

**SPECTROSCOPIC STUDIES ON SOME SCHIFF BASES
DERIVED FROM 4-AMINOANTIPYRINE**

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ABSTRACT

The electronic absorption spectra of some Schiff bases derived from 4-amino- antipyrine were investigated in organic solvents of different polarities and aqueous universal buffer solutions of different pH values. The pk values of the different examined compounds were calculated and compared with the acidity and basicity of the compounds. The important bands in the ir spectra of the investigated compounds were assigned.

INTRODUCTION

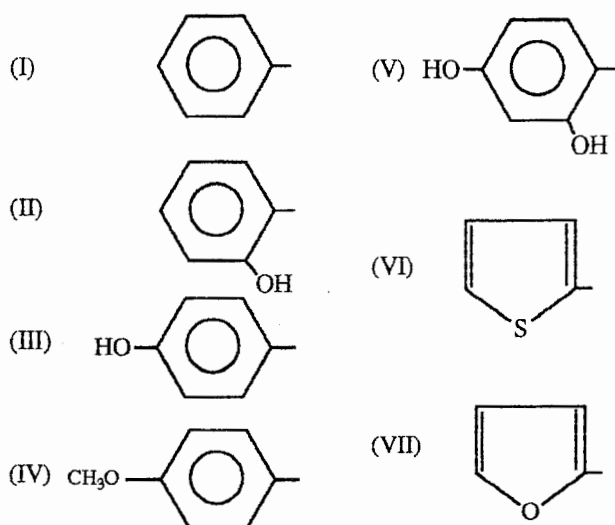
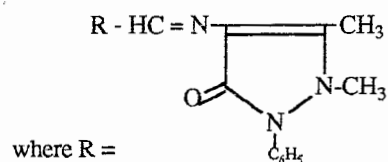
Because of the importance of antipyrine derivatives as analgesic compounds and having antirheumatic activity it is important to study their structures in solution¹⁻⁴ and effect of pH on these structure,.

Although the work on Schiff bases drew the attention of many workers yet it seems that little attention has been payed for the spectral behaviour of those derived from 4-aminoantipyrine. Accordingly, the present artical is devoted to study the electronic absorption spectra of these compounds in organic solvents and in aqueous universal buffer solutions. In addition, the main ir bands are assigned.

EXPERIMENTAL

Reagents :

All materials were reagent grade chemical and used without further purification. The Schiff bases were prepared by the method described previously⁵. The compounds under the present investigation have the following general formula :



Physical Measurements :

The electronic absorption spectra were recorded by the aid of pye Unicam Sp 8000 spectrophotometer using 1 cm matched silica cells.

The ir spectra were recorded in the solid state on a pye Unicam Sp 1000 using the KBr disc technique.

RESULTS AND DISCUSSION

A. Electronic Absorption Spectra :

The electronic absorption spectra of Schiff bases derived from 4- aminoantipyrine were carried out in organic solvents of varying polarity Fig. (1) and in aqueous universal buffer solutions of different pH values Fig. (2).

The electronic absorption spectra of the compounds under investigation on ethyl alcohol Table (1), display mainly four bands (A,B,C and D). Band (C) is observed only in the spectra of compounds II (0 - OH) and V (2,4-diOH).

The bands (A) and (B) appear within the 210-218 nm and 228-258 nm ranges. These bands can be assigned to π - π^* electronic transition $IL_a \leftarrow 1A$ and $IL_b \leftarrow 1A$ states of phenyl ring respectively.

Band (C) appears at 308 and 325 nm for compounds (II) and (V) respectively. This band can be assigned to a transition within the chelate ring formed through intramolecular hydrogen bonding between the lone pair of electrons of the azomethine linkage and the OH group⁶.

Table (1) : Electronic absorption spectra of the compounds under investigation.

Compound	Solvent	Wavelength (nm)			
		A	B	C	D
I	Ethanol	218	258	-	340
	Chloroform	-	253	-	344
	Benzene	-	-	-	345
	Cyclohexane	325	255	-	344
II	Ethanol	-	234	315	343, 360 (Sh)
	Chloroform	-	-	325	346, 360 (Sh)
	Benzene	-	-	320	351, 363 (Sh)
	Cyclohexane	-	235	318	348, 362 (Sh)
III	Ethanol	-	228	-	328
	Chloroform	-	-	-	330
	Benzene	-	-	-	327
	Cyclohexane	-	-	-	330, 348 (Sh)
IV	Ethanol	-	250	-	333
	Chloroform	-	-	-	334
	Benzene	-	-	-	335
	Cyclohexane	210	253	-	335, 350 (Sh)
V	Ethanol	-	244	308	346, 362 (Sh)
	Chloroform	-	-	310	347
	Benzene	-	-	310	348, 362 (Sh)
	Cyclohexane	-	246	308	345, 362 (Sh)
VI	Ethanol	-	250	-	324
	Chloroform	-	-	-	329
	Benzene	-	-	-	330
	Cyclohexane	-	253	-	327
VII	Ethanol	-	250	-	333
	Chloroform	-	-	-	334
	Benzene	-	-	-	335
	Cyclohexane	210	253	-	235 (SHO), 350

The electronic absorption spectra of all compounds exhibit band (D) within the 334 - 346 nm range. This band assigned to the charge transfer interaction through the whole molecule. The C.T. band displays a slight shift to red with increasing polarity of the solvent. This shift is due to specific solute solvent interaction leading to the formation of some sort of molecular complexes, this would possibly results from intermolecular hydrogen bonding leading to solute-solvent association^(7,8).

The electronic absorption spectra of the compounds under investigation in aqueous universal buffer solutions of varying pH values (representative spectra are given in Fig. (2) show regular changes which are more or less identical for all compounds. The electronic absorption spectra of 6.4×10^{-5} M solutions of all compounds show that in acid solution, $\text{pH} < 6$, the band within the 334-346 nm range which was assigned to the CT within the whole molecule, decreases in intensity compared to those in pure ethyl alcohol. By decreasing the $\text{pH} \leq 4$, this band completely disappeared. The disappearance of this band is attributed to the protonation of the azomethine group which eliminates lone pair of electrons on the nitrogen atom and prevent the charge transfer transition. In alkaline solutions the electronic spectra of compounds (I) and (IV) are unchanged i.e are identical to those in pure ethanol, while the spectra of compounds (II), (III) and (V) show that the C.T. band is red shifted in solutions of pH 7-8. By increasing the pH to more than 8 a new band near 355 nm was gradually developed and its intensity increases with increase of pH attaining the limiting value above pH 12. This band corresponds to the ionised species. An

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isobestic point is observed in the spectra of compounds (II), (III), (IV) and (V). The presence of such an isobestic point denotes the existence of acid-base equilibrium. The equilibrium set in solutions would be the protonation of the azomethine nitrogen in acidic media as well as the splitting of a proton from the aromatic OH group in alkaline solutions. The plot of absorbance -pH curves for compounds (I), (IV), (VI) and (VII) Fig. (3), is S-shaped indicating that one acid-base equilibrium is established in acid solutions. This equilibrium would be the protonation of the azomethine nitrogen, while the absorbance-pH curves for compounds (II), (III) and (V), Fig. (3), show two steps i.e the compound shows two separate equilibria. The first step represents the protonation of azomethine nitrogen in acid media and the second one represents the ionisation of phenolic OH group in alkaline media.

The acid dissociation constant for the various equilibria set in solution are determined applying the collerter method⁹ as modified for acid-base equilibria¹⁰, as well as the corrected limiting absorbance and isobestic point method¹¹, making use of the variation of absorbance with pH. The obtained values were shown in Table 2.

B- The Infrared Spectra :

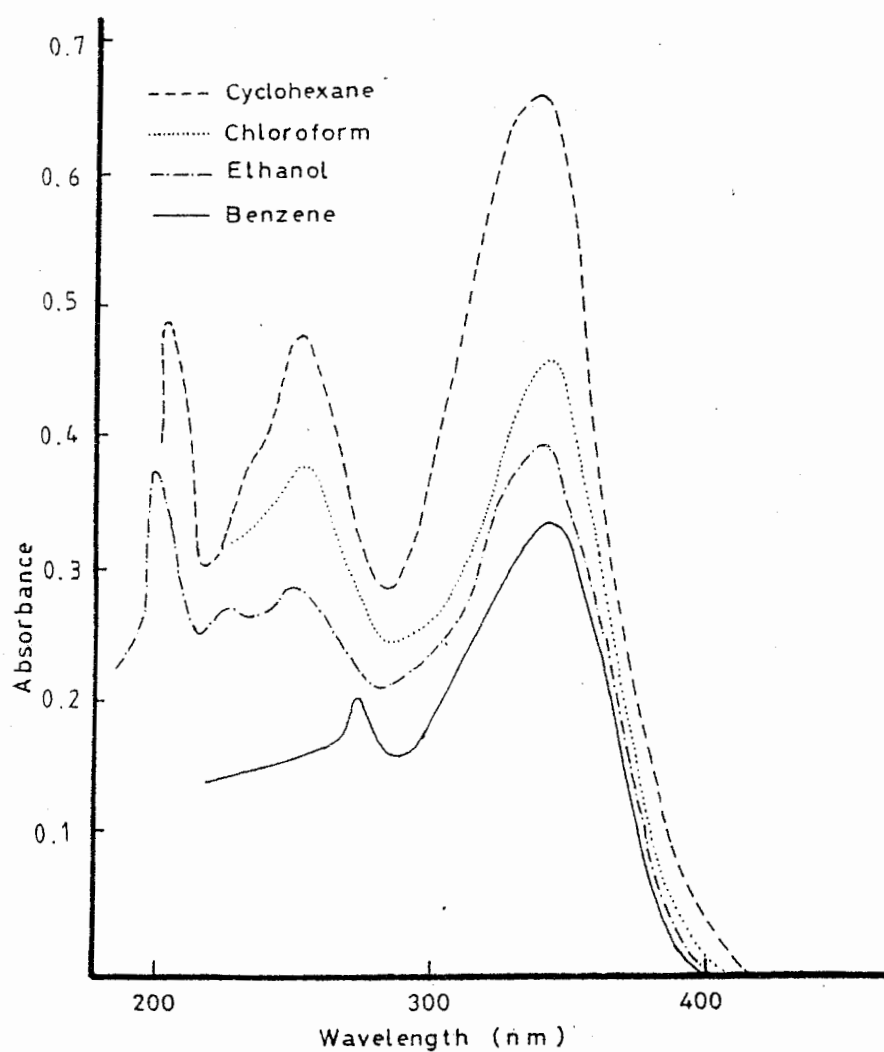
The ir bands of diagnostic importance are depicted in Table (3). The ir spectra of compounds (II), (III) and (V) show a band in the 3100 - 3300 cm^{-1} which can be assigned to ν OH (phenolic). The ir spectra of all compounds show a strong band in the 1670 - 1680 cm^{-1} range which can be assigned to ν C = O. The band around 1600 cm^{-1}

Table (2) : Cumulative data of ionization constants of 4-amino antipyrine Schiff bases.

Compound	pka ₁	pka ₂
I	3.50	-
II	3.10	10.40
III	5.00	9.10
IV	5.80	-
V	3.20	8.40
VI	3.90	-
VII	4.90	-

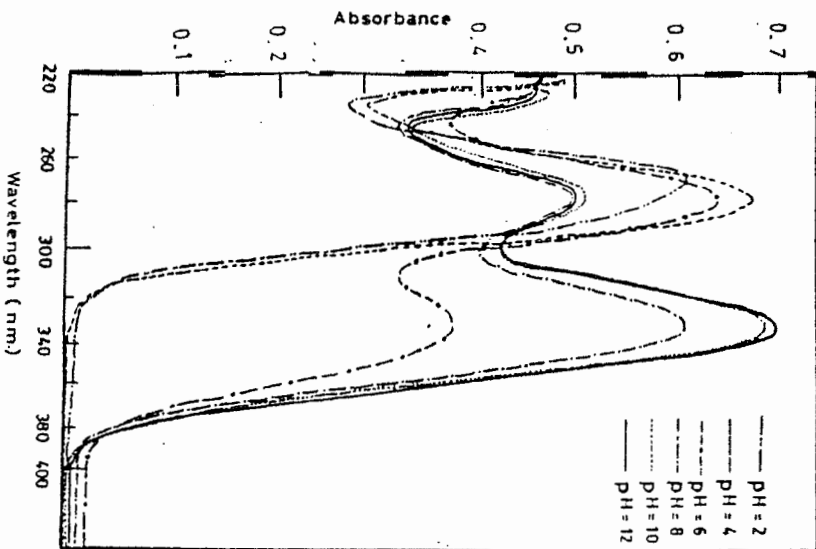
Table (3) : The assignment of the important bands in the infrared spectra of compounds I-VII.

Assignment	I	II	III	IV	V	VI	VII
C = N	1580	1600	1570	1590	1600	1570	1590
C = O	1670	1680	1675	1670	1670	1675	1675
OH	-	3100	3200	-	3200	-	-
C - OH	-	1185	1170	-	1170	-	-
γ CH	775	868, 780	780	780	715	776	796

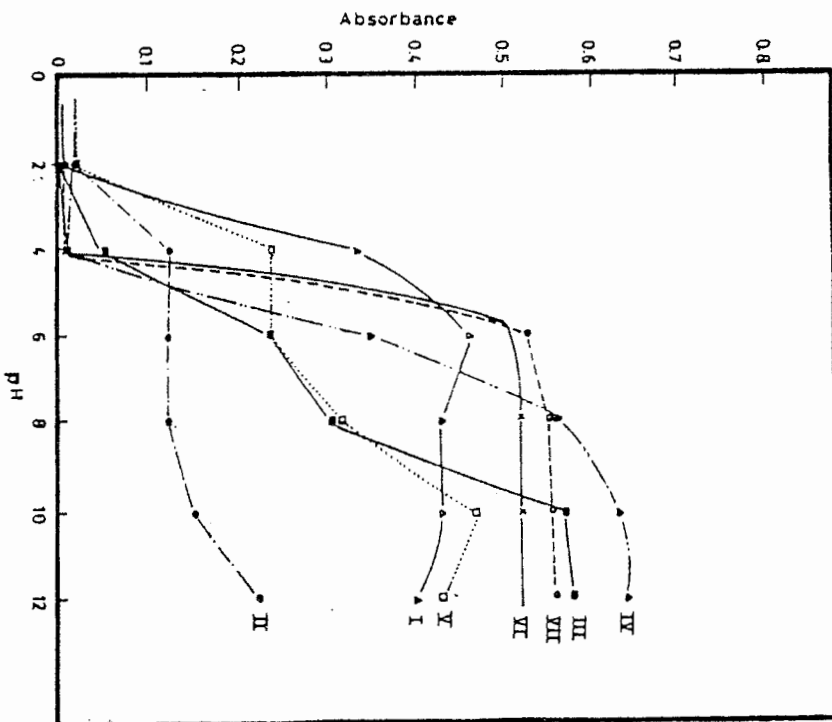


Fig(1): Electronic absorption spectra of (I) in organic solvents .

Fig(2):Electronic Absorption Spectra of IV in Buffer Solutions



Fig(3):Absorbance - pH Curve



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can be assigned to stretching vibration of the C=N group¹². The skeletal vibrations of the aromatic ring were obtained at 1600, 1580 and 1500 cm⁻¹, whereas the out-of-plane deformation of the phenyl ring appeared at 760 - 750 cm⁻¹. The out-of-plane deformation vibration of the aromatic C-H groups lead to the bands within 700 - 800 cm⁻¹. The ir spectra of the compounds (VI) and (VII) show strong bands at 885 - 875 cm⁻¹ and 750 - 690 cm⁻¹ which may be due to thiophene and furan rings respectively.

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الملخص العربى

دراسات طيفية على بعض قواعد شيف المشتقه من ٤-أمينو أنتيبيرين

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الهيئة القومية للرقابه الدوائيه والبحوث

نظراً لأهمية مركب الأنتيبيرين ومشتقاته فى مجالات الدواء فهو يستخدم لعلاج الروماتيزم والإلتهابات مثل إلتهابات الأذن ونظراً لنشاطه البيولوجى والإكلينكى ويستخدم أيضاً لتعين بعض العناصر فقد تم فى هذا البحث دراسة طيف الأشعه فوق البنفسجيه والمرئيه لبعض قواعد شيف المشتقه من ٤-أمينو أنتيبيرين وقد تم دراسة تأثير المذيبات مختلفه القطبيه على هذه الأطياف وقد تم دراسة تأثير تغير الأس الهيدروجينى على هذه المركبات لدراسة الإترانات التى تحدث فى المحاليل وتم أيضاً دراسة طيف الأشعة تحت الحمراء لهذه المركبات .