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N,N'-dipyridoxyl Schiff bases: Synthesis, experimental and theoretical characterization

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ABSTRACT

Three N,N'-dipyridoxyl Schiff bases (**L1**, **L2** and **L3**) have been newly synthesized and characterized by IR, ¹H NMR, mass spectrometry and elemental analysis. Their optimized geometries together with the theoretical assignment of the vibrational frequencies and the ¹H NMR chemical shifts of them have been computed by using density functional theory (DFT) method. In the optimized structures of the Schiff bases, two pyridine rings are not in a same plane; however the substitutions are essentially in the same plane with the pyridine rings. Also, the benzene ring(s) in the bridge region is (are) not in the same plane with the pyridine rings and azomethine moieties. In all the species, engagement in intramolecular-hydrogen bonds causes to weakness of the phenolic O–H bonds. Consistency between the theoretical results and experimental evidence confirms suitability of the optimized geometries for the synthesized Schiff bases.

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1. Introduction

Due to their structural varieties and very unique characteristics Schiff bases are the most versatile studied ligands in coordination chemistry [1,2]. Also, because of a variety of applications, including biological [3–5], analytical [6] and industrial use as catalysts [7], the Schiff-base ligands and their complexes are of great importance.

From biological point of view, study on the Schiff bases of pyridoxal and their metal complexes are attractive from different aspects, the significance of which are: the pyridoxal is a close analogue of pyridoxine (Vitamin B_6) [8], the manganese dipyridoxyl diphosphate is a contrast agent for magnetic resonance imaging of the liver [9,10], use of a copper(II) complex of pyridoxal in the treatment of diabetic complications [11], and so on.

In continuation of our studies [12,13], here we report the synthesis and characterization of three dipyridoxyl Schiff bases by IR, ¹H NMR, mass spectrometry and elemental analysis. The newly synthesized Schiff bases are N,N'-dipyridoxyl (1,2-diphenyldiamine)=**L1**, N,N'-dipyridoxyl (2,4-toluendiamine)=**L2** and N,N'-dipyridoxyl (4,4'-diaminodiphenylether)=**L3**. Also, geometry optimizations and theoretical assignment of the IR and ¹H NMR spectra of them have been performed using DFT method, which is widely used as a remarkable method in many areas of the

computational chemistry, such as kinetics and mechanism studies, spectroscopic assignments and so on [12–19].

2. Experimental

2.1. Materials and methods

All the chemicals and solvents were purchased from Merck except for pyridoxal hydrochloride which obtained from Fluka. They were used as recieved. The IR spectra were recorded on a Perkin Elemer 783 infrared spectrophotometer. Melting points were determinated by using an electrothermal 9100 melting point apparatus. Elemental analysis (C, H, N) was performed on a Heraeus elemental analyzer CHN-O-Rapid. Mass spectra were scanned on a Shimadzu-GC-Mass-Qp 1100 Ex. The ¹H NMR spectra were recorded on a Bruker Drx-500 Avance spectrometer (500.13 MHz), with (CD₃)₂CO as a solvent.

2.2. Synthesis of the Schiff bases

Pyridoxal hydrochloride (611 mg, 3mmol) was dissolved in 5 mL of methanol, and then was added to a methanolic solution of Et_3N (303 mg, 3 mmol in 5 mL). This mixture was stirred for a few minutes. Then, a methanolic solution of diamine (1.5 mmol in 5 mL) was slowly added to the mixture, where diamine is benzene-1,2-diamine, 4-methylbenzene-1,3-diamine and 4-(4-aminophenoxy)benzenamine for the **L1**, **L2** and **L3** Schiff bases, respectively. The mixture was stirred for 5 h. The solid was filtered,

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washed with cold methanol and dried in air (for L1, L2 and L3: Yield: 77, 73 and 89%, respectively, and Decomp. P.: 199, 208.5 and 197.5 °C, respectively).

2.3. Computational details

All the present calculations have been performed by using the gradient-corrected DFT method with the B3LYP functional [20], where the 6-311+G(d, p) basis set was employed. The Gaussian 98 program package [21] was used with its default procedures.

First, geometries of the Schiff bases were fully optimized in the gas phase. The optimized geometries were confirmed to have no imaginary frequency of the Hessian. Then, the gas phase optimized geometries were used to compute theoretical vibrational frequencies of them. The use of finite basis sets and incomplete treatment of electron correlation result in the higher DFT vibrational wavenumbers in comparison with the experimental ones. This can be corrected by applying the scaling of wavenumbers. Here, the scale factor of 0.9614 was used for calculated wavenumbers [22]. Also, their ¹H NMR chemical shifts were predicted with respect to tetramethylsilane. The GIAO method was used for prediction of the DFT nuclear shielding [23].

3. Results and discussion

3.1. Chemistry

The newly synthesized Schiff bases (**L1**, **L2** and **L3**) were characterized by the elemental and spectroscopic analysis (IR, ¹H NMR and Mass).

Theoretical investigation of the IR and NMR spectra can be employed as an important tool for identification of chemical species, especially analyzing of proposed geometries for compounds with undetermined X-ray structure [12–16,22]. Here, we used this approach for identification of the newly synthesized compounds.

3.2. Elemental analysis and mass spectroscopy

The elemental analysis results of the **L1–L3** species are given in Table 1, serving as a basis for the determination of their empirical formulas. Also, the mass losses of the compounds were found in consistent with the proposed formulas, which may be taken as extra evidence for the correctness of these formulas. The molecular ion peaks, m/z (M⁺), observed in the mass spectra of the synthesized Schiff bases are given in Table 1.

3.3. Geometry optimization

No single crystal has been obtained for the investigated compounds. Hence, their structural parameters have been determined theoretically. The optimized structures of the **L1–L3** species with labeling of their atoms are shown in Fig. 1. From structural point of view, the most difference between them is the –N–R–N– region, which bridges two pyridoxal moieties. The selected structural parameters of the Schiff bases are gathered in Table 2, which are in agreement with the structural data reported for the similar compounds [10,11,24–31].

As seen, the optimized structure of the **L1** molecule is V shape. Each of the benzene ring and two pyridine rings are in a separate plane, where the pyridine rings make approximately a 20° dihedral angle to each other. For example, the calculated N3–C5–C13–N4 and C1–O1–O2–C9 dihedral angles are 22.4 and –170.5°, respectively. In the bridge region, the azomethine nitrogens are bonded to the *ortho* positions of the benzene ring. In comparison with the species **L1**, other notable changes are observed in the shape of the **L2**, where the planes of two pyridine rings are perpendicular to each other. The calculated C2–C4–C10–C12 and C8–N1–N2–C16 dihedral angles are 98.7 and 89.7° , respectively.

In the species L3, longer bridge causes more deformation in its molecular structure. The pyridine rings make a dihedral angle of about 100° to each other. The calculated C1–O1–O2–C9 and C8–N1–N2–C16 dihedral angles are –102.9 and 98.7°, respectively. The benzene rings of the L3 species are twisted relative to each other, so that they are not in the same plane. For example, the calculated C17–C19–C24–C18 dihedral angle is 65.5°. 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 35° . In the bridge region, an oxygen atom binds two benzene rings, where the C–O bond length and C–O–C angle are 138.0 pm and 121°, respectively.

In the structure of each of three Schiff bases: the pyridine rings are essentially planar, where the bond lengths of C=C (141.2–141.7 pm) and C=N (128.9 pm) bonds are in the expected range [28]. The pyridine–C bond lengths for the –CH₂OH and –CH₃ substitutions are 152.1 and 150.2 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 azomethine moieties are essentially in the same plane with the pyridine rings, but make a dihedral angle about 40° with the benzene ring. The C8–N1–C17–C19 dihedral angle is 42°.

In all of the three species, the phenolic –OH groups are essentially in the same plane with the corresponding pyridine rings (Table 2). 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 species **L1–L3** are about 171.7 pm, showing a strong hydrogen bonds. Due to this interaction, the phenolic O–H bonds are longer than the alcoholic ones (96.3 pm). The calculated parameters for the investigated compounds are in agreement with the previously reported values for the similar compounds [10,11,24–31].

In the metallic complexes, the dipyridoxyl Schiff-bases act usually as a dianionic tetra dentate ligand in N,N,O⁻,O⁻ manner, via phenolic oxygens and azomethine nitrogens. According to the optimized geometries, complexation tendencies of the species is expected to be of order of L1 > L2 > L3. Since, the steric hindrance around the coordinating nitrogens increases from the L1 to L3 species.

3.4. ¹ H NMR spectra

The experimental and theoretical ¹H NMR chemical shifts (δ) of the **L1**, **L2** and **L3** Schiff bases are given in Table 3, 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 [12,13,32].

The calculated chemical shifts are in good agreement with the experimental values, confirming suitability of the optimized geometries for the species **L1–L3**. The only exception is the chemical shift of the H9 and H17 atoms, where the calculated chemical shifts are significantly lower than the experimental ones. These alcoholic protons may be engaged in intermolecular hydrogen bonds. On the other hand, the experimental data are from (CD₃)₂CO solutions but the calculations correspond to the isolated molecule

Table 1

The CHN analysis and the molecular ion peak of the species L1-L3.

Compound	Calculation			Found			$m/z (\mathrm{M}^+)$
	С	Н	N	С	Н	N	
$L1 = C_{22}H_{22}N_4O_4$	65.00	5.47	13.79	64.78	5.34	13.43	406
$L2 = C_{23}H_{24}N_4O_4$	65.69	5.76	13.33	65.13	5.76	13.27	420
$L3 = C_{28}H_{26}N_4O_5$	67.45	5.27	11.24	67.18	5.24	11.37	498



Fig. 1. The B3LYP optimized geometries of the L1, L2 and L3 N,N'-dipyridoxyl Schiff bases.

in the gas phase. Obviously, the solvent molecules interact with the alcoholic protons.

3.5. Vibrational spectroscopy

The selected vibrational frequencies of the species **L1–L3** together with their intensities are gathered in Table 4. The vibrational modes were analyzed by the results of DFT calculations and the previously reported data [12,13,24–30]. As seen, the calculated results have good consistency with the experimental ones. In the infrared spectra of the investigated species, a strong doublet band is appeared at $1100-1020 \,\mathrm{cm^{-1}}$, deconvolution of which is given in Table 4. The very intensive band in the $1660-1500 \,\mathrm{cm^{-1}}$ region is diagnostic of the IR spectra of Schiff bases [12,13,24-27]. For the **L1** to **L3** Schiff bases, this band is appeared at 1612, 1623 and $1631 \,\mathrm{cm^{-1}}$, respectively, which is related to the stretching modes of the azomethine C=N bonds.

In the $3600-2000 \,\mathrm{cm}^{-1}$ region of the IR spectra, overlapping of stretching vibrations of the O–H and C–H bonds leads to band broadening [30,33], the deconvolution of which is given in Table 4. The most intensive bands are related to the stretching vibrations

Table 2 Calculated structural parameters for the species L1–L3.

	L1	L2	L3		L1	L2	L3
Bond lengths (pm)				Dihedral angles (°)			
C1-01	133.9	134.0	134.1	H1-O1-C1-C5	-1.5	-0.3	-0.7
C1-C2	141.7	141.2	141.6	01-C1-C5-C8	0.5	-0.3	0.5
C2-N3	132.4	132.5	132.5	C1-C2-N3-C3	-0.2	0.2	-0.3
C2-C6	150.2	150.2	150.2	C3-N3-C2-C6	-179.8	-179.9	180.0
C5-C8	145.4	145.5	145.5	C1-C5-C4-C7	-179.8	179.9	180.0
C8-N1	128.9	128.9	128.9	C2-C1-C5-C8	-179.4	179.4	-179.4
N1-C17	140.5	140.9	140.7	C1-C5-C8-N1	-0.1	-0.2	0.3
N1-N2	276.1	484.8	997.0	01-N1-N2-02	48.1	42.9	-46.5
01-02	408.0	879.4	1326.6	C1-01-02-C9	-170.5	-98.6	-102.9
01-H1	99.4	99.4	99.4	C8-N1-C17-C19	42.0	36.9	34.1
N1-H1	171.6	171.8	171.7				
N1-01	260.5	261.0	260.8				
Angles (°)							
H1-01-C1	107.6	107.4	107.4				
01-C1-C5	122.8	122.6	122.7				
C1-C5-C8	120.3	120.4	120.4				
C5-C8-N1	122.1	122.3	122.1				
C1-01-02	110.7	133.3	138.8				
C8-N1-N2	143.7	144.8	148.8				

Table 3

Experimental and theoretical ¹H NMR chemical shifts of the L1–L3 in (CD₃)₂CO solution, δ [ppm].

L1			L2			L3		
Atom position	Exp.	Theo.	Atom position	Exp.	Theo.	Atom position	Exp.	Theo.
H17	5.32	0.17	H17	5.46	0.12	H17	5.45	0.08
H9	5.32	0.24	H9	5.46	0.18	H9	5.45	0.13
H ^a	2.58	2.61	H ^b	2.40	1.9	H ^a	2.42	2.57
H (CH2)	4.92	5.13	H ^a	2.43	2.57	H (CH2)	4.78	5.1
H°	6.96	7.03	H ^a	2.45	2.62	H21, H26	7.18	7.07
H ^m	7.56	7.48	H (C15–H)	4.79	5.07	H ^c	7.58	7.26
H3, H11	8.02	8.59	H (C7–H)	4.82	5.12	H3, H11	7.99	8.48
H10, H18	9.28	8.93	H19	7.44	6.88	H10, H18	9.18	8.71
H2	13.95	13.11	H20	7.46	6.98	H2	13.91	13.62
H1	13.95	13.24	H21	7.59	7.37	H1	13.91	13.66
			H3	8.00	8.51			
			H11	8.02	8.52			
			H10	9.19	8.61			
			H18	9.22	8.74			
			H2	13.92	13.60			
			H1	13.98	13.82			

 H^a = methyl hydrogen of the pyridine-substituted rings; H^b = methyl hydrogen of the methyl-substituted benzene ring; H^c = H_{19} - H_{20} and H_{22} - H_{25} atoms; H^m = *meta* hydrogen of benzene with respect to the N atom; H^o = *ortho* hydrogen of benzene with respect to the N atom.

Table 4

Selected experimental and calculated IR vibrational frequencies (cm⁻¹) of the species L1-L3.

L1		L2	L2			Vibrational assignment
Exp.	Cal. (intensity)	Exp.	Cal. (intensity)	Exp.	Cal. (intensity)	
836 (m)	813 (118)	846 (w)	829 (62) 863 (32)	852 (m)	835 (109)	$\delta_{ m op}(m O-H)$ phenolic $\delta_{ m op}(m C-H19)$
1020 (s)	1021 (94)	1038 (m)	1024 (74)	1041 (m)	1023 (68)	δ (C–H) Me + υ (py–C)
1033 (s)	1058 (136)	1056 (s)	1059 (89)	1056 (m)	1059 (50)	v _{asym} (py-C-O) alcoholic
1206 (s)	1177 (147)	1182 (m)	1187 (79)	1185 (m)	1171 (118)	υ(C-C, C-N) ^a
_	_	_	_	1222 (vs)	1216 (919)	$v_{asym}(C-O-C)$ bridge
1262 (w)	1268 (39)	1275 (m)	1266 (86)	1283 (m)	1271 (90)	v(ph-C)
1378 (vs)	1369 (198)	1412 (vs)	1371 (199)	1421 (s)	1372 (209)	v(C-O) phenolic
	1521 (39)	1508 (m)	1521 (67)	$1510(m_{c})$	1474 (254)	v(pyridine ring)
1546 (w)	1550 (93)	1566 (w)	1555 (150)	1510(VS)	1459 (428)	v(benzene ring)
1612 (vs)	1595 (239)	1623 (s)	1599 (146)	1631 (s)	1596 (340)	υ(C=N)
2020	2877 (37)		2875 (41)	2775	2872 (39)	$v_{\rm sym}$ (CH) alcoholic
2820	2916 (16)	2072(1)	2913 (23)	2775	2915 (19)	U _{sym} (CH) Me
2020	2952 (37)	2873 (Dr)	2929 (43)	2865	2953 (50)	$\upsilon(C_8H_{10}) + \upsilon(C_{16}-H_{18})$
3020	2961 (20)		2960 (13)		2960 (13)	$v_{\rm asym}({\rm CH}){\rm Me}$
	3048-3073 (35)		3044-3066 (25)		3056-3077 (30)	υ(C-H) aromatic
3165 (br,s)	3078 (486)	3170 (br,s)	3069 (885)	3189 (br,s)	3063	v(O–H) phenolic
	3154 (38)		3674 (35)		3674	υ (O–H) alcoholic

Abbreviations: a: except for C=N azomethine; w, weak; m, medium; s, strong; vs, very strong; br, broad.

of the phenolic O–H bonds. These vibrations are observed at lower energies than the alcoholic O–H ones, which is consistent with the weaker phenolic O–H bonds with respect to the alcoholic ones. Also, the stretching vibrations of the aromatic C–H bonds have lower energies than the aliphatic ones.

In the IR spectrum of the **L3**, a strong band was appeared in the $1550-1500 \text{ cm}^{-1}$ region. This broad and doublet band arises from the overlapping of the stretching vibrations of the aromatic rings (Table 4). Also, appearance of a new intensive band at 1222 cm^{-1} was assigned to the asymmetric stretching vibration of the C21–O5–C26 bonds. As expected, no band is observed in this region of the IR spectra of the species **L1** and **L3**.

4. Conclusion

In continuation of our previous works [12,13], herein, three dipyridoxyl Schiff-bases (**L1–L3**) have been newly synthesized and experimentally characterized. The geometries of the Schiff bases were optimized using the B3LYP level and 6-311 + G(d, p) basis sets. Also, the ¹H NMR chemical shifts and IR vibrational frequencies of the species have been calculated at the same computational level. The obtained results are in good agreement with the experimental evidence, confirming validity of the optimized geometries for the species **L1–L3**. The DFT results can be used for analysis of the similar compounds, too.

However, the substituted groups are in the same plane with the pyridine rings, the optimized geometries of the new Schiff bases are not planar. Each of the aromatic rings lies in a separate plane. Change in the bridge region affects considerably the structure of the pyridoxal Schiff base, especially the dihedral angle between two pyridine rings, which is increased in going from the species **L1** to **L3**.

The phenolic protons are engaged in the intramolecularhydrogen bonds with the azomethine nitrogens, which leads to weakness of the phenolic O–H bond and considerable upfield shift in the chemical shifts of the phenolic protons.

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