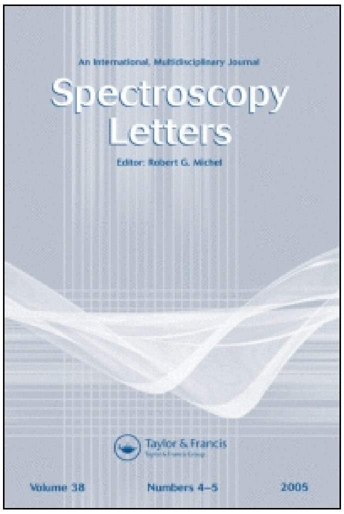

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Substitution and Solvent Effect of Some Substituted Hydroxy Schiff Bases

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SUBSTITUTION AND SOLVENT EFFECT OF SOME SUBSTITUTED HYDROXY SCHIFF BASES

Key words:UV-visible spectroscopy,schiff bases,solvent effect,substitution effect.

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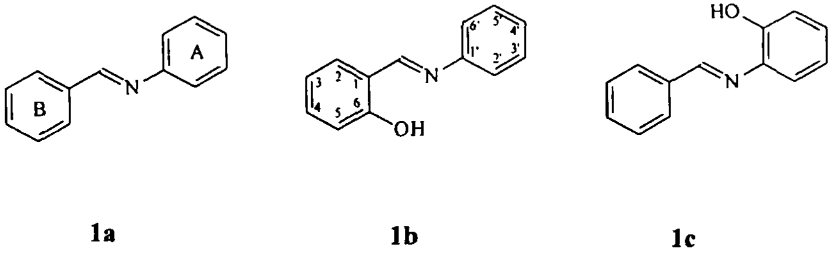
ABSTRACT:

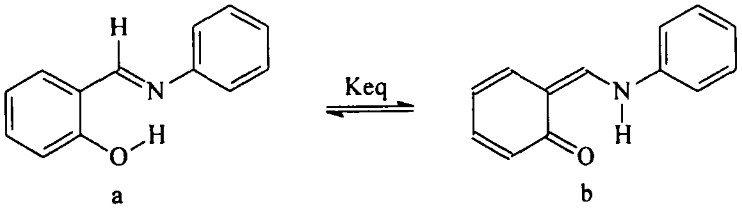
The uv-vis spectra of eight ortho-hydroxy- andpara-hydroxy schiff bases were recorded in different solvents.Inductive and resonance effect of the substituents affect the electronic spectra of those molecules,while,intra-molecular hydrogen bond formation or breakage have little effect on the uv-visible spectra.

INTRODUCTION:

The phenyl rings A and B in the N-benzylideneaniline **1a** are not coplaner[1,2].This results from the twist of the phenyl ring(ring A) from the PhCH=N plane.Non coplanerity is additionally strengthened by the steric interaction of the azomethine nitrogen atom and hydrogen atoms in the ortho positions of the aniline ring[3,4].This interaction should be stronger in the benzylideneaniline carrying larger substituents in these positions.The N-benzylideneaniline **1a** and its derivatives have been the subject of a number of investigations,including studies employing IR[5],NMR[6,7],X-ray crystallography[8] and molecular orbital calculations[9].However, the effect of electron-donating substituent(such as OH)in the 2-position as in N-(2-hydroxybenzylidene)aniline **1b** cause the molecule to be coplaner via a six-membered intramolecular hydrogen bond[10,11] and the transition metals complex[12].For 2-hydroxy-N-(benzylidene)aniline **1c**,it was suggested that the five membered intramolecular hydrogen bond(IAMHB) is absent[13],while other studies indicated their presence[15,16].the solvent effects was studied for some of the N-(2-hydroxybenzylidene)- anilines **1b**[17-19].It was indicated that these compounds may exist in equilibrium between the enol and the keto form such as **a⇌b** (scheme 2) and showing that the keto form predominates in polar solvents and a new band at 400 nm in the uv-vis spectra developed.There are no studies concerning tautomerism in 2-hydroxy-N-(4-



Scheme 1



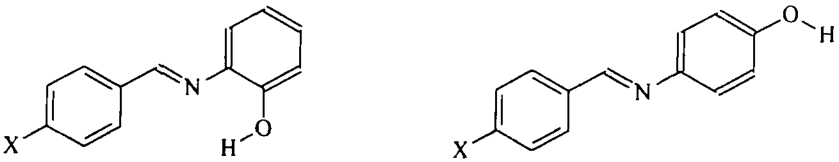
Scheme 2

subst.benzylidene)anilines **2-6** and 4-hydroxy-N-(4- subst.benzylidene)anilines **7-9** (Scheme 3).

Detailed uv-vis study on the substitution effect, solvent effect and tautomerism is lacking for this series. The aim of this work is to present such data for compounds **2-9**.

EXPERIMENTAL:

Anils **2-9** were prepared by refluxing 50 mmol of 2-hydroxyaniline or 4-hydroxyaniline and 50 mmol of 4-substituted benzaldehydes in 75 mL of



2 x=H **5** x=NO2

3 x=CH3 **6** x=N(CH3))2

4 x=OCH3

7 x=H

8 x=CH3

9 x=NO2

Scheme 3

absolute ethanol for 2 hr.After the mixtures cooled,the schiff bases precipitated and were recrystallized from absolute ethanol.The melting points of the purified compounds agree with the literature values[15,20]. Cyclohexane,chloroform,ethanol and dimethylsuphoxide(DMSO) were of spectrosol grade(BDH),and were used without further purification.The uv-visible spectra were recorded on a Pye-Unicam SP8-100 spectrophotometer for solution of optimum concentrations of 5×10^{-5} using a quartz cell of 1.0 cm path length.

RESULT AND DISCUSSION:

The positions and extinction coefficients of the bands in the uv-vis spectra of the anils **2-9** in cyclohexane,Chloroform ,Ethanol and DMSO are given in Tables 1 and 2.The uv-vis spectra of compounds **3** and **4** in different

TABLE 1

Solvent effect on the UV-visible spectra of compounds 2-6

Compound	Solvent	A band		B band	
		$\lambda_1$max(nm)	ε_1(m^2mol^{-1})	$\lambda_2$max(nm)	ε_2(m^2mol^{-1})
2	Cyclohexane	280	5600	355	6800
	Chloroform	276	8400	350	11000
	Ethanol	282	9200	364	4100
	DMSO	264	10800	354	4800
3	Cyclohexane	278	13000	354	10400
	Chloroform	280	13400	352	11800
	Ethanol	270	15400	342	8600
	DMSO	-	-	354	8000
4	Cyclohexane	286	8400	354	8600
	Chloroform	286	9000	354	12800
	Ethanol	282	15600	350	4800
	DMSO	280	16000	346	10400
5	Cyclohexane	276	8000	385	8400
	Chloroform	280	9400	385	8400
	Ethanol	278	10600	380	8200
	DMSO	-	-	390	8100
6	Cyclohexane	324	15000	370	14000
	Chloroform	328	7000	382	20400
	Ethanol	238	11800	350	20400
	DMSO	-	-	370	15600

TABLE 2

Solvent effect on the UV-visible spectra of compounds 7-9

Compound	Solvent	A band		B band	
		$\lambda_1$max(nm)	ε_1(m^{2}mol^{-1})	$\lambda_2$max(nm)	ε_2(m^{2}mol^{-1})
7	Cyclohexane	266	8600	336	8800
	Chloroform	266	11000	334	10400
	Ethanol	266	9000	334	10200
	DMSO	-	-	340	10500
8	Cyclohexane	270	14200	336	13400
	Chloroform	272	16600	336	14100
	Ethanol	270	14400	336	14400
	DMSO	-	-	340	13800
9	Cyclohexane	264	17200	380	10600
	Chloroform	258	13600	382	13600
	Ethanol	260	11200	380	12000
	DMSO	-	-	390	11000

solvents are shown in figures 1 and 2 respectively as typical examples.On the basis of the data outlined in Tables 1 and 2,one can draw the following notes:

The formation of IAMHB between the hydroxy proton and the nitrogen atom of the azomethine group(compare compounds **2**and **3** with that of **7**and **8**)cause a red shift for λ_1 and to a larger extent to λ_2.For compound **9**,the formation of IAMHB cause a small red shift to λ_1,and namely no effect on λ_2,while ε_1 and ε_2 decreased.On comparing compound **2** with **3-6** ,it is

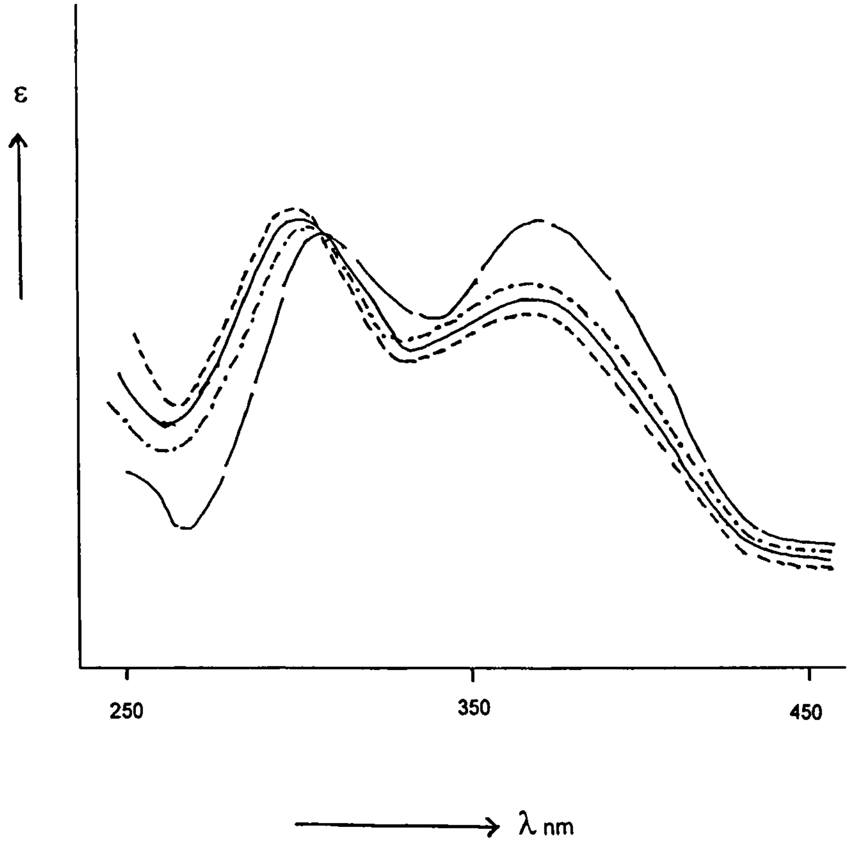


Figure 1. Effect of solvents on the long wavelength bands in the spectrum of compound **4**. ethanol—–,(3ethanol - 2cyclohexane)______, (2ethanol -3cyclohexane)-·-·-·-,cyclohexane__ __ __,schiff base concentration 5x 10^{-5} mol dm^{-3}.

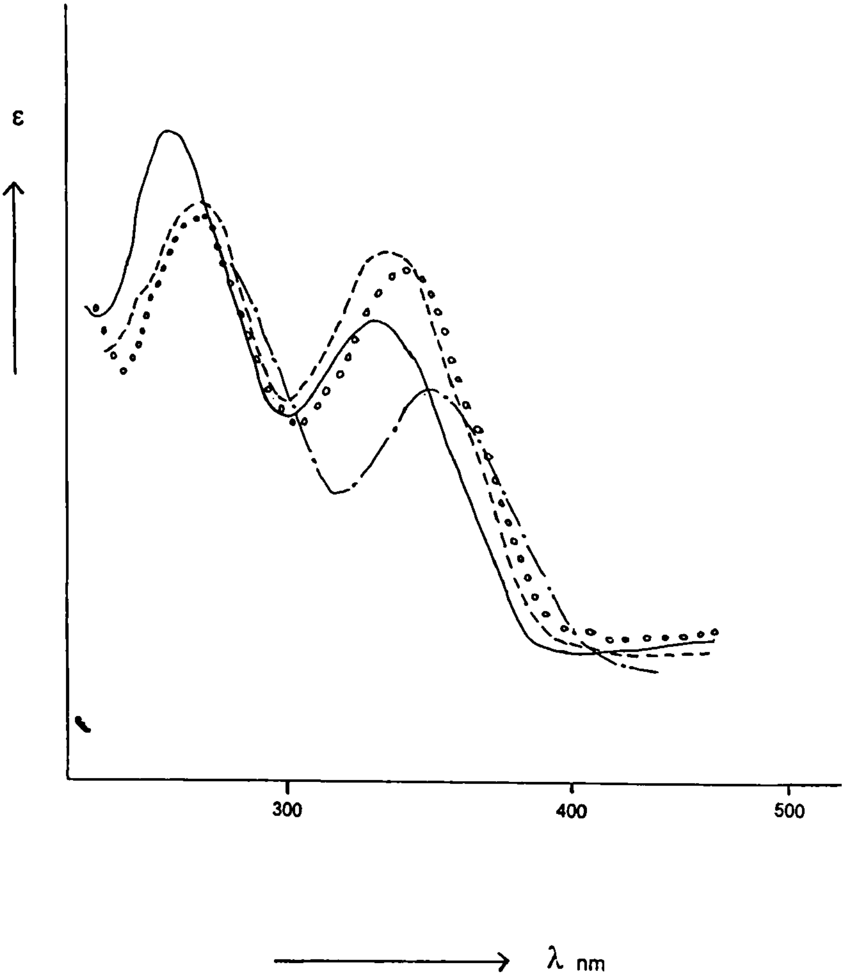


Figure 2. Effect of solvents on the long wavelength bands in the spectrum of compound 3. ethanol———, chloroform----, cyclohexane ooooo, DMSO __ __ , schiff base concentration 5x 10^{-5} mol dm^{-3}.

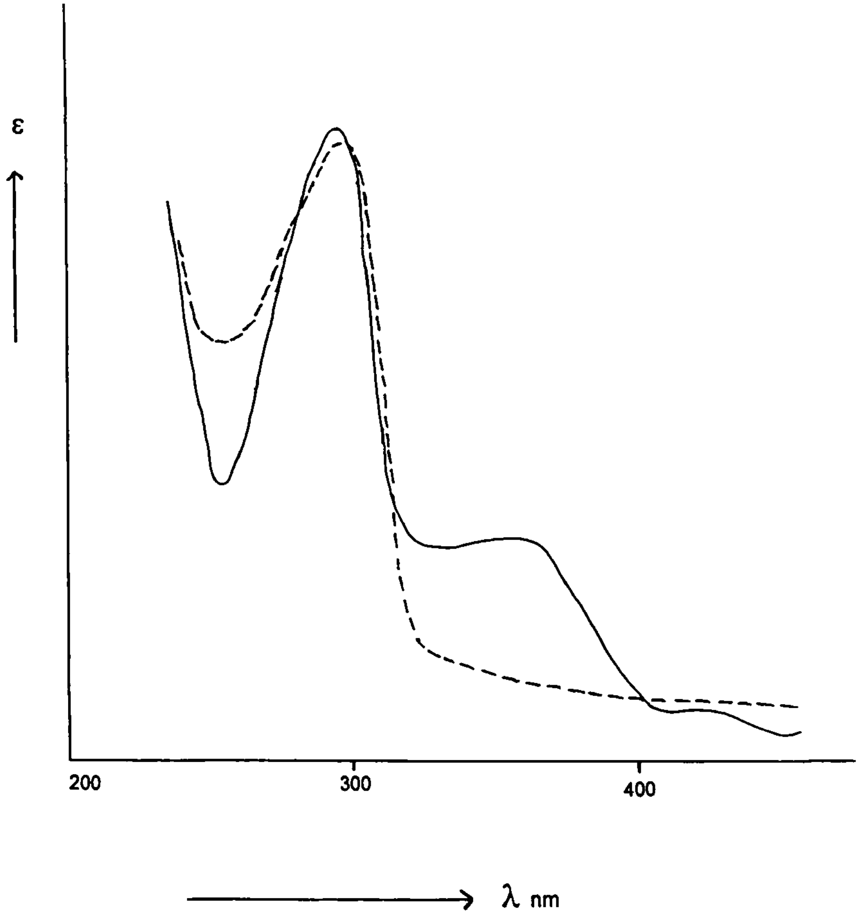


Figure 3. Effect of sodium metal on the long wavelength bands in the spectrum of compound **4**. In ethanol——, and in ethanol + Na metal ---, schiff base concentration 5x 10^{-5} mol dm^{-3}.

obvious that substitution of an CH_3 and OCH_3 at the 4-position increase ε_1 and ε_2 ,but have little effect on λ_1 and λ_2.Substitution of an N(CH3)2 at the 4-position cause the largest red shift on both λ_1 and λ_2, ε_1, and ε_2.On switching from nonpolar to polar solvent have little effect on λ_1 and λ_2, but significant increase of ε_1 and ε_2 was noticed.The above remarks indicates that the changes in λ_1 and λ_2 can be attributed to the change in the basisty of the nitrogen atom as a result of the change in the resonance and inductive effects of different substituents.The uv-visible data presnted in the Table 1 and 2 can hardly be explained by the formation and the breakage of the IAMHB,since these are not the magor factors in determining the uv absorption of those molecules,because,it is not sensative to solvent polarity.In a separate experiment a mixture of different proportions of cyclohexane and ethanol did not give a clear isobestic point,but addition of sodium matal to ethanolic solution of compound 4 and recording the spectra just after the reaction of sodium had ceased,cause the band at 350 nm to disapear(fig.3).This result might indicates the presence of a small proportion of the keto form in ethanolic solution,while the enol form dominates in all solvents.

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