## <sup>1</sup>H NMR, IR and UV/VIS Spectroscopic Studies of Some Schiff Bases Derived From 2-Aminobenzothiazole and 2-Amino-3-hydroxypyridine

Raafat M. Issa, Abdalla M. Khedr\* and Helen Rizk Chemistry Department, Faculty of Science, Tanta University, Tanta, Egypt

By condensing 2-aminobenzothiazole with 2-hydroxy-1-naphthaldehyde, 2-hydroxybenzaldehyde, 4-methoxybenzaldehyde, 4-hydroxybenzal-dehyde, benzaldehyde and 4-dimethylaminobenzaldehyde, and five Schiff bases Ia-Ie are prepared. Also, two Schiff bases IIa and IIb are prepared by condensation of 2-amino-3-hydroxypyridine with 2-hydroxy-1-naphthaldehyde and 2-hydroxybenzaldehyde. The <sup>1</sup>H NMR, IR and UV/Vis spectra of these seven Schiff bases are investigated. The signals of the <sup>1</sup>H NMR spectra as well as the important bands in the IR spectra are considered and discussed in relation to molecular structure. The UV/Vis absorption bands in ethanol are assigned to the corresponding electronic transitions and the electronic absorption spectra of Schiff bases Ib and IIb are studied in organic solvents of different polarities. The UV/Vis absorption spectra of 2-amino-3-hydroxypyridine Schiff bases IIa and IIb are investigated in buffer solutions of different pH values containing 5% (v/v) methanol, and the results are utilized for the determination of  $pK_a$  and  $\Delta G^*$  of the ionization of the phenolic OH-groups. The fluorescence spectra of IIa and IIb are studied in organic solvents of different polarities.

The obtained spectral results are confirmed by some molecular calculations using the atom super position and electron delocalization molecular orbital theory for the Schiff base IIb.

**Keywords:** 2-Aminobenzothiazole; 2-Amino-3-hydroxypyridine; Benzaldehyde derivatives; Schiff bases; Spectral studies; Molecular orbital calculations.

### **1. INTRODUCTION**

Although there are wide applications of Schiff bases and their metal chelates in biological systems,<sup>1,2</sup> catalysis,<sup>3,4</sup> dying processes,<sup>5,6</sup> and analytical applications,<sup>7</sup> the spectral studies of the Schiff bases containing a heterocyclic ring are comparatively minor.<sup>7-9</sup>

In the present article, the <sup>1</sup>H NMR, IR and UV/Vis spectra of seven Schiff bases derived from 2-aminobenzo-thiazole and 2-amino-3-hydroxypyridine (Scheme I) are





considered. The UV/Vis absorption spectra of Schiff bases Ib and IIb as well as the fluorescence spectra of IIa and IIb are investigated in organic solvents of different polarities and discussed with respect to different solvent parameters. The ionization of phenolic OH-groups of 2-amino-3-hydroxypyridine Schiff bases IIa and IIb is studied in aqueous buffer solutions of varying pH values. The results of spectral studies are supported by some molecular orbital calculations using the ASED-MO theory for the Schiff base IIb.

### 2. EXPERIMENTAL

All compounds used in the present study were of pure grade available from BDH, Aldrich or Sigma. The solvents used for the spectral study were spectroscopic grade from Aldrich.

The Schiff bases were obtained by refluxing equimolar quantities of the aromatic amine and the aldehyde (0.01 mole of each in 25 mL ethanol) on a water bath for 2-5 hrs.<sup>10</sup> The Schiff base compounds precipitated on cooling, were then filtered and purified by recrystallisation

\* Corresponding author. E-mail: abkhedr2001@yahoo.com; Tanta, P. O. 31527.

from the appropriate solvent (yield 70-80%).

The <sup>1</sup>H NMR spectra were obtained by the aid of a Bruker DMX 750 (500 MHz) spectrometer using  $d_6$  DMSO as a solvent and TMS as internal standard. The IR spectra were recorded on a Perkin Elmer 1430 ratio recording infrared spectrometer using the KBr wafer technique. The UV/Vis spectra were measured at room temperature within the 200-600 nm range on a Perkin Elmer Lambda 4B using 1.0 cm matched silica cells. The fluorescence quantum yield for solutions having an absorbance of less than 0.1 at the excitation wavelength were determined using a Shimadzu RF 510 spectrofluorometer and referenced to fluorescence in 0.1 N NaOH ( $\phi_f = 0.93$ ).<sup>11</sup> Molecular orbital calculations were carried out on Schiff base IIb using the ASED-MO method.

### **3. RESULTS AND DISCUSSION**

### 3.1. <sup>1</sup>H NMR spectra

The signals observed in the <sup>1</sup>H NMR spectra of the Schiff bases under study (Figs. 1 and 2) are collected in Table 1. The spectra exhibit a multiplet at 6.50-8.18 ppm for



Fig. 1. <sup>1</sup>H NMR spectrum of 2-aminobenzothiazole-2-hydroxy-1-naphthaldehyde (Ia).



Fig. 2. <sup>1</sup>H NMR spectrum of 2-amino-3-hydroxypyridine-2-hydroxy-1-naphthaldehyde (IIa).

the hydrogens of the aromatic rings. The azomethine hydrogen (-CH=N-) leads to a singlet of integration intensity equivalent to one hydrogen at 8.32-9.71 ppm. The spectra of Ic and If display signals at 3.41 ppm or 3.08 and 3.12 ppm due to the hydrogens of the OCH<sub>3</sub> or  $-N(CH_3)_2$  groups. The spectra of Id, IIa and IIb show a singlet with an integration equivalent to one hydrogen at 10.62, 8.70 and 9.33 ppm corresponding to the hydrogen of the free OH-group, while Ia, Ib, IIa and IIb exhibit a signal due to the hydrogen bonded hydroxyl group at 9.28-10.03 ppm.

It is worth mentioning that the signal of the azomethine hydrogen appears as two singlets in the spectra of Ic and Ie ( $\Delta \delta = 0.03$  ppm) with a total integrated intensity corresponding to one hydrogen. This behavior can be ascribed to the existence of these compounds as a mixture of anti and syn forms.

The higher field singlet is assigned to the azomethine hydrogen in the syn form while that at lower field is due to the anti form. Also, the high-resolution spectra of Ia and IIa (Fig. 1) show the signal of the N=CH hydrogen as a doublet

		Cor	npound nun	nber			Assignment
Ia	Ib	Ic	Id	Ie	IIa	IIb	Assignment
		3.41					CH <sub>3</sub>
7.73-8.78	6.97-7.70	6.82-7.72	6.93-8.05	6.89-7.72	6.30-8.15	7.50-7.75	C-H (Ar)
8.81	9.0	8.92, 8.95	9.05	8.96, 8.99	8.50	8.03	N=CH
			10.62		9.70	9.33	OH free
10.03	9.28				9.85	9.72	OH bonded

 Table 1. Data from <sup>1</sup>H NMR spectra of 2-aminobenzothiazole and 2-amino-3-hydroxypyridine

 Schiff bases

Scheme II The anti and syn forms in Schiff bases Ic and Ie



Scheme III Keto-enol toutomerism in Schiff base Ia



at 8.81 ppm (J = 7.8 Hz) and 8.50 ppm (J = 10.20 Hz) of a total integration intensity equivalent to one hydrogen. This splitting can be explained on the bases of a coupling with a neighboring –NH hydrogen, which resonates as a doublet at 7.27 ppm (J = 7.8 Hz), and the existence of keto-enol toutomerism (Scheme III). The presence of the singlet at 10.03 ppm, due to the H-bonded OH-group, indicates a high contribution of the enolic structure.

### 3.2. IR Spectra

The IR spectra of the Schiff bases under study (Figs. 3 and 4) are recorded in the solid state using the KBr disc technique. Selected bands of diagnostic importance are collected in Table 2.

The spectra of compounds Id, IIa and IIb having free OH groups display somewhat broadened bands within the 3434-3425 cm<sup>-1</sup> region. The presence of OH-groups involved in intramolecular hydrogen bonding for Ia, Ib, IIa and IIb give the v(OH) as a shallow, very broad band ex-

tending within the 3300-2700 cm<sup>-1</sup> region. The stretching vibrations of the aromatic C-H groups give medium to weak bands within the 3072-3043 [v(C-H)<sub>asym</sub>] and 3057-3026 cm<sup>-1</sup> [v(C-H)<sub>sym</sub>] ranges. The azomethine hydrogen gives three bands at 3004-2915 cm<sup>-1</sup> [v(N=C-H)], 1279-1200 cm<sup>-1</sup> [ $\delta$ (N=C-H)] and 1046-1010 cm<sup>-1</sup> [ $\gamma$ (N=C-H)]. The v(C=N) bands are observed at 1645-1557 cm<sup>-1</sup>; the position of these bands varies with the molecular structure, though no regularity can be pointed out. The spectra of compounds Ia-If exhibit a medium to sharp band at 1606-1560 cm<sup>-1</sup> corresponding to v(C=N) of the thiazole ring



Fig. 3. IR spectra of Schiff bases Ia, Ib, Ic and Id.

	5 515							
			Compou	nd numbe	er			A :
Ia	Ib	Ic	Id	Ia	If	IIa	IIb	Assignment
			3425			3434	3434	v(OH) free
not defined	not defined					not defined	not defined	v(OH) bonded
3059	3064	3069	3043	3065	3069	3072	3070	v(CH) asym
3047	6050	3057	3026	3053	3052	3055	3055	v(CH) sym
2969	2915	3004	2917	2956	2916	2929	2982	$\nu$ (N=CH)
1620	1642					1624	1598	v(C=O)
1597	1622	1637	1645	1636	1635	1579	1557	v(C=N) (Schiff)
1560	1606	1595	1600	1599	1612	1534	1539	v(C=N) (ring)
1280	1268		1340			1300	1289	δ(OH)
1237	1235	1235	1279	1256	1258	1200	1234	δ(N=CH)
1170	1170		1148			1148	1191	ν(C-OH)
1033	1010	1023	1013	1017	1015	1046	1029	γ(CH=N)
921	889		929			935	913	γ(OH)

 

 Table 2. Selected bands of diagnostic importance from the IR spectra of 2-aminobenzothiazole and 2-amino-3-hydroxypyridine Schiff bases

while IIa and IIb have the C=N vibrations of the pyridine ring at 1534 and 1539 cm<sup>-1</sup>, respectively. Compounds containing OH groups display bands at 1340-1268 cm<sup>-1</sup> [ $\delta$ (OH)], 1191-1148 cm<sup>-1</sup> [ $\nu$ (C-OH)] and 935-889 cm<sup>-1</sup> [ $\gamma$ (OH)]. The



Fig. 4. IR spectra of Schiff bases Ie, If, IIa and IIb.

spectra of all compounds show medium to sharp bands within the 870-630 cm<sup>-1</sup> range due to the out-of-plane deformations of the aromatic C-H groups.<sup>12</sup>

# 3.3. The electronic absorption spectra 3.3.1. Spectra in ethanol

The electronic absorption spectra of the Schiff bases included in the present study (Fig. 5 and Table 3) exhibit mainly four bands. The two bands on the higher energy side, within the 210-231 and 252-270 nm ranges, are due to the excitation of the  $\pi$  electrons ( $\pi$ — $\pi^*$  transitions) of the aromatic rings. The third band within the 275-353 nm range is assigned to the  $\pi$ — $\pi^*$  transition within the C=N group, while the longer wavelength band at 325-471 nm is due to an intramolecular charge transfer (CT transition) involving the whole molecule. The CT transition is influenced by the aldehyde rest. This is confirmed by calculating the  $E_{CT}$  values from  $\lambda_{max}$  using the relation:

$$E_{CT} = 1241.6 / \lambda_{\text{max}}^{CT} \text{ (eV)}$$
 (1)

and comparing the values obtained with the data calculated using the Briegleb equation:<sup>13</sup>

$$E_{CT} = (I_P - E_A) + C \tag{2}$$

in which I<sub>P</sub> is the ionization potential of the donor,  $E_A$  is the electron affinity of the C=N acceptor (-1.3 eV) and C is the coulomic force between the electron transferred and the positive hole left behind (-5.2 or -5.6 eV).<sup>13</sup>

Compound number								Cal.		
Ia	Ib	Ic	Id	Ie	If	IIa	IIb	Values for IIb		Assignment
221	217	221	218	221	221	210, 230	214, 231	215,	$\lambda_{max}$	Band A ( $\pi$ - $\pi$ * Ar)
2.4	3.3	2.8	2.6	2.9	3.3	2.1, 2.8	1.9, 1.3	235	$\epsilon_{max}$	
252	2.65	265	268	266	255	230, 255	255, 270	252,	$\lambda_{max}$	Ban d B (π-π* Ar)
0.7	1.2	1.3	0.6	1.6	1.2	2.8, 1.4	0.9, 0.6	270	$\epsilon_{max}$	
306	278	290	310	275	297	324, 353	306, 334	307,	$\lambda_{max}$	Band C ( $\pi$ - $\pi$ * of
0.3	1.2	0.6	1.0	0.7	0.6	0.8, 0.6	0.6, 0.8	329	$\epsilon_{max}$	C=N group)
349, 427	325, 375	356	360	344	341, 427	446, 471	362, 433	359	$\lambda_{max}$	Band D (CT)
0.5, 0.9	1.1, 1.4	0.7	2.5	0.4	2.5, 0.5	2.0, 2.2	0.8, 0.2		$\epsilon_{max}$	
3.6, 2.9	3.8, 3.3	3.5	3.4	3.6	3.6, 2.9	2.8, 2.6	3.4, 2.9	E <sub>CT</sub> (	(ev) from	n equation (1)
, 3.2	3.6, 3.1	3.7,	3.7,	3.8,	, 3.2	3.2, 3.0	3.7, 3.2	E <sub>CT</sub> from	n Breig	leb equation $(2)^{13}$
, 2.7		3.2	3.2	3.3	, 2.7	2.7, 2.5	3.2, 2.7			
, 0.15	, 0.25	0.21	0.80	0.08	, 0.45	0.23,	0.34, 0.03		(	<i>(f</i> )
, 0.21	, 0.23				, 0.09	0.19				
, 7.41	, 7.7	7.9	7.8	8.0	, 7.41	7.3, 7.2	7.8, 7.4		$I_{P1}$ (	(ev) <sup>15</sup>
, 6.88	, 7.2	7.4	7.3	7.5	, 6.88	6.8, 6.6	7.3, 6.9		$I_{P2}$ (	$(ev)^{16}$
, 7.14	, 7.4	7.5	7.5	7.6	, 7.14	7.1, 7.0	7.5, 7.1		$I_{P3} (ev)^{17}$	
, 7.14	, 7.5	7.6	7.56	7.7	, 7.14	7.1, 6.9	7.6, 7.1	Ν	Iean I <sub>P</sub>	(ev) values

Table 3. UV/Vis spectral data of 2-aminobenzothiazole and 2-amino-3-hydroxypyridine Schiff bases in ethanol

 $\lambda_{\text{max}}$  in (nm),  $\varepsilon_{\text{max}}$  (L mol<sup>-1</sup> cm<sup>-1</sup> × 10<sup>-4</sup>) and f is the oscillator strength (L mol<sup>-1</sup> cm<sup>-2</sup>)

The data calculated for  $E_{CT}$  from Eq. 2 using the two values of C are in satisfactory agreement with the  $E_{CT}$  obtained from the experimental data using Eq. 1 (Table 3).

It is worth mentioning that the spectra of the Schiff bases Ia, Ib, IIa and IIb display the bands due to the  $\pi - \pi^*$ of the C=N linkage and the CT bands as two adjacent peaks. This can be ascribed to the existence of these compounds in two tautomeric forms (Scheme III). The bands at shorter wavelength are assigned to the absorption of the hydroxy aryl form while those at longer wavelength sides are due to the quinine-like structure.<sup>14</sup>

The spectra of If display a broad shallow band with  $\lambda_{max}$  427 nm which originates from the contribution of a *p*-quinone-like structure,<sup>14</sup> originating from the possible mesomeric shift (Scheme IV).

The electronic absorption spectra were used to calcu-



Wavelength (nm)

Fig. 5. Electronic absorption spectra of the Schiff bases under study.

Scheme IV Hydroxy aryl and quinonid structures of If



Hydroxy aryl structure

late the ionization potentials of the compounds under study using the relation:

$$Ip = a + b E_{CT}$$
(3)

in which a and b are constants having the values (4.93 & (0.857), <sup>15</sup> (5.156 & 0.778)<sup>16</sup> or (5.11 & 0.701).<sup>17</sup> The calculated values together with the mean values are depicted in Table 3.

The oscillator strength (f) of the CT band for some compounds was also determined (Table 3) using the relation:18

$$f = 4.6 \times 10^{-9} \,\varepsilon_{\rm max} \,\Delta v_{1/2} \tag{4}$$

where  $\epsilon_{max}$  is the molar extinction coefficient at  $\lambda_{max}$  and  $\Delta v_{1/2}$  is the band width at half absorbance values.

### 3.3.2. Spectra in organic solvents of different polarities

The electronic absorption spectra of Ib and IIb were measured in six organic solvents of different polarities namely ethanol, methanol, DMF, chloroform, tetrachloromethane and cyclohexane (Table 4). These spectra indicated that the bands due to localized electronic transitions are slightly influenced by the nature of the solvent used. On the other hand, the CT band displayed in general a red shift with increasing the solvent polarity which reflects an increased solvent stabilization of the excited state in more polar solvents.

The application of the dielectric relations of Gati and Szalay<sup>19</sup> or those of Suppan<sup>20</sup> to the data of the CT band did not give linear relationships denoting that the dielectric constant of the medium did not play an important role in the CT band solvent shift. Also, the plot of  $E_{CT}^{\max}$  in different solvents as a function of the solvent parameters Z, <sup>21</sup>  $E_T$ , <sup>22</sup>  $\alpha$ (acidity),  $\beta$  (basicity) and  $\pi^*$  (dipolarity),<sup>23</sup> showed nonlinear relationships. This behaviour denotes that each solvent parameter will have its effective contribution to the  $E_{CT}^{max}$ band which depends also on the nature of the solute under study. Accordingly, it can be concluded that the change of  $E_{CT}^{\max}$  with solvent is the result of the influence of all these parameters. These effects can be additive, counteracting or even may cancel out each other.

Table 4. UV/Vis spectral data of Schiff bases Ib and IIb in organic solvents of varying polarities

C	G 1	Ban	d (A)	Ban	d (B)	Band (C)		Band (D)	
Com.	Solvent -	λ	З	λ	3	λ	3	λ	3
Ib	Methanol	221	30.3	269	13.8	332	7.6	374	9.2
	DMF			268	38.8	329	38.0	373	46.2
	CHCl <sub>3</sub>	240	11.2	273	10.0	333	14.1	377	18.5
						349	15.2		
	$CCl_4$	232	8.3	273	11.1	332	14.9	378	20.8
		248	9.0			349	16.0		
	Cyclohexane	216	22.1	271	11.0	329*	20.9	377	20.0
		232*	15.5			344*	15.5		
IIb	Methanol	213	17.6	268	9.5	339	12.2	358	13.7
		229*	15.9					453	1.8
	DMF			269	10.4			368	15.1
								436	3.1
	CHCl <sub>3</sub>	240	9.9	270	10.2	341	12.8	362	16
	CCl <sub>4</sub> **			269		341		366	
	Cyclohexane**	215		269		322*		362	
		230				341*			

\* Shoulder, \*\* Saturated solution,  $\varepsilon_{max} \times 10^{-3}$  (l mol<sup>-1</sup> cm<sup>-1</sup>),  $\lambda_{max}$  (nm).

### 3.3.3. Absorption spectra of IIa and IIb in buffer solutions of varying pH

2-Amino-3-hydroxypyridine Schiff bases IIa and IIb are considered as dibasic acids. The dissociation of these acids can be represented by the following equilibrium:

Scheme V The acid-base equilibrium of the Schiff bases under study

$$H_2L \xrightarrow{K_1} HL^- + H^+$$
 and  $HL^- \xrightarrow{K_2} L^{2-} + H^+$ 

where  $K_1$  and  $K_2$  are the dissociation constants for each step.

The absorption spectra in the UV/Vis region (200-600 nm) of Schiff bases IIa and IIb are studied in universal buffer solutions of varying pH values containing 5% (v/v) methanol. The spectra obtained reveal that the pH of the medium has an obvious effect on both the position and extinction of the absorption peaks which can be explained in the following points:

a. The spectra of IIa showed two peaks with  $\lambda_{max}$  at 300 and 395 in the strong acidic medium (pH < 4) corresponding to the H<sub>2</sub>L form. The absorbance of these peaks decreased with increasing the pH of solution with the appearance of a new absorption peak with  $\lambda_{max} = 480$  nm corresponding to formation of HL<sup>-</sup> and L<sup>2-</sup>. The extinction of this peak increases with increasing pH of the medium.

b. For Schiff base IIb; the spectra show only one peak with  $\lambda_{max} = 310$  nm in solution having pH < 6 corresponding to the H<sub>2</sub>L form. The extinction of this peak decreased with increasing pH value of the solution while a new absorption peak appeared at pH  $\ge$  6 with  $\lambda_{max} = 380$  nm corresponding to the HL<sup>-</sup> form. The absorbance of this peak increased with increasing pH value of the solution until pH = 8 and remains constant to pH = 9, then it began to increase after pH = 9 until pH = 12 which can be attributed to the formation of L<sup>2-</sup>.

The pH-absorbance curves of Schiff bases IIa and IIb for the longer wavelength bands are typical S-shaped (Fig. 6). The presence of two steps in each pH-absorbance curve supports the existence of two types of equilibria (Scheme V). These curves were utilized for the determination of the two acid dissociation constants of these Schiff bases using the half-height methods<sup>24</sup> and the limiting absorbance methods.<sup>25</sup> The values of pK<sub>1</sub> equal 5.4 and 7.1, whereas pK<sub>2</sub> is equal to 8.3 and 9.6 for IIa and IIb, respectively. Also, the pK values were used in calculating the free energy changes ( $\Delta G^*$ ) of each ionization step. The  $\Delta G^*$  values were found to be 31.3 and 48.2 kJ mol<sup>-1</sup> in the case of IIa and 41.2 and 55.7 kJ mol<sup>-1</sup> in the case of IIb for the first and second ionization steps, respectively.

### 3.4. Fluorescence spectra

The fluorescence spectra of 2-amino-3-hydroxypyridine Schiff bases IIa and IIb were investigated in organic solvents of different polarities (Table 5). The results obtained reveal that both the fluorescence quantum yield ( $\phi_f$ ) and emission  $\lambda_{max}$  depend on the molecular structure of the Schiff base and the solvent used as medium. Also, Schiff bases IIa and IIb give good fluorescence spectra and satisfactory values for the fluorescence quantum yield ( $\phi_f$ ). This behavior is good evidence for the formation of strong hydrogen bonding in these compounds (Scheme III) which increased the stability of the molecule in the excited state.<sup>26</sup>

The solvent effect on emission spectra of IIb and IIe is actually the result of the influence of various solvent parameters. This fact appeared clearly on plotting the values of  $E_{\max}^{emm}$  as a function of macro- or microscopic solvent parameters, which gave nonlinear relationships, as in the case of the ground state spectra.

### 3.5. Molecular orbital calculations

The atom superposition and electron delocalization molecular orbital (ASED-MO) method<sup>27,28</sup> is used to inves-



Fig. 6. The pH-absorbance curves of Schiff bases IIb ( $\lambda = 380$  nm) and IIe ( $\lambda = 480$  nm).

C = 1t	Schiff b	ase IIa	Schiff base IIb		
Solvent	$\lambda_{emm}$ (nm) $\phi_{f}$		$\lambda_{emm}\left(nm\right)$	$\phi_{\rm f}$	
Ethanol	492	0.039	500	0.035	
Methanol	496	0.036	502	0.031	
DMF	505	0.023	506	0.19	
Acetone	495	0.018	498	0.013	
$CH_2Cl_2$	501	0.061	504	0.058	
Toluene	510	0.015	527	0.009	

 Table 5. Data obtained from the emission spectra of Schiff bases

 IIa and IIb in organic solvents of varying polarities

 $\lambda_{ennm}$  is the emission wavelength and  $\varphi_f$  is the fluorescence quantum yield.

tigate the geometric and electronic structures as well as the types of electronic transitions in the Schiff base IIb (Fig. 7). This technique has already been applied for predicting molecular structures, reaction mechanism, and electronic and vibrational properties.<sup>29-34</sup> The input data consists of ionization potentials<sup>35</sup> (VSIP) and valence-state Slater orbital exponents<sup>36</sup> for the constituent atoms. Atomic parameters used in the calculations are reported in Table 6; in all calculations the C-H bond lengths are kept constant at 1.10 Å.

As shown in Fig. 4, the *trans* form is found to be the stable structure of Ib. The calculations indicated that the phenyl ring is out of plane with respect to the pyridine moiety. Strong distribution and rotation begin from  $C_8$  and continue for  $C_9$ ,  $C_{10}$ ,  $C_{11}$ ,  $C_{12}$ ,  $C_{13}$ ,  $C_{14}$  and  $O_{15}$ . The Schiff base formation is confirmed by the values of bond orders (bond lengths) of  $C_1$ - $N_7$ ,  $N_7$ - $C_8$ , and  $C_8$ - $C_9$  bonds which are equal to 0.8545 (1.40), 1.0723 (1.33) and 0.8430 (1.44 Å), re-



Fig. 7. The investigated molecular structure of the Schiff base IIb using ASED-MO theory.

Table 6.	Atomic parameters used in the calculations: principle
	quantum numbers, n; ionization potentials, IP (eV);
	orbital exponents, $\zeta$ (au)

		-	-			
A 4		s			р	
Atom	n	IP	ζ	n	IP	ζ
С	2	16.590	1.8580	2	11.260	1.8180
Ν	2	18.330	1.9240	2	12.530	1.9170
0	2	28.480	2.2459	2	13.620	2.2266
Н	1	13.600	1.2000			

spectively, with the double bond character for  $N_7$ - $C_8$  bond. Also, the proposed keto-enol tautomerism (Scheme III) is supported by the partial double bond character of  $C_{14}$ - $O_{15}$ with high contribution of the enolic form as mentioned before. The calculations reveal the formation of a hydrogen bond ( $N_7$ - $H_{18}$ ) as assumed before with bond order = 0.0403 and bond length 1.89 Å. The calculated bond orders and bond lengths over the whole-investigated molecule IIb are shown in Table 7.

The ASED-MO calculations for the different types of electronic transitions in Schiff base IIb denote the following points:

a. The lowest energy electronic transition between the HOMO (-13.39562 eV) and the LUMO levels (-9.93915 eV) equals 3.45647 eV corresponding to CT electronic transition. The calculated wavelength of this transition is equal to 358.5 nm in satisfactory agreement with the exper-

 Table 7. The calculated bond orders and bond lengths (Å) of

 Schiff base IIb obtained from ASED-MO theory

Bond	Bond order	Bond length
C <sub>1</sub> -C <sub>2</sub>	0.9136	1.4100
$C_2-C_3$	1.0012	1.3600
C <sub>2</sub> -O <sub>16</sub>	0.7653	1.3000
C <sub>3</sub> -C <sub>4</sub>	0.9718	1.3800
C <sub>4</sub> -C <sub>5</sub>	0.9753	1.3800
C <sub>5</sub> -N <sub>6</sub>	0.9771	1.3500
$C_1-N_6$	0.9560	1.3704
$C_1-N_7$	0.8545	1.4000
N <sub>7</sub> -C <sub>8</sub>	1.0723	1.3300
C <sub>8</sub> -C <sub>9</sub>	0.8430	1.4400
$C_9-C_{10}$	0.9274	1.4200
$C_{10}$ - $C_{11}$	0.9970	1.3800
$C_{11}$ - $C_{12}$	0.9656	1.3800
$C_{12}$ - $C_{13}$	0.9960	1.3700
C <sub>13</sub> -C <sub>14</sub>	0.9862	1.3600
$C_{9}-C_{14}$	0.9818	1.3663
C <sub>14</sub> -O <sub>15</sub>	0.7424	1.3200

imental value (362 nm).

b. The  $\pi \rightarrow \pi^*$  transition within the C=N group gives two bands at 306.9 and 329.1 nm with high coefficients on N<sub>7</sub>, C<sub>8</sub>, C<sub>14</sub> and O<sub>15</sub> atoms. The experimental wavelengths are equal to 306 and 334 nm, respectively, which is good evidence for the proposed keto-enol tautomerism (Scheme III).

c. The third electronic transition is a  $\pi$ - $\pi$ \*(Ar) transition with greater coefficients on C<sub>1</sub>, C<sub>3</sub>, C<sub>4</sub>, and N<sub>6</sub> atoms within 252 and 269.7 nm where the experimental values are 255 and 270 nm, respectively.

d. The fourth type is  $\pi$ - $\pi$ \*(Ar) transition at 214.8 and 225 nm which could be described by an electron excitation from the levels at 15.70624 and 15.45083 eV, significantly, characterized by coefficients of C<sub>10</sub>, C<sub>12</sub>, C<sub>13</sub>, C<sub>14</sub> and C<sub>14</sub> atoms to the LUMO level with a complete  $\pi$ \* character. The experimental wavelengths are 214 and 231 nm, respectively.

### ACKNOWLEDGMENT

The authors are grateful to Prof. Dr. Mohamed Khaled Awad for his assistance in the molecular orbital calculation carried out in this work.

Received December 25, 2007.

### REFERENCES

- (a) Calvin, M. Science 1974, 184, 375. (b) Cooper, S.-R.; Calvin, M. Science 1974, 188, 376.
- Maurer, R.-I.; Blover, P.-I.; Dilworth, J.-R.; Reynoh, C.-A. J. Med. Chem. 2002, 45, 1420.
- 3. Selbin, J. Coord. Chem. Rev. 1966, 1, 293.
- Vasin, S.-V.; Cetralla, J.; Genogel, R.-A.; Bernal, J. Inorg. Chem. 1990, 29, 885.
- 5. Maki, M.; Hashimato, H. Bull. Chem. Soc. (Japan) 1952, 25, 411; 1954, 27, 602.
- 6. Papie, S.; Kaprivanae, N.; Grabarie, Z.; Paracosterman, D. *Dyes Pigments* **1994**, *25*, 229.
- Khedr, A.-M.; Gaber, M.; Issa, R.-M.; Erten, H. Dyes Pigments 2005, 67, 117.

- Cimerman, Z.; Miljanic, S.; Antolic, J. Spectr. Lett. 1999, 33, 181.
- 9. Issa, R.-M.; Khedr, A.-M.; Rizk, H.-F. *Spectrochimica Acta A*, **2005**, *62*, 621.
- 10. Saw, H.-D. J. Am. Chem. Soc. 1967, 101, 154.
- 11. Melhuish, W.-H. J. Phys. Chem. 1961, 65, 229.
- 12. Katritzky, A.-R. et al., J. Chem. Soc. 1959, 2051; 3607.
- Breigleb, G.; Delle, H. Z. Electrochem. (Ber. Bausengesell. Physiki Chem.) 1960, 64, 347; Z. Physiki Chem. (Frankfurt) 1960, 24, 359.
- 14. Bruyneel, W.; Charette, T.-J.; De Hoffman, E. J. Am. Chem. Soc. **1966**, *88*, 3808.
- 15. Masten, F.-A. J. Chem. Phys. 1958, 24, 602.
- Becker, R.-S.; Wentworth, W.-F. J. Am. Chem. Soc. 1962, 84, 4263; 1963, 85, 2210.
- Wheast, C. D. Hand Book of Chemistry and Physics, 5<sup>th</sup> ed.; The Chemical Rubber Company: Ohio, 1969.
- Reisey, A.; Leyshon, L.-J. Saundevs, D.; Mijavic, M.-V., Bright, A.; Bogie, J. J. Am. Chem. Soc. 1972, 94, 2414.
- 19. Gati, L.; Szalay, L. Acta Phys. Chem. 1959, 5, 87.
- 20. Suppan, P. J. Chem. Soc. 1968, 2, 3125.
- 21. Kosower, E.-M. J. Am. Chem. Soc. 1956, 78, 5700.
- 22. Reichardt, C.; Dimoorth, K. Chem. Forsch. 1986, 11, 1.
- 23. Kamlet, M.-J.; Taft, R.-W. J. Am. Chem. Soc. 1976, 98, 377.
- 24. Issa, R.-M. Egypt. J. Chem. 1971, 14, 133.
- Issa, R.-M.; Maghrabi, J.-Y. Z. Phys. Chem. (Leipzig) 1975, 56, 1120.
- 26. Forster, T. Z. Elektochem. (Ber. Bunsengesell. Physik. Chem.) 1950, 54, 43.
- 27. Anderson, A.-B. J. Chem. Phys. 1975, 62, 1187.
- Anderson, A.-B.; Grimes, R.-W.; Hong, S.-Y. J. Phys. Chem. 1987, 91, 4245.
- 29. Abd El-Halim, S.-T.; Awad, M.-K. J. Phys. Chem. **1993**, 97, 3160.
- Awad, M.-K.; Shehata, A.; El-Dissouki, A. Trans. Met. Chem. 1993, 20, 6.
- 31. Awad, M.-K. Polym. Degrad. Stab. 1995, 49, 339.
- 32. Awad, M.-K.; Habeeb, M. J. Mol. Struct. 1996, 378, 103.
- 33. Awad, M.-K. J. Mol. Struct. (Theochem) 2000, 505, 185.
- Awad, M.-K. Mahgoob, F.; El-iskandrani, M. J. Mol. Struct. (Theochem) 2000, 531, 105.
- 35. Lotz, W. J. Opt. Soc. Am. 1970, 60, 206.
- 36. Clementi, I.; Raimondi, D.-L. J. Chem. Phys. 1963, 38, 2680.