

## Experimental and theoretical characterization of a new Schiff-base ligand

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Abstract- Here, new N,N'-dipyridoxyl(4,4'-diaminodiphenylether) Schiff-base ligand has been synthesized and characterized by IR, <sup>1</sup>H NMR and mass spectrometry. Also, geometry optimization and theoretical assignment of IR spectrum of the ligand have been computed by employing density functional theory (DFT) method. Two pyridine rings and benzene rings in the bridge region are not in the same plane. The calculated results are good in agreement with the experimental ones, confirming validity of the optimized structure for the ligand.

**Keywords:** DFT; IR Assignment; NMR; Schiff base; Dipyridoxyl

## INTRODUCTION

Study on the Schiff-base compounds is of great importance from different aspects, the most significant of which are: versatile metal bonding ability [1-4], biological activities [5-8] and industrial uses as catalyst [9-10] and dyes [11].

The Schiff bases of pyridoxal and their metal complexes show attractive biological activities due to the pyridoxal is a close analogue of pyridoxine [12]. In this work, we report the synthesis and experimentally characterization of the N,N'-dipyridoxyl(4,4'-diaminodiphenylether) = **H<sub>2</sub>L** Schiff-base ligands by IR, <sup>1</sup>H NMR and mass spectrometries.

Also, geometry optimizations and theoretical assignment of the IR spectrum of the ligand have been calculated using DFT method, which is widely used in investigation of kinetics and mechanism of the chemical reactions [13-15] and identification of the chemical compounds [16-21].

## EXPERIMENTAL

*Materials and methods*

All of used chemicals and solvents were purchased from Merck except for pyridoxal hydrochloride which obtained from Fluka. They were used as received. Melting points were determined by using an electrothermal 9100 melting point apparatus. The IR spectra were recorded on a Perkin Elemer 783 infrared spectrophotometer. The  $^1\text{H}$  NMR spectra were recorded on a Bruker Drx-500 Avance spectrometer (500.13 MHz), with  $(\text{CD}_3)_2\text{CO}$  as a solvent. Mass spectra were scanned on a Shimadzu-GC-Mass-Qp 1100 Ex.

#### *Synthesis of the ligand*

Pyridoxal hydrochloride (3mmol) was dissolved in 5 mL of methanol, and then was added to methanolic NaOH (3mmol in 5 mL). This mixture was stirred for a few minutes. Then, a methanolic solution of 4-(4-aminophenoxy)benzenamine (1.5 mmol in 5 mL) was slowly added to the mixture. The mixture was stirred for 5 hours. The yellow solid was filtered, washed with cold methanol and dried in air (Yield: 76.7, and Decomp. P.: 197.5 °C,  $m/z$  ( $\text{M}^+$ ) = 498).

#### *Computational Methods*

In this work, all calculations have been performed by using the B3LYP functional [22] of the DFT method and 6-31G(d,p) basis sets. The Gaussian 98 program package [23] was used with its default procedures.

Geometry of the ligand was fully optimized, which confirmed that has no imaginary frequency of the Hessian. Theoretical vibrational frequencies of the ligand have been calculated on the its optimized geometry.

## **RESULT AND DISCUSSION**

### *Chemistry*

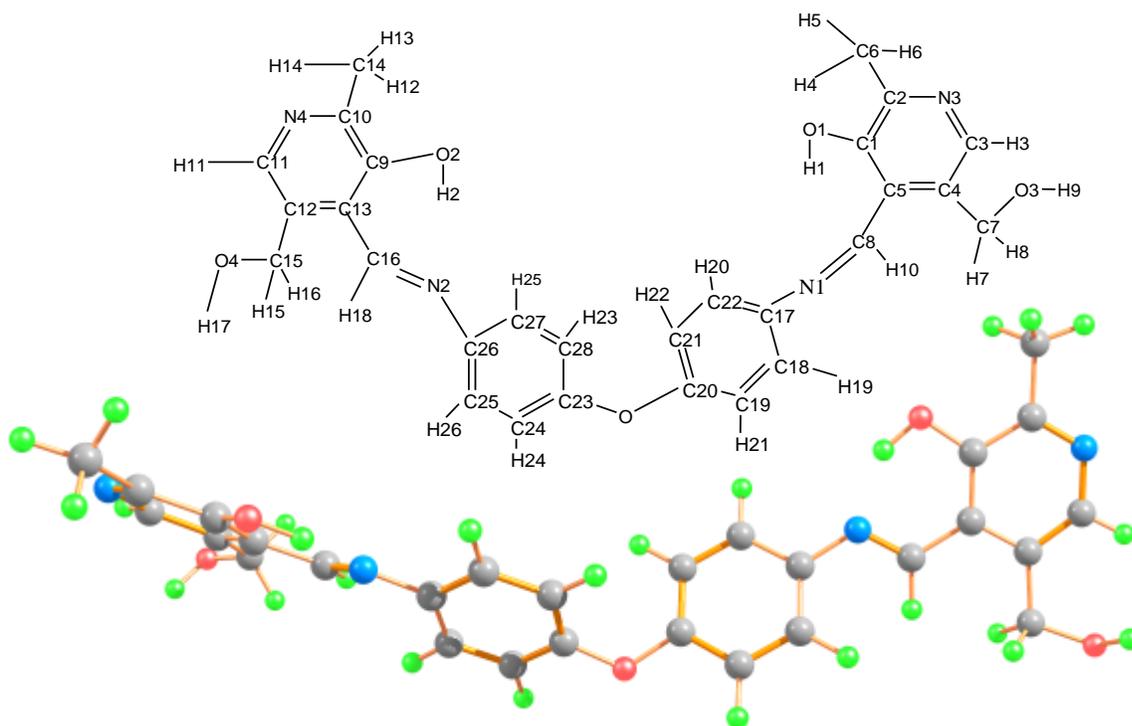
The new synthesized **H<sub>2</sub>L** Schiff-base ligand was characterized by the spectroscopic approaches (IR,  $^1\text{H}$  NMR and Mass). The decomposition mass losses of the ligand were found in consistent with the proposed formula weight. Also, the DFT approach was employed for identification of the new synthesized ligand.

### *Geometry optimization*

No single crystal has been obtained for the investigated ligand. Therefore, geometry optimization can be used as a replacement procedure for the X-ray analysis in determination of its structural parameters. The optimized structure of the **H<sub>2</sub>L** ligand with labeling of its atom is shown in Fig. 1. The calculated

structural parameters of the ligands are consistent with the values reported for the similar compounds [18-20,24,25].

As seen in Fig. 1, the pyridine rings are not essentially in the same plane, but make a dihedral angle of about  $103^\circ$  to each other. The calculated C1-O1-O2-C9 and C8-N1-N2-C16 dihedral angles are  $-104.3$  and  $97.2^\circ$ , respectively. The benzene rings are twisted relative to each other, so that they are not in the same plane. The calculated C18-C21-C24-C27 dihedral angle is  $105.3^\circ$ . Also, the benzene rings are not in the same plane with the pyridine rings. The dihedral angle between C=N azomethine and benzene ring is about  $37^\circ$ . In the bridge region, an oxygen atom bonds two benzene rings, where the C-O bond length and C-O-C angle are 139.8 pm and  $120^\circ$ , respectively.



**Figure 1.** B3LYP optimized geometry of the N,N'-dipyridoxyl(4,4'-diaminodiphenylether) ligand together with their labeling.

The pyridine rings are essentially planar and the bond distances of C=C (141.5 pm) and C=N (129.8 pm) bonds in these rings are in the expected range [26]. The pyridine-carbon bond lengths for the –CH<sub>2</sub>OH and –CH<sub>3</sub> substitutions are 153.2 and 1520.1 pm, respectively, which are appropriate sizes for the pyridine-carbon bond. The substituted groups are essentially in the same plane with the pyridine rings. For example, the calculated C6-C2-C1-C5, C7-C4-C5-C1 and H11-C11-N4-C10 dihedral angles

are 179.9, 179.8 and 179.2°, respectively. Also, the C=N azomethine bonds are essentially in the same plane with the pyridine rings, But make a dihedral angle about 42° with the plane of benzene ring.

The phenolic hydrogens are engaged in the intramolecular-hydrogen-bond interactions with the azomethine-nitrogen atoms, which elongates the phenolic O-H bonds. The calculated OH...N distances of the ligand are about 171.7 pm, showing a strong hydrogen bonds. The calculated parameters are well in agreement with the reported values for the similar compounds [18-20,24,25].

#### *<sup>1</sup>H NMR spectra*

The <sup>1</sup>H NMR chemical shifts (δ) of the **H<sub>2</sub>L** Schiff-base ligand are given in Table 1, where the atom positions are numbered as in Fig. 1. The appearance of a signal at about 14 ppm is attributed to the phenolic protons (H1, H2), where their engagement in the intramolecular hydrogen bond interaction (O-H...N), shifts their signals upfield [18-20].

**Table 1.** The <sup>1</sup>H NMR chemical shifts of the **H<sub>2</sub>L** ligand in (CD<sub>3</sub>)<sub>2</sub>CO solution, δ [ppm].

Atom position	δ
H methyl	2.42
H (CH <sub>2</sub> )	4.78
H <sub>9</sub> ,H <sub>17</sub>	5.45
H <sub>19</sub> ,H <sub>20</sub> ,H <sub>25</sub> ,H <sub>26</sub>	7.18
H <sub>21</sub> ,H <sub>22</sub> ,H <sub>23</sub> ,H <sub>24</sub>	7.58
H <sub>3</sub> , H <sub>11</sub>	7.99
H <sub>10</sub> , H <sub>18</sub>	9.18
H <sub>1</sub> ,H <sub>2</sub>	13.91

#### *Vibrational spectroscopy*

Theoretical description of vibrational spectra is of practical importance for the identification of compounds and has become an important tool of spectrochemical investigations [18-20,27]. The IR spectrum of N,N'-dipyridoxyl(4,4'-diaminodiphenylether) ligand was analyzed by comparing its vibrational modes with those from the literature reports [28-33] together with the results of our DFT calculations. The selected vibrational frequencies of the ligand are gathered in Table 2. As seen, the calculated results are in good agreement with the experimental values, confirming suitability of the optimized geometry of the studied ligand.

**Table 2.** Selected experimental and calculated IR vibrational frequencies ( $\text{cm}^{-1}$ ) of the **H<sub>2</sub>L** ligand.

frequencies ( $\text{cm}^{-1}$ )		Vibrational assignment
Exp	Cal.	
852 (m)	869	$\delta_{\text{op}}(\text{O-H})$ phenolic
982 (w)	1025	$\delta_{\text{ip}}(\text{C-H})$ benzene
1041 (m)	1064	$\delta(\text{C-H})$ Me + $\nu(\text{ph-C})$
1056 (m)	1101	$\nu_{\text{asym}}(\text{py-C-O})_{\text{alcoholic}}$
1185 (m)	1218	$\nu(\text{C-C}, \text{C-N})$
1222 (vs)	1265	$\nu_{\text{asym}}(\text{C-O-C})_{\text{bridge}}$
1283 (m)	1322	$\nu(\text{ph-C})$
1421 (s)	1427	$\nu(\text{C-O})$ phenolic
1510 (vs)	1533	$\nu(\text{pyridine ring})$
	1518	$\nu(\text{benzene ring})$
1631 (s)	1660	$\nu(\text{C=N})_{\text{azomethine}}$
2775	2987	$\nu_{\text{sym}}(\text{CH})_{\text{alcoholic}}$
	3032	$\nu_{\text{sym}}(\text{CH})$ Me
	3072	$\nu(\text{C}_8\text{H}_{10}) + \nu(\text{C}_{16}\text{-H}_{18})$
2865	3079	$\nu_{\text{asym}}(\text{CH})$ Me
	3179-3201	$\nu(\text{C-H})$ aromatic
3189 (br,s)	3186	$\nu(\text{O-H})$ phenolic
	3821	$\nu(\text{O-H})$ alcoholic

The very intensive band in the 1660-1500  $\text{cm}^{-1}$  region of the IR spectra is a diagnostic of the Schiff-base ligands [18-20,28-30,33]. For the ligand, this band is appeared at 1631  $\text{cm}^{-1}$ , respectively, which is related to the stretching modes of the azomethine C=N bonds.

In the 3600-2000  $\text{cm}^{-1}$  region of the IR spectra, overlapping of stretching vibrations of the O-H and C-H bonds leads to band broaden [31-33]. The deconvolution of which is given in Table 2. The most intensive bands of the ligands are related to the stretching vibrations of the phenolic O-H bonds. Also, the stretching vibrations of the aromatic C-H bonds involve lower frequencies than the aliphatic ones. In the IR spectrum of the ligand, a strong and broad band was appeared at 1510  $\text{cm}^{-1}$ , which arises from overlapping of the stretching vibrations of the aromatic rings (Table 2).

## CONCLUSION

In this work, new N,N'-dipyridoxyl(4,4'-diaminodiphenylether) Schiff-base ligand has been synthesized and experimentally characterized. Also, the optimized structure and IR vibrational frequencies of the ligand have been calculated using the DFT method. The obtained results are in good agreement with the experimental evidence, confirming suitability of the optimized geometry for the ligand.

Structure of the ligand is not planar, but the benzene and pyridine rings are not in the same plane. However, the substituted groups are in the same plane with the pyridine rings. The phenolic protons are engaged in the intramolecular-hydrogen bonds with the azomethine nitrogens, which results in weakness of the phenolic O-H bonds.

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