

## Syntheses and Characterization of the Structure for an $N_2O_2$ -Donor Atom Set in a Symmetrical Tetradentate Schiff-Base Ligand Derived from Salicylaldehyde

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Tetradentate bis-(3-methoxy salicylaldimine)-1,6-diamino hexane Schiff base with ( $N_2O_2$ ) donor sets, prepared by condensation of 1,6-diaminohexane and 3-methoxy salicylaldehyde and characterized by various spectroscopic methods. Semi-empirical calculations have been used for investigation of the electronic properties of this tetradentate Schiff base compound.

**Key Words:** Schiff base, Semi-empirical method, 3-Methoxy Salicylaldehyde, 1,6-diaminohexane.

### INTRODUCTION

Schiff-base compounds result from the condensation of primary amine with ketone or aldehyde to give imines containing a  $C=N$  bond. An aryl group bonded to the nitrogen or carbon stabilizes the compounds, known as Schiff-base<sup>1</sup>. The complexes are usually synthesized by carrying out the condensation reaction in the presence of a new ion and when the free ligands are not stable, the template effect can be very important.

In the present time, there has been an increasing interest during recent years in Schiff bases with bi-, tri- and tetradentate ligands in the range of both hard and soft donor groups. Also Schiff bases are attractive analytical reagents, because they enable simple and expensive determinations of various organic and inorganic substances<sup>2,3</sup>.

On the other hand, theoretical calculations are very useful for prediction of some electronic properties of compounds like the number and the behaviour of coordination sites, solvatochromic behaviour of a compound, inhibition properties of a compound, hydrogen bonding, etc.<sup>4-6</sup> In the past, the design and synthesis of some bidentate Schiff-base compounds containing N, O-donor sets<sup>7-9</sup> have been reported.

This paper is devoted to the theoretical study of a tetradentate Schiff-base ligand and the most stable conformation for the compound has been determined.

## EXPERIMENTAL

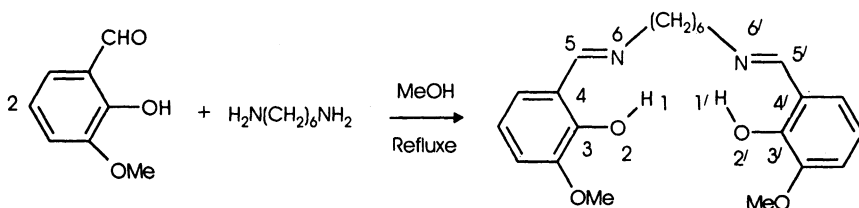
All the reagents and solvents used were of analytical grade and purchased commercially. 3-Methoxy salicylaldehyde and 1,6-diaminohexane were obtained from Merck and used without further purification.

Elemental analyses for C, H and N were performed using a Heraeus C, H, N and O rapid elemental analyzer. Infrared (FTIR) spectra were recorded by using KBr discs on an FT-IR Unicam-4000. The electronic spectra in the range of 200–900 nm were recorded in DMF solvent on Shimadzu UV-265 FW spectrophotometer. <sup>1</sup>H and <sup>13</sup>C NMR spectra were taken in CDCl<sub>3</sub> on a Bruker spectrosopin Avance 400 MHz ultrashield spectrometer and chemical shifts are indicated in ppm relative to tetramethylsilane (Table-1).

TABLE-1  
<sup>1</sup>H AND <sup>13</sup>C NMR DATA FOR BIS-(3-METHOXY SALICYLALDIMINE)-  
1,6-DIAMINOHEXANE SCHIFF BASE COMPOUND

<sup>1</sup> H NMR (ppm)	<sup>13</sup> C NMR (ppm)
14.01 (br, 2H, OH)	(2C, aliphatic) 56.11, 56.96
9.89 (s, 2H, iminic)	(6C, aliphatic) 77.29, 77.04, 76.54, 76.21, 75.89, 76.92
3.78 (s, 6H, aliphatic)	(2C, aromatic) 152.68, 150.44
4.05 (s, 12H, aliphatic)	(6C, aromatic) 122.72, 118.94, 118.59, 117.41, 119.91, 121.88

**Synthesis of Schiff-base ligand:** Schiff base compound, bis-(3-methoxy salicylaldehyde)-1,6-diaminohexane was prepared by standard method<sup>10</sup> by condensation of 3-methoxy salicylaldehyde with 1,6-diaminohexane in MeOH solution (**Scheme-1**). The yellow solution was gently refluxed for about 4 h. On evaporation of the solvent the Schiff-base was obtained as yellow microcrystals. The microcrystals were filtered off, washed with 3 mL cold methanol and then recrystallized from ethanol. The analytical and physical data of this teradentate compound are presented in Table-2.



**Scheme-1**

TABLE-2  
SOME PHYSICAL PROPERTIES FOR BIS-(3-METHOXY SALICYLALDIMINE)-  
1,6-DIAMINOHEXANE SCHIFF BASE LIGAND

Empirical formula	Formula weight	Yield (%)	Colour	m.p. (°C)	Analysis, % Found (Calcd.)		
					C	H	N
C <sub>22</sub> H <sub>28</sub> N <sub>2</sub> O <sub>4</sub>	384	55	Yellow	65-67	67.50 (68.75)	7.00 (7.29)	6.90 (7.29)

## RESULTS AND DISCUSSION

**Computational studies:** A full optimization of the structure of bis-(2-methoxysalicylaldehyde)-1,6-diaminohexane compound was done with semi-empirical methods. All calculations were carried out using Hyperchem 5.1 program Package<sup>11</sup>.

Full geometry optimization was performed using AM1, PM3, MNDO and MINDO/3 semi-empirical methods and all the data for comparison with the other were reported along with some important bond lengths and bond angles (Table-3). This table shows the best conformation for this tetradentate Schiff base compound optimized by MINDO/3 Hamiltonian, because this form has the minimum heat of formation energy. The optimized geometry and also the net charges that MINDO/3 calculated on coordination sites for this symmetrical ligand are reported in Fig. 1.

TABLE-3  
COMPARISON OF SELECTED BOND LENGTHS (Å) FOR SCHIFF BASE LIGAND BY  
AM1, PM3, MNDO AND MINDO/3 SEMI-EMPIRICAL METHODS

Bond	AM1	PM3	MNDO	MINDO/3
H(1)-O(2)	0.9714	0.9675	0.9506	0.9501
H'(1)-O'(2)	0.9717	0.9772	0.9482	0.9501
O(2)-C(3)	1.3657	1.3543	1.3639	1.3287
O'(2)-C'(3)	1.3649	1.3541	1.3574	1.3291
C(3)-C(4)	1.4020	1.4068	1.4246	1.4362
C'(3)-C'(4)	1.4024	1.4067	1.4272	1.4354
C(4)-C(5)	1.4686	1.4629	1.4882	1.4901
C'(4)-C'(5)	1.4684	1.4630	1.4883	1.4901
C(5)-N(6)	1.2867	1.2968	1.2880	1.2519
C'(5)-N'(6)	1.2869	1.2970	1.2879	1.2521
ΔH <sub>f</sub> (kcal/mol)	-92.8180	-100.0750	-105.320	-128.720

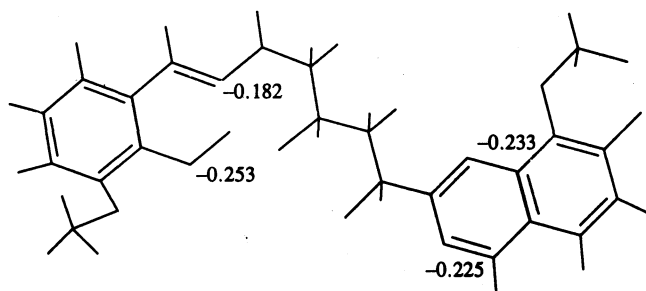


Fig. 1. MINDO/3 optimized geometry of bis-(2-methoxysalicylaldehyde)-1,6-diaminohexane Schiff-base ligand

Table-3 shows the main structure for this Schiff-base ligand and it has been optimized by MINDO/3 Hamiltonian. The structure has two hydrogen bonding between hydroxyl groups and nitrogen atoms of C=N groups.

On the other hand the MINDO/3 semi-empirical calculated data of molecular orbitals (MOs) for the anionic form of the tetradentate Schiff base compound are shown in Table-4. The MOs are named  $\Psi_1$ ,  $\Psi_2$  etc. in ascending energy order. Only the highest occupied MOs are shown, since lower lying orbitals are unlikely to play an important role in coordination<sup>12</sup>.

TABLE-4  
SOME CALCULATED PROPERTIES OF MOLECULAR ORBITAL FOR THE ANIONIC FORMS OF BIS-(2-METHOXYSALICYLALDIME)-1,6-DIAMINOHEXANE SCHIFF-BASE LIGAND

MO	Symmetry	Energy (eV)	Contribution of AO to the MO			
			O <sub>(2)</sub>	O <sub>(2)</sub>	N <sub>(6)</sub>	N <sub>(6)</sub>
$\Psi_{66}$	$\pi$	-6.16538	0.00014	0.00112	0.00001	0.60273
$\Psi_{67}$	$\sigma$	-6.12456	0.00000	0.71809	0.00011	0.00030
$\Psi_{68}$	$\pi$	-5.16755	0.00016	0.00000	0.59786	0.00010
$\Psi_{69}$	$\sigma$	-5.15866	0.71149	0.00001	0.00038	0.00111
$\Psi_{70}$	$\pi$	-4.35897	0.00000	0.00001	0.00013	0.00000
$\Psi_{71}$	$\pi$	-4.35537	0.00001	0.00003	0.00000	0.00000
$\Psi_{72}$	$\pi$	-4.10293	0.00000	0.00011	0.00000	0.00000
$\Psi_{73}$	$\pi$	-4.09162	0.00000	0.00008	0.00000	0.00001
$\Psi_{74}$	$\pi$	-2.34599	0.00000	0.00004	0.00000	0.00003
$\Psi_{75}$	$\pi$	-2.34162	0.00000	0.00001	0.00004	0.00001

From Table-4, we can deduce that the MOs more likely to combine with the metal orbitals are  $\Psi_{66}$  and  $\Psi_{68}$  that are located mainly on  $N_{(6)}$  and  $N_{(6)}$  atoms, and  $\Psi_{69}$  and  $\Psi_{67}$  are located mainly on  $O_{(2)}$  and  $O_{(2)}$  atoms in the structure of this tetradentate monoazo Schiff base ligand.

Table-4 shows that the bis-(3-methoxysalicylaldehyde)-1,6-di-amino-hexane compound has four strong negative coordination sites for combination with the metal ions for preparation of planar or coplanar geometry for Co(II) complexes<sup>13</sup>.

## Conclusion

In this work, a new stable  $N_2O_2$ -coordinated symmetrical tetradentate Schiff-base ligand has been reported. Semi-empirical calculation methods are very fast compared to high-level quantum chemical methods. Also our results show that both OH and C=N groups are hydrogen-bonded to the others in the symmetrical tetradentate ligand and the methoxy group has not any important role as coordination site in this structure.

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