SPECTROSCOPIC STUDY OF KETO-ENOL TAUTOMERISM IN N-ARYLSALICYLALDIMINE DERIVATIVES- HYDROGEN BONDING AND ELECTRONIC EFFECTS OF *P*-SUBSTITUENTS

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Abstract: Keto-enol tautomerism in some N-arylsalicylaldimine derivatives has been evaluated from spectroscopic data. The effect of substituents on the hydrogen bonded ortho-hydroxyl Schiff bases were studied using different *p*-substituents with varying nucleophilicity. The N-aryl salicylaldimine derivatives were characterized with elemental analysis, infrared, NMR and UV/Visible spectral data. The Schiff bases exist mainly as the phenol-imine tautomers. However, keto-amine tautomers were observed in methanol which is a protic solvent. The extent of the intra-molecular hydrogen bonding in the Schiff bases was evaluated from Hammett substituents' constant. There was a positive correlation between the band intensity and the substituents nucleophilicity; and consequently with the basicity of the imine nitrogen.

Keywords: Keto-enol tautomerism, Nucleophilicity, Hammett substituent's constant, N-arylsalicylaldimine, Hydrogen bonding

Introduction

Ortho-hydroxyl Schiff bases are of great importance due to the existence of proton tautomerism between the enol-imine and the keto-enol tautomers (Asiri and Badahdah, 2007). The presence of ortho-hydroxyl group in salicylaldimine free ligands enables the formation of intra-molecular hydrogen bonding (O-H---N and O---H-N), Fig. 1, and this is responsible for the keto-enol-tautomerism usually observed in Schiff bases (Cristovao and Miroslaw, 2015). Consequently, the question of the exact structure of salicylaldimines has long been controversial (Charette, 1963), because the keto-amine/enol-imine tautomer (Scheme 1) is sensitive to factors such as the physical state, the nature of solvent, as well as the effects of substituents (Ledbetter, 1968). In particular, some cases have been reported (Charette, 1963) where a ketimine form seems to have greater stability than the enol-imine tautomer. Tautomerism in salicylaldimine bases occur either via an intramolecular (or intermolecular, in protonic solvents) hydrogen transfer to the imine nitrogen or through hydrogen transfer from the hydroxyl proton (Ledbetter, 1968). Therefore, an increase in the imine basicity and or hydroxyl acidity would favour keto-enol tautomerism in salicylaldminine Schiff base ligands.
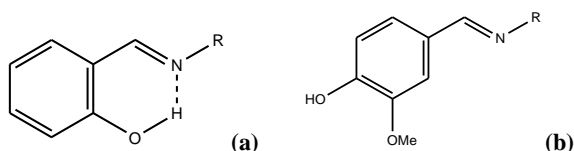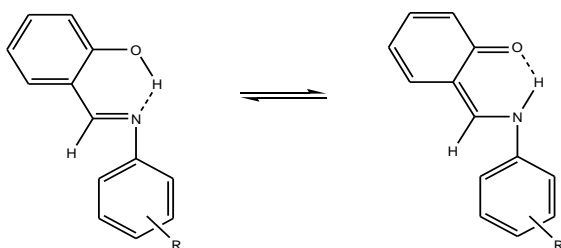

Fig. 1: (a) Hydrogen bonding in salicylaldimines (b) Vanillin-derived Schiff bases

Scheme 1: Tautomerism in N-arylsalicylaldimine Schiff bases

The use of analytical data from infrared, nuclear magnetic resonance and electronic spectroscopic techniques has been of great importance in establishing the prevailing tautomer of given ortho-hydroxyl imine bases (Dudek and Dudek, 1971; Asiri and Badahdah, 2007; Ledbetter, 1968). In general, the diagnostic infrared bands for tautomers arising from ortho-hydroxyl salicylaldimines are due to the absorption associated with the phenolic stretching (ν_{OH}), carbonyl stretching ($\nu_{C=O}$) and imine stretching ($\nu_{C=N}$) vibrational frequencies. Electronic spectroscopy has equally been used to study the existence of tautomerism between the enol-imine and the keto-imine forms of ortho-hydroxyl Schiff bases (Ledbetter, 1968; Antonov, 2000; Salman *et al.*, 1990). The absorption band at greater than 400 nm indicates a keto-imine form of the Schiff base while the enol form has no appreciable absorbance in this region (Ledbetter, 1968; Salman *et al.*, 1990; Saeed *et al.*, 1988; Asiri and Badahdah, 2007).

In the NMR study, however, the azomethine proton and the enol proton chemical shifts provide information on the position of the keto-amine/enol-imine tautomer equilibrium of the Schiff bases. Any significant presence of the keto-amine tautomer is expected to split the methine proton, with the concomitant loss of the hydroxyl proton. The positions of the chemical shifts are also sensitive to the electronic effects of substituents, and this may be correlated with the Hammett substituent constant (σ) (Percy and Thornton, 1972; Tabei and Saitou, 1969; Khoo, 1979). Any significant presence of the keto-amine tautomer is also expected to be reflected in the aromatic protons, with the quinoidal form undergoing downfield shifts (Pretsch *et al.*, 2000). A better differentiation between the quinoidal and the benzoid forms can be obtained from the ^{13}C-NMR spectra.

The aim of this study, therefore, was to investigate the position of keto-amne/enol-imine tautomer and study the electronic effects of *p*-substituents on some hydroxybenzaldimines derived from the condensation of salicylaldehyde, 3-methoxy-2-hydroxybenzaldehydye (*o*-vanillin), 4-methoxy-2-hydroxybenzaldhyde (*p*-vanillin) and 3-methoxy-4-hydroxybenzaldehyde (vanillin) with *p*-substituted anilines using nuclear magnetic resonance (^{1}H-NMR and ^{13}C-NMR), infrared and electronic spectral data.

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Materials and Methods

All the chemicals and reagents used were of analytical grade. The ^1H- and ^{13}C- NMR spectra were recorded on a Bruker Avance 400 MHz NMR spectrometer in $CDCl_3$ with TMS as internal standard. The mid-infrared absorption frequencies (4000-700 cm^{-1}) were recorded on a Perkin Elmer Spectrum 100 FT-IR equipped with universal attenuated total reflectance (ATR) accessory. The UV/Visible spectra were obtained from Perkin Elmer Lambda 25 spectrophotometer. The elemental analysis, CHN, was done on a Vario MICRO V1.6.2 elemental analysen systeme GmbH. The melting points (uncorrected) of the compounds were determined using Galenkemp melting point apparatus.

Synthesis of the N-aryl Schiff bases

The N-aryl Schiff bases, $L_1 - L_{27}$, were obtained by refluxing equimolar amount of salicylaldehyde and its derivatives with the *p*-substituted anilines (Sobola *et al.*, 2014) as shown in Scheme 2. The detail description of the synthesis is presented in the supplementary report while selected spectroscopic data for the salicylaldehyde and *o*-vanillin based ligands are presented in Table 1.
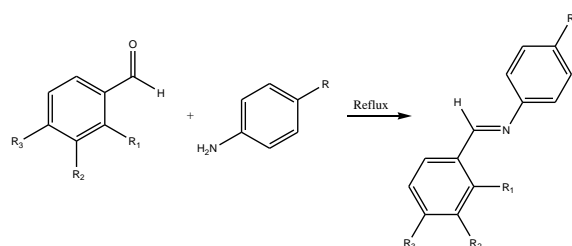
Scheme 2: Synthesis of the Schiff base ligands (L₁- L₂₈)

R = H; Cl; Br; CH_3; OCH_3; OH and NO_2

R_1 = OH/H; R_2 = H/OMe; R_3 = H/OMe/OH

Table 1: List of the N-aryl Schiff bases

L_1 - L_7	L_8 - L_{14}	L_{15} - L_{21}	L_{22} – L_{27}
R_1 = OH	R_1 = OH	R_1 = OH	R_1 = H
$R_2 = R_3$ = H	R_2 = OMe	R_2 = H	R_2 = OMe
	R_3 = H	R_3 = OMe	R_3 = OH

Results and Discussion

Microanalysis of the compounds

The CHN values of the synthesized compounds are presented in the experimental section. There is a high coherence between the theoretical and the experimental values. This suggests the compounds were obtained in high purity. In addition, the compounds were obtained in very high yield with varying brilliant colours.

NMR study

The NMR spectral data for the compounds were recorded in deuterated chloroform and dimethylsulfoxide (for the *p*-hydroxy derivatives); and the chemical shift values are presented in the experimental section. The hydroxyl proton absorbed far downfield at δ 13.97 – 12.54 ppm (Reddy *et al.*, 2008) due to extensive hydrogen bonding between the imine nitrogen (HC=N) and the OH group as shown in Fig. 1a. This is in contrast to the free hydroxyl proton of the vanillin-derived Schiff base analogues, Fig. 1b, which resonated at 9.53 – 6.10 ppm. It has been reported (Percy and Thornton, 1972) that strong intra-molecular hydrogen bonding leads to a large downfield shift of the hydroxyl proton resonance which is related to the electronic effects of the substituents as measured by their Taft (Newman, 1956) substituent's parameters, σ*. A plot of δ_{OH} of *o*-vanillin Schiff bases (L_8 –

L_{14}) against Hammett substituent's constant (σ) is presented in Fig. 2.

The electronic effect of the substituents on hydrogen bonding was understood to occur directly by modifying the capacity of the nitrogen atom for participation in hydrogen bonding rather than through the conjugation of the heterocyclic ring which would have favoured a keto-imine tautomer (Percy and Thornton, 1972). The electron withdrawing group decreases the basicity of the imine N and thus weakens the effect of hydrogen bonding on the resonating frequency of the hydroxyl proton (δ_{OH}).
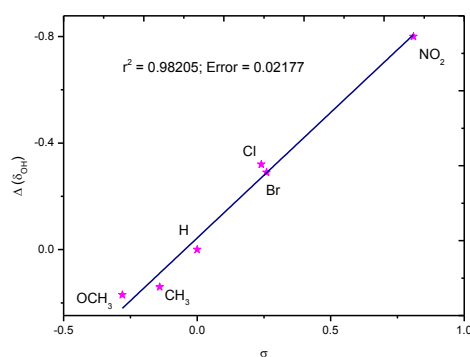

Fig. 2: Plot of δ_{OH} of o-vanillin Schiff bases (L_9 – L_{14}) against Hammett substituent's constant (σ)
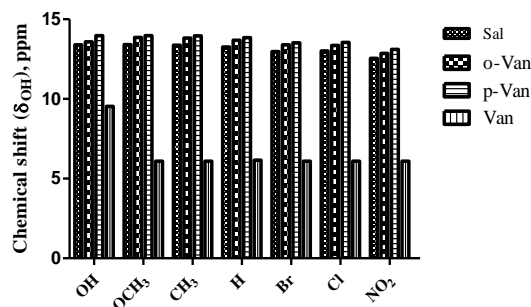

Fig. 3: Chart showing effect of the methoxyl group on the strength of hydrogen bonding on δ_{OH} of the *o*-vanillin (L_8 – L_{14}) and the *p*-vanillin (L_{15} – L_{21}) derivatives

In addition, the hydrogen bonding effect was more pronounced in the *o*-vanillin and the *p*-vanillin analogues as indicated in Fig. 3. This may be due to the inductive and electronic effects of the methoxyl group located at the meta-position of the aldehyde moiety of the ligands. The azomethine proton, HC=N, appeared as a strong singlet at 8.80 – 8.35 ppm for all the synthesized compounds. The non-splitting of the methine proton implied the compounds exist solely in the phenol-form (Dudek and Dudek, 1965). This was corroborated by the absence of the quinodal C=O signal (δ= 180 – 200 ppm) in the ^{13}C-NMR spectra of the ligands.

Infrared study

The stretching vibration for the azomethine band, $\nu_{C=N}$, of the salicylaldimine-type Schiff bases (L_1 – L_{21}) was observed at a lower value, 1616 – 1598 cm^{-1}, than expected (Reddy *et al.*, 2008) due to the effect of a strong intra-molecular hydrogen bonding as indicated in Fig. 1a. A value of 1623 – 1622 cm^{-1} was, however, recorded for the $\nu_{C=N}$ of the non-hydrogen bonded vanillin analogues, Fig. 1b.

Furthermore, the internally hydrogen bonded O-H stretching vibration (Kovacic, 1967; Percy and Thornton, 1972) was observed as a broad, weak band having some fine structure in

the region 3100-2000 cm^{-1} of the IR spectra (Kovacic, 1967, Percy and Thornton, 1972). Intra-molecular hydrogen bonds in Schiff bases may form six- or five -membered cycles. The hydrogen bonding participating in six-membered rings are essentially stronger than those of five-membered rings due to acquisition of a quasi-aromatic type in the former case (Garnovskii *et al.*, 1993). The phenolic C-O stretching for the compounds was observed as a strong band at 1289-1273 cm^{-1}(Kovacic, 1967; Percy and Thornton, 1972). The absence of the quinoidal (C=O) band at 1690-1720 cm^{-1} implied the absence of the keto tautomer for the Schiff base ligands (Asiri and Badahdah, 2007).

The electronic study of the ligands

The electronic spectral data for the Schiff base ligands were recorded in methanol (a protic solvent) and dimethylformamide (DMF). The spectral data are presented in the experimental section. Solvent effect is dependent upon the ability of solvents to form hydrogen bonding both as proton donors and as proton acceptors, thereby permitting proton transfer that result in formation of the keto form. The Schiff base ligands exhibit two absorption bands at 231 – 208 nm and 306 – 240 nm due to the delocalization of the phenyl electrons over the molecule and thus corresponding to the $\pi \rightarrow \pi*$ electronic transition (Sidir *et al.*, 2016). The third band at 312 – 374 nm is assigned to$\pi \rightarrow \pi*$ transition of the HC=N moiety of the Schiff base ligands (Köse *et al.*, 2015; Sutradhar *et al.*, 2013; Golcu *et al.*, 2005). In addition, the methanol solution of most of the Schiff bases exhibited a new band in the visible region at 463 – 412 nm, Fig. 4, due to n $\rightarrow$ $\pi*$ transition of the azomethine moiety. This absorption band at greater than 400 nm is sensitive to solvents and it indicates a keto-imine form of the Schiff bases; the enol form has no appreciable absorbance in this region (Ledbetter, 1968; Salman *et al.*, 1990; Saeed *et al.*, 1988).
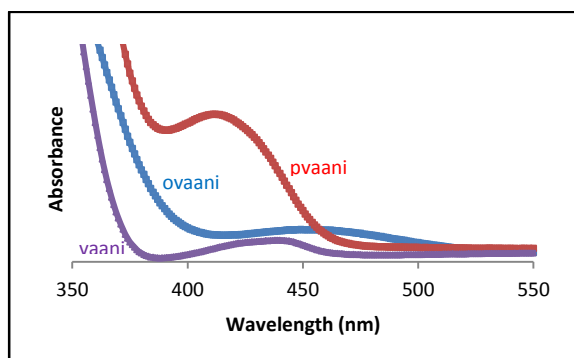

Fig. 4: UV spectra of ligands L$_8$, L$_{15}$ and L$_{22}$; showing the quinoid band at > 400 nm
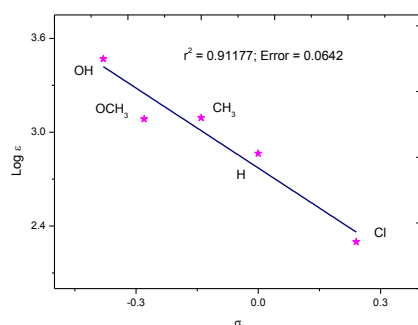

Fig. 5: Correlation of the 'Quinoid band' of the *o*-vanillin Schiff bases (L8 – L14) with the Hammett substituent's constant, showing the electronic effect of the *p*-substituents on band intensity
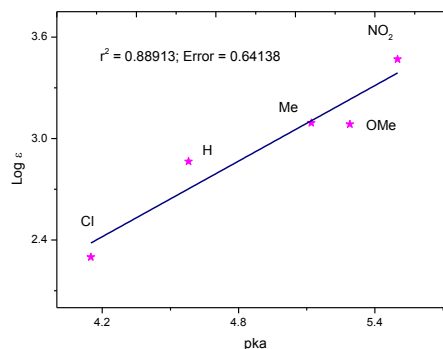

Fig. 6: Correlation of the intensity of the 'quinoid band' of the *o*-vanillin analogues against ionization constant of the *p*-substituted anilines

The extent of the keto-enol tautomerism as measured by the molar absorptivity of the band at greater than 400 nm is presented in Figs. 5 and 6. The molar absorptivity values were plotted against Hammet substituent constant, σ, and the pKa of the corresponding amine. There was a positive correlation between the band intensity and the substituents nucleophilicity; and consequently with the basicity of the imine nitrogen.

Conclusion

Schiff bases derived from N-aryl salicylaldimines and its methoxyl derivatives exist as phenol-imine tautomers. There is a direct correlation between the nucleophilicty of the *p*-substituents and the extent of the intramolecular hydrogen bonding. The strong intramolecular hydrogen bonding present in the ligands leads to very broad and weak hydroxyl absorption near 2700 cm^{-1}. Consequently, the NMR spectra are more informative than the IR spectra with respect to the nature of the O-H bonding.

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