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# UV–vis, IR and <sup>1</sup>H NMR spectroscopic studies of some Schiff bases derivatives of 4-aminoantipyrine

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#### Abstract

Five Schiff bases derived from 4-aminoantipyrine and benzaldehyde derivatives (I) are prepared and their UV–vis, IR, <sup>1</sup>H NMR and fluorescence spectra are investigated and discussed. The electronic absorption spectra of the hydroxy 4-aminoantipyrine Schiff bases Ib and Ie as well as the fluorescence spectra of Ie are studied in the organic solvents of different polarity. The UV–vis absorption spectra of 4-aminoantipyrine Schiff bases Ib, Id and Ie are investigated in aqueous buffer solutions of varying pH and utilized for the determination of  $pK_a$  and  $\Delta G$  of the ionization process. The reactions of the hydroxy compounds Ib and Ie with Ni(II) and Cu(II) ions are also studied. The results of spectral studies are supported by some molecular orbital calculations using an atom superposition and electron delocalization molecular orbital theory for a compound Ib.

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# 1. Introduction

A considerable number of articles have been published on the spectral behavior of Schiff bases [1–4]. This originated from the fact that the Schiff bases and their metal complexes exhibit wide applications in biological systems [5,6] and industrial uses, especially in catalysis [7,8] and dying [9–11].

Although Schiff bases containing a heterocyclic nucleus have efficient biological activities, yet spectral studies of these compounds are comparatively minor [12–14].

In the present work, the UV–vis, IR, <sup>1</sup>H NMR and fluorescence spectra of some Schiff bases obtained from 4aminoantipyrine and benzaldehyde derivatives (Scheme 1) are investigated. The UV–vis absorption bands are assigned to corresponding electronic transitions; the IR bands and the <sup>1</sup>H NMR signals of diagnostic importance are considered and discussed. The reactions of some compounds with Ni(II) and Cu(II) ions are also investigated. The electronic absorption spectral data for Schiff base Ib are supported by using the molecular orbital calculations.

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# 2. Experimental

All compounds used were pure grade chemicals from BDH, Aldrich or Sigma. The solvents used for spectral measurements were spectroscopic grade from Aldrich.

The Schiff bases were prepared by refluxing a mixture of 10 mmole of 4-aminoantipyrine and 10 mmole of aldehyde in 25 ml of ethanol on a water bath for 2–5 h [15]. The Schiff base, precipitated on cooling, was filtered off and purified by repeated crystallization from the appropriate solvent (yield 70–80%).

The UV–vis spectra were recorded at room temperature in the range of 200–600 nm on a Perkin-Elmer Lambda 4B using a 1.0 cm matched silica cells. The IR spectra were recorded in the solid state as KBr discs on a Perkin-Elmer 1430 ratio recording infrared spectrometer. The <sup>1</sup>H NMR spectra were obtained on a Brooker DMX 750 (500 MHz) using d<sub>6</sub> DMSO as a solvent and TMS as an internal standard. The fluorescence spectra were recorded on a Schimadzu RF 510 spectrofluorometer. The fluorescence quantum yield for the solutions having absorbances less than 0.1 at the excitation wavelength and refereed to fluorescene in 0.1 N NaOH ( $\phi_f = 0.93$ ) [16]. The X-band ESR spectra of

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R= Ph (Ia), o-OH-Ph(Ib), p-OCH<sub>3</sub>-Ph(Ic), p-OH-Ph(Id) and 2-OHl-naphthaldhyde (Ie)

Scheme 1. Structure of the Schiff bases under investigation in which R: Ph (Ia), *o*-OH-Ph (Ib), *p*-OCH<sub>3</sub>-Ph (Ic), *p*-OH-Ph (Id), and 2-OH-1-naphthaldhyde (Ie).

the solid Cu(II)-complexes were recorded on a Joel-X-band spectrometer equipped with an E-101 microwave bridge. Molecular orbital calculations were carried out on compound Ib using the atom superposition and electron delocalization molecular orbital (ASED-MO) theory.

## 3. Results and discussion

### 3.1. The electronic absorption spectra

The electronic absorption spectra of Ia–Ie in ethanol (Fig. 1) displays four main bands (Table 1). The first (210–234 nm) and second (240–281 nm) bands (A and B) are assigned to the  $\pi$ – $\pi$ \* transitions of the aromatic rings. The third band (C) at 301–334 nm involves  $\pi$ – $\pi$ \* transition of the C=O and C=N groups; this band appears splitted in the spectra of Ib and Ie where the C=N group is involved in an intramolecular hydrogen bond which causes a decrease of the  $\pi$ – $\pi$ \* energy of the C=N group relative to that of the C=O group. The longer wavelength band (D) at 325–396 nm can be assigned to an intramolecular charge transfer interaction. The charge transfer will originate from 4-aminoantipyrine



Fig. 1. Electronic absorption spectra of 4-aminoantipyrine Schiff bases in ethanol.



Scheme 2. Keto-enol tautomerism in Schiff base Ie.

ring as an origin to the C=N group as a sink. This can be confirmed by determining the energy of this charge transfer band from  $\lambda_{max}$  values using the relation:

$$E_{\rm CT} = \frac{1241.6}{\lambda_{\rm max}^{\rm CT}} \tag{1}$$

and comparing the values thus obtained with those calculated from the Briegleb relation [17]:

$$E_{\rm CT} = I_{\rm P} - (E_{\rm A} + C) \tag{2}$$

in which  $I_P$  is the ionization potential of the donor part,  $E_A$  is the electron affinity of the C=N acceptor group (-1.3 eV) and *C* is the coulombic force between the electron transferred and the positive hole left behind (C = 5.2 or 5.6 eV) [17]. The values obtained for  $E_{CT}$  from Eq. (1) lie between the two values calculated from Eq. (2) by using the two values of *C* with maximum difference of 0.26 eV (Table 1).

It is worthy to mention that the charge transfer band is splitted into two bands in the spectrum of Ie at 381 and 396 nm. For Ib the spectrum displays a shoulder on the longer wavelength side. This behavior can be ascribed to the possible existence of a tautomeric shift between the C=N and *o*-OH group according to the equilibrium in Scheme 2.

The absorption at shorter wavelength is assigned to the enolic form (II) while that at longer wavelength is due to the ketonic structure (III) [18].

The oscillator strength (*f*) of the CT band was also determined from the relation [19]:

$$f = 4.6 \times 10^{-9} \varepsilon_{\text{max}} \,\Delta\nu_{1/2} \tag{3}$$

in which  $\Delta v_{1/2}$  is the bandwidth at half absorbance value and  $\varepsilon_{\text{max}}$  is the maximum molar extinction coefficient.

In cases where the CT band overlaps with the band C, the band envelope was completed by considering it to follow a Gaussian curve. The *f*-values determined are given in Table 1.

The ionization potentials of the 4-aminoantipyrine Schiff bases under study were determined from the electronic absorption spectra applying the relation:

$$I_{\rm P} = a + b\nu \tag{4}$$

in which *a* and *b* are constants having the values (4.93 and 0.857) [20], (5.156 and 0.778) [21] or (5.11 and 0.701) [22];  $\nu$  is the energy of the lowest  $\pi - \pi^*$  transition. The values obtained together with the mean values determined from the above three values are given in Table 1.

Table 1
Data from UV-vis and fluorescence spectra of 4-aminoantipyrine Schiff bases in ethanol

Compound number						Assignment		
Ia	Ib	Ic	Id	Ie				
210, 234	212, 234	213, 230	213	212	$\lambda_{max}$	Band A $(\pi - \pi^* Ar)$		
1.58, 1.79	1.88, 1.99	1.64, 1.51	1.70	3.32	$\varepsilon_{\rm max}$			
252	262	281	242	240	$\lambda_{max}$	Band B ( $\pi$ – $\pi^*$ Ar)		
1.76	1.27	1.41	1.70	3.28	$\varepsilon_{\rm max}$			
313	301, 317	307	317	321, 334	$\lambda_{max}$	Band C ( $\pi$ - $\pi^*$ of C=O or C=N)		
1.81	1.24, 1.49	1.90	2.14	1.24, 1.36	$\varepsilon_{\rm max}$			
325	346,	329	330	381, 396	$\lambda_{max}$	Band D (CT)		
2.16	2.24	2.64	2.90	2.26, 1.86	$\varepsilon_{\rm max}$			
3.82	3.59	3.77	3.76	3.26, 3.14	$E_{\rm CT}$ (eV	7) from Eq. (1)		
8.13	7.95	8.09	8.07	7.69, 7.50	$I_{\rm P1}$ (eV)	)		
7.66	7.47	7.62	7.61	7.18, 7.08	$I_{\rm P2}~({\rm eV})$	)		
7.79	7.63	7.75	7.74	7.40, 7.31	$I_{\rm P3}$ (eV)	)		
$7.86 \pm 0.24$	$7.68 \pm 0.24$	$7.82\pm0.24$	$7.81 \pm 0.24$	$7.42 \pm 0.26, 7.30 \pm 0.21$	Mean $I_{\rm F}$	(eV) values		
1.01	0.51	0.74	0.66	0.29, 0.21	f			
3.96	3.78	3.92	3.91	3.52, 3.40	$E_{\rm CT}$ from	m Eq. (2) $[C=5.2 \mathrm{eV}]$		
3.56	3.38	3.52	3.51	3.12, 3.00	$E_{\rm CT}$ from	m Eq. (2) $[C = 5.6 \mathrm{eV}]$		
325	346	329	330	381	$\lambda_{\max}^{exc}$	• • • • •		
No fluorescence	434	No fluorescence	No fluorescence	480	$\lambda_{\max}^{emm}$			
	0.064			0.1131	$\phi_{ m f}$			

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

Despite the fact that the position of the CT band is influenced by the substituent on the phenyl ring being shifted to longer wavelength with the increasing donor character of the substituent, yet it is not possible to have a quantitative treatment because the shift is of a small magnitude. However, the hydrogen bond formation between the C=N group and the *o*-OH group on the phenyl or naphthyl ring shifts the CT band obviously to longer wavelength. The magnitude of shift is higher for the naphthyl derivative.

The spectra of Ib and Ie are measured in organic solvents of different polarity and the values of  $\varepsilon_{\lambda_{max}}^{CT}$  and  $\lambda_{max}$  are listed in Table 2. The obtained results indicate that the position of the bands due to the localized transitions is slightly influenced by solvent polarity. The CT band displays a general red shift with an increased solvent polarity denoting the higher stabilization of the excited state with increased solvent polarity. The application of the dielectric relations of Gati and Szalay [23] or Suppan [24] to the data of the CT band did not lead to linear relationships. This reveals that the dielectric constant of the solvent does not play an important role in the band shift. The plot of  $E_{\rm CT}^{\rm max}$  in different solvents as a function of the various microscopic solvent parameters:  $\alpha$  (acidity),  $\beta$  (basicity),  $\pi^*$  (dipolarity) [25], Z [26] as well as  $E_{\rm T}$  [27] showed nonlinear relations indicating that these solvent parameters are not the main factors affecting the CT band position. Accordingly, it can be assumed that the shift of the CT band is the resultant of the influence of all these parameters. These effects may be additive, counteracting or even may cancel out each other.

Table 2 Data from UV-vis spectra of 4-aminoantipyrine Schiff bases Ib and Ie in organic solvents of different polarity

Solvent	$\lambda_{CT}^{max}$ of Ib	$\varepsilon_{\rm CT}^{\rm max}$ of Ib	$\lambda_{CT}^{max}$ of Ie	$\varepsilon_{\rm CT}^{\rm max}$ of Ie	$\lambda_{max}^{emm}$ of Ie	$\phi_{\mathrm{f}}$ of Ie			
Methanol	346	2.22	380, 395 (sh)	2.62, 2.12	467	0.1156			
Ethanol	343	2.24	381, 396 (sh)	2.26, 1.86	480	0.1131			
Acetone	355	1.94	382, 398 (sh)	2.08, 1.90	477	0.0754			
DMF	357	2.82	386	2.74	484	0.0762			
DMSO	348	2.66	388	2.70	_	_			
CHCl <sub>3</sub>	345	2.70	382, 398 (sh)	2.68, 2.24	-	_			
CCl <sub>4</sub>	346	2.42	381, 395 (sh)	2.60, 2.14	476	0.1087			
CH <sub>2</sub> Cl–CH <sub>2</sub> Cl	346	2.60	380, 395 (sh)	2.68, 2.24	475	0.0792			
CH <sub>2</sub> Cl <sub>2</sub>	347	2.62	383, 397 (sh)	2.64, 2.18	482	0.0876			
Toluene	344	2.61	381, 396 (sh)	2.60, 2.22	475	0.1105			
Benzene	344	2.70	380, 395 (sh)	2.88, 2.36	-	_			
Ethylacetate	347	2.72	380, 395 (sh)	2.76, 2.30	_	-			

 $\varepsilon_{max} \times 10^{-4}$  (l mol<sup>-1</sup> cm<sup>-1</sup>),  $\lambda_{max}$  (nm),  $\phi_f$  is the fluorescence quantum yield.

3.2. Electronic absorption spectra of 4-aminoantipyrine Schiff bases Ib, Id and Ie in buffer solutions of varying pH and spectrophotometric determination of their acid dissociation constant  $(pK_a)$ 

The 4-aminoantipyrine Schiff bases Ib, Id and Ie are considered as monobasic acids and their dissociation can be represented by the following equilibrium:

$$HL \stackrel{K_a}{\rightleftharpoons} L^- + H^+$$

where  $K_a$  is the acid dissociation constant for the compound.

The absorption spectra of 4-aminoantipyrine Schiff bases Ib, Id and Ie are studied in universal buffer solutions of varying pH values containing 5% (v/v) methanol in the UV–vis region (200–600 nm). The spectra obtained indicate that the absorbance values and position of the absorption bands changes with the pH of the medium due to the following:

- 1. In case of Ib, in solution having pH <6, the absorption spectra showed an absorption peak with  $\lambda_{max} = 280 \text{ nm}$  corresponding to HL form, the extinction of this peak increases with increasing pH values of solution until pH 6 and begin to decrease with increasing pH value, while another absorption peak appeared at pH  $\geq$ 6 with  $\lambda_{max} = 350 \text{ nm}$  corresponding to the L<sup>-</sup> form. The absorbance of this peak increases with increasing the pH value of the solution until pH 10. This behavior indicates that, in solution of pH <6, Ib exist essentially as undissociated molecules, whereas at pH >10 the L<sup>-</sup> form exist; at pH 6–10 the undissociated and dissociated forms are present in different ratios.
- 2. The spectra of Id showed two different peaks with  $\lambda_{max} = 250$  and 364 nm corresponding to HL and L<sup>-</sup>, respectively. The extinction of the first peak due to the undissociated form (HL) decreases with increasing pH of the solution, while the absorbance of the second peak of the dissociated form (L<sup>-</sup>) increases with increasing pH values.
- 3. The spectra of ligand Ie showed a peak with  $\lambda_{max} = 292 \text{ nm}$ and two broad peaks with  $\lambda_{max} = 330$  and 395 nm. The extinctions of the three peaks increases with increasing pH of the solution due to the change from undissociated form to the dissociated one with increasing pH.

The pH-absorbance curves of 4-aminoantipyrine Schiff bases Ib, Id and Ie at different wavelengths corresponding to  $\lambda_{max}$  are of typical Z- or S-shaped (Fig. 2). This behavior is utilized for the determination of the acid dissociation constant (p $K_a$ ) of these compounds by applying the limiting absorbance [28] and the half-height methods [29] (Table 3).

The values of  $pK_a$  were used in calculating the free energy change  $(\Delta G^*)$  of the ionization process from the relationship

$$\Delta G^* = -2.303RT \log K \quad (\text{at } 303 \text{ K}) \tag{5}$$

The  $\Delta G^*$  value (Table 3) of Ib (*o*-OH) is higher than  $\Delta G^*$  value of Id (*p*-OH), although they have the same molecular



Fig. 2. Absorbance-pH curves of 4-aminoantipyrine Schiff base (Ib).

configuration except in the position of the OH group. This can be attributed to the formation of hydrogen bond in case of *o*-OH which retards the liberation of H<sup>+</sup> proton relative to *p*-OH substituent. The strength of the hydrogen bond can be taken as equal to the difference in energy in both cases  $(8.70 \text{ kJ mol}^{-1})$ .

# 3.3. IR spectra

Selected bands of diagnostic importance are discussed in this part (Table 4). The spectra of all compounds exhibit two medium intensity bands at 3174–3038 and 3087–3036 cm<sup>-1</sup> corresponding to asymmetric and symmetric stretching vibrations of the aromatic C–H groups. All compounds display an intense band at 1648–1617 cm<sup>-1</sup> corresponding to  $\nu$ (C=O) of the antipyrine ring. The  $\nu$ (C=N) band is observed at 1591–1576 cm<sup>-1</sup> being shifted to lower wave numbers for Ib and Ie due to the contribution of the C=N in these two compounds in an intramolecular hydrogen bond.

The aliphatic CH<sub>3</sub>-groups lead to two small bands at  $2984-2917 \text{ cm}^{-1}$  due to the stretching modes, while their deformation vibrations give strong bands at  $1200-1160 \text{ cm}^{-1}$ .

Table 3	
The values of $pK_a$ for 4-aminoantipyrine Schiff bases Ib, Id and	ıd Ie

Schiff base	λ (nm)	pK <sub>a</sub>		$\Delta G^*$ (kJ mol <sup>-1</sup> )	
		LAM	HHM	Av. V	
Ib	350	7.54	7.08	7.31	42.41
Id	346	5.88	5.73	5.81	33.71
Ie	395	5.66	5.15	5.41	31.39

HHM: half-height method; LAM: limiting absorbance method; Av. V: average value;  $\Delta G^*$ : free energy change.

Table 4 Some selected bands of diagnostic importance from the IR spectra of 4aminoantipyrine Schiff bases

Compo	Assignment				
Ia	Ib	Id	Ie	4-Aminoantipyrine	
_	_	_	_	3424	$\nu(NH_2)$ as
_	_	_	_	3317	$\nu(NH_2)$ s
_	3450	3630	3427	-	ν(OH)
3087	3087	3138	3080	3174	v(CH) as (Ar)
3036	3056	3060	3043	3087	v(CH) s (Ar)
2935	2928	2935	2926	2984	$\nu$ (CH) as (CH <sub>3</sub> )
2920	2918	2916	2917	2917	v(CH) s (CH <sub>3</sub> )
1644	1648	1617	1634	1641	С=0
1591	1590	1576	1587	_	C=N
1417	1410	1418	1417	1406	N-CH <sub>3</sub>
1370	1369	1305	1326	1310	C—N
1305	1304	1250	1312	_	$\delta(OH)$
1179	1180	1160	1155	1200	$\delta(CH_3)$
1070	1115	1093	1087	_	ν(C-OH)
1017	1020	1024	1027	_	$\gamma$ (CH=N)
870	860	865	870	_	γ(OH)
675	673	674	641	728	$\gamma$ (CH) ring

The spectrum of Id exhibits the v(OH) as a sharp medium band at  $3630 \,\mathrm{cm}^{-1}$ , while for Ib and Ie it appears as a broad band at 3450 and  $3427 \,\mathrm{cm}^{-1}$ , respectively. The OH deformation bands lie at  $1326-1250 \text{ cm}^{-1}$  while the  $\nu$ (C–OH) bands are observed at 1115–1070 cm<sup>-1</sup> and  $\gamma$ (OH) at  $870-860 \text{ cm}^{-1}$ .

The aromatic rings give a group of intense bands due to skeletal and CH deformations at different positions characteristic for the type of substitution.

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

The <sup>1</sup>H NMR spectra of the antipyrine Schiff bases (Table 5) display two sharp signals at 2.35-2.5 and 3.10-3.19 ppm with an integration equivalent to three hydrogens corresponding to the N-(CH)<sub>2</sub> and C-CH<sub>3</sub> groups. The aromatic rings give a group of multi signals at 6.82–7.92 ppm. The CH=N hydrogen for (Ia–Id) resonates at 9.49–9.84 ppm as a sharp singlet. For Schiff bases Ib and Ie two doublets are observed: the first at 9.48 and 8.27 due to the azomethine

Table 5	
<sup>1</sup> H NMR spectral data of 4-aminoantipyrine Schiff bases in	CDCl <sub>3</sub>

hydrogen coupled with the N-H hydrogen which resonates as a doublet at 6.82 and 7.12 ppm for Ib and Ie, respectively. This behavior supports the occurrence of the keto-enol tautomerism given above (Scheme 2).

# 3.5. Fluorescence spectra

The fluorescence spectra of 4-aminoantipyrine Schiff bases were investigated in ethanol as a solvent. The data are collected in Table 1. The spectra were also obtained for Ie in solvents of different polarity; the results are collected in Table 2. These results indicate that the values of the emission  $\lambda_{\text{max}}$  and fluorescence quantum yield ( $\phi_{\text{f}}$ ) depend on the molecular structure and solvent used as a medium. Also, compounds Ib and Ie give good fluorescence spectra and satisfactory values for the fluorescence quantum yield ( $\phi_f$ ) whereas compounds Ia, Ic and Id do not give the convincing fluorescence spectra. This behavior may be attributed to the formation of hydrogen bonding in case of Ib and Ie which increase the stability of the molecule in the excited state, which is not possible in case of the other Schiff bases Ia, Ic and Id [30]. The fluorescence spectra of Ie were recorded in some organic solvents of varying polarity (Fig. 3 and Table 2). The data reflect that both  $\lambda_{\max}^{\text{emm}}$  and  $\phi_{\text{f}}$  are solvent dependent.

The plot of  $\lambda_{\text{max}}^{\text{emm}}$  as a function of macro- or microscopic solvent parameters gave nonlinear relationships indicating that the solvent effect on emission spectra, as in the case of ground state spectra, is actually the resultant of the influence of the various solvent parameters.

# 3.6. Spectral studies on the metal complexes of Ib and Ie with $Ni^{2+}$ and $Cu^{2+}$ ions

The addition of Ni(II) or Cu(II) ions to a solution of Ib or Ie leads to the appearance of a new absorption band with  $\lambda_{max} = 410$  and 450 nm for Ib and Ie, respectively. The extinctions of these bands increase with increasing the metal ion concentration which is a good evidence for the specification of these bands to the formed metal complexes in the solution. The stoichiometry of the formed metal complexes was determined using the mole ratio [31] and continuous vari-

Compound number								
Ia	Ib	Ic	Id	Ie	4-Aminoantipyrine			
2.5	2.339	2.45	2.42	2.42	2.13	C-CH3		
3.19	3.15	3.10	3.12	3.16	2.82	N-CH <sub>3</sub>		
-	_	_	_	-	2.98	NH <sub>2</sub>		
-	-	3.28	-	-	_	OCH <sub>3</sub>		
-	6.82	-	-	7.17 <sup>a</sup>	_	NH(tout)		
7.25-7.92	7.26-7.52	6.92-7.82	6.84-7.68	7.39-7.80	7.20-7.50	Ar H		
9.78	9.48 <sup>b</sup>	9.71	9.49	8.27 <sup>a</sup>	_	CH=N		
_	9.84 <sup>b</sup>	_	9.94	10.85	-	OH		

<sup>a</sup> Doublet.

<sup>b</sup> N=CH overlapping with OH.



Fig. 3. Emission spectra of a  $1 \times 10^{-5}$  M solution of the compound (Ie) in organic solvents of varying polarity.

ation methods [32]. Also, their stability constants and free energy changes are calculated [33]. The results obtained are collected in Table 6.

In order to investigate the molecular structure of the formed Cu(II)- and Ni(II)-complexes with 4-aminoantipyrine Schiff bases Ib and Ie, some solid complexes were prepared and characterized. The prepared solid complexes were found to have the following molecular compositions:  $[CuLAcO(H_2O)_2]\cdot 2H_2O$  (1),  $[CuLAcO]\cdot 2H_2O$  (2),  $[CuLCI]\cdot 2H_2O$  (3),  $[CuL(NO_3)]$  (4) and  $[NiL_2]$  (5) where L refers to the deprotonated ligand Ib in case of complex (1) and Ie for complexes (2–5).

The data of elemental analysis of the complexes are in good agreement with the suggested formulae (Table 7).

The IR spectra of the metal complexes (Table 7) compared with those of the ligands showed that the C=O and C=N bands are shifted to lower wave numbers by  $10-30 \text{ cm}^{-1}$ 

#### Table 6

Electronic absorption spectral data of Ni(II) and Cu(II) chelates with 4aminoantipyrine Schiff bases Ib and Ie

Compound	Metal ion	$\lambda_{\text{max}}$	Stoichio	ometry	$\log \beta_n$	$-\Delta G^*$	
			MRM	CVM			
Ib	Ni(II)	410	1:1 1:2	1:1 -	12.78 19.16	17.72 26.56	
	Cu(II)		1:1 1:2	1:1 1:2	12.38 24.38	17.16 33.80	
Ie	Ni(II)	450	1:1 1:2	1:1 1:2	9.94 18.79	13.78 26.05	
	Cu(II)		1:1 -	1:1 1:2	10.16 20.62	14.09 28.59	

 $\log \beta_n$ : log stability constant;  $-\Delta G^*$ : free energy change (k cal mol<sup>-1</sup>).

denoting the contribution of these two groups with the metal ion. The bands due to the various vibrations of the phenolic OH-group disappeared from the spectra of the complexes denoting displacement of the phenolic proton through the metal ion. Thus, the SB-Ib and SB-Ie would act as monobasic tridentate ligands towards the metal ion [34].

The copper(II) nitrate complex displayed a strong band at  $1290 \text{ cm}^{-1}$  characteristic for monodentate coordinated nitrate anion while the spectra of the acetate complexes contain two bands near 1575 and 1535 cm<sup>-1</sup> corresponding to a monodentate acetate anion [35].

The IR spectra of all complexes exhibit two bands at 500–480 and 445–425 cm<sup>-1</sup> corresponding to  $\nu$ (M–O) and  $\nu$ (M–N) stretching modes [36].

The magnetic moment values for the Cu(II)-complexes amounted to 1.49 for (1), 1.99 for (2) and 1.54 BM for (4) supporting the octahedral, square planar and tetrahedral geometries for Cu(II)-complexes 1, 2 and 4, respectively. The Ni(II)-complexes had a magnetic moment of 2.8 BM which is the normal value for octahedral nickel(II)-complexes; this is quite close to the spin-only value for the two unpaired electrons [37].

The electronic absorption spectra of the prepared solid complexes were recorded in the range of 200–1000 nm as nujol mull. The electronic absorption spectra of Cu(II)- and Ni(II)-complexes compared with those of the free Schiff bases exhibit new bands or shoulders at longer wavelengths around 700 nm for Cu(II)-complexes and at 639 nm for Ni(II)-complex (Table 7). The position of  $\lambda_{max}$  and the shape of the new bands are relevant to an octahedral structure of Cu(II)-complex (1), square planar geometry for Cu(II)-complex (2), distorted tetrahedral geometry for Cu(II)-complexes (3 and 4) and octahedral geometry for Ni(II)-complex (5) [38].

The molar conductance values for  $10^{-3}$  M solution of Cu(II)-complexes in DMF were found to lie within the 10–15  $\Omega^{-1}$  which reflects the non-electrolyte nature of the complexes. This indicates that the anions are involved in the coordination sphere of the metal ion [39].

Table 7	
Elemental analysis, IR spectra and UV-vis band of the solid complexes (1–5	6

No.	Empirical formula (molecular formula)	Color (for. wt.)	Microanalysis results <sup>a</sup>			IR spectra					UV-vis band due	
			%C	%H	%N	%M	vOH	vCH=N	vC=O	vМ—О	vM–N	to d–d transition
1	[CuL(AcO)(H <sub>2</sub> O) <sub>2</sub> ]· 2H <sub>2</sub> O (C <sub>20</sub> H <sub>27</sub> CuN <sub>3</sub> O <sub>8</sub> )	Green (501.00)	47.6 (48.0)	5.9 (5.4)	8.7 (8.4)	13.0 (12.8)	3416	1576	1603	478	408	715
2	$[CuL(AcO)] \cdot 2H_2O$ $(C_{24}H_{25}CuN_3O_6)$	Brown (515.02)	55.5 (56.0)	4.5 (4.9)	8.5 (8.2)	12.0 (12.3)	3477	1555	1618	452	428	670
3	$[CuLCl] \cdot 2H_2O$ $(C_{22}H_{22}ClCuN_3O_4)$	Brown (491.43)	53.5 (53.8)	4.2 (4.5)	8.4 (8.6)	13.2 (12.9)	3455	1573	1604	496	430	730
4	$[CuL(NO_3)]$ $(C_{22}H_{18}CuN_4O_7)$	Green (513.95)	51.8 (51.4)	3.6 (3.5)	10.9 (10.9)	11.9 (12.4)	3445	1578	1602	498	431	675
5	[NiL <sub>2</sub> ] (C <sub>44</sub> H <sub>36</sub> NiN <sub>6</sub> O <sub>4</sub> )	Green (771.50)	68.1 (68.5)	4.6 (4.7)	11.0 (10.9)	7.2 (7.6)	3436	1579	1609	489	441	639

The reaction yield was 80-85%.

<sup>a</sup> %F (%C), all complexes (1–5) decompose without melting above 300 °C.

The results obtained from the X-band ESR spectra of the solid Cu(II)-complexes (1, 2 and 4) at room temperature indicate the following:

- 1. The ESR spectrum of Cu(II)-complex (1) gives three anisotropic signals ( $g_{\perp} = g_x = 2.4295$ ,  $g_{\parallel} = g_z = 2.7468$  and  $g_y = 2.6186$ ) and  $g_{\text{eff}} = 2.6015$  which confirm the octahedral geometry around the Cu(II) ion.
- 2. The ESR spectrum of Cu(II)-complex (2) show one signal with pattern with  $g_{\text{eff}}$  value (2.1569) indicating a square planar geometry around the Cu(II) ion.
- 3. The ESR spectrum of Cu(II)-complex (4) show two sharp anisotropic signals ( $g_{\perp} = g_x = 1.8488$  and  $g_{\parallel} = g_z = 1.8957$ ). The observed ESR pattern and  $g_{\text{eff}}$  value (1.8724) indicate a tetrahedral geometry around the Cu(II) ion [40].

Based on the knowledge gained above for the metal complexes, the bonding in the Cu(II)-complexes (2–4) can be formulated as follows (Scheme 3).

## 3.7. Molecular orbital calculations

The atom superposition and electron delocalization molecular orbital theory [41,42] is used. This is a semiempirical theoretical approach based on partitioning the molecular density function ( $\rho_{mol}$ ) into rigid atomic components and a



Scheme 3. The bonding in the Cu(II)-complexes (2–4). X: AcO<sup>-</sup>, n = 2 (2); Cl<sup>-</sup>, n = 2 (3); and NO<sub>3</sub><sup>-</sup>, n = 0 (4).

non-rigid or non-perfectly following  $(\rho_{npf})$  component. For the example of a diatomic molecule (ab),

$$\rho_{\rm mol} = \rho_{\rm a} + \rho_{\rm b} + \rho_{\rm npf} \tag{6}$$

where  $\rho_a$  and  $\rho_b$  are atomic charge densities centered on nuclei (a) and (b), and  $\rho_{npf}$  is an electron delocalization or bond charge density. According to the electrostatic theorem, the forces on the nucleus (a) has two nonzero components; a repulsive one due to the nucleus and electronic charge distribution of atom (b) and an attractive force due to  $\rho_{npf}$ . These forces are integrated, yielding the potential energy E(R), where *R* is the internuclear distance

$$E(R) = E_{\rm r}(R) + E_{\rm npf}(R) \tag{7}$$

 $E_{\rm r}(R)$  is the repulsive energy due to atom superposition and  $E_{\rm npf}(R)$  is the attractive energy due to electron delocalization.  $E_{\rm npf}$  is approximated as the change in the total one-electron valence orbital energy that is due to bond formation

$$E \cong E_{\rm r} + \Delta E_{\rm MO} \tag{8}$$

 $\Delta E_{\rm MO}$  is determined by using a modified extended Hückel Hamiltonian. When this approximation to  $E_{npf}$  is employed, the more electronegative atom is used to provide the density function for  $E_{\rm r}$ . This technique has already been applied for predicting molecular structures, reaction mechanism, and electronic and vibrational properties [43-48]. The input data consist of ionization potentials [49] (VSIP) and valence-state Slater orbital exponents [50] for the constituent atoms. These parameters are sometimes altered, particularly in treating ionic heteronuclear molecules to ensure reasonably accurate calculations of ionicities and bond lengths in the diatomic fragment molecules. In this way electronic charge self-consistency is taken into account [42]. Atomic parameters used in the calculations are given in Table 8. Because of ionicity, the ionization potentials for N 2s and 2p are decreased by 2.0 eV from the atomic values [49]. The C 2s and 2p Slater exponents are increased by 0.20 from the atomic values of Clementi and Raimondi [50] to get a reasonable bond length. In all reported resulted for

Table 8 Atomic parameters used in the calculations: principle quantum numbers, n; ionization potentials,  $I_P$  (eV); orbital exponents,  $\zeta$  (a.u.)

s			р				
n	IP	ζ	n	IP	ζ		
2	16.590	1.8580	2	11.260	1.8180		
2	18.330	1.9240	2	12.530	1.9170		
2	28.480	2.2459	2	13.620	2.2266		
1	13.600	1.2000					
	s n 2 2 2 1	s n I <sub>P</sub> 2 16.590 2 18.330 2 28.480 1 13.600	s           n         I <sub>P</sub> ζ           2         16.590         1.8580           2         18.330         1.9240           2         28.480         2.2459           1         13.600         1.2000	$\begin{array}{c c c c c c c c c c c c c c c c c c c $	$\begin{array}{c ccccccccccccccccccccccccccccccccccc$		

equilibrium structures, the bond lengths are variationally optimized to the nearest degree. In all calculations the C–H bond lengths are kept constant at 1.10 Å.

Quantum chemical calculations using ASED-MO theory are used to investigate the geometry and electronic structure of the Schiff base Ib. The optimization of bond lengths, bond angles and dihedral angles (Table 9) produces a stable structure with a minimum energy. It is shown that the stable structure of Ib is in the trans form as shown in Fig. 4. The molecular orbital calculations shows that the phenyl moiety is out of plane with respect to both diazole and OH-phenyl rings. The distortion from planarity takes place through rotation around C<sub>4</sub>-C<sub>7</sub>, C<sub>7</sub>-C<sub>8</sub>, C<sub>8</sub>-C<sub>9</sub>, C<sub>9</sub>-N<sub>12</sub> and N<sub>12</sub>-C<sub>13</sub> by 3, 32, 2, 1 and 20°, respectively. The bond lengths (bond orders) of C<sub>9</sub>-N<sub>12</sub>, N<sub>12</sub>-C<sub>13</sub>, and C<sub>13</sub>-C<sub>14</sub> bonds are equal to 1.38 (0.8653), 1.32 (1.1007) and 1.49 Å (0.7690), respectively, and the double bond character of N<sub>12</sub>-C<sub>13</sub> bond is a good evidence for Schiff base formation. The C19-O20 bond length (bond order) 1.27 Å (0.8174) donates some double bond character of this bond. The partial double bond character of the C-O bond confirms the proposed keto-enol tautomerism represented in Scheme 2 since the bond would

Table 9

The calculated bond lengths (Å), bond order, bond angle and dihedral angles of compound Ib obtained from ASED-MO theory

Bond	Bond length	Bond order	Bond angle	Dihedral angle
$C_1 - C_2$	1.38	0.9806	120	0
$C_2 - C_3$	1.38	0.9821	120	180
$C_3 - C_4$	1.38	0.9735	120	0
$C_4 - C_5$	1.39	0.9579	120	0
$C_5 - C_6$	1.38	0.9872	120	0
$C_4 - N_7$	1.39	0.8484	120	177
$N_7 - C_8$	1.34	0.9725	131	328
$C_8 - C_9$	1.35	0.9850	119	182
$C_9 - C_{10}$	1.38	0.9516	106	0
C <sub>10</sub> -N <sub>11</sub>	1.39	0.9857	104	0
C9-N12	1.38	0.8653	117	181
$N_{12}-C_{13}$	1.32	1.1007	140	340
$C_{13} - C_{14}$	1.49	0.7690	124	180
$C_{14} - C_{15}$	1.36	1.1181	120	181
$C_{15} - C_{16}$	1.43	0.8476	119	180
$C_{16} - C_{17}$	1.39	0.9947	120	0
$C_{17} - C_{18}$	1.39	0.9579	120	0
$C_{18} - C_{19}$	1.39	0.9679	120	0
$C_{19} - O_{20}$	1.27	0.8174	120	180
$C_8 - O_{21}$	1.30	0.7508	120	2
$C_{10} - C_{22}$	1.50	0.6950	120	179
$C_{11} - C_{23}$	1.50	0.6667	120	181



Fig. 4. The molecular structure of Schiff bases Ib obtained from ASED-MO theory.

have resonance character between a double bond and a single one. The calculations reveal the formation of strong hydrogen bond,  $N_{12}$ – $H_{39}$ , as assumed before with bond length (bond order) equal to 1.58 Å (0.1745), and confirmed by the presence of the negative charge on  $N_{12}$  equal to 0.23388 e.

The calculation of the charge distribution over the whole skeleton of the molecule indicates the presence of relatively high electron density on atoms  $C_1$  (-0.00964),  $C_3$  (-0.02482),  $C_5$  (-0.02624),  $C_9$  (-0.07978),  $N_{12}$  (-0.23388),  $C_{14}$  (-0.07271),  $C_{16}$  (-0.10965),  $C_{18}$  (-0.13964) and the highest electron density is present on  $O_{20}$  (-0.54970) and  $O_{21}$  (-1.20709). Whereas an electron deficient are found on atoms  $C_2$  (0.03381),  $C_4$  (0.16864),  $C_6$  (0.03277),  $C_7$  (0.33902),  $C_8$  (0.56451),  $C_{10}$  (0.09393),  $N_{11}$  (0.33290),  $C_{13}$  (0.20748),  $C_{15}$  (0.03768),  $C_{17}$  (0.04199),  $C_{19}$  (0.47925),  $C_{22}$  (0.06759) and  $C_{23}$  atoms (0.16712).

The calculated types of electronic transitions in the Schiff base Ib revealed the following points:

- 1. The lowest energy electronic transition between the HOMO (-12.9827 eV) and the LUMO levels (-9.4163 eV) equals to 3.5664 eV corresponding to CT electronic transition with greater coefficients on C<sub>14</sub>, C<sub>15</sub>, C<sub>17</sub>, C<sub>18</sub> and O<sub>21</sub> atoms. The calculated wavelength of this transition is equal to 347.41 nm, which is in a good agreement with the experimental value (346 nm).
- 2. The second type of electronic transition is a  $\pi \pi^*$  transition with low energy (4.1002 eV) and high coefficients on C<sub>19</sub>, O<sub>20</sub> and O<sub>21</sub> atoms, which is a new evidence for

the occurrence of the keto–enol tautomerism. The calculated and experimental wavelengths are equal to 302.18 and 301 nm, respectively.

- 3. The third electronic transition is a  $\pi \pi^*$ (Ar) transition with greater coefficients on C<sub>1</sub>, C<sub>5</sub>, C<sub>6</sub>, C<sub>10</sub> and C<sub>11</sub> atoms with an energy and wavelength equal to 5.2266 eV and 237.06 nm, respectively (exp. value = 234 nm).
- 4. The highest energy excitation (5.8482 eV) corresponds to another  $\pi - \pi^*$ (Ar) transition which could be described by an electron excitation from the level at 15.2645 eV, significantly characterized by the coefficients of C<sub>1</sub>, C<sub>4</sub>, C<sub>7</sub>, C<sub>8</sub> and C<sub>9</sub> atoms to LUMO level with complete  $\pi^*$  character. The calculated wavelength (211.80 nm) is nearly equal to experimental value (212 nm).

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