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Synthesis, crystal structure and spectroscopic study of *para* substituted 2-hydroxy-3-methoxybenzalideneanilines

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Abstract

Eight Schiff bases derived from 2-hydroxy-3-methoxybenzaldehyde and different *para* substituted anilines have been synthesized and their structures were elucidated by physical measurements and FT-IR. NMR assignments were made using ¹H, ¹³C NMR and aided by 2D COSY homonuclear, HMQC and HMBC heteronuclear correlation techniques. IR spectral analysis of the model compounds was found useful in understanding the degree of stabilization upon this series of enol-imino tautomers, which possess different substituents in the aniline fragment. In order to rationalize the stabilization of tautomer in solid state, the crystallography data of 1-{(4-methylphenylimino)methyl}- and 1-{(4-chlorophenylimino)methyl}-2-hydroxy-3-methoxyphenol were adopted wherein the 4-chloro (4-Cl) and 4-methyl (4-CH₃) containing compounds crystallized into orthorhombic lattice with a non-centrosymmetric space group $P2_12_12_1$. The relationship between the stabilization of bonding involved in heteronuclear six-membered ring of the tautomer and the conformation of the molecules in crystal phase was reported. © 2003 Elsevier B.V. All rights reserved.

Keywords: 2-Hydroxy-3-methoxybenzaldehyde; Schiff bases; FT-IR; NMR; Single crystal X-ray diffraction analysis

1. Introduction

It has well been documented that Schiff bases are important in diverse fields of chemistry and biochemistry owing to their biological activities [1,2]. Apart from the biological activities, photochromism is another characteristic of these materials leading to its application in various areas such as the control and measurement of radiation intensity, display systems and optical computers. In view of the importance and also the usefulness of these compounds, the chemists

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In the field of coordination chemistry, this type of *ortho* hydroxylated Schiff bases has received an overwhelming attention particularly on the study of complex formation [4-7]. Recently, the liquid crystals researchers have also made a significant

are prompted to generate the derivatives by introducing different substituents into the existing skeleton of the molecule. The presence of *ortho* hydroxyl group, for instance, has been regarded as one of the importance elements which favours for the existence of intramolecular hydrogen bonding $(O-H \cdots N \text{ and } O \cdots H-N)$ and also the tautomerism which accounts for the formation of either enol-imino or keto-amino tautomer [3].



revelation that the introduction of lateral polar hydroxy group will enhance the molecular polarizability as well as to stabilize the liquid crystalline compounds [8]. One of the typical examples is the study on the effect of lateral hydroxyl group on mesomorphism of azobenzene derivatives [9].

In this paper, we report a series of Schiff bases wherein the substituents of 2-hydroxy and 3-methoxy in the aldehyde ring were remained unaltered. However, the aniline used in the reaction with this aldehyde was either non-substituted or substituted by F, Cl, Br, NO₂, CH₃, OCH₃ and CN at *para* position. The effects attributed to the emergence of the tautomeric conformers in crystal and liquid phases were studied by spectroscopic methods and X-ray diffraction analysis.

2. Experimental section

4-Bromoaniline, 4-chloroaniline and 4-aminophenol were obtained from Merck (Germany). 4-Nitroaniline and 4-methylaniline were purchased from Riedel-de Haen (Germany). Aniline, 4-fluoroaniline and 4-aminobenzonitrile and 4-methoxyaniline were obtained from BDH (England), Acros Organics (USA) and Fluka Chemie (Switzerland), respectively. 2-Hydroxy-3-methoxybenzaldehyde (*o*vanilin) was purchased from TCI Chemical Company (Japan).

2.1. Synthesis of Schiff bases

The Schiff bases were synthesized by mixing equimolar amounts of *o*-vanilin with the appropriate aniline, both dissolved in absolute ethanol. The reaction mixture was refluxed for 5 h and the precipitate thus formed upon cooling to room temperature (300 K) was filtered. The solid residue was crystallized from absolute ethanol or chloroform and dried under reduced pressure. The representation of Schiff bases with numbering scheme is shown in Scheme 1.

2.2. FT-IR measurements

The FT-IR spectra of Schiff bases of *o*-vanilin were recorded by using a Perkin Elmer 2000-FT-IR

spectrophotometer in the frequency range $4000-400 \text{ cm}^{-1}$. All samples were prepared in KBr discs.

2.3. NMR measurements

NMR spectra were recorded in CDCl₃ at 298 K on a Bruker 400 MHz Ultrashield Spectrometer equipped with a 5 mm BBI inverse gradient probe. Chemicals shifts were referenced to internal TMS. The concentration of solute molecules was 150 mg in 1.0 ml CDCl₃. Standard Bruker pulse programs [10] were used throughout the entire experiment. The spectroscopic details of NMR were summarized in Table 1.

2.4. X-ray data collection, structure solution and refinement for 1-{(4-methylphenyl-imino)methyl}-2hydroxy-3-methoxyphenol (3) and 1-{(4methylphenylimino)-methyl}-2-hydroxy-3methoxyphenol (6)

Crystal data are given in Table 2. Whist the final coordinates and equivalent isotropic displacement parameters are given in Table 3, the selected bond lengths, angles and torsion angles are given in Table 4. The molecular structures with



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Table 1 Acquisition parameters used in the NMR measurements

| Parameters* | Experiment | | | | | | | | |
|-------------|------------------------------|-------------------------------|-----------------------------|--|---|--|--|--|--|
| | ¹ H NMR | ¹³ C NMR | 2D COSY | 2D HMQC | 2D HMBC | | | | |
| SF | 400.1 MHz | 100.6 MHz | 400.1 MHz | $F_1 = 100.6 \text{ MHz}$ $F_2 = 400.1 \text{ MHz}$ | $F_1 = 100.61 \text{ MHz}$ $F_2 = 400.1 \text{ MHz}$ | | | | |
| SW | 20 ppm | 250 ppm | 18 ppm | $F_1 = 200 \text{ ppm}$ $F_2 = 20 \text{ ppm}$ | $F_1 = 200 \text{ ppm}$ $F_2 = 20 \text{ ppm}$ | | | | |
| PW | 8.3 μ s (30° flip angle) | 20.0 μ s (90° flip angle) | 8.3 μs (90° flip angle) | 8.3 μ s (90° flip angle) | 8.3 μ s (90° flip angle) | | | | |
| AQ | 4.0 s | 1.3 s | 0.3 s | 0.09 s | 0.4 s | | | | |
| D1 | 1.0 s | 2.0 s | 2.0 s | 1.0 s | 1.0 s | | | | |
| NS | 16 | 1879 | 8 | 20 | 18 | | | | |
| TD | 66 K | 65 K | $F_1 = 256$ $F_2 = 2048$ | $F_1 = 512$ $F_2 = 1024$ | $F_1 = 512$ $F_{2=}4096$ | | | | |

*Abbreviations: F₁, ¹³C channel; F_2 , ¹H channel (except 2D COSY where F_1 and F_2 are ¹H channels); SF, spectrometer frequency; SW, spectral width; PW, pulse width; AQ, acquisition time; D1, relaxation delay, NS, number of scan; TD, number of data points.

the atom-numbering scheme for **3** and **6** are shown in Fig. 1(a) and (b), respectively.

Intensity data were collected at 293 K using the imaging-plate diffractometer Rigaku R-axis Rapid with Mo K α radiation monochromated by a graphite plate. The cylindrically shaped imaging plate covers the two-theta angular range between -60 and 140° with a crystal-film distance of 127.4 mm. The diffraction pattern was recorded on an imaging plate by oscillating the crystal around the ω axis by 3° at a speed of 240° per second for **3**, and by 2° at a speed of 120° per second for **6**. In all, 173 images for **3** were taken successfully by varying ω with three sets of different χ and φ values, and 178 images with two sets for **6**. Overlaps of 0.2° in ω were taken into consideration at both ends of each scan.

Cell dimensions were refined together with other offset parameters of the diffractometer using all reflections with $I > 2\sigma(I_0)$ measured in the 2θ range between -60 and 140° . Since there are virtually no significant reflections at 2θ angles higher than 55°, all data in this region was eliminated. Equivalent reflections were merged using the Rapid-auto program package. Friedel pairs were considered as equivalent for the merge.

In all, 2749 independent reflections with $R_{int} = 0.099$ were retrieved from 13,021 measured reflections for **3**, and 1721 independent reflections with

 $R_{\text{int}} = 0.103$ from 13,827 measured ones for **6**, and used for structure determination and the refinement procedure.

The structures were solved by the direct method using SHELXS [11] and SIR2002 [12]. The positional and atomic displacement parameters (ADPs) were refined using SHELXL [13]. All the hydrogen atom positions were found from the difference Fourier map. The ranges of the C-H and O-H bond distances found for compounds **3** and **6** were 0.83(7) - 1.18(9) Å and 0.81(4) - 1.09(5) Å, respectively. The positional and isotropic atomic displacement parameters of hydrogen atoms were refined together with other structural parameters by the full-matrix least-squares procedure based on the squared value of the structure factors. The weighting scheme $\omega = 1/[\sigma^2(F_0^2) +$ $(0.1226P)^2 + 0.5279P$ where $P = (F_o^2 + 2F_c^2)/3$ was used for **3** and $\omega = 1/[\sigma^2(F_o^2) + (0.0254P)^2 +$ 0.0000*P*] where $P = (F_o^2 + 2F_c^2)/3$ were used for **6**. The final R(F) and $\omega R(F^2)$ values became 0.0841 and 0.2579 for 3, and 0.0453 and 0.1056 for 6.

3. Results and discussion

All title compounds formed solid with sharp melting points. The structural formula of these compounds is shown in Scheme 1.

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Table 2

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Summary of crystal data, intensity data collection and structure refinement for compounds ${\bf 3}$ and ${\bf 6}$ at 298 K

| Table 3 | a |
|---------|---|
|---------|---|

Fractional atomic coordinates and isotropic temperature factors (\mathring{A}^2) , with standard deviations in the least significant digits in parentheses for compound **3**. For anisotropic atoms, the equivalent isotropic temperature factors are shown

| Compound | 3 | 6 |
|--------------------------------------|--------------------------------------|---|
| Formula | C ₁₄ H ₁₂ ClNO | C ₁₅ H ₁₅ NO ₂ |
| Data collection | 298 | 298 |
| temperature (K) | | |
| M _r | 261.7 | 241.28 |
| Crystal colour | Orange, | Orange, |
| | transparent | transparent |
| Crystal | $0.25 \times 0.38 \times 0.99$ | $0.19 \times 0.29 \times 0.35$ |
| dimension | | |
| Crystal system, | $P2_{1}2_{1}2_{1}$ | $P2_12_12_1$ |
| space group | | |
| Unit cell parameters | | |
| a (Å) | 4.9076(2) | 5.9190(2) |
| <i>b</i> (Å) | 12.5700(4) | 9.2428(3) |
| <i>c</i> (Å) | 20.1739(8) | 23.3431(6) |
| $V(Å^3)$ | 1244.50(8) | 1277.06(7) |
| Ζ | 4 | 4 |
| $D_c ({\rm g}{\rm cm}^{-3})$ | 1.397 | 1.255 |
| $\mu (\mathrm{mm}^{-1})$ | 0.299 | 0.083 |
| F(000) | 544 | 512 |
| 2θ range for | 54.90 | 54.96 |
| data collection | | |
| (degrees) | | |
| h, k, 1 range | $-6 \le h \le 6,$ | $-7 \le h \le 7$, |
| | $-16 \le k \le 16,$ | $-12 \le k \le 12,$ |
| | $-26 \le l \le 26$ | $-30 \le l \le 30$ |
| No. of measured | 13,021 | 13,827 |
| reflections | | |
| No. of independent | 2749 | 1721 |
| reflections | | |
| No. of refined | 211 | 223 |
| parameters | | |
| R | 0.084 | 0.045 |
| Rw | 0.258 | 0.1056 |
| Goodness of | 1.048 | 0.754 |
| fit on S | | |
| Max. residual | 0.283 | 0.148 |
| electron density ($e A^{-3}$) | 0.000 | 0.465 |
| Min. residual $\frac{3}{2}$ | -0.292 | -0.165 |
| electron density (e A ³) | | |

3.1. IR spectroscopy

IR frequencies of various diagnostic bands in the solid state (KBr) are collected in Table 5. The IR spectra of 1, 4, 5, 6 and 8 are shown in Fig. 2 as representative illustration. The exact positions of the characteristic bands discussed in the later part of this section vary from one compound to another since the substituent in the aniline fragment is different.

| Atom | x/a | y/b | z/c | U (Å ²) |
|------|-------------|-----------|-----------|---------------------|
| CL1 | 0.2704(3) | 0.5657(1) | 0.0051(1) | 0.086 |
| N1 | -0.5636(9) | 0.6020(3) | 0.2164(2) | 0.067 |
| 01 | -0.8442(9) | 0.7241(3) | 0.2958(2) | 0.076 |
| O2 | -1.2178(9) | 0.7436(3) | 0.3903(2) | 0.082 |
| C1 | -0.3675(10) | 0.5892(4) | 0.1664(3) | 0.066 |
| C2 | -0.2561(12) | 0.4906(4) | 0.1476(3) | 0.068 |
| C3 | -0.0626(12) | 0.4849(4) | 0.0986(3) | 0.072 |
| C4 | 0.0225(10) | 0.5746(4) | 0.0671(2) | 0.068 |
| C5 | -0.0781(12) | 0.6731(4) | 0.0848(3) | 0.078 |
| C6 | -0.2695(13) | 0.6782(4) | 0.1342(3) | 0.076 |
| C7 | -1.2938(12) | 0.5511(5) | 0.3907(3) | 0.075 |
| C8 | -1.2277(13) | 0.4531(5) | 0.3655(3) | 0.082 |
| C9 | -1.0367(12) | 0.4443(5) | 0.3171(3) | 0.080 |
| C10 | -0.9001(11) | 0.5341(4) | 0.2924(3) | 0.066 |
| C11 | -0.9653(10) | 0.6350(4) | 0.3182(3) | 0.065 |
| C12 | -1.1669(10) | 0.6420(4) | 0.3676(3) | 0.069 |
| C13 | -0.6989(11) | 0.5225(4) | 0.2414(3) | 0.070 |
| C14 | -1.4337(13) | 0.7549(6) | 0.4364(3) | 0.085 |
| | | | | |

Table 3b

Fractional atomic coordinates and isotropic temperature factors (\mathring{A}^2) , with standard deviations in the least significant digits in parentheses for compound **6**. For anisotropic atoms, the equivalent isotropic temperature factors are shown

| | x/a | y/b | z/c | U (Å ²) |
|-----|-------------|-----------|------------|---------------------|
| 02 | 0.0940(5) | 0.5743(3) | 0.0149(1) | 0.066 |
| 01 | 0.4204(5) | 0.5271(3) | 0.0888(1) | 0.060 |
| N1 | 0.5707(6) | 0.3773(3) | 0.1763(1) | 0.053 |
| C1 | 0.7119(7) | 0.3599(4) | 0.2250(1) | 0.050 |
| C11 | 0.2626(7) | 0.4248(4) | 0.0835(1) | 0.047 |
| C10 | 0.2641(7) | 0.2971(4) | 0.1171(1) | 0.051 |
| C13 | 0.4284(9) | 0.2799(4) | 0.1630(1) | 0.057 |
| C12 | 0.0851(8) | 0.4461(4) | 0.0437(1) | 0.051 |
| C4 | 1.0063(7) | 0.3410(4) | 0.3194(2) | 0.057 |
| C8 | -0.0736(9) | 0.2125(5) | 0.0686(2) | 0.065 |
| C7 | -0.0756(9) | 0.3408(5) | 0.0366(2) | 0.061 |
| C14 | -0.1015(11) | 0.6115(6) | -0.0186(2) | 0.074 |
| C9 | 0.0952(10) | 0.1925(4) | 0.1081(2) | 0.065 |
| C6 | 0.9125(8) | 0.4351(4) | 0.2258(2) | 0.059 |
| C5 | 1.0603(8) | 0.4233(5) | 0.2721(2) | 0.062 |
| C2 | 0.6551(8) | 0.2777(5) | 0.2726(2) | 0.062 |
| C15 | 1.1636(11) | 0.3273(8) | 0.3695(2) | 0.081 |
| C3 | 0.8004(8) | 0.2698(5) | 0.3191(2) | 0.063 |
| | | | | |

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|---------|------------|---------|--------------|--------------|---------|---------|
|---------|------------|---------|--------------|--------------|---------|---------|

Table 4b

Table 4a

Bond lengths (Å), bond angles (degrees) and torsion angles (degrees) for compound ${\bf 3}$

Bond lengths (Å), bond angles (degrees) and torsion angles (degrees) for compound ${\bf 6}$

| CL1-C4 | 1.749(5) | N1-C1 | 1.404(7) | O2-C12 | 1.364(4) | O1-C11 | 1.335(4) |
|-----------------|----------|----------------|----------|-----------------|----------|----------------|----------|
| N1-C13 | 1.301(7) | O1-C11 | 1.346(6) | N1-C1 | 1.419(4) | N1-C13 | 1.272(5) |
| O2-C12 | 1.379(6) | O2-C14 | 1.417(8) | C1-C6 | 1.376(6) | C1-C2 | 1.387(5) |
| C1-C2 | 1.407(7) | C1-C6 | 1.381(8) | C11-C10 | 1.417(5) | C11-C12 | 1.416(5) |
| C2-C3 | 1.372(8) | C3-C4 | 1.359(8) | C10-C13 | 1.456(5) | C10-C9 | 1.406(6) |
| C4-C5 | 1.380(8) | C5-C6 | 1.372(9) | C12-C7 | 1.371(6) | C4-C5 | 1.377(6) |
| C7-C8 | 1.372(8) | C7-C12 | 1.382(8) | C4-C15 | 1.502(6) | C4-C3 | 1.385(5) |
| C8-C9 | 1.358(9) | C9-C10 | 1.404(8) | C8-C7 | 1.402(5) | C8-C9 | 1.371(6) |
| C10-C11 | 1.408(7) | C10-C13 | 1.434(8) | C6-C5 | 1.395(5) | C2-C3 | 1.388(6) |
| C11-C12 | 1.408(7) | | | C14-O2 | 1.438(6) | | |
| C1-N1-C13 | 122.7(5) | C12-O2-C14 | 116.5(5) | C1-N1-C13 | 120.3(3) | N1-C1-C6 | 117.5(3) |
| N1-C1-C2 | 124.2(5) | N1-C1-C6 | 118.9(5) | N1-C1-C2 | 124.1(4) | C6-C1-C2 | 118.3(4) |
| C2-C1-C6 | 116.9(5) | C1-C2-C3 | 120.6(5) | O1-C11-C10 | 122.4(3) | O1-C11-C12 | 118.7(3) |
| C2-C3-C4 | 120.4(5) | CL1-C4-C3 | 119.7(4) | C10-C11-C12 | 118.9(3) | C11-C10-C13 | 120.2(4) |
| CL1-C4-C5 | 119.4(4) | C3-C4-C5 | 120.9(5) | C11-C10-C9 | 119.0(3) | C13-C10-C9 | 120.6(3) |
| C4-C5-C6 | 118.3(5) | C1-C6-C5 | 122.9(6) | N1-C13-C10 | 123.0(3) | O2-C12-C11 | 114.6(4) |
| C8-C7-C12 | 120.8(5) | C7-C8-C9 | 120.1(6) | O2-C12-C7 | 125.7(4) | C11-C12-C7 | 119.7(4) |
| C8-C9-C10 | 121.3(6) | C9-C10-C11 | 119.0(5) | C5-C4-C15 | 121.8(5) | C5-C4-C3 | 117.6(4) |
| C9-C10-C13 | 120.2(5) | C11-C10-C13 | 120.9(5) | C15-C4-C3 | 120.6(4) | C7-C8-C9 | 118.6(4) |
| O1-C11-C10 | 121.7(4) | O1-C11-C12 | 119.7(5) | C12-C7-C8 | 122.0(4) | C10-C9-C8 | 121.7(4) |
| C10-C11-C12 | 118.6(5) | O2-C12-C7 | 124.9(5) | C1-C6-C5 | 120.9(4) | C4-C5-C6 | 121.2(4) |
| O2-C12-C11 | 114.9(4) | C7-C12-C11 | 120.2(5) | C1-C2-C3 | 120.4(4) | C4-C3-C2 | 121.6(4) |
| N1-C13-C10 | 123.5(5) | | | C12-O2-C14 | 116.4(4) | | |
| C13-N1-C1-C2 | -13.6 | C13-N1-C1-C6 | 168.3 | C1-N1-C13-C10 | 173.9 | C13-N1-C1-C6 | 156.0 |
| C1-N1-C13-C10 | - 179.9 | C14-O2-C12-C7 | - 5.9 | C13-N1-C1-C2 | -27.2 | N1-C1-C6-C5 | - 179.9 |
| C14-O2-C12-C11 | 175.3 | N1-C1-C2-C3 | -179.2 | N1-C1-C2-C3 | -178.1 | C2-C1-C6-C5 | 3.1 |
| C6-C1-C2-C3 | -1.0 | N1-C1-C6-C5 | -180.0 | C6-C1-C2-C3 | -1.4 | O1-C11-C10-C13 | 6.0 |
| C2-C1-C6-C5 | 1.7 | C1-C2-C3-C4 | -0.6 | O1-C11-C10-C9 | -178.4 | O1-C11-C12-O2 | -1.0 |
| C2-C3-C4-CL1 | 179.7 | C2-C3-C4-C5 | 1.7 | O1-C11-C12-C7 | 178.4 | C10-C11-C12-O2 | 177.8 |
| CL1-C4-C5-C6 | -179.1 | C3-C4-C5-C6 | -1.0 | C12-C11-C10-C13 | -172.7 | C10-C11-C12-C7 | -2.8 |
| C4-C5-C6-C1 | -0.8 | C12-C7-C8-C9 | -0.3 | C12-C11-C10-C9 | 2.9 | C11-C10-C13-N1 | 2.2 |
| C8-C7-C12-O2 | -179.4 | C8-C7-C12-C11 | -0.6 | C11-C10-C9-C8 | -1.5 | C9-C10-C13-N1 | -173.2 |
| C7-C8-C9-C10 | 0.9 | C8-C9-C10-C11 | -0.6 | C13-C10-C9-C8 | 174.0 | O2-C12-C7-C8 | - 179.2 |
| C8-C9-C10-C13 | 179.9 | C9-C10-C11-O1 | -179.0 | C11-C12-C7-C8 | 1.5 | C15-C4-C5-C6 | 180.0 |
| C9-C10-C11-C12 | -0.3 | C13-C10-C11-O1 | 0.5 | C3-C4-C5-C6 | 0.3 | C5-C4-C3-C2 | 1.5 |
| C13-C10-C11-C12 | 179.2 | C9-C10-C13-N1 | -179.6 | C15-C4-C3-C2 | -178.2 | C7-C8-C9-C10 | 0.1 |
| C11-C10-C13-N1 | 0.8 | 01-C11-C12-O2 | -1.5 | C9-C8-C7-C12 | -0.1 | C1-C6-C5-C4 | -2.7 |
| O1-C11-C12-C7 | 179.6 | C10-C11-C12-O2 | 179.8 | C1-C2-C3-C4 | -1.0 | | |
| C10-C11-C12-C7 | 0.9 | | | | | | |

The absorption bands assignable to the stretching of C=N bond for compounds 1-8 were observed at frequencies range of $1613-1619 \text{ cm}^{-1}$ and these values conform with that reported in the IR spectrum for unsubstituted aromatic Schiff base which possesses the formulation of C₆H₅CH=NC₆H₅ [14,15]. A band assignable to the stretching of O-H bond is found to be broadened within the frequency range of $3000-2500 \text{ cm}^{-1}$. This observation implies that the H atom from the O-H group in compounds 1-8 has

a tendency to migrate to azomethine N atom via the $O-H\cdots N$ intramolecular hydrogen bonding as that observed for *meta* substituted 5-methoxysalicylaldimine isomer [(Sal-*m*-OH-ph)H] in the solid state [16].

Although the probable structures for compounds 1-8 have been postulated as enol-imino tautomer resembling (Sal-*m*-OH-ph)H, but further inspection upon the IR spectra have revealed that the stabilization of the enol-imino tautomer may vary depending on the type of *para* substituent. This conformational

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Fig. 1. ORTEP drawings with atom-numbering scheme for (a) Schiff base 3, and (b) Schiff base 6.

study was based on the comparison of IR spectra of all Schiff bases 1-8 at different vibrational regions similar to the experimental observation carried out earlier on salicylidineaniline and naphthylidinequino-lineamine [15,17].

A first comparison was made among compounds 2-4 wherein the compound was substituted by F, Cl or Br atom, respectively. The presence of the most electronegative F atom in compound 2 gave rise to

the highest C=N stretching frequency. The discrepancy can be ascribed to the stabilization of C=N bond resulting from the resonance effect whereby the lone-pair electrons from the F atom were delocalized via π -bonding in the conjugated skeleton comprising aniline fragment and the exocyclic C=N. The presence of very strong intensity of ν (O– H) also suggests that the azomethine C=N is not affected by H atom through intramolecular hydrogen



Table 5 Infrared frequencies (cm^{-1}) of compounds 1-8 in the solid state (KBr)

| Compound | ν (C=N) | ν (C=C) _{arom} | ν (C–O) |
|----------|---------|-----------------------------|---------|
| 1 | 1615 vs | 1589 s | 1270 s |
| 2 | 1618 vs | 1600 m | 1278 s |
| 3 | 1615 vs | 1572 m | 1273 m |
| 4 | 1614 s | 1570 w | 1274 m |
| 5 | 1613 m | 1572 m | 1273 w |
| 6 | 1617 s | 1595 s | 1275 s |
| 7 | 1619 vs | 1580 m | 1276 s |
| 8 | 1619 s | 1592 vs | 1283 m |

Abbreviations: s, strong; m, medium; w, weak; v, very

bonding. The information with respect to the intensity of the band assigned for ν (C=C) within the aromatic skeleton in compound 2 also supports that the percentage of enol-imine is comparatively higher than 3 and 4 [17].

The stabilization of C=N bond which is accountable partially for the existence of enol-imino tautomer can also be inferred from the IR spectra of 6-8 in which the σ -electron donors of CH₃, OCH₃ and the π -electron density from cynide (CN)

substituent caused the intensities of ν (C=N) band increased in comparison with compound **5** which possesses electron withdrawing NO₂ group. Another feature is that there are bands corresponding to the stretching of phenolic C–O bond in different intensity at 1283–1270 cm⁻¹ resemble that reported for *ortho* hydroxyl group [16]. Again, the comparison among compounds **2–4** substantiates that the compound **2** with strong band at 1278 cm⁻¹ possesses highest percentage of enol-imino tautomer due to the stabilization of phenolic C–O bond.

3.2. NMR spectroscopy

The ¹H and ¹³C NMR data recorded in CDCl₃ solutions are shown in Tables 6 and 7, respectively. The assignments with respect to the different resonances in Tables 6 and 7 are obtained by means of ${}^{1}\text{H}{-}^{1}\text{H}$ and ${}^{13}\text{C}{-}^{1}\text{H}$ correlation spectroscopic measurements.

For compound 1, two signals each appeared as a singlet at $\delta = 8.60$ and 13.75 ppm can be ascribed to CH=N and OH, respectively. The appearance of both signals indicated that the tautomeric equilibrium



Fig. 2. FT-IR spectra of compounds 1, 4, 5, 6 and 8 in the solid state (KBr).

Table 6 ¹H NMR chemical shifts (ppm) of Schiff bases **1–8** in CDCl₃

| Compounds | Chemical shifts (ppm) | | | | | | | | | | |
|-----------|-----------------------|----------------------|-----------------------------|---------------|-----------------------------|----------|----------|-----------|---------------|--|--|
| | H2, H6 | H3, H5 | H7 | H8 | H9 | H13 | H14 | ОН | R | | |
| 1 | 7.28-7.29 (m) | 7.40-7.44 (m) | 6.99-7.00 (dd) ^a | 6.85-6.89 (t) | 6.97-7.02 (dd) ^a | 8.60 (s) | 3.92 (s) | 13.75 (s) | 7.26-7.27 (t) | | |
| 2 | 7.20-7.23 (m) | 7.04-7.08 (m) | $6.96 (d)^{a}$ | 6.82-6.86 (t) | $6.94 - 6.98 (dd)^{a}$ | 8.53 (s) | 3.89 (s) | 13.51 (s) | - | | |
| 3 | 7.15-7.17 (m) | 7.31-7.33 (m) | 6.95-6.96 (dd) ^a | 6.82-6.86 (t) | 6.94-6.97 (dd) ^a | 8.54 (s) | 3.89 (s) | 13.41 (s) | _ | | |
| 4 | 7.12-7.14 (m) | 7.49-7.51 (m) | 6.98-6.99 (dd) ^a | 6.85-6.89 (t) | 6.97-7.00 (dd) ^a | 8.56 (s) | 3.91 (s) | 13.40 (s) | _ | | |
| 5 | 7.37-7.40 (m) | 8.30-8.33 (m) | $7.07 - 7.08 (dd)^a$ | 6.93-6.97 (t) | 7.06-7.09 (dd) ^a | 8.66 (s) | 3.96 (s) | 12.90 (s) | - | | |
| 6 | $7.22 (d)^{b}$ | 7.22(d) ^b | 6.99-7.00 (dd) ^a | 6.86-6.90 (t) | 6.97-7.02 (dd) ^a | 8.61 (s) | 3.94 (s) | 13.88 (s) | 2.38 (s) | | |
| 7 | 7.22-7.26 (m) | 6.89-6.92 (m) | $6.95 - 6.96 (t)^{a}$ | 6.82-6.86 (t) | 6.93-6.98 (dd) ^a | 8.55 (s) | 3.91 (s) | 13.90 (s) | 3.79 (s) | | |
| 8 | 7.28-7.30 (m) | 7.64-7.66 (m) | $7.01 - 7.04 \ (m)^a$ | 6.86-6.90 (t) | $7.01 - 7.04 \ (m)^a$ | 8.59 (s) | 3.90 (s) | 12.74 (s) | _ | | |

S = singlet, d = doublet, dd = double doublets, t = triplet, m = multiplet. TMS used as internal standard. ^a The peaks attributed to H2, H3, H5 and H6 atoms overlapped with each other giving rise to a doublet. ^b The peak for H7 atom overlapped with the peak for H9 atom.

| Table 7 | |
|--|--|
| 13 C NMR chemical shifts (ppm) of Schiff bases $1-8$ in CDCl ₃ | |

| Compounds | Chemical shifts (ppm) | | | | | | | | | | | | | | |
|-----------|-----------------------|---------------------|---------------------|---------------------|---------------------|---------------------|--------|--------|--------|--------|---------------------|--------|--------|-------|--------|
| | C1 | C2 | C3 | C4 | C5 | C6 | C7 | C8 | C9 | C10 | C11 | C12 | C13 | C14 | R |
| 1 | 151.87 | 121.59 ^a | 129.83 ^b | 127.42 | 129.83 ^b | 121.59 ^a | 115.18 | 118.97 | 124.25 | 119.58 | 148.47 | 145.30 | 163.03 | 56.57 | _ |
| 2 | 151.58 | 122.97 ^a | 116.67 ^b | 160.81 | 116.67 ^b | 122.97 ^a | 115.19 | 119.03 | 124.20 | 119.39 | 148.79 | 144.61 | 162.78 | 56.50 | - |
| 3 | 151.67 | 122.85 ^a | 129.87 ^b | 132.88 | 129.87 ^b | 122.85 ^a | 115.38 | 119.10 | 124.30 | 119.33 | 148.79 | 146.97 | 163.31 | 56.53 | - |
| 4 | 151.71 | 123.23 ^a | 132.87 ^b | 120.85 | 132.87 ^b | 123.23 ^a | 115.45 | 119.14 | 124.32 | 119.35 | 148.83 | 147.52 | 163.40 | 56.58 | - |
| 5 | 151.90 | 122.33 ^a | 125.63 ^b | 148.95 ^c | 125.63 ^b | 122.33 ^a | 116.24 | 119.08 | 124.69 | 119.55 | 148.95 ^c | 146.55 | 165.86 | 56.65 | - |
| 6 | 151.87 | 121.40 ^a | 130.43 ^b | 137.42 | 130.43 ^b | 121.40 ^a | 114.97 | 118.86 | 124.11 | 119.58 | 148.87 | 145.85 | 162.00 | 56.57 | 21.47 |
| 7 | 151.65 | 122.69 ^a | 114.99 ^b | 159.30 | 114.99 ^b | 122.69 ^a | 114.80 | 118.83 | 123.98 | 119.67 | 148.79 | 141.27 | 160.67 | 56.53 | 55.87 |
| 8 | 151.77 | 122.47 ^a | 133.89 ^b | 110.45 | 133.89 ^b | 122.47 ^a | 116.11 | 119.08 | 124.69 | 119.48 | 148.81 | 146.21 | 165.50 | 56.58 | 114.77 |

TMS used as internal standard.

^a C2' and C6' are equivalent.
^b C3' and C5' are equivalent.

^c Overlapped.

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favors the enol-imino form in the solution (CDCl₃) as that reported by Nazir and his coworkers [18]. This phenomenon has further been supported by NMR technique as that reported by Alarcon et al. [19] wherein the *ortho* hydroxy group attached to the aldehyde ring in HOC₆H₅CH=NC₆H₅ exists as an enol-imino tautomer when left in the solution (CDCl₃). A singlet assignable to the chemically and magnetically equivalent protons in methoxy group was observed at $\delta = 3.92$ ppm [20]. Compounds **2–8** show similar characteristic as those discussed in compound **1**.

The signal attributed to H7 atom in 1-8 appeared in different patterns (Table 6). It appeared as double doublets in compounds 1, 3–6, doublet in 2, triplet in 7 and as indisguishable multiplet in compound 8. Actually the signals assignable to H7 atom in compounds 1–7 occurred between a pair of doublets which resulted from the resonance of H9 atom. The complexity of this region is well confirmed through dimensional 2D heteronuclear-correlated spectroscopic technique (2D ¹³C–¹H HMQC) with the aid of 2D ¹H–¹H COSY experiment. The couplings between the different protons in 1–8 as inferred from the 2D COSY correlation studies are tabulated in Table 8. The representative spectra of 2D COSY experiment and the relationship between different protons in 2 are shown in Fig. 3.

Assignment of protonated carbons was made by two 2D ${}^{13}C-{}^{1}H$ HMQC experiment using delay values which corresponds to ${}^{1}J(C,H)$ [21,22]. From HMQC, CH₃ and CH carbons were assigned unambiguously (Table 7). Heteronuclear multiplebond correlation (${}^{1}H-{}^{13}C$ HMBC), a modified version of HMQC was applied on 7 in order to determine the long range ${}^{1}H-{}^{13}C$ connectivities [21,22]. The long range ${}^{1}H-{}^{13}C$ correlations for 7 (Table 9) and its two dimensional spectra are shown in Fig. 4.

Inspection from COSY and HMBC for 7 can be summarized as follows:

- (a) By 2D COSY experiment, hydroxyl proton (O– H) was found to be not correlated with any other protons.
- (b) However, observation from HMBC experiment showed that the hydroxyl proton (O–H) correlated with C1, C10 and C11 atoms.
- (c) The hydroxyl proton (O–H) was located nearer to C1 rather than H13 owing to the relationship observed for hydroxyl proton with C1 atom via ${}^{1}\text{H}{-}{}^{13}\text{C}$ correlation.

Table 8

| $^{1}H^{-1}$ | Η | correlations | from | 2D | COSY | for | Schiff | bases | 1 - 8 |
|--------------|---|--------------|------|----|------|-----|--------|-------|-------|
|--------------|---|--------------|------|----|------|-----|--------|-------|-------|

| Atom H | ¹ H ⁻¹ H COSY correlations | | | | | | | | |
|--------|--|---------------------------------|------------------|------------------|--------|-------------------------------|----------------|----------|--|
| | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | |
| 2 or 6 | 3 or 5, 7, 9, 14, Y | 3 or 5, 7, 9 | 3 or 5, 7 | 3 or 5, 7, 9 | 3 or 5 | 7, 9, 13, 14, Y | 3 or 5, 13, Y | 3 or 5 | |
| 3 or 5 | 2 or 6, 7, 13, Y | 2 or 6, 7, 9 | 2 or 6 | 2 or 6, 7, 9 | 2 or 6 | 7, 9, 13, 14, Y | 2 or 6, 13, Y | 2 or 6 | |
| 7 | 2 or 6, 8, 9 | 2 or 6, 3 or 5, 8, 9, 13, 14 | 2 or 6, 8, 9, 14 | 2 or 6, 8, 9, 14 | 8, 9 | 2 or 3 or 5 or 6, 8, 9, 14 | 8, 9, 14 | 8, 9 | |
| 8 | 7, 9 | 7, 9 | 7, 9 | 7, 9 | 7, 9 | 7, 9 | 7, 9 | 7, 9 | |
| 9 | 2 or 6, 7, 8, 13 | 2 or 6, 3 or 5, 7, 8, 13, 14 | 7, 8, 13 | 2 or 6, 7, 8, 13 | 7, 8 | 2 or 3 or 5 or 6, 7, 8, 13 | 7, 8 | 7, 8, 13 | |
| 13 | 3 or 5, 9 | 7, 9, 14 | 9 | 9 | - | 2 or 3 or 5 or 6, 9 | 2 or 6, 3 or 5 | 9 | |
| 14 | 7 | 7 | 7 | 7 | - | 2 or 3 or 5 or 6, 7, Y | 7 | - | |
| OH | - | _ | - | _ | _ | _ | _ | - | |
| Y | 2 or 6, 3 or 5 | - | - | - | - | 2 or 3 or 5 or 6, 14 | 2 or 6, 3 or 5 | - | |

Y = proton in the substituent R (1: R = H; 6: $R = CH_3$; 7: $R = OCH_3$).





Fig. 3. (a) Homonuclear ${}^{1}H-{}^{1}H$ 2D COSY spectrum, and (b) ${}^{1}H-{}^{1}H$ relationships as inferred from 2D COSY and supported by HMQC spectra of compound **2**.

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|---|
|---|

Table 9 $2D \ ^{1}H - \ ^{13}C \ HMQC$ and HMBC correlations for 7

| Atom | HMQC | HMBC [J(C, H)] | | | | | |
|------|---------|----------------|-------------|---------|-------------|--|--|
| | ^{1}J | ^{2}J | ^{3}J | ^{4}J | $^{intra}J$ | | |
| Y* | Z* | _ | C4 | _ | _ | | |
| H14 | C14 | - | _ | C11 | - | | |
| H8 | C8 | _ | C10 | C11 | _ | | |
| H3 | C3 | C4 | _ | - | C12, C13 | | |
| H5 | C5 | C4 | _ | _ | C12, C13 | | |
| H9 | C9 | _ | C11 | _ | C10 | | |
| H7 | C7 | _ | _ | _ | C13 | | |
| H2 | C2 | _ | _ | C4 | C12 | | |
| H6 | C6 | _ | _ | C4 | C12 | | |
| H13 | C13 | C10 | C1, C9, C11 | C12 | - | | |
| OH | - | C11 | C10 | - | C1 | | |

*Atoms in the R substituent whereby Y = hydrogen and Z = carbon intra = intramolecular interaction.

The summary from (a)-(c) suggest that the probable conformation for compound 7 in CDCl₃ solution can be depicted in Fig. 5.

The molecular structure as postulated for compound 7 shows that the azomethine proton was located at the other side opposing to the OH group. As such, the hydroxyl proton (O-H) lies nearer to the aromatic C1 atom, which is adjacent to the azomethine N imine atom.

3.3. X-ray crystal structures

From Fig. 1(a) and (b), the compounds can be described as comprising of central part of C=N bridging 3-methoxy-2-hydroxybenzaldehye and *para* substituted aniline fragments. The figures show that the azomethine proton of H4 and H2 in compounds **3** and **6** are lying on the other side opposite to



Fig. 4. The HMBC spectrum resulted from long range ${}^{1}H-{}^{13}C$ connectivities on Schiff base 7 (Y = proton in the substituent, in this case the methoxy group OCH₃).

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Fig. 5. The stereoisomer structure of compound 7 at ambient temperature in CDCl₃.

the hydroxyl protons H4 and H2, respectively. This result conforms with the postulated structure (Fig. 5) as inferred from the NMR spectra whereby the compound dissolved in CDCl₃. Data in Table 3 have clearly illustrated that the bond distance of C=N in compound **3** [1.301(7) Å] is found to be longer than that in its analogue 6 [1.272(6) Å]. This piece of information suggests that the bond strength associated with the effective charge of C=N bond in compound 6 is comparatively higher in comparison with that in compound 3. As such, the stretching frequency of C=N in compound 6 (1617 cm⁻¹) was found lying at higher frequency than compound **3** (1615 cm⁻¹). The elongation of C=N bond in compound 3 can also be substantiated from the presence of six-membered pseudoaromatic chelate rings which possess OH-C=C-C=N (enol-imino tautomer) heterodienic moieties. The rings are formed by an intramolecular hydrogen bond whereby the phenolic H atom (H12 in compound 3) appeared to be directed to the azomethine N atom, which resulted in a decrease in electron density at N1 atom. As a consequence, the bond strength of C=N become lesser than that in compound 6.

Fig. 1(a) and (b) also show that the phenolic H atoms in molecules **3** and **6** are located at phenolic O atom. This observation can be rationalized by the stabilization effects experienced by enol-imino tautomers as that discussed in IR section wherein the characteristic of C=N bonds in all compounds 1-8 were remained unchanged even though the strength of this bond was found to be altered from one compound to another owing to the presence of different substituents R in the aniline fragment. Although the bond distance of N1···H12(O1) in compound **3** [1.65(7) Å] is found to be much shorter than that in

its analogue 6 [1.95(3) Å], both compounds still exist as predominant form of enol-imines in solid state. One of the factors could be due to the position of phenolic H atom from azomethine N atom in compounds 3 and 6 resulting from the strain incurred by heteronuclear six-membered ring in which the bond angles O1-C11-C10 were found to be 121.7(4)° and 122.4(3)°, respectively. As such, both phenolic H atom in 3 and 6 were positioned at the distance not favourable for the formation of keto-imino tautomer. This result was also evident from the $N \cdots O$ atomic distances in compounds **3** [2.611(6) Å] and **6** [2.624(4) Å] which favoured the formation of enol-imines. The dominance of enol-imino tautomer in the presence compounds can also be exemplified by the range of C11-O1 bond length [1.335(5)-1.346(6) Å] (Table 4) which is comparable or higher than the single bond values in enols [1.333(7) Å] [23]. Another evidence could be deduced from the dihedral angles [C13-N1-C1-C2] of **3** (-13.6) and **6** [-27.2] which indicate that the present molecules are not coplanar. As a result, the transfer of the hydrogen in the ground state with small energy requirement is not likely to occur [24,25].

4. Supplementary material

Crystallographic data for the structures 3 and 6 in this paper have been deposited at Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK and can be obtained upon request. Structure factors table is available from the authors.

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