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# Pyridazine-based Schiff base ligands with $N_4O_xS_2$ (x = 2, 4) donor set atoms: Synthesis, characterization, spectral studies and <sup>13</sup>C chemical shifts computed by the GIAO-DFT and CSGT-DFT methodologies

## Hamid Khanmohammadi\*, Malihe Erfantalab

Department of Chemistry, Arak University, Arak 38156, Iran

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### 1. Introduction

Schiff base compounds have attracted considerable attention due to their impressive and useful chemical and physical properties [1–4]. The instant and enduring popularity of Schiff base compounds undoubtedly stem from the ease with which they can be synthesized and their wide ranging complexing ability [5–7]. On the other hand, a wide variety of Schiff base ligands and their metal complexes have been extensively investigated because of their potential applicability as catalyst [8–11], their magnetic properties [3,12] and so on.

Among the various Schiff base ligands, the heterocycle-coupled salicylaldimines have received special attention because of their mixed soft-hard donors (O, N and S donor sites), versatile coordination behavior [13–15] and their pharmacological properties [16–19]. Although the most straightforward protocol for synthesis of salicylaldimines is the condensation reaction of salicylaldehyde, or its derivatives, with the appropriate amines in high boiling point volatile organic solvents, this protocol often provides only low to moderate yields of products followed by extensive recrystallization and/or chromatography. This has led to the recent disclosure of several improved reaction protocols for synthesis of salicylaldimines,

#### ABSTRACT

Six pyridazine-based Schiff base ligands,  $H_2L^n$  (n = 1-5) and  $H_4L$ , with  $N_4O_2S_2$  and  $N_4O_4S_2$  donor set atoms, respectively, were prepared by condensation reaction of 3,6-bis-((2-aminoethyl)thio)pyridazine with various salicyladehyde derivatives in ethanol and under solvent-free polyphosphate ester catalyzed conditions. The acid-base properties of  $H_2L^2$  and  $H_2L^3$  in DMSO/water (1:1) solution have been studied by spectrophotometric method at 25 °C. Optimized geometries of all compounds were also obtained at the B3LYP level of theory. Additionally, the <sup>13</sup>C chemical shielding of gas phase  $H_2L^1$  and  $H_2L^2$  were studied by the gauge independent atomic orbital (GIAO) and continuous set of gauge transformations (CSGT) methods at the level of density functional theory (DFT). The 6-311++G\* basis set was utilized for all of the atoms.

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either by the solvent-free under microwave irradiation [20,21] or by the solvent-free acid-catalyzed conditions [22,23].

With the assistance of solvent-free acid-catalyzed conditions, it was found that the condensation reaction of salicylaldehyde and amines could proceed fast and efficiently with high yield. In addition, the absence of solvent reduces the risk of hazardous explosions when the reactions take place in a mild condition.

In order to promote conditions that would favor the formation and interception of bis-imine pyridazine-based salicylaldimine ligands we have now investigate the condensation reaction of 3,6-bis((aminoethyl)thio)pyridazine (PTA) with salicylaldehyde, 5-Br-salicyladehyde, 3-OH-salicylaldehyde, 3-MeO-salicylaldehyde, 3,5-di-(t-Bu)-butylsalicylaldehyde and 5-MeO-3-(t-Bu)-salicylaldehyde in boiling ethanol and also under solvent-free polyphosphate ester (PPE)-catalyzed condition (Scheme 1). The high yields and overall low waste generation of PPE-catalyzed solvent-free approach, gives this attractive green chemistry metrics along with remarkable versatility. The solid products were purified simply and characterized by spectroscopic methods (<sup>1</sup>H NMR, <sup>13</sup>C{<sup>1</sup>H} NMR, UV-vis and IR) as well as microanalysis.

The acid-base properties of the prepared compounds have also studied by monitoring of changes in the electronic absorption spectra in DMSO/water (1:1) solution at pH range of 2–11, as far as possible. The results indicated each two identical protons of the soluble compounds are liberated at basic condition.

<sup>\*</sup> Corresponding author. Tel.: +98 861 2777401; fax: +98 861 4173406. *E-mail address:* h-khanmohammadi@araku.ac.ir (H. Khanmohammadi).

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$H_2L^n$	$H_2L^1$	$H_2L^2$	$H_2L^3$	$H_2L^4$	$H_2L^3$	$H_4L$
$R_1$	Н	Н	OMe	t-Bu	t-Bu	OH
$\mathbf{R}_2$	Н	Н	Н	Н	Н	Н
$R_3$	Н	Br	Н	OMe	t-Bu	Н

Scheme 1. The synthesized compounds.

On the other hand, the comparison between experimental and theoretical NMR data may be helpful in making correct assignments and understanding the relationship between chemical shielding and molecular structure. Therefore, nowadays the Gauge Independent Atomic Orbitals/Density Functional Theory (GIAO/DFT) [24,25] and Continuous Set of Gauge Transformations/Density Functional Theory (CSGT/DFT) [26,27] approaches are widely used for the calculation of chemical shifts for a variety of compounds [28–31]. According to our knowledge, there are only few computational NMR studies on heterocycle-based Schiff base compounds [32,33]. At this work, the <sup>13</sup>C NMR isotropic chemical shieldings of gas phase  $H_2L^1$  and  $H_2L^2$  was also systematically studied by the GIAO and CSGT methods at the level of density functional theory (DFT) with 6-311++G\* basis set. The computed <sup>13</sup>C NMR chemical shieldings are compared with the experimental data.

### 2. Experimental

### 2.1. General information

All chemicals and solvents were of reagent grade and purchased commercially. 3,5-di-(t-Bu)-butylsalicylaldehyde [34], 5-MeO-3-(t-Bu)-salicylaldehyde [34], 3,6-bis((aminoethyl)thio)pyridazine (PTA) [35] and polyphosphate ester (PPE) [36] were prepared as described previously. <sup>1</sup>H and <sup>13</sup>C{<sup>1</sup>H} NMR spectra were obtained with a Bruker Avance 300 MHz spectrometer. Electronic spectral measurements were carried out using Perkin-Elmer Lamda spectrophotometer in the range 200–600 nm. The pH measurements were made using a Metrohm 691 pH meter equipped with a glass calomel combined electrode. Elemental analyses were performed on an Elementar Vario EL III elemental analyzer. Infrared spectra were recorded as pressed KBr discs,

using a Unicom Galaxy Series FT-IR 5000 spectrophotometer (400–4000  $\rm cm^{-1}$ ).

# 2.2. Procedure for pH dependence study of the electronic absorption spectra of $H_2L^n$ n = 1-5

To record electronic absorption spectra as a function of pH, the pH of the DMSO/water (1/1) solution containing each ligands, 25 mL of  $1.0 \times 10^{-5}$  M (for H<sub>2</sub>L<sup>1</sup>, H<sub>2</sub>L<sup>2</sup> and H<sub>2</sub>L<sup>4</sup>) and  $2.0 \times 10^{-5}$  M (for H<sub>2</sub>L<sup>3</sup>, H<sub>2</sub>L<sup>5</sup>), was adjusted in the range of 2–11 by adding hydrochloric acid and potassium hydroxide solutions, as far as possible. Then, the solution transferred through the flow cell and the absorbance at 190–800 nm was recorded at 1 nm increments. All experiments were carried out at the temperature  $(25 \pm 0.5)$ °C. After each pH adjustment, the spectra were recorded and data were collected for subsequent treatment. The calibration of the pH meter was done in the usual way using two standard buffer solutions (Metrohm) in aqueous media.

### 2.3. Theoretical calculations

The structures and NMR chemical shifts of the compounds were calculated using Gaussian 03 [37] series of programs. A starting molecular mechanics structure for the DFT calculations was obtained using the HyperChem 5.02 program [38]. The geometry of all compounds were fully optimized at the B3LYP/6-31G\* level. Vibrational frequency analyzes, calculated at the same level of theory, indicate that the optimized structures are at the stationary points corresponding to local minima without any imaginary frequency. The calculations of <sup>13</sup>C NMR chemical shieldings of H<sub>2</sub>L<sup>1</sup> and H<sub>2</sub>L<sup>2</sup> were performed using GIAO/DFT [24,25] and CSGT/DFT [26,27] methods at 6-311++G\* basis set. The <sup>13</sup>C NMR chemical shift was referenced to TMS.

Table 1Bis-imine isolated products.

Compounds	Solvent free, yield (%)	Ethanol, yield (%)
$H_2L^1$	82	70
$H_2L^2$	92	80
$H_2L^3$	90	76
$H_2L^4$	83	70
$H_2L^5$	76	56
H <sub>4</sub> L	75	60

# 2.4. General procedure for the solvent-free PPE-catalyzed synthesis of the compounds

In a typical solvent-free experiment, the 3,6bis((aminoethyl)thio)pyridazine (0.5 mmol) was added to the mixture of aldehyde (1 mmol) and PPE. The mixture was agitated at 40 °C (ca. 2 min), affording an oil (ranging from yellow to orange in colour). On further grinding (ca. 15 min) the solid product was formed. The product was washed with cooled *n*-hexane/ethanol (4/1), and dried in air. If required, analytically pure product can be obtained by recrystallization.

# 2.5. General procedure for the synthesis of the compounds in ethanol

A solution of 3,6-bis((aminoethyl)thio)pyridazine (1 mmol) in absolute EtOH (10 ml) was added to a stirring solution of aldehyde (2 mmol) in absolute EtOH (30 ml) at 50 °C over a period of 10 min. The solution was heated in water bath for 3 h at 70 °C with stirring, then cooled and let to stand at 0 °C. The obtained solid was filtered off, washed with cooled *n*-hexane/ethanol (4/1), and dried in air. The characterization data of the synthesized compounds are given in Tables 1 and 2.

### 2.5.1. 3,6-Bis((2-aminoethylsalicyliden)thio)pyridazine ( $H_2L^1$ )

 $^{1}\text{H}$  NMR (d<sub>6</sub>-DMSO, 300 MHz, RT, ppm):  $\delta_{\text{H}}$  3.59 (t, 4H), 3.90 (t, 4H), 6.88 (m, 4H), 7.31 (m, 2H), 7.46 (m, 4H), 8.57 (s, 2H), 13.22 (br, 2H).  $^{13}\text{C}\{^{1}\text{H}\}$  NMR (d<sub>6</sub>-DMSO, 300 MHz, RT, ppm):  $\delta_{\text{C}}$  167.4, 161.0, 158.6, 132.9, 132.1, 126.6, 119.01, 119.04, 116.9, 57.7, 30.8.  $\lambda_{\text{max}}$  (nm) ( $\varepsilon(\text{M}^{-1}\,\text{cm}^{-1})$ ): 269 (21230), 317 (5330) in DMSO.

# 2.5.2. 3,6-Bis((2-aminoethyl-5-Br-salicyliden)thio)pyridazine $(H_2L^2)$

<sup>1</sup>H NMR (d<sub>6</sub>-DMSO, 300 MHz, RT, ppm):  $\delta_{\rm H}$  3.58 (t, 4H), 3.93 (t, 4H), 6.83 (d, 2H, *J* = 8.80 Hz), 7.45 (dd, 2H, *J* = 8.80 Hz and 2.40 Hz), 7.47 (s, 2H), 7.66 (d, 2H, *J* = 2.40 Hz), 8.55 (s, 2H), 13.14 (br, 2H). <sup>13</sup>C{<sup>1</sup>H} NMR (d<sub>6</sub>-DMSO, 300 MHz, RT, ppm):  $\delta_{\rm C}$  166.1, 160.4, 158.5, 135.3, 133.9, 126.6, 120.7, 119.5, 109.6, 57.7, 30.6.  $\lambda_{\rm max}$  (nm) ( $\varepsilon$ (M<sup>-1</sup> cm<sup>-1</sup>)): 263 (29650), 322 (9290) in DMSO.

# 2.5.3. 3,6-Bis((2-aminoethyl-3-MeO-salicyliden)thio)pyridazine $(H_2L^3)$

<sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz, RT, ppm):  $\delta_{\rm H}$  3.58 (t, 4H), 4.04 (t, 4H), 3.77 (s, 6H), 6.80 (m, 2H), 7.01 (m, 4H), 7.49 (s, 2H), 8.55 (s, 2H),

13.44 (s, 2H). <sup>13</sup>C{<sup>1</sup>H} NMR (CDCl<sub>3</sub>, 300 MHz, RT, ppm):  $\delta_{C}$  168.3, 158.2, 151.7, 148.5, 125.9, 124.5, 123.1, 118.1, 114.3, 57.7, 56.1, 30.8.  $\lambda_{max}$  (nm) ( $\varepsilon$ (M<sup>-1</sup> cm<sup>-1</sup>)): 268 (30170), 329 (4890) in DMSO.

### 2.5.4.

# 3,6-Bis((2-aminoethyl-5-MeO-3-t-Bu-salicyliden)thio)pyridazine $(H_2L^4)$

<sup>1</sup>H NMR (d<sub>6</sub>-DMSO, 300 MHz, RT, ppm):  $\delta_{\rm H}$  1.34 (s, 18H), 3.60 (t, 4H), 3.88 (t, 4H), 3.69 (s, 3H), 6.86 (dd, 4H), 7.50 (s, 2H), 8.53 (s, 2H), 13.59 (s, 2H). <sup>13</sup>C{<sup>1</sup>H} NMR (d<sub>6</sub>-DMSO, 300 MHz, RT, ppm):  $\delta_{\rm C}$  168.1, 158.5, 154.5, 151.2, 138.2, 126.5, 118.2, 118.1, 112.4, 57.8, 55.8, 34.9, 30.2, 29.5.  $\lambda_{\rm max}$  (nm) ( $\varepsilon$ (M<sup>-1</sup> cm<sup>-1</sup>)): 268 (30650), 346 (9300) in DMSO.

## 2.5.5.

# 3,6-Bis((2-aminoethyl-3,5-di-t-Bu-salicyliden)thio)pyridazine $(H_2L^5)$

<sup>1</sup>H NMR (d<sub>6</sub>-DMSO, 300 MHz, RT, ppm)  $\delta_{\rm H}$ : 1.32 (s, 18H), 1.46 (s, 18H), 3.69 (t, 4H), 4.01 (t, 4H), 7.12 (s, 2H), 7.16 (br, s, 2H), 7.42 (d, 2H, *J*=2.10 Hz), 8.46 (s, 2H), 13.40 (br, 2H). <sup>13</sup>C{<sup>1</sup>H} NMR (d<sub>6</sub>-DMSO, 300 MHz, RT, ppm)  $\delta_{\rm C}$ : 167.5, 158.2, 153.5, 150.4, 137.2, 126.0, 120.1 117.6, 114.4, 57.4, 35.1, 34.2, 31.7, 30.1, 29.5.  $\lambda_{\rm max}$  (nm) ( $\varepsilon$ (M<sup>-1</sup> cm<sup>-1</sup>)): 267 (23700), 327 (5920) in DMSO.

# 2.5.6. 3,6-Bis((2-aminoethyl-3-OH-salicyliden)thio)pyridazine (H<sub>4</sub>L)

 $^{1}\text{H}$  NMR (d<sub>6</sub>-DMSO, 300 MHz, RT, ppm)  $\delta_{\text{H}}$ : 3.59 (t, 4H), 3.93 (t, 4H), 6.66 (m, 2H), 6.84 (m, 4H), 7.50 (s, 2H), 8.52 (s, 2H), 13.20 (br, 2H).  $^{13}\text{C}\{^{1}\text{H}\}$  NMR (d<sub>6</sub>-DMSO, 300 MHz, RT, ppm)  $\delta_{\text{C}}$ : 167.6, 158.5, 151.4, 146.3, 126.6, 122.4, 118.6, 118.3, 118.2, 56.8, 30.8.  $\lambda_{\text{max}}$  (nm) ( $\varepsilon(\text{M}^{-1}\,\text{cm}^{-1})$ ): 272 (28200), 332 (2900) in DMSO.

## 3. Result and discussion

The main goal of this work is the synthesis and characterization of six bis-imine pyridazine-based compounds (four of which are previously unpublished) by (i) a solvent-free PPE-catalyzed method and (ii) using organic solvent, ethanol, as a reaction medium. All prepared compounds are air stable solid and soluble in DMSO and DMF at ambient temperature. The characterization data are given in Section 2, Tables 1 and 2.

An overview of the synthetic details is summarized in Scheme 1. Typically in the solvent-free PPE-catalyzed reaction, the bis-imine product is formed in near-quantitative yield by low intensity grinding of the diamine with two molar equivalents of the aldehyde using a pestle and mortar over a period of ca. 15 min, associated with constant agitation of the mixture. During the reaction the product was formed as a yellow to orange solid. As the product solidifies from the reaction mixture, care needs to be taken to prevent it coating small quantities of the starting materials.

Analysis of the bulk product by <sup>1</sup>H and <sup>13</sup>C NMR show only the pure products (typically >90%) and the unreacted starting materials. Potential limitations in the solvent-free method may be overcome using ultra high intensity grinding in a

Tab	le 2	2

The characterization data of the prepared compounds.

Compounds	Color	Mol. formula	mp °C	Analysis (%) found (calculated)			
				С	Н	Ν	S
$H_2L^1$	Yellow	$C_{22}H_{22}N_4O_2S_2$	109–110	60.25 (60.1)	5.06 (4.8)	12.78 (12.5)	14.62 (14.7)
$H_2L^2$	Yellow	$C_{22}H_{20}Br_2N_4O_2S_2$	178-180	44.5 (44.31)	3.6 (3.38)	9.5 (9.39)	10.9 (10.75)
$H_2L^3$	Orange	$C_{24}H_{26}N_4O_2S_2$	142-143	57.7 (57.81)	5.4 (5.26)	11.3 (11.24)	12.7 (12.86)
$H_2L^4$	Cream	$C_{32}H_{42}N_4O_4S_2$	80-81	62.8 (62.91)	7.0 (6.93)	9.3 (9.17)	10.3 (10.50)
$H_2L^5$	Yellow	$C_{38}H_{54}N_4O_2S_2$	150-151	68.9 (68.84)	8.4 (8.24)	8.2 (8.45)	9.6 (9.67)
H <sub>4</sub> L	Orange	$C_{22}H_{22}N_4O_4S_2\\$	156–158	56.21 (56.15)	4.9 (4.71)	11.8 (11.91)	13.8 (13.63)

130 **Table 3** 

Tentative assignments of some selected IR<sup>a</sup> frequencies (cm<sup>-1</sup>) and UV-vis data of the prepared compounds.

Compound	ν(C-O)	$\nu$ (Ar–H)	ν(C=N/C=C)	v(Phenol ring)	ν(N–N)	$\lambda_{max}$ (nm) ( $\epsilon$ (M <sup>-1</sup> cm <sup>-1</sup> )) in DMSO
$H_2L^1$	1281	3065	1635, 1610, 1497	1578	1232	269 (21230), 317 (5330)
$H_2L^2$	1271	3050	1634, 1604, 1479	1570	1248	263 (29650), 322 (9290)
$H_2L^3$	1271	3062	1632, 1601, 1472	1466	1260	268 (30170), 329 (4890)
$H_2L^4$	1278	3040	1636, 1601, 1470	1451	1237	268 (30650), 346 (9300)
$H_2L^5$	1273	3030	1632, 1595, 1470	1441	1252	267 (23700), 327 (5920)
H <sub>4</sub> L	1252	3085	1643, 1586, 1460	1540	1220	272 (28200), 332 (2900)

<sup>a</sup> KBr disc.







Fig. 2. The electronic absorption spectra of protonated  $\rm H_2L^4$  in DMSO/water solution of pH 2–5.



Fig. 3. The electronic absorption spectra of protonated  $\rm H_2L^2$  in DMSO/water solution of pH 2–5.

ball mill. We predict that the implementation of a spinning disk/cylinder reactor will also lead to improved conversion without additional purification steps. Traces of PPE can be



Fig. 4. The pH-absorbance curve of  $H_2L^2$  (385 nm band).



Fig. 5. The electronic absorption spectra of ligands: (a)  $H_2L^2$  and (b)  $H_2L^3,$  in DMSO/water solution of different pH.



H<sub>4</sub>L Fig. 6. B3LYP/6-31G\* geometry optimized structure of compounds.

removed from the product by washing with small amount cooled n-hexane/ethanol (4/1). The obtained results are shown in Table 1.

The second method implemented in this study utilizes ethanol as an alternative solvent system without additional purification steps. Typically, the diamine and two molar equivalents of the aldehyde were heated in a minimal volume ( $\approx$ 40 ml) of ethanol and stirred until the reaction was complete, as determined by TLC. The pure product precipitates out of the reaction medium on cooling and can be collected by filtration. For comparison purposes the obtained results are shown in Table 1. It was found that significantly lower yields (8–20%) were obtained using in boiling ethanol rather than the solvent-free PPE-catalyzed method.

#### 3.1. IR spectra of the compounds

The positions of some of the prominent bands in the IR spectra of the prepared compounds and their assignments based on extensive data available for related compounds [39,40] are given in Table 3. The IR spectra of all compounds show bands at 1630–1660 and 1240–1280 cm<sup>-1</sup> assigned for  $v_s$  and  $v_{as}$  of the C=N and C–O groups, respectively. The band in the IR spectrum of H<sub>2</sub>L<sup>4</sup> at approximately 826 cm<sup>-1</sup> can be assigned to the C–Br stretching mode.

### 3.2. NMR spectra of the compounds

The <sup>1</sup>H NMR and <sup>13</sup>C $\{^{1}H\}$  NMR spectral results, obtained for all compounds at ambient temperature in d<sub>6</sub>-DMSO and/or CDCl<sub>3</sub>, are

given in Section 2. All compounds show a slightly broad singlet in the region  $\delta_{\rm H}$  13.10–13.60 ppm assigned to OH proton, as was confirmed by deuterium exchange when D<sub>2</sub>O was added to solutions. The CH=N imine protons exhibit a singlet resonance in the region  $\delta_{\rm H}$  8.40–8.60 ppm. The <sup>1</sup>H NMR spectra of all compounds show two set of triplets ( $\delta_{\rm H}$  3.58–3.61 and 3.90–4.05 ppm) assigned to the CH<sub>2</sub> protons ( ${}^{3}J_{H-H} \approx 5.50 \text{ Hz}$ ).

### 3.3. Electronic spectra of the compounds

The electronic spectra of  $H_2L^n$  (n = 1-5) in DMSO display main features at 265-272 and 315-345 nm (Fig. 1 and Table 1). The intense absorption band at short wavelengths may be assigned for  $\pi - \pi^*$  aromatic rings transitions [41]. The weak broad absorption band at 315–345 nm may be assigned to the n- $\pi^*$  and  $\pi$ - $\pi^*$ electronic transition associated with the C=N linkages [41].

### 3.4. The electronic absorption spectra of the prepared compounds in DMSO and in buffer solutions of different pH values

All of the prepared compounds contain available active centres for proton attacks and are appropriate for use as pH probes. In the light of previous studies of the acid-base properties of salicylaldimines [42],  $H_2L^n$  (n=1-5) ligands are to be considered as bi-basic acids while H<sub>4</sub>L would be tetra-basic acid. Protonation–deprotonation equilibrium of  $H_2L^n$  (n=1-5) ligands are shown as follows:

$$\underset{n=1-5}{\text{H}_2\text{L}^n \stackrel{K_1}{\rightleftharpoons} \text{H}_2\text{L}^{n-} + \text{H}^+, \quad \text{H}_2\text{L}^{n-} \stackrel{K_2}{\rightleftharpoons} \text{L}^{n2-} + \text{H}^+$$

The absorption spectra of  $H_2L^n$  (n=1-5) in DMSO/water (1:1) solution of pH 2-11 were investigated in the UV-vis region (200-600 nm). The obtained spectra indicate that the absorbance and position of the absorption bands changed with pH of the medium according to the following:

- 1. The extinction of the all bands of protonated forms of  $H_2L^1$ , H<sub>2</sub>L<sup>4</sup>, H<sub>2</sub>L<sup>5</sup> and H<sub>4</sub>L decreases with increasing pH. Unfortunately, the monitoring of electronic absorption spectra at pH > 5 in DMSO/water (1:1) solution of these compounds is impossible because of formation an unsoluble precipitate (Fig. 2).
- 2. Absorption spectra of  $H_2L^2$  and  $H_2L^3$ , in solution having pH < 5, showed two absorption bands with  $\lambda_{max} \approx 265 \text{ nm}$  and  $\lambda_{\text{max}} \approx 325 \text{ nm}$  corresponding to protonated forms of H<sub>2</sub>L<sup>n</sup> (n = 2, 3) (Fig. 3).

The extinction of these bands decrease with increasing pH values of solution while additional absorption band appeared at pH>5 with  $\lambda_{max} \approx 385 \text{ nm}$  corresponding to the (HL<sup>n</sup>)<sup>-</sup> and/or  $(L^n)^{2-}$  forms. The extinction of newly appeared band was increase with increasing pH values of the solution until pH 11. The changes of absorbance with pH of the solution (Fig. 4) lead to the appearance of isobestic point at  $\approx$ 350 nm for both H<sub>2</sub>L<sup>2</sup> and  $H_2L^3$  (Fig. 5) indicating the existence of an acid-base equilibrium between two different forms of these compounds as given above.

#### 4. Computational studies

In spite of our many efforts, single crystals suitable for Xray crystallography have not been obtained for newly prepared compounds. The structural parameters of all compounds were assessed by undertaking density functional theory calculations. This was done by undertaking a full geometry optimization at the B3LYP/6-31G\* level of theory. The calculations predicate a symmetric structure ( $C_s$  configuration) for  $H_2L^1$  and  $H_2L^2$ , which are

#### Table 4

Selected carbon chemical shifts ( $\delta$ , ppm) in d<sub>6</sub>-DMSO and calculated magnetic isotropic shielding tensors (s) for  $H_2L^1$  and  $H_2L^2$ .



Atoms	$H_2L^1$ , X = H			$H_2L^2$ , X = Br	
	$\sigma_{C}$ (Cal)	$\delta_C$ (Exp)		$\sigma_{C}$ (Cal)	$\delta_C$ (Exp)
C <sub>1</sub>	57.87ª 59.09 <sup>b</sup>	126.6	C <sub>1</sub>	61.14 61.76	126.6
C <sub>2</sub>	12.72	158.6	C <sub>2</sub>	8.49 10.71	158.5
C <sub>3</sub>	138.65	30.8	C <sub>3</sub>	141.70	30.6
C <sub>4</sub>	118.39	57.7	C <sub>4</sub>	117.52	57.7
C <sub>5</sub>	20.04	167.4	C <sub>5</sub>	16.59 17.23	166.1
C <sub>10</sub>	21.62	161.0	C <sub>7</sub>	47.13	109.6
C <sub>11</sub>	56.33 59.20	116.9	C <sub>10</sub>	19.04	160.4
	22.20		C <sub>11</sub>	54.06 55.73	120.7

<sup>a</sup> Computed data at GIAO, B3LYP/6-311++G\* for all atoms.

<sup>b</sup> Computed data at CSGT, B3LYP/6-311++G\* for all atoms.

closely related to the structure of these compounds in solution. The resulting optimized structures and atom numbering are displayed in Fig. 6. The selected bond lengths, bond angles and torsion angles of the minimum energy structures are given in Table 4.

The <sup>13</sup>C NMR chemical shifts of selected carbons were calculated on the optimized structures of H<sub>2</sub>L<sup>1</sup> and H<sub>2</sub>L<sup>2</sup> using GIAO/DFT and CSGT/DFT methods with 6-311++G\* basis set for all atoms. Calculated and measured <sup>13</sup>C chemical shifts of selected atoms are tabulated in Tables 3 and 4.

The following conclusions can be straightforwardly derived based on presented data. On an absolute scale, the computed NMR chemical shifts for  $H_2L^1$  and  $H_2L^2$  at the DFT level of theory are in acceptable agreement with the experimental data. Differences between the calculated and measured values may be a result of solvent interactions. Regarding the method for achievement of <sup>13</sup>C chemical shifts, for the present case, at the B3LYP level, the CSGT algorithm is slightly superior to GIAO. The relation between the experimental <sup>13</sup>C chemical shifts and the computed (CSGT/DFT method) magnetic isotropic shielding tensors for  $H_2L^1$  and  $H_2L^2$ are shown in Fig. 7. The correlation is linear and it is described by the equation:

$$\delta_{\exp} = a + b\sigma$$

Parameters *a* and *b* for  $H_2L^1$  and  $H_2L^2$  are

$$\delta_{13C} = -0.9802\sigma + 177.4(R^2 = 0.9758)$$
 for H<sub>2</sub>L<sup>1</sup>

and

$$\delta_{13c} = -1.0094\sigma + 177.4(R^2 = 0.9553)$$
 for H<sub>2</sub>L<sup>2</sup>



**Fig. 7.** Plot of experimental chemical shifts *vs.* magnetic isotropic shielding tensors from the CSGT B3LYP/6-311++G<sup>\*</sup> calculation: (a)  $H_2L^1$  and (b)  $H_2L^2$ .

#### 5. Conclusion

During this feasibility study, we found that solvent-free PPEcatalyzed method is a general, eco-friendly and straightforward method for the library synthesis of pyridazine-based Schiff bases  $(H_2L^n, n = 1-5 \text{ and } H_4L)$ . The acid-base behavior of  $H_2L^2$  and  $H_2L^3$  in DMSO/water (1:1) solution indicated that each two identical protons from both sides of the molecule are liberated at basic condition.

The <sup>13</sup>C NMR chemical shieldings of gas phase  $H_2L^1$  and  $H_2L^2$  were systematically studied by GIAO/DFT and CSGT/DFT methods. The CSGT <sup>13</sup>C relative shift values correlate better with the experimental ones than the GIAO. The proposed approach can be potentially useful in an extended way to predict the chemical shifts of the heterocycle-based Schiff bases.

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