SYNTHESIS AND CHARACTERIZATION OF VARIOUSLY SUBSTITUTED HYDROXYBENZALDIMINES DERIVED FROM THE CONDENSATION OF ANILINE OR 1-AMINONAPHTHALENE WITH SALICYLADEHYDE AND ITS DERIVATIVES

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ABSTRACT

The condensation of salicylaldehyde, *o*-vanillin, *p*-vanillin or vanillin with aniline or 1-aminonaphthalene had been used to produce variously substituted hydroxybenzaldimines. The compounds were characterized using elemental analyses, FT-IR, UV-vis, ^{1}HNMR and ^{13}CNMR. The effects of the replacement of aniline with aminonaphthalene on the vibrational and electronic properties were reported. The spectroscopic methods were used to confirm the tautomeric nature of the 2-OH or 4-OH substituted hydroxybenzaldimines which showed that most of the Schiff bases existed predominantly as enol-imine tautomer. The various spectroscopic techniques of the compounds were found useful in understanding the degree of stabilization of the tautomeric nature of the Schiff bases. It was observed that the variously substituted substituents and the type of solvent used for the spectroscopic examination determined the existence of intra or intermolecular hydrogen bonding, hence the formation of tautomer.

Keywords: Aniline, 1-Aminonaphthalene, Substituted-hydroxybenzaldimines; Tautomerism

INTRODUCTION

Schiff bases are compounds mostly obtained from the condensation of aldehydes and primary amines. They are well known in diverse fields of chemistry and biochemistry owing to their physical, chemical and biological activities (Hodnett, and Dunn, 1970; Garnovskii *et al.,* 1993 and Voet and Voet, 1995). The aromatic Schiff bases with an *ortho*-hydroxy substituent are known to possess a characteristic reversible colour change. The reversible change is induced by a change in temperature, termed thermochromism or by a change in irradiation termed photochromism (Ogawa *et al.*, 2001). It has been established that the presence of the *ortho* hydroxyl group favours the existence of intramolecular proton transfer resulting in hydrogen bonding and also resulting in the inter-conversion between the enol-imine or keto-amine tautomer formed (Ferringa, 1993; Rontoyianni, 1994; Elmali *et al.,* 2000). The proton transfer causes a change in the π electronic system. The tautomeric equilibrium is influenced by the intermolecular hydrogen bonding. The position of the proton in the tautomeric equilibrium affects the interactions and plays a very significant role in determining the physical, chemical, and biological properties of *o*-hydroxy Schiff bases (Krygowski *et al.*, 2008). It has also been established that parent aromatic aldehyde as well as solvent obviously plays important roles in determining the equilibrium position of the tautomers formed (Shaibu and Watkins, 2015).

The present study reports the synthesis of eight Schiff bases derived from variously substituted hydroxybenzaldehyde and aniline or 1-aminonaphthalene. The Schiff bases have been characterized by using elemental analysis, UV-vis, FT-IR, low resolution mass spectrometry, ^{1}HNMR and ^{13}CNMR. The analytical and spectroscopic data have been used to investigate the type of tautomer formed by the various synthesized Schiff bases. The effects of substituents of the asymmetric carbon, the type of amine as well as the effect of the protic and aprotic solvents on the vibrational and electronic properties of the isolated Schiff bases were also examined.

EXPERIMENTAL

Materials

1-aminonaphthalene, *o*-vanillin, *p*-vanillin and vanillin were purchased from Sigma Aldrich and were used without further purification. Salicylaldehyde and aniline were distilled before

use. The solvents were distilled and dried according to standard procedures before use.

Physicochemical Measurements

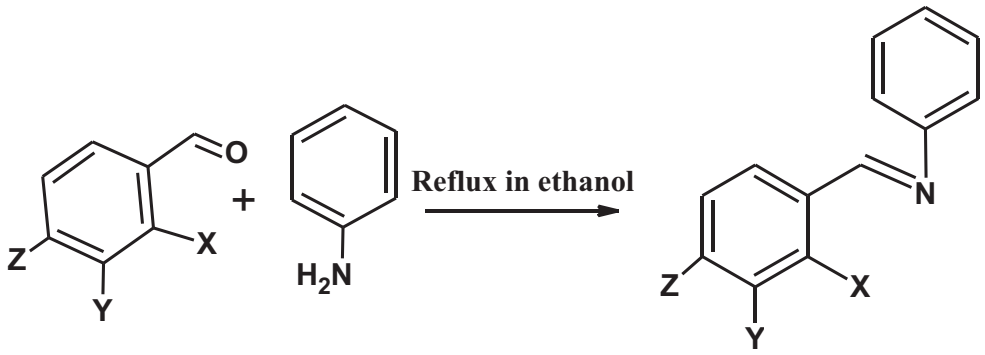
Mid infrared spectra were recorded on a Perkin-Elmer spectrum 2000 FT-IR spectrometer. The spectra were determined using a KBr beam splitter and a DTG detector, in the region 4000 - 400 cm^{-1} with typical 16 scans at an average resolution of 4 cm^{-1}. Samples were run as mulls in Nujol on KBr windows. NMR spectra were recorded in $CDCl_3$ at 298 K on a Bruker 400 MHz Ultrashield Spectrometer equipped with a 5 mm BBI inverse gradient probe. Chemical shifts were reference to internal TMS. The concentration of Schiff base molecules for the NMR analyses was 120 mg in 1.0 ml $CDCl_3$. Carbon, hydrogen and nitrogen combustion microanalyses were carried out using a Fisons Elemental Analyzer 1108 CHNS-O, at the University of KwaZulu-Natal, South Africa. Melting points were determined using a Gallenkamp melting point apparatus. The results were uncorrected. The ultraviolet-visible (UV/vis) spectra were recorded on a Varian Cary 500 spectrophotometer. The concentration of the Schiff bases used for the determinations of the electronic properties was approximately C ~ 5.0 x 10^{-4} M in DMF or methanol. All spectra from the spectroscopic methods are submitted as supplementary material.

General Procedure for Schiff Base Synthesis:

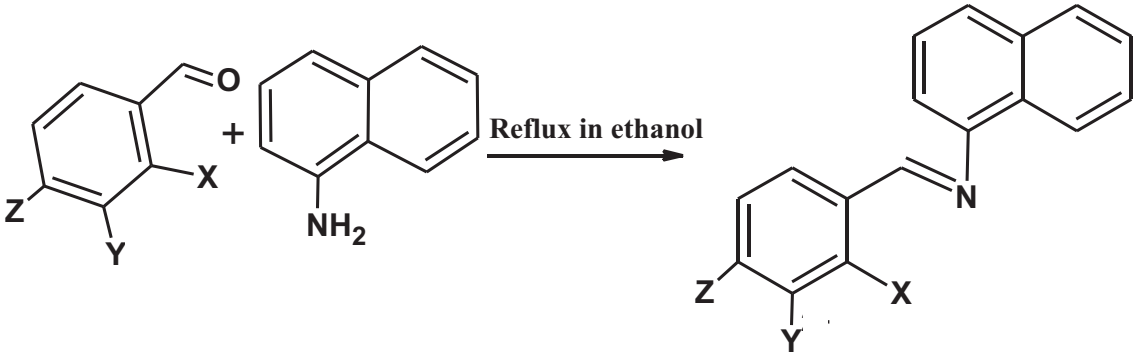
Equimolar quantities (5 mmol) of each of the four aromatic aldehydes and aniline or 1-aminonaphthalene, listed in Table 1, were dissolved in 10 ml of warm ethanol and refluxed for 2 hours (Schemes 1a and 1b). After cooling, the crystalline products were filtered and recrystallized from ethanol, and then dried under reduced pressure over silica. The isolated Schiff bases with their ^{1}H NMR and ^{13}C NMR are listed in the results and discussion section.

Table : The position of the substituents on Schiff bases

X	Y	Z
OH	H	H
OH	3-OCH_3	H
OH	H	4-OCH_3
H	3-OCH_3	4-OH



Scheme 1a: Synthetic route for Schiff bases **GL1a - GL1d**



Scheme 1b: Synthetic route for the Schiff bases **GL2a - GL2b**

RESULTS AND DISCUSSION

The microanalysis and the analytical data for the Schiff bases are listed in Table 2. The theoretical composition of the Schiff bases agreed with micro analytical data. Direct reaction of one equivalent of the amine (aniline or 1-aminonaphthalene) with one equivalent of salicyaldehyde, vanillin, *o*-vanillin or *p*-vanillin in ethanol gave the corresponding Schiff base.

2-((pheylimino)methyl)phenol (GL1a): ^{1}H NMR (400 MHz, $CDCl_3$) 13.22 (br, 1H, C-OH), 8.62 (s, 1H, CH=N), 7.44-7.35 (m, 4H, ArH), 7.30-7.25 (m, 3H, ArH), 7.04-7.02 (d, 1H, ArH), 6.96-6.92 (ddd, 1H, ArH) ^{13}C NMR (400 MHz, $CDCl_3$) 162.6 (C-OH), 161.1 (C=N), 148.5 (C-N), 133.1 (CH), 132.3 (CH), 129.4 (CH), 126.9 (CH), 121.2 (CH), 119.2 (CH), 119.0 (CH), 117.2 (CH).

5-methoxy-2-((phenylimino)methyl)phenol (GL1b): ^{1}H NMR (400 MHz, $CDCl_3$) 13.78 (br, 1H, C-OH), 8.55 (s, 1H, CH=N), 7.45-7.41 (t, 2H, ArH), 7.31-7.27 (m, 4H, ArH), 6.54 (d, 1H, ArH), 6.53-6.50 (dd, 1H, ArH), 3.87-3.86 (d, 3H, O-CH_3), ^{13}C NMR (400 MHz, $CDCl_3$) 164.0 (C-OCH_3), 161.5 (C-OH), 160.1 (C=N), 148.2 (C-N), 55.5 (O-CH_3).

2-methoxy-6-((pheylimino)methyl)phenol (GL1c): ^{1}H NMR (400 MHz, $CDCl_3$) 13.65 (br, 1H, C-OH), 8.63 (s, 1H, CH=N), 7.44-7.40 (m, 2H, ArH), 7.30-7.25 (m, 3H, ArH), 7.03-7.01 (dd, 1H, ArH), 7.00-6.98 (dd, 1H, ArH), 6.90-6.86 (t, 1H, ArH), 3.93-3.92 (d, 3H, O-CH_3), ^{13}C NMR (400 MHz, $CDCl_3$) 162.6 (C=N), 151.1 (C-OH), 56.2 (O-CH_3).

2-methoxy-4-((phenylimino)methyl)phenol (GL1d): ^{1}H NMR (400 MHz, $CDCl_3$) 8.35-8.34 (d, 1H, CH=N), 7.63 (d, 1H, ArH), 7.41-7.37 (t, 1H, ArH), 7.27-7.19 (m, 5H, ArH), 7.01-6.98 (dd, 1H, ArH), 6.13 (d, 1H, ArH), 3.98-3.97 (d, 3H, O-CH_3), ^{13}C NMR (400 MHz, $CDCl_3$) 160.1 (CH=N), 152.2 (C-OH), 149.0 (C-OCH_3), 147.1 (CH), 129.1 (CH), 125.6 (CH), 125.2 (CH), 120.8 (CH), 114.2 (CH), 108.43 (CH), 56.07 (O-CH_3).

2-((naphthalene-1ylimino)methyl)phenol (GL2a): ^{1}H NMR (400 MHz, $CDCl_3$) 13.43 (s, 1H, C-OH), 8.75 (s, 1H, CH=N), 8.32-8.29 (m, 1H), 7.97-7.91 (m, 1H, ArH), 7.84-7.82 (d, 1H, ArH), 7.61-7.57 (m, 2H, ArH), 7.56-7.52 (t, 1H, ArH), 7.51-7.45 (dddd, 2H, ArH), 7.23-7.21 (dd, 1H, ArH), 7.15-7.13 (d, 1H, ArH), 7.05-7.01 (ddd, 1H, ArH) ^{13}C NMR (400 MHz, $CDCl_3$) 163.6 (C-OH), 161.2 (C=N), 146.2 (C-N), 133.9 (CH), 133.4 (CH), 132.4 (CH), 128.2 (CH), 127.9 (CH), 126.9 (CH), 126.7(CH), 125.9 (CH), 123.2 (CH), 119.5 (CH), 119.2 (CH), 117.3 (CH), 114.0 (CH).

5-methoxy-2-((naphthalene-1-ylimino)methyl)phenol (GL2b): ^{1}H NMR (400 MHz, $CDCl_3$) 13.80 (br, 1H, C-OH), 8.55 (s, 1H, CH=N), 8.21-8.18 (m, 1H), 7.81-7.79 dd, 2H, ArH), 7.69-7.67 (d, 1H, ArH), 7.49-7.45 (m, 3H, ArH), 7.43-7.40 (t, 2H, ArH), 7.28-7.26 (d, 1H, ArH), 7.18 (s, 1H, ArH), 7.10-7.08 (d, 1H, ArH), 6.51 (d, 1H, ArH), 6.48-6.45 (dd, 1H, ArH), 3.80 (s, 3H, O-CH_3) ^{13}C NMR (400 MHz, $CDCl_3$) 164.2 (C-OCH_3), 163.9 (C-OH), 162.6 (C=N), 146.3 (CH), 134.0 (CH), 133.7 (CH), 128.3 (CH), 127.9 (CH), 126.6 (CH), 126.5 (CH), 126.4 (CH), 126.0 (CH), 123.3 (CH), 114.0 (CH), 113.5 (CH), 107.3 (CH), 101.2 (CH), 55.6 (O-CH_3).

2-methoxy-6-((naphthalen-1-ylimino)methyl)phenol (GL2c): ^{1}H NMR (400 MHz, $CDCl_3$) 13.94 (d, 1H, C-OH), 8.74-8.72 (d, 1H, CH=N), 8.31-8.29 (t, 1H), 7.89-7.87 (dd, 1H, ArH), 7.80-7.78 (t, 1H, ArH), 7.56-7.49 (m, 2H, ArH), 7.56-7.52 (t, 1H, ArH), 7.51-7.45 (dddd, 2H, ArH), 7.23-7.21 (dd, 1H, ArH), 7.15-7.13 (m, 3H, ArH), 7.23-7.21 (dd, 1H, ArH), 7.10-7.04 (m, 2H, ArH), 6.95-6.93 (t, 1H, ArH), 3.98-3.97 (d, 3H, O-CH_3) ^{13}C NMR (400 MHz, $CDCl_3$) 163.4 (C=N), 151.5 (C-N), 148.5 (C-OH), 145.7 (C-OCH_3), 134.0 (CH), 128.2 (CH), 127.9 (CH), 127.1 (CH), 126.5 (CH), 125.9 (CH), 123.8 (CH), 123.2 (CH), 119.4 (CH), 118.7 (CH), 114.8 (CH), 113.4 (CH), 56.2 (O-CH_3).

2-methoxy-4-((naphthalen-1-ylimino)methyl)phenol (GL2d): ^{1}H NMR (400 MHz, $CDCl_3$) 8.47 (s, 1H, CH=N), 8.36 (d, 1H), 7.90-7.80 (d, 1H, ArH), 7.80 (s, 1H, ArH), 7.75-7.73 (d, 1H, ArH), 7.56-7.48 (d, 3H, ArH), 7.39-7.37, 7.30 (d, 3H, ArH), 7.08-7.06 (d, 2H, ArH),

6.11 (br, s, 1H) 4.07 (s, 3H, O-C<u>H</u>$_3$); ^{13}C NMR (400 MHz, $CDCl_3$) 163.8 (<u>C</u>=N), 152.0 (<u>C</u>-N), 149.0 (<u>C</u>-OH), 146.1 (<u>C</u>H), 134.4 (<u>C</u>H), 128.7 (<u>C</u>H), 128.9 (<u>C</u>H), 127.5 (<u>C</u>H), 127.1 (<u>C</u>H), 127.0 (<u>C</u>H), 126.3 (<u>C</u>H), 124.2 (<u>C</u>H), 123.6 (<u>C</u>H), 119.8 (<u>C</u>H), 119.1 (<u>C</u>H), 115.3 (<u>C</u>H), 114.3 (<u>C</u>H), 56.6 (O-<u>C</u>H$_3$).

All the compounds were isolated as solid with good yields and each with sharp melting point. Mass spectra data of compound confirmed the proposed structure of the Schiff bases. The spectra mass of the seven out of the eight isolated Schiff bases showed the molecular ion peak corresponding to their formulation. The resulting Schiff bases were intensely coloured. The colour intensity was attributed to different positions of the hydroxyl and methoxy present as substituents on the asymmetric carbon as well as the difference in amine. The colour of the product of the salicyaldehyde-based Schiff bases **GL1a** and **GL2a** were yellow while others with methoxy were of distinct different colours. The colour difference of the Schiff bases was attributed to the presence of different positions of the substituent on the asymmetric carbon. This observation was further supported by spectroscopic data obtained from the various techniques used for their characterization after the synthesis.

Table 2: Microanalysis and analytical data for the Schiff bases **GL1a - Gl2d**

No.	Molecular formula	% Found (Calculated)			Colour	Yield (%)	M.p. (°C)	Molar mass	M+
		% C	% H	% N					
GL1a	$C_{13}H_{11}NO$	78.68 (79.16)	5.73 (5.62)	6.93 (7.10)	Yellow	90	51-52	197	197
GL1b	$C_{14}H_{13}NO$	74.15 (73.99)	5.70 (5.77)	5.96 (6.16)	Bright Yellow	57	65-66	227	226
GL1c	$C_{14}H_{13}NO$	74.97 (73.97)	5.74 (5.77)	6.09 (6.16)	Orange	97	82-83	227	227
GL1d	$C_{14}H_{13}NO$	74.01 (73.99)	5.95 (5.77)	6.09 (6.16)	Cream	81	102-104	227	226
GL2a	$C_{17}H_{15}NO$	82.11 (82.57)	5.30 (5.30)	5.77 (5.66)	Dark brown	85	43-44	247	247
GL2b	$C_{18}H_{15}NO_2$	77.64 (77.96)	5.39 (5.45)	4.90 (5.05)	Light brown	97	69-70	277	277
GL2c	$C_{18}H_{15}NO_2$	77.62 (77.96)	5.45 (5.45)	4.89 (5.05)	Orange	90	90-92	277	277
GL2d	$C_{18}H_{15}NO_2$	77.64 (77.96)	5.39 (5.45)	4.90 (5.05)	Dark brown	90	100-101	277	N/A

IR Spectroscopy

Selected bands of diagnostic importance are listed in Table 3 while the FTIR spectra of the Schiff bases under study are included in the supplementary material. In the FTIR spectra of products, the presence of characteristic bands of azomethine moiety ($C=N_{(imine)}$) at the frequency ranges of 1622-1609 cm^{-1} were observed for all the isolated Schiff bases. The stretching frequencies for the *ortho* hydroxyl substituent Schiff bases were known (Suydam, 1963, Gavranic *et al*., 1996, **Bilge** et al., **2009**) to be relatively lower than the Schiff bases with unsubstituted phenyl group or those without *ortho* hydroxyl substituent (**GL1d** and **GL2d**). These has been attributed to the effect of intramolecular H-bonding between $C=N_{(imine)}$ and the *ortho* hydroxyl groups (Curran and Siggia, 1970, Yildz *et al*., 1998). In addition, Shaibu and Watkins, (2015) observed that the presence of the electron donating methoxy group in the **GL1b**, **GL1c**, **GL2b** and **GL2c** usually resulted in further reduction in stretching frequency of $C=N_{(imine)}$ when compared with Schiff bases (**GL1a** and **GL2a**) without methoxy substituent. This was attributed to mass effect. The absence of bands of the carbonyl and amine moieties, revealed the formation of the Schiff bases.

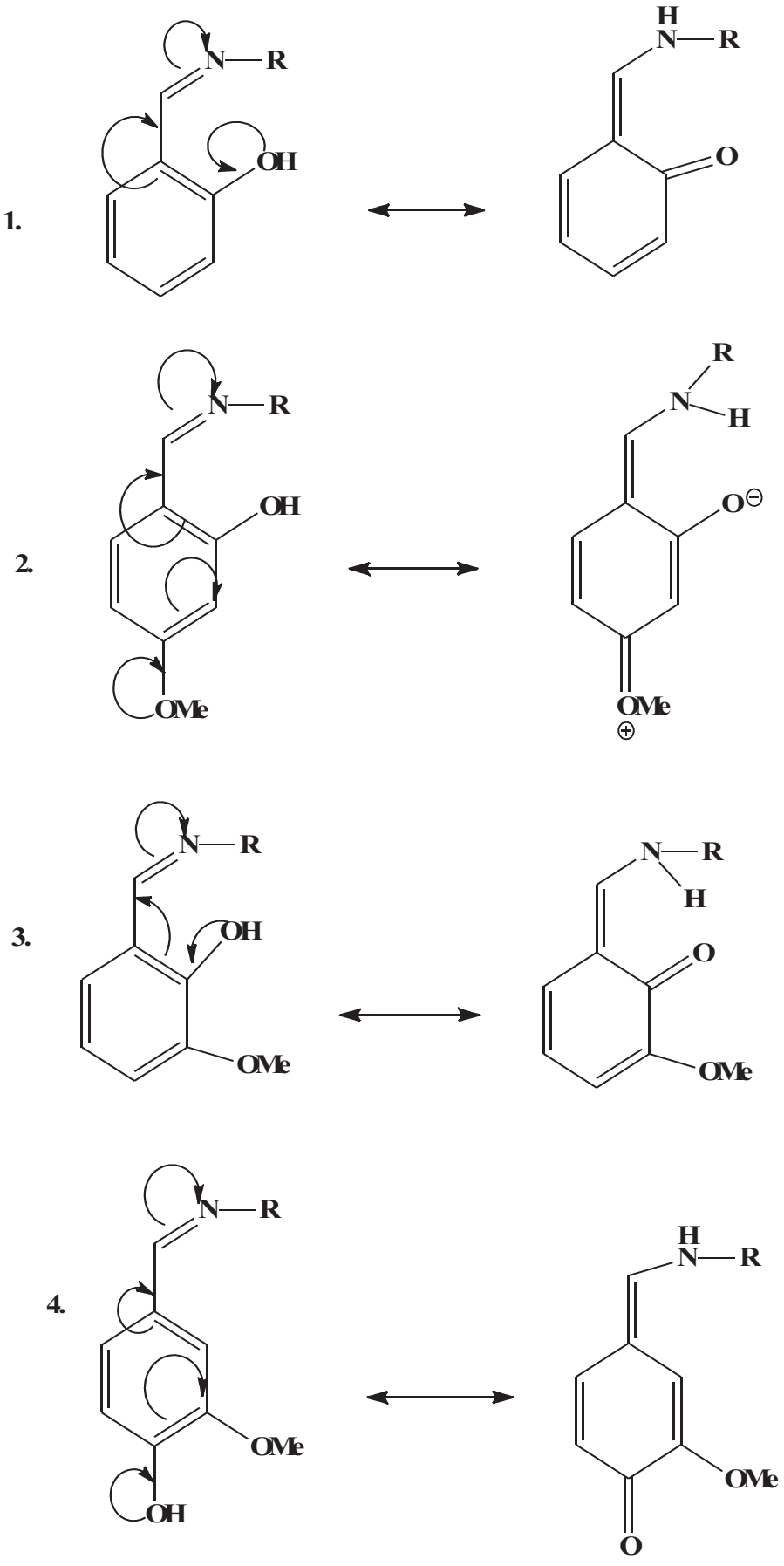
The stretching frequencies observed signifies the existence of intramolecular hydrogen bonding interaction between the *ortho* hydroxyl and the

$C=N_{(imine)}$ bond in **GL1a-GL1c**, **GL2a-GL2c** analogues (Bilge *et al.*, 2009). Freedman (1961) observed that internal hydrogen bond is not possible for p-hydroxybenzylideneaniline which absorbs at 3580 cm^{-1} in dilute chloroform. *o*-hydroxybenzylideneaniline and *p*-hydroxybenzylideneaniline were known to have 1622 cm^{-1} (s) and 1629 cm^{-1} (wv). The Schiff bases **GL1d** and **GL2d** are closely related to the *p*-hydroxybenzylideneaniline, hence can only have intermolecular hydrogen bonding because of the presence of the strongly electron-donating hydroxyl group in the *p*-position (Freedman, 1961). However, the similarity in the stretching frequency of the $C=N_{(imine)}$ bond of **GL1d** (1622 cm^{-1}) and **GL2d** (1621 cm^{-1}) to the **a – c** analogues can be attributed to conjugation caused by the presence of hydroxyl in the para position. The effects of ring substituents (hydroxyl or methoxy) in the resonance interaction and the effect of hydrogen bonding on the C=N absorption frequency obtained is depicted in Scheme 2. In addition, the possibility of existence of intramolecular interaction between the *para*-hydroxyl and the *meta*-methoxy substituent on the asymmetric carbon is being suggested.

Table 3: Electronic absorption spectra data of the isolated Schiff bases in methanol**, (Dimethylformamide)** in nm and mid infrared stretching frequencies in cm^{-1}.

S/N	$\pi \rightarrow \pi^*$		$\pi \rightarrow \pi^*$		$\pi \rightarrow \pi^*$	$n \rightarrow \pi^*$	νO-H	νC=N (imine)	νC-O
GL1a	206	226	272	300	315 (**318**)	337 (**334**)	3440	1621	1285
GL1b	220		235	290	335, 355 (**308**)	410	3442	1619	1290
GL1c	220		235	290	305, 315 (**308**)	450	3443	1616	1254
GL1d	215	233		270	(317)	401 (**361**)	3444	1622	1284
GL2a		230	260		(**300**)	354 (**346**)	3420	1618	1281
GL2b	215	230		287 (**278**)		353 (**349**)	3442	1613	1290
GL2c	215	225		275 (**274**)		345 (**336**)	3440	1609	1254
GL2d		226	234		(**290**)	364 (**336**)	3439	1621	1284

The bands in the region 1290 – 1254 cm^{-1} are ascribed to the phenolic C–O stretching vibration. These vibrations signify that the eight Schiff bases exist as enol-imine tautomers (Hokelek *et al.*, 2006; Bilge *et al.*, 2009). The evidence of hydrogen bond interaction in the isolated Schiff bases is shown by the presence of slightly medium and broad OH band with lower vibration frequency of between 3444 – 3420 cm^{-1} when compared with free OH value of 3600 cm^{-1} (Bellamy, 1970; Ligtenbarg *et al.*, 1999).



Scheme 2: The effects of ring substituents in the resonance interaction and tautomer formation

It was observed that the aminonaphthalene-based Schiff bases **GL2a – GL2d** appeared at lower frequencies relative to the aniline analogues due to mass effect. The presence of methoxy in 3-position resulted in red shifting of the stretching vibrations of both $C=N_{(imine)}$ and C–O more than it shifted these vibrations in the other analogous.

NMR Spectroscopy

GL1a, (Jain *et al*., 2006), **GL1c** (Yeap *et al*., 2003) and **GL2c** (Unver *et al*., 2005) were found to have been previously reported in the literature. It has been established that the Schiff base **GL1a** exists solely in the phenol-imine form. This is in agreement with this study's findings which also observed that the hydroxyl of all the Schiff bases was generally broad. The relative acidity of the hydroxyl proton can be judged by its chemical shift. While introduction of the methoxy group to the salicylaldimine results in a slightly increased acidity and a downfield shift for the OH by δ = 0.45 – 0.55 (**GL1a – GL1c**), the reverse was observed for the aminonaphthalene analogous (**GL2a – GL2c**).

The vanillin based Schiff bases are the least acidic (δ = 6.14), and intramolecular proton transfer to the imine is not favoured for the hydroxyl group in the *para* position. As a consequence, the ^{13}C chemical shift for the hydroxyl containing carbon is noticeably up-field compared with that for the deshielded p-vanillin salicylaldimine derivative (δ =164.0). This difference is similarly noticeable in the parent aldehydes (*C*-4: δ = 152.3 for vanillin *cf. C*-2: δ = 164.99 for p-vanillin (Pelter *et al*., 1976).

Only the azomethine proton of **GL2c** split. This implies slight presence of the keto-amine tautomer. The suggestion of slight keto-amine tautomer existence is because the OH proton that is expected to be lost if significant keto-amine is present appeared at 13.4. The aromatic protons are also slightly affected. The differences between the aromatic and quinoid forms expected in the ^{13}C NMR spectra were not noticed. This may imply mixture of the tautomers with the keto-amine tautomer likely to be dominant.

It was observed that the presence of methoxy in *meta* position caused a small shift to higher field of the azomethine proton (**GL1c**, **GL2c**), because of the increase in electron density on the carbon atom. Conversely, the presence of methoxy in the 4-position caused a shift to lower field of the azomethine. As observed in the infrared spectroscopy, the NMR technique also confirms that the spectroscopic properties of **a** – **c** analogous are different from spectroscopic properties observed for the **d**-analogous (**GL1d**, **GL2d**).

Tabei and Saitou (1969) and Khoo (1979) observed and generalized that the electronic structure of the azomethine group are more sensitive to substitution in the benzaldehyde ring than in the amine ring. The study showed that the electron donating substituent on the asymmetric carbon caused a small shift to higher field of the azomethine proton because of the increase in electron density on the carbon atom (Tabei and Saitou, 1969; Khoo, 1979). The position of the substituent determines the type of effect on the structure and the spectroscopic properties of the isolated Schiff bases.

A decrease in the shielding of the OH proton is produced by the presence of electron donating substituents which have the effect of increasing the electron density in the N-H bond. The large downfield shift of the hydroxyl proton resonance observed implies strong intramolecular hydrogen bonding in the Schiff bases caused by the electronic inductive effects of the substituents.

Electronic Absorption Spectra

The electronic spectra data of all Schiff bases are listed in Table 3. Electronic spectra were measured in protic solvent (methanol) and aprotic solvent dimethylformamide (DMF). The wavelengths obtained from DMF were put in brackets in Table 3 to differentiate them from the data obtained from methanol. The electronic absorption spectra of the Schiff bases in methanol produced four main bands while those of DMF produced one main band. In methanol, the transition due to $\pi \rightarrow \pi^*$ of the aromatic rings were observed at higher energy between 217 – 230 nm and 260 – 265 nm respectively (Bosnich, 1968; **Bilge** et al., **2009**). The bands within 315 – 362 nm is assigned to the $\pi \rightarrow \pi^*$ of the $(C=N)_{imine}$ while the bands appearing within the 380 – 425 nm are due to the $n \rightarrow \pi^*$ of

the imine (Dowing and Urbach, 1966). The presence of the band above 400 nm for the methoxy substituted **GL1b**, **GL1c** and **GL1d** respectively confirms the predominance of the keto-amine tautomeric form in methanol. This is attributed to solvation and resonance stabilization caused by the presence of the methoxy group or the use of the protic solvent (Dudek, 1963). The band above 400 nm was absent in DMF. This implies that the enol-imine predominates in the aprotic solvent (Dudek, 1963; Yildiz *et al.* 1998; Nazir, 2000). The interactions of enol-imine with a hydrogen bond forming solvent most probably reduced the O–H bond strength and facilitated proton transfer to the nitrogen centre. As a result, the hydrogen-bond forming solvents methanol favoured the formation of the keto-amine. This is because methanol solvates strongly via hydrogen bonding hence disrupting the H-bonding between N and H in the molecule. A blue shift of the keto-amine band caused by increased DMF polarity implies a decrease in the polar quinoid resonance forms (Ferguson and Kelly, 1951). This behaviour is ascribed to the stabilization of the ground state by the solvent (Ibrahim and Al-Deeb, 2006). The presence of the band confirming keto-amine tautomeric form in methanol and the absence of the band in DMF signifies the importance of solvent in the formation of enol-imine or keto-amine tautomer. The electronic absorption results obtained corroborate the mid-IR, ^{1}H-NMR and ^{13}C-NMR results obtained.

The increase in the solvent polarity of the DMF caused the electronic spectra of the isolated Schiff bases to suffer a loss in vibrational fine structure which serves as a measure of the extent of the solvent-ligand interaction (Ungnade, 1953).

The benzenoid band around 272 nm observed for Schiff base **GL1a,** blue shifted in all the other three aniline-based ligands showing the effect of the methoxy substituent. The general trend was that the bands assigned to $\pi\rightarrow\pi^*$ and $n\rightarrow\pi^*$ seen for the (**GL2a** – **GL2d**) 1-aminonaphthalene-based Schiff bases in both solvents shifted to lower energy in DMF when compared with the (**GL1a** – **GL1d**) aniline-based analogues. This shift in energy to higher energy can be attributed to increased conjugation which created smaller energy gap between $\pi\rightarrow\pi^*$ and $n\rightarrow\pi^*$ orbitals of the aminonaphthalene-based Schiff bases ligands. The absence of a band above 400 nm for the isolated 1-aminonaphthalene-based Schiff bases, implies that replacement of aniline with 1-aminonaphthalene lead to the predominance formation of enol-imine tautomers (Antonov *et al.*, 2000; Joshi *et al.*, 2001).

CONCLUSION

On the basis of spectroscopic and analytical data, it could be concluded that intramolecular hydrogen bonding exists for all the Schiff bases **GL1a**, **GL1b**, **GL1c**, **GL2a**, **GL2b** and **GL2c** while **GL1d** and **GL2d** have intermolecular hydrogen bonding. The spectra data from the spectroscopic techniques suggest mixture of tautomers with enol-imine dominance. The spectra data of UV/vis and IR spectra (supplementary material) results indicated a significant influence of parent aldehyde and solvent on the tautomerization process. The protic and aprotic solvents caused the proton transfer reversible process, *i.e.*, tautomer changing from the OH to NH form or vice versa. Parent aromatic aldehyde, solvent type as well as the type of amine used while designing the Schiff base obviously plays important roles in determining the equilibrium position of the tautomer formed, hence the tautomer that will predominate.

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