

## AM1 Semi-Empirical Study of the Structural Property of Two Thio-triazine Schiff Bases

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Two novel Schiff bases (**L**<sub>1</sub> and **L**<sub>2</sub>) were prepared by condensation of 4-amino-6-methyl-1,2, 4-triazine-3-thione-5-one with 2-methoxybenzaldehyde and 4 methoxybenzaldehyde. The structures of **L**<sub>1</sub> and **L**<sub>2</sub> were determined by X-ray analysis and reported. **L**<sub>2</sub> imine has three forms intermolecular hydrogen bonding but **L**<sub>1</sub> compound does not have any hydrogen bonding. In this study, AM1 semi-empirical calculations are used to investigate the structure and hydrogen bonding with nitrogen, oxygen and hydrogen in N-H group containing in these compounds.

**Key Words:** Thio-triazine Schiff base, AM1, Single crystal structure.

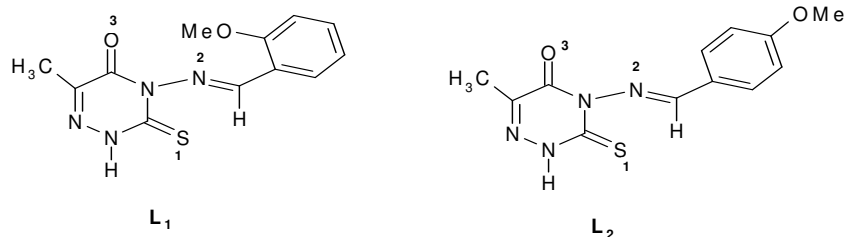
### INTRODUCTION

By condensation of primary amines with aldehydes or ketones gives imines containing a C=N bond. An aryl group bonded to the nitrogen or carbon stabilizes the compounds, are known as Schiff bases<sup>1</sup>. It is well documented that Schiff base and its metal complexes are important in diverse fields of chemistry and biochemistry owing to their biological activities<sup>2,3</sup> and catalytic properties<sup>4,6</sup>. Some of the Schiff bases have been used as analytical reagents because they enable simple and inexpensive determinations of various organic and inorganic substances. In addition, Schiff bases and their metal complexes have potential applications as metallomesogens and in the development of photonic devices<sup>7</sup>.

Theoretical calculations have been used for investigation of the electronic properties of compounds. Recently, the structural and optical properties of some azo Schiff base compounds have been reported<sup>8-10</sup>. In the present study, the electronic structure of two thio triazine Schiff base compounds **L**<sub>1</sub> and **L**<sub>2</sub> (**Scheme-I**) has been discussed. These ligands have three coordination sites N, O and S atoms in the imine group C=N (**Scheme-I**).

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**Scheme-I** Chemical structure of **L<sub>1</sub>** and **L<sub>2</sub>** Schiff base ligands

## EXPERIMENTAL

The MOPAC 7.0<sup>11</sup> program is used and a full optimization of the structure of two imine ligands was performed at Austin Model 1<sup>12</sup> AM1 semi-empirical method. A starting semi-empirical structure for MOPAC 7.0 calculations was optimized using the Hyperchem 7.0 program<sup>13</sup>.

## RESULTS AND DISCUSSION

The calculated structural property of **L<sub>1</sub>** and **L<sub>2</sub>** Schiff bases are given in Table-1.

TABLE-1  
SOME IMPORTANT CALCULATED PROPERTY OF **L<sub>1</sub>** AND **L<sub>2</sub>**  
COMPOUNDS BY AM1 METHOD

Compd.	DH	Surface	Volume	E <sub>HOMO</sub> *	E <sub>LUMO</sub> **	DE	μ (Debye)
<b>L<sub>1</sub></b>	69.198	479.54	780.38	-8.9269	-0.9700	7.9569	2.525
<b>L<sub>2</sub></b>	68.016	478.24	773.37	-8.8660	-1.0508	7.8152	0.682

\*Highest occupied molecular orbital \*\*Lowest unoccupied molecular orbital

Table-1 shows that **L<sub>1</sub>** compound is more polar molecule than the **L<sub>2</sub>** compound and **L<sub>2</sub>** Schiff base compound is more stable than **L<sub>1</sub>** compound.

The optimized structures of two Schiff base ligands are shown in Fig. 1. Fig. 1. shows the coordination sites for binding to the metal orbitals for

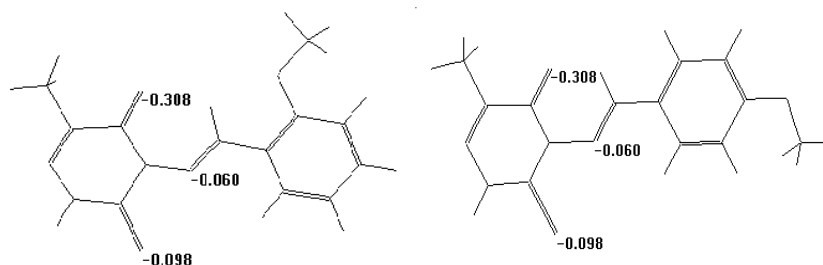


Fig. 1. Optimize structures of **L<sub>1</sub>** and **L<sub>2</sub>** imines with AM1 semi-empirical method (the net charges are shown on the N, O and C=N coordination sites)

$L_1$  and  $L_2$  Schiff base ligands, in other hand we calculated the contribution of atomic orbital (AO) to the molecular orbital (MO) for these compounds (Table-1).

From Table-2, it is deduced that the MO more likely to combine with the metal orbital are  $\Psi_{49}$ ,  $\Psi_{44}$  and  $\Psi_{40}$  for  $L_2$  compound that are located mainly on S(1), N(2) and O(3) atoms and  $\Psi_{49}$ ,  $\Psi_{44}$  and  $\Psi_{41}$  are located mainly on S(1), N(2) and(O3) atoms in the structure of  $L_1$  Schiff base ligand.

Geometry optimization for  $L_1$  and  $L_2$  compound were done by AM1 semi-empirical method by using MOPAC 7.0 program package. Some important bond lengths, bond angles and torsion angles for these compounds were shown in Table-2. (Fig. 2 and Table-3).

TABLE-2  
SOME CALCULATED PROPERTIES OF MOLECULAR ORBITAL  
FOR  $L_1$  AND  $L_2$  COMPOUND

MO	Energy (eV)	Contribution of AO to the MO		
		S(1)	N(2)	O(3)
<b><math>L_2</math></b>				
$\Psi_{40}$	-12.4930	0.0000	0.0023	<b>0.9280</b>
$\Psi_{41}$	-12.2848	0.0010	0.0000	0.0031
$\Psi_{42}$	-11.9049	0.0012	0.0004	0.0032
$\Psi_{43}$	-11.7963	0.0124	0.0000	0.0018
$\Psi_{44}$	-10.6194	0.0006	<b>0.5685</b>	0.0003
$\Psi_{45}$	-10.4467	0.1345	0.0000	0.0000
$\Psi_{46}$	-9.9904	0.0000	0.0061	0.0001
$\Psi_{47}$	-9.4715	0.0000	0.0000	0.0000
$\Psi_{48}$	-9.0360	0.0000	0.0000	0.0000
$\Psi_{49(\text{HOMO})}$	-8.8660	<b>0.9384</b>	0.0001	0.0002
<b><math>L_1</math></b>				
$\Psi_{40}$	-12.6393	0.0000	0.0109	0.0030
$\Psi_{41}$	-12.2885	0.0000	0.0020	<b>0.8334</b>
$\Psi_{42}$	-12.0868	0.0000	0.0000	0.0000
$\Psi_{43}$	-11.9473	0.0002	0.0001	0.0000
$\Psi_{44}$	-10.8171	0.0000	<b>0.5813</b>	0.0000
$\Psi_{45}$	-10.3404	0.0000	0.0049	0.0000
$\Psi_{46}$	-9.7180	0.0000	0.0002	0.0000
$\Psi_{47}$	-9.3624	0.0000	0.0001	0.0000
$\Psi_{48}$	-9.0252	0.0001	0.0030	0.0000
$\Psi_{49(\text{HOMO})}$	-8.9269	<b>0.9393</b>	0.0003	0.0000

TABLE-3  
 SELECTED BOND LENGTHS (Å), BOND ANGLES (°) AND TORSION  
 ANGLES (°) FOR L<sub>1</sub> AND L<sub>2</sub> SCHIFF BASES CALCULATED BY AM1  
 SEMI-EMPIRICAL METHOD AND BY X-RAY ANALYSIS

Selected bonds or angles	Bond lengths (Å) and bond angle (°) calc. By AM1 semi-empirical method	Bond lengths (Å), by X-ray analysis	Bond lengths (Å) and bond angle (°) calc. by AM1 semi- empirical method	Bond lengths (Å), by X-ray analysis
	L <sub>1</sub>	L <sub>1</sub>	L <sub>2</sub>	L <sub>2</sub>
S(1)-C(1)	1.585	1.624	1.586	1.659
N(1)-N(2)	1.355	1.426	1.355	1.418
N(1)-C(2)	1.432	1.397	1.432	1.407
N(3)-N(4)	1.315	1.360	1.315	1.359
N(4)-C(1)	1.419	1.354	N(4)-C(3) 1.316	1.289
O(2)-C(1)	1.239	1.226	O(1)-C(2) 1.238	1.210
N(1)-C(1)	1.432	1.379	1.432	1.383
N(2)-C(5)	1.305	1.276	1.305	1.274
N(2)-N(1)-C(2)	126.8	118.3	136.7	120.7
N(1)-N(2)-C(5)	124.5	113.5	124.3	115.0
N(3)-N(4)-C(1)	127.3	127.5	118.6	116.9
N(1)-C(2)-C(3)	116.3	114.3	116.4	113.7

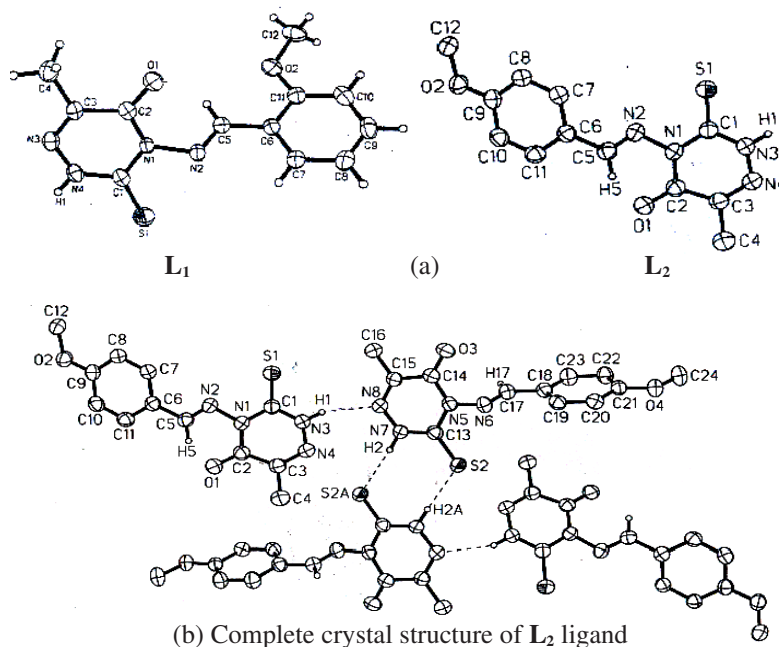


Fig. 2. The crystal structures of L<sub>1</sub>, L<sub>2</sub> (a) and the complete crystal structure of L<sub>2</sub> ligands (b)

### Conclusions

(a) **L**<sub>1</sub> and **L**<sub>2</sub> compounds have three coordination sites S(1), N(2) and O(3). (b) OCH<sub>3</sub> group has not any role in the net charges of coordination sites in the structures of **L**<sub>1</sub> and **L**<sub>2</sub> Schiff bases. (c) **L**<sub>1</sub> compound is polar molecule; also the volume and surface of **L**<sub>1</sub> compound are bigger than **L**<sub>2</sub>. (d) Theoretical calculation has a good agreement with those in the X-ray experimental data.

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