

Spectroscopic Studies and Keto-Enol Tautomeric Effect of Newer Schiff Bases of *ortho*-Hydroxybenzaldehyde/naphthaldehyde with 1,2-Phenylenediamine and 4-Aminophenyl Ether

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Hydroxyl Schiff bases derived from 1,2-phenylenediamine and 4-aminophenyl ether with *o*-hydroxy benzaldehyde or *o*-hydroxyl naphthaldehyde were used to investigate enol-imine and keto-amine tautomeric analysis. UV-visible spectra of the compounds have been investigated tautomeric equilibrium (enol-imine O-H...N, keto-amine O...H-N forms) in different polar and non-polar solvents systems. From FTIR spectra of these model compounds, were possible to assign the IR absorption for the C=O and C=N groups in both keto-amine and enol imine forms, respectively. The keto-enol forms was observed in basic solution of polar and nonpolar solvents such as ethanol, chloroform, DMF, benzene, cyclohexane, *n*-hexane and in acidic solutions of CHCl₃, benzene and *n*-hexane not in ethanol and DMF. FTIR results were showed that all Schiff bases studied, favoured the enol-imine form over the keto form in a weakly polar solvent.

Key Words: Schiff base, Tautomerism, Keto-enamine, Enol-imine, Solvent effect.

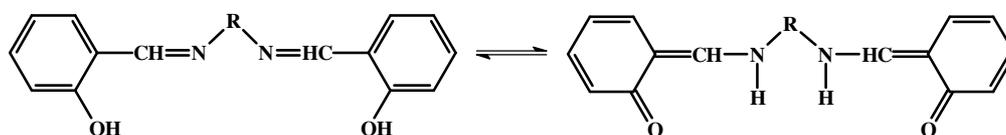
INTRODUCTION

Schiff bases with an -OH group on the *ortho* position to the imine group and their complexes derived from *o*-hydroxyl benzaldehyde and *o*-hydroxyl naphthaldehyde, were extensively studied and a number of them are being used as model for biological system¹⁻⁴. *ortho*-Hydroxyl Schiff base ligands are of prime interest mainly due to the presence of (O-H...N and O...H-N) type hydrogen bonding in tautomerism between enol-imine and keto-enamine forms (**Scheme-I**).

Popovic *et al.*⁵ gave the first example of co-existence of the keto-amine or enol-imine forms of diamines with Schiff bases of naphthaldimine compound of *N,N'*-bis-(1-naphthaldimine) *o*-phenylenediamine chloroform (1/1) at 200 K. In these compounds, the short H-bonds between the -OH group on the *ortho* position to the imino group and imine nitrogen were played important role due to the stereochemistry of imine compounds. Different spectroscopic techniques were used to find the tautomeric effect in *o*-hydroxy Schiff bases, both in

solid state and in solutions⁶⁻¹¹. UV-VIS spectroscopy of *o*-hydroxy Schiff bases were studied in both solid state and in solutions^{12,13}.

Herzfeld *et al.*^{14,15} examined initially the role of acidity and basicity of the solvent in spectra of some Schiff bases and also observed their solvent effect in different solvents. In UV-visible spectra of *o*-hydroxy Schiff bases, a new band is observed at greater than 400 nm, in polar and non-polar solvents. This result indicated that the absorption band at 400 nm belongs to the keto-amine form of the Schiff base. This tautomer is always observed when Schiff base is derived from 2-hydroxynaphthaldehyde and aromatic amines. In the *o*-hydroxybenzaldehyde and aromatic amines, the keto amine is not observed in polar and non-polar solvents, but it is observed in acidic media^{16,17}. 2-Hydroxy naphthaldehyde was shown two bands in the visible region located above 400 nm, which are assigned to the keto form. In the solid state, 2-hydroxy benzaldehyde, both forms are possible and O-H...N and O...H-N intramolecular hydrogen bonding can occur^{18,19}. Antonov *et al.*²⁰



Scheme-I: Tautomerism in newer *ortho*-hydroxy Schiff bases

studied the tautomerism of 2-hydroxy naphthaldehyde Schiff bases but Fernandez²¹ reported the structure and solvent effect of *ortho*-hydroxyl Schiff bases ligands. The effect of substitutions on the keto-enol equilibrium mostly observed in crystalline state and extra stabilization of keto form is derived from molecular association, thus leading to its crystallization²².

Recently, Zawadiak *et al.*²³ investigated that the position of substituted hydroxyl group of compound was shown clear influence on UV absorption spectrum and keto enol equilibrium exist constantly²⁴. This present work reports spectroscopic studies of Schiff base formed by the reaction of 2-hydroxybenzaldehyde or 2-hydroxyl naphthaldehyde by the reaction with different diamines; 1,2-phenylenediamine and 4-amino phenyl ether, respectively.

EXPERIMENTAL

Melting points were recorded on a Gellenkamp capillary melting apparatus (Gallenkemp, England), without correction. Infrared spectra were recorded on a Nicolet Avatar 330 FT-IR (Thermo Nicolet Electron Corporation, USA) with attenuated total reflectance (ATR) accessory (Smart partner) within 4000-600 cm^{-1} . Spectrophotometric studies were carried out in dimethyl formamide (DMF) and *n*-hexane on double beam Hitachi 220 spectrophotometer [Hitachi (Pvt.) Tokyo, Japan], with dual 1 cm silica cuvettes within 185-700 nm. All reagents and chemicals were analytical grade, obtained from Aldrich Chemical Company (USA).

Preparation of Schiff base: The Schiff bases was synthesized by reported method, which was the following²⁵: The Schiff base was synthesized by reacting (0.01 M) of diamine compounds (1,2-phenylenediamine or 4-aminophenyl ether dissolved in 10 mL of MeOH with (0.02 M) of *o*-hydroxybenzaldehyde/hydroxynaphthaldehyde in the presence of 0.5 gm of anhydrous sodium acetate. After one hour of reflux at 70 °C. The contents were cooled. The obtained precipitate were filtered and recrystallized in ethanol. The Schiff bases were isolated as a light yellow crystalline solid.

Bis-(*o*-hydroxybenzaldehyde)1,2-phenylenediimine: Yield: 84.6 %; m.p.: 182.9 °C. Analysis of ($\text{C}_{28}\text{H}_{20}\text{N}_2\text{O}_2$): Calcd.: C; 80.7 %, H; 4.8 %, N; 6.7 %. Found: C; 79.9 %, H; 4.69 %, N; 6.3 %. IR $\nu(\text{cm}^{-1})$; 1610 (C=N), 1488 (C=C), 1277 (C-O) and 1183 (C-N).

Bis-(*o*-hydroxybenzaldehyde)4-aminophenylether: Yield: 90 %; m.p.: 290.4 °C. Analysis of ($\text{C}_{20}\text{H}_{16}\text{N}_2\text{O}_2$): Calcd.: C; 75.9 %, H; 5.06 %, N; 8.8 %. Found: C; 73.8 %, H; 4.89 %, N; 8.13 %. IR $\nu(\text{cm}^{-1})$; 1608 (C=N), 1486 (C=C), 1276 (C-O) and 1182 (C-N).

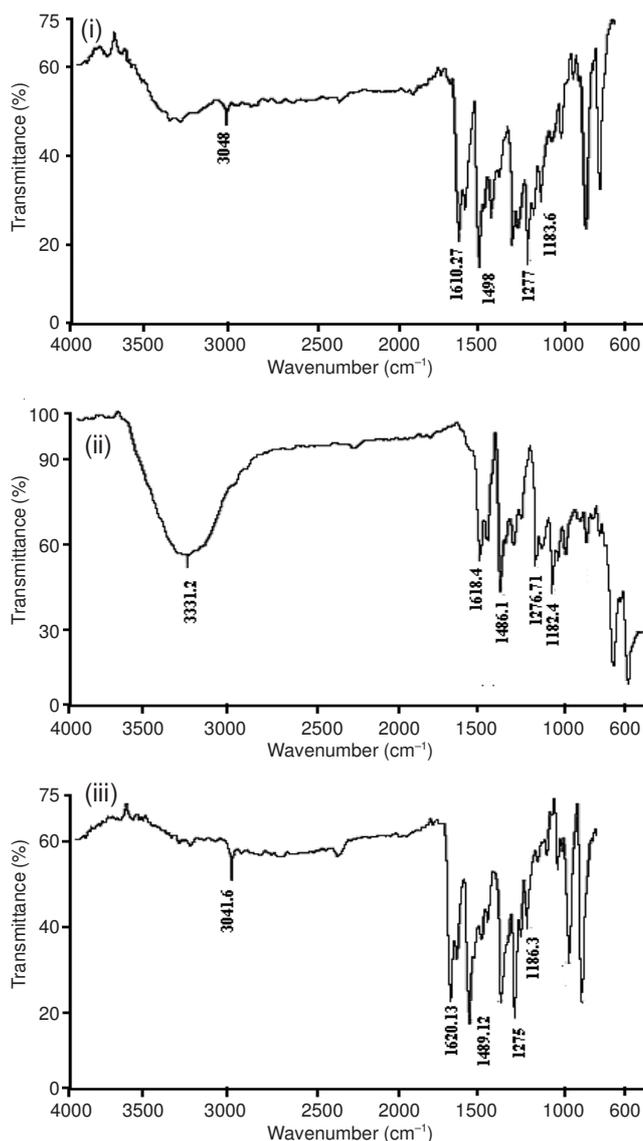
Bis-(*o*-hydroxynaphthaldehyde)1,2-phenylenediimine: Yield: 73.9 %; m.p.: 176.6 °C. Analysis of ($\text{C}_{34}\text{H}_{24}\text{N}_2\text{O}_3$): Calculate: C; 80.3 %, H; 4.72 %, N; 5.51 %. Found: C; 79.8 %, H; 4.89 %, N; 5.13 %. IR $\nu(\text{cm}^{-1})$; 1610 (C=N), 1488 (C=C), 1275 (C-O) and 1186 (C-N).

Bis-(*o*-hydroxynaphthaldehyd)4-aminophenylether: Yield: 89.7 %; mp: 177.2 °C. Analysis of ($\text{C}_{26}\text{H}_{20}\text{N}_2\text{O}_3$): Calculate: C; 76.4 %, H; 4.9 %, N; 6.8 %. Found: C; 75.8 %, H; 4.89 %, N; 6.13 %. IR $\nu(\text{cm}^{-1})$; 1611 (C=N), 1491 (C=C), 1241 (C-O) and 1156 (C-N).

RESULTS AND DISCUSSION

Newly synthesized Schiff bases from 1,2-phenylenediimine and 4-aminophenyl ether were shown in (Fig. 1). FT-IR spectra of all compounds showed weak and broad absorption bands in the 3400-3200 cm^{-1} region. This is interpreted to be a sign of the presence of the enol forms schiff bases. Other vibration bands with the wave numbers of 1625-1610 cm^{-1} $\nu(\text{C}=\text{N})$, 3080-3040 cm^{-1} $\nu(\text{CH}, \text{Ar-H})$, 1600-1580 cm^{-1} $\nu(\text{C}=\text{C})$ and 1293-1046 cm^{-1} $\nu(\text{C-O-C})$ were observed. From the FTIR spectra of compounds, it was possible to assign the IR absorption for C=O and C=N group in both keto and enol form, it was also possible to assign other absorption which were specific either to the keto or enol forms⁸. Such as the compound *o*-hydroxy naphthaldehyde crystallized as a mixture of enol and keto forms with both amines. The enol form was infrareded from the presence of strong absorption in the region of 3400-3200 cm^{-1} , while the keto form shown by the strong absorption in the 1700-1660 cm^{-1} region¹¹.

The existence of intramolecular hydrogen bonding (O...H-N) in solution, has been confirmed by ¹H NMR spectroscopy. Mostly all compounds shown the enol-imine form dominates



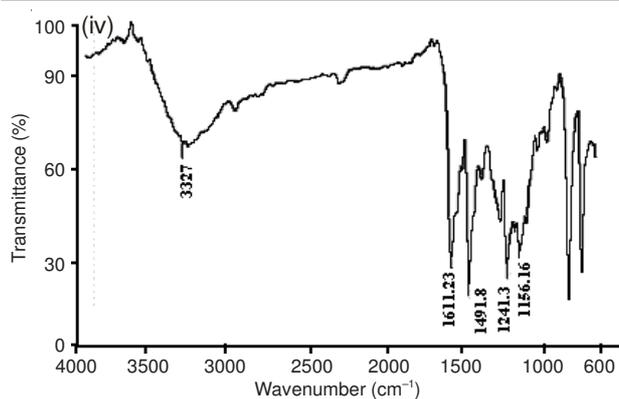


Fig. 1. IR spectra of new Schiff bases: (i) *Bis*-(*o*-hydroxybenzaldehyde)1,2-phenylenediimine; (ii) *Bis*-(*o*-hydroxynaphthaldehyde)1,2-phenylenediimine; (iii) *Bis*-(*o*-hydroxybenzaldehyde)4-aminophenylether; (iv) *Bis*-(*o*-hydroxynaphthaldehyde)4-aminophenylether

in CDCl_3 . The signals at proton of OH and NH groups were involved in the intra molecular hydrogen bonding. According to NMR spectra, the proton exists in the spectra of all four compounds indicated the presence of enol forms except the Schiff base *o*-hydroxynaphthaldehyde due to the mixture of keto-enol forms⁴.

Electronic absorption spectral properties: The UV-visible spectra of the compounds were studied in polar DMF and non-polar to *n*-hexane solvents¹³. The spectra are presented in Figs. 2-5 and summarized in Table-1. All compounds studied show one absorption band in the range of less than 400 nm but the new band (greater than 400 nm) belongs to the keto form of the *o*-hydroxy Schiff bases in polar and non-polar solvents^{15,16}. The band was observed in *o*-hydroxy naphthaldehyde 1,2-phenylenediimine at greater than 400 nm in both polar DMF and non-polar *n*-hexane solutions. The enol-imine tautomer is dominant only in the polar solutions of DMF, in contrast to the keto-enamine tautomer. Solvent effects can be explained in term of the capability of solvents to form hydrogen bonding both as proton donors and as proton acceptors, thereby permitting proton transfers that result in formation of the keto form.

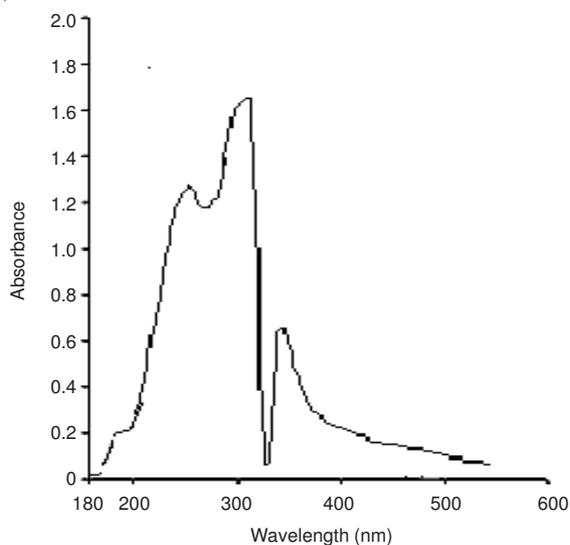


Fig. 2. UV-visible spectra of compound *bis*-(*o*-hydroxybenzaldehyde)1,2-phenylenediimine in *n*-hexane

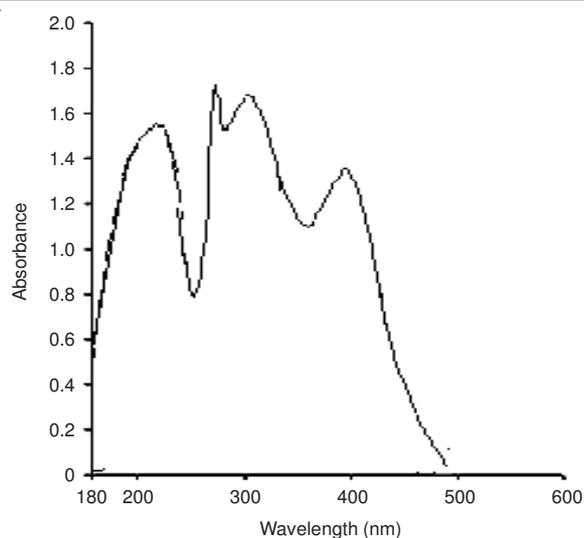


Fig. 3. UV-visible spectra of compound *bis*-(*o*-hydroxynaphthaldehyde)1,2-phenylenediimine in *n*-hexane

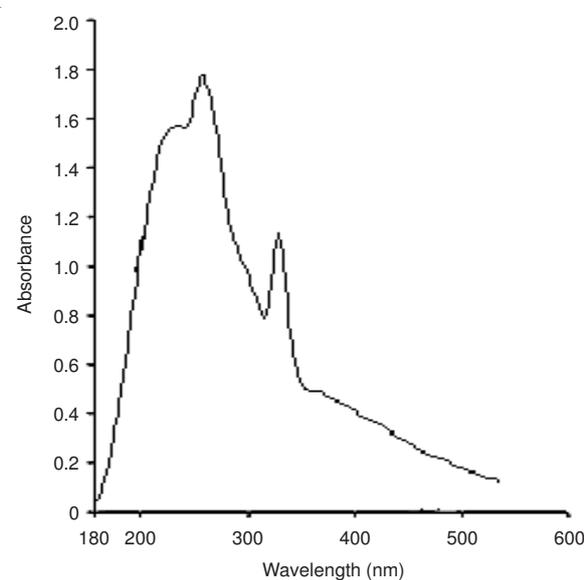


Fig. 4. UV-visible spectra of compound *bis*-(*o*-hydroxybenzaldehyde)4-amino phenylether in *n*-hexane

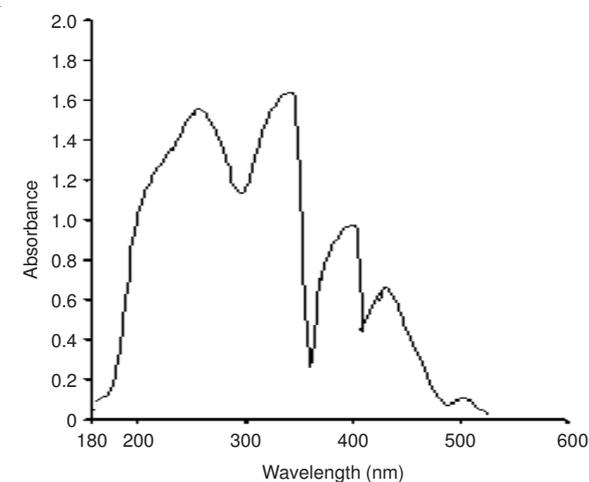


Fig. 5. UV-visible spectra of compound *bis*-(*o*-hydroxynaphthaldehyde)4-amino phenylether in *n*-hexane

TABLE-1
ELECTRONIC SPECTRAL DATA OF
COMPOUNDS 2-HYDROXY SCHIFF BASE

Compound	<i>n</i> -Hexane λ_{max} (nm)	DMF λ_{max} (nm)	Molar coefficient
<i>Bis</i> -(<i>ortho</i> -hydroxybenzaldehyde) 1,2-phenylenediimine	240	220	66560
	285	270	91520
	310	300	33280
<i>Bis</i> -(<i>ortho</i> -hydroxynaphthaldehyde) 1,2-phenylenediimine	195	265	52140
	265	315	56880
	296	355	53720
	412	430	44240
<i>Bis</i> -(<i>ortho</i> -hydroxybenzaldehyde) 4-aminophenylether	226	220	78400
	265	260	88200
	305	310	56840
<i>Bis</i> -(<i>ortho</i> -hydroxynaphthaldehyde) 4-aminophenylether	305	340	26650
	234	230	106680
	312	290	111760
	375	380	58420
	415	430	50800

As a proton donor, the solvent interacts with the non-bonding electron pair of the azomethine nitrogen. Thus, it may be assumed that, in those Schiff base derivatives where a non-bonding electron pair is no longer available, a solvent effect will not be observed.

The spectroscopic data suggest that these compounds exist mainly in the enol-imine form in solid state for *o*-hydroxybenzaldehyde compounds and a mixture of enol and the keto form for *o*-hydroxynaphthaldehyde compound.

Conclusion

On the basis of spectroscopic data, the *o*-hydroxy Schiff bases or derivatives have a course of an additional role in the process, which played by intramolecular hydrogen bonding. In contrast with the formation of keto form, the possibility of enol form is raised in all compounds because when a molecule pass from keto to enol then a H- bonding exist which make it more stable. And the compound *o*-hydroxynaphthaldehyde have a mixture of keto-enol forms in both polar and non-polar solvents.

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