 = OH$



IV

Scheme 1

The molecular structure of Schiff bases



Scheme 2

The molecular structures of Schiff bases in the acidity, basicity and neutrality media

Charge – Transfer (CT) Complexes

It is well known that Schiff bases act as electron donors in the CT processes with various electron acceptors [13, 16]. Chloranil (CA) is used as electron acceptor with Schiff bases I – IV as electron donors in chloroform to estimate their ionization potentials (IP) as well the equilibrium constants (K_{CT}), molar extinction coefficients (ε_{CT}) of the CT complexes, and the dissociation energies of their excited states (**w**) using the following equations [15,16]:

$$I_p = \frac{(h\upsilon_{CT} - b)}{a} \quad (1)$$

$$W = I_P - Ea - h\upsilon_{CT} \quad (2)$$

$$\frac{[CA]\ell}{OD_{CT}} = \frac{1}{\varepsilon_{CT}.K_{CT}} \cdot \frac{1}{[SB]} + \frac{1}{\varepsilon_{CT}} \quad (3)$$

Where (a) and (b) are constants of the acceptor CA, 0.89 and -5.13 eV respectively, and (Ea) its electron affinity (=1037 eV) [16] , $h\upsilon_{CT}$ is transition energy of the CT complex, [CA] and [SB] are the initial concentrations of CA and Schiff base respectively, (OD_{CT}) is the optical density of the CT complex λ_{max}, and (ℓ) is the optical path length of the absorption cell (=1.0 cm). Equation 3 is applicable only when [SB] >> [CA]. The plot of [CA]/OD_{CT} vs. 1/[SB] gives straight line of intercept and slope equal to 1/ ε_{CT} and 1/(ε_{CT} . K_{CT}) respectively, division of the intercept by the slope can obtain K_{CT}.

A series of solution were prepared in chloroform in which [CA] = 10^{-4} mol.dm^{-3} is constant in all measurements, and [SB] is variable ranging from (10-50)x10^{-4} mol dm^{-3}. In every case, the electronic spectrum recorded to determine λmax of the CT complex. We were unable to calculate (K_{CT}) and (ε_{CT}) of the complex of III due to its insolubility in chloroform. Figure 4 represents the electronic spectrum of CT complex of compound II in chloroform atypical example, and Figure 5 shows the equation 3 plots for determination of the values of (K_{CT}) and (ε_{CT}) of CT complexes of I , II and IV. Table 6 exhibits the values of λmax, $h\upsilon_{CT}$, K_{CT},ε_{CT} ,W of the CT complexes, and Ip of the Schiff bases I -IV .

The values of Ip are very close to each other's and are agree with the values of other Schiff bases which were estimated from their complexes with various acceptors, the values are ranged between 6.53 – 9.57 eV [10,16,17] compared with our estimated values 8.38 – 8.98 eV (Table 6)

The values of K_{CT} of II and IV are greater than that of I, this is obvious since the presence of OH group in the structure of II and IV increase the electronic density of the azomethine group (- CH = N-) of the Schiff base molecule and makes it a better n-electron donor to π* orbital of the CA molecule in the formation of n→ π* CT complexes [18-20].

The values of W are also very close to each other; the closeness within ± 0.01 (Table 6) i.e. within 99.8%. This means that the excited state of CT complexes of compounds I – IV have almost similar structures.

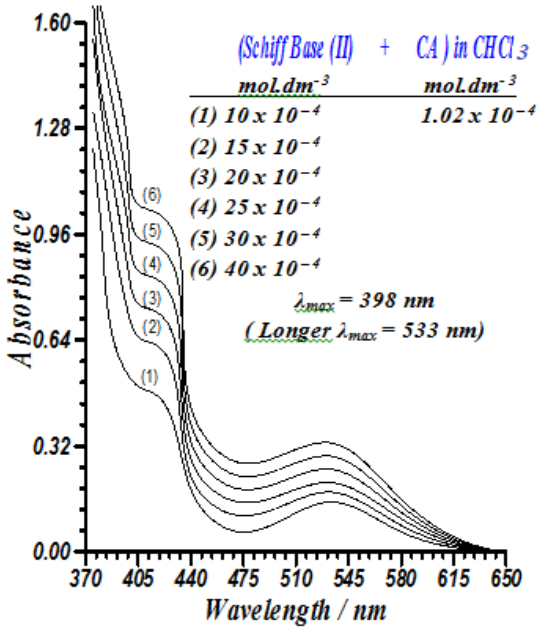


Figure 4- The electronic spectrum of CT complexes of SB (II) in chloroform at different concentrations

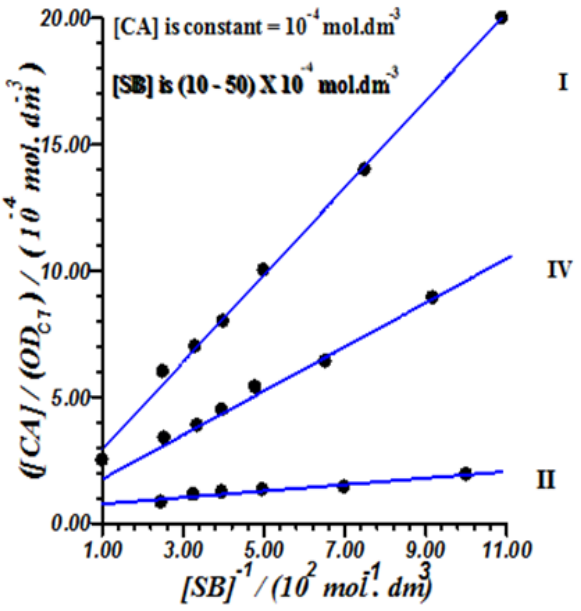


Figure 5- Equation 3 plots for determination of the value of k and ε for CT complexes in $CHCl_3$

Table 6 – The value of I_P, $\mathcal{E}_{CT}$, K_{CT}, W, $h\nu_{CT}$ *and* λ_{max} of the CT complexes of compounds I – IV with chloranil in chloroform.

Compound	λ_{max} / nm CTC	$h\nu_{CT}$ / eV	I_P / eV	W / eV	K_{CT} /($mol^{-1}.dm^3$)	$\mathcal{E}_{CT}$ / ($m^2.mol^{-1}$)
I	465	2.67	8.76	4.72	86.3	670
II	533 398	2.33 ----	8.38 —	4.68 ----	----- 446.3	----- 1590
III*	450	2.75	8.85	4.73	-----	-----
IV	434	2.86	8.98	4.75	207.1	600

*The Spectrum was measurement without exact concentrations, by addition of few drops of CA solution to the saturated solution of Schiff base III in chloroform; this done owing to improper solution of this compound in chloroform (see the text).

Conclusions

The data of absorption peaks of the stretching and bending vibrations of compounds I –IV and some of their starting materials, confirm the molecular structures that they can be outlined as follow: (i) the asymmetric and symmetric stretching vibrations of the free O-H bonds in compounds II and IV are located at 3460 and 3360 cm^{-1} and at 3380 and 3330 cm^{-1} respectively. These absorption peaks have not observed in the spectrum of 2,6- dihydroxyacetophenon, although the bonded O-H was observed at 3300 cm^{-1}. This indicates that the O-H of 2,6- dihydroxyacetophenone is completely bonded with its carbonyl groups, where as II and IV present as a tautomeric mixtures in which the O-H groups is free and bonded with the azomethine group of the molecule.

The absorption bands at 203 and 205 nm of I – IV at 250 nm of I represent the local excitation 4 transitions of pyridine and acetophenone rings. We indicated that the intensity of the band at 250 nm of I is greater than the total intensities of the bands at 224 and 247 nm of II, equal to the total intensities of the bands at 229 and 246 nm of III, and approximately equal to the intensity of the band at 228 nm of IV.

The values of Ip and W of Schiff bases (I – IV) are very close to each other's and are agree with the values of other Schiff bases which were estimated from their complexes with various acceptors.

The values of K_{CT} of II and IV are greater than that of I, this is obvious since the presence of OH group in the structure of II and IV increase the electronic density of the azomethine group of the Schiff base molecule and makes it a better n-electron donor.

References

1. Al-Garawi Z. S., Hamed I. and Al-Daraji A. S., **2012**, "Synthesis and characterization of new amino acid- Schiff base and studies their effects on the activity of ACP, PAP and enzymes", *J. Chem.*, 9(2), pp: 962-969.
2. Sanchez C. O., Huaiquimilla D. M. Sobrazo P., Abello R. and Silva R., **2013**, "Low band gap Schiff base polymers obtained by complexation with Lewis acids", *Polym. Bull*., 70, pp:971-980.
3. Naeimi H. and Karshenas A., **2013**, "Highly regioselective conversion of epoxides to b-hydroxy nitriles using metal (II) Schiff base complexes as new catalysis under mild condition", *Polyhedron*, 49, pp: 234-238.
4. Liu Y., Lion G., Yin D. and Su B., **2013**, "Synthesis, characterization and biological activity of ferrocenc based Schiff base ligands and their metal (II) complexes" , *Spectrochimica Acta Part A*, 100, pp: 131-137.
5. Shaabani B., Khandar A. A., Dusek M., Pojrova M. and Mahmoudi F., **2013**, "Synthesis, crystal structure antimicrobial activity and electrochemistry study of chromium (III) and copper (II) complexes', *Chimica. Acta*, 394, pp: 652-661.
6. Fugu M. B., Ndahi N. P., Paul B. B. and Mustapha A. N., **2013**, "Synthesis, characterization, and antimicrobial studies of some vanillin Schiff base metal (II) complexes", *J. Chem. Pharm. Res*., 5(4), pp: 22-28.
7. Kiafar A. H. and Abroshan I., **2013**, "Spectrophotometric study of complexiation between some salen type Schiff bases and dimethyltin (IV) dichloride", *Chem. Sci. Trans*., 2(1), pp: 17-24.

8. Patil S. A. , Unki S. N., Badami P. S., **2013**, "Synthesis, characterization, biological and thermal behavior of Co (II), Ni (II) and cu (II) complexes with Schiff bases having coumarin moieties", *J. Therm. Analy.*, 111, pp: 1281-1290.

9. Calu L., Badea M., Falcescu D. Duca D., Marinescu D. and Olar R., **2013**, "Thermal study on complexes with Schiff base derived from 1,2,4-triazole as potential antimicrobial agents", *J. therm. Analy.*, 111, pp: 1725-1737.

10. Abdul-Rahman K. A. and Laila A. J., **2009**, "Spectral study of some charge- transfer complexes derived from Schiff base of 3-Methoxy-4-hydroxy benzaldehyde with some electron acceptors", *J. Al-Anbar Univ. Sci*., 3(1), pp: 38-44.

11. Refat M. S., Aqeel S.M and Grabtcher I.K, **2004**, "Spectroscopic and physicochemical studies of charge of charge-transfer complexes of some benzanthrone derivatives "Luminophore Dyes" with iodine as 6-acceptor", *J. Appl. Sci*., 49(4), pp: 258-266.

12. Ali A. H. S, Anwar T. M. and Ali M. S, **2002**, "Estimation of the physical constants of the electron acceptors 1,4-benzoquinone and 9,10-anthraquinone from their charge-transfer complexes with some Schiff bases in chloroform", *Iraqi J. Chem*., 28(2), 245-257.

13. Silverstein R. M., Bassler G. C. and Morrill T. C., **1989**, *"Spectrometric Identification of Organic Compounds*", 4th ed., John Wiley and sons.

14. Jaffe H. H. and M. Orchin, **1966**, *"Theory and application of ultraviolet spectroscopy*", 1st ed., John Wiley and Sons Inc.

15. Subhani M. S., Aslam S., Qureshi R. and Rahman A., **2008**, "UV spectroscopic studies of charge-transfer complexes of 2-hydroxy-1,4-naphthoquinone", *J. Chem. Soc. Pok*., 20, pp:2-14.

16. Foster R., **1969**, *"Organic charge-transfer complexes*", 1st ed., Academic Press, London & New York.

17. Ali A. H. S., Razaq K. A. and Kunda B. H., **1993**, "Estimation of ionization potentials of some Schiff bases from their charge-transfer complexes with various electron acceptors", *Iraqi J. Chem*., 18(1), pp: 1-10.

18. Kosower E. M., **2007**, "*An Introduction to physical organic chemistry*", 2nd ed., John Wiley and Sons Inc., New York.

19. Ali A. H. and Azzawy A.R. J, **1992**, "Spectrophotometric study on the charge-transfer complexes of iodine acceptor with some Schiff bases n-donors", *Spectroscopy Letters*, 25(6), pp:777-788.

20. Anwar T. M., Nisreen K. M. and Ali S. E., **2013**, "Spectroscopic and thermodynamic studies of charge-transfer complexes formation between cytosine, uracil and thymine with electronic acceptors", *J. Al-Nahrain Univ*., 16(2), pp: 37-47.