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UV–vis, IR and ^{1}H NMR spectroscopic studies of some Schiff bases derivatives of 4-aminoantipyrine

Raafat M. Issa, Abdalla M. Khedr*, Helen F. Rizk

Chemistry Department, Faculty of Science, Tanta University, Tanta, Egypt

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Abstract

Five Schiff bases derived from 4-aminoantipyrine and benzaldehyde derivatives (I) are prepared and their UV–vis, IR, ^{1}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 ΔG 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.

Keywords: 4-Aminoantipyrine; Schiff bases; Spectral studies; Metal chelates

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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, ^{1}H NMR and fluorescence spectra of some Schiff bases obtained from 4-aminoantipyrine and benzaldehyde derivatives (Scheme 1) are investigated. The UV–vis absorption bands are assigned to corresponding electronic transitions; the IR bands and the ^{1}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.

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 ^{1}H NMR spectra were obtained on a Brooker DMX 750 (500 MHz) using d_6 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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* Corresponding author. Fax: +20 40 3350804.
E-mail address: abkhedr2001@yahoo.com (A.M. Khedr).

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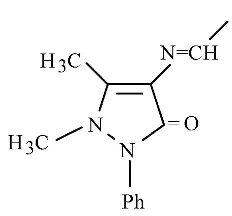


(I)

R= Ph (Ia), o-OH-Ph(Ib), p-OCH$_3$-Ph(Ic), p-OH-Ph(Id) and 2-OH-1-naphthaldhyde (Ie)

Scheme 1. Structure of the Schiff bases under investigation in which R: Ph (Ia), *o*-OH-Ph (Ib), *p*-OCH3-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

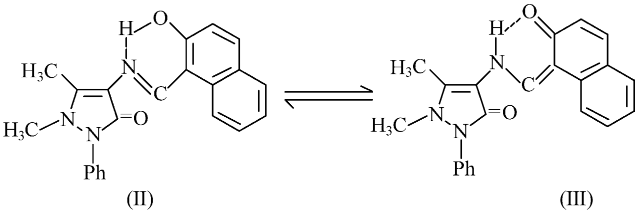
The electronic absorption spectra of Ia–Ie in ethanol (Fig. 1) displays four main bands (Table 1). The first (210–234 nm) and second (240–281 nm) bands (A and B) are assigned to the π–π^* transitions of the aromatic rings. The third band (C) at 301–334 nm involves π–π^* transition of the C=O and C=N 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 π–π^* 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 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:

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

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

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

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).



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

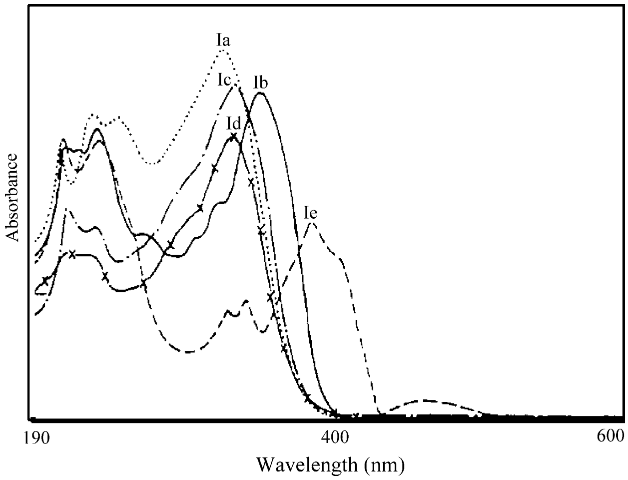


Fig. 1. Electronic absorption spectra of 4-aminoantipyrine Schiff bases in ethanol.

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]:

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

in which $\Delta\nu_{1/2}$ is the bandwidth at half absorbance value and $\varepsilon_{\max}$ 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:

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

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]; ν is the energy of the lowest π–π^* transition. The values obtained together with the mean values determined from the above three values are given in Table 1.