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Some Quantum Chemical Study about the Second-Order Non-linearity of Two Imino Chromophores Containing Salen Group

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Abstract: Two new trident imine compounds 4-nitrophenylazo- N-(2-hydroxy propylamine) saliciliden [L_1] and phenylazo- N-(2-hydroxy propylamine) saliciliden [L_2] have been synthesized and characterized by some spectroscopy techniques. The electrical dipole moment (μ) and the first hyperpolarizability (β) and amount of charge density on all coordination atoms, HOMO energy and LUMO energy of L_1 and L_2 compounds were calculated by using AM1 Semi-empirical method. The calculation results reveal this π -conjugated systems have a good NLO property in second harmonic generation technique (SHG). The calculated β (NLO property) for L_1 compound is 134.55 times of that Urea.

Key words: Nonlinear optical property, AM1, Schiff base, Semi-empirical method

INTRODUCTION

Materials possessing nonlinear optical (NLO) properties change the propagation characteristics (polarization, phase, frequency, etc.) of the incident light. The molecules with large optical nonlinearities have recently become the focus of most researches in view of their potential applications in various photonic technologies, including all-optical switching (Kanchana *et al.*, 2002) and data processing especially in optical fibers communication and optical computing which makes the maximum use of light characteristics such as parallel and spatial processing capabilities and high speed (Prasad and Williams, 1990).

A molecule with π -electron system possess many attractive nonlinear optical (NLO) characteristics and show enhanced NLO properties. The design of most efficient organic materials for the nonlinear effect is based on molecular unit containing highly delocalized π -electron moieties and extra electron donor and electron acceptor groups on the opposite sides of the molecule at appropriate positions on the ring to enhance the conjugation. We have reported some compounds with NLO property elsewhere (Sheikhsboaie, 2003; Sheikhsboaie and Mashhadizadeh, 2003, 2005).

Nonlinear optics is currently an active area of research, development of NLO compounds aim at to optimize higher-order polarizabilities at the molecular as well as material levels (Nalwa and Miyata, 1997).

In the present study we synthesized two new tridentate Schiff base ligands L_1 and L_2 (Fig. 1) and

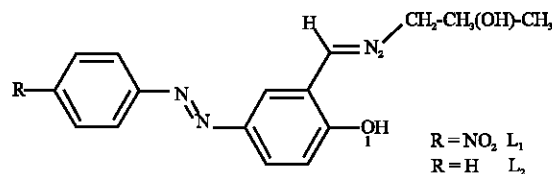


Fig. 1: Chemical structure of L_1 and L_2 imine compounds

characterized the structures and also we studied their structural properties by using AM1 semi-empirical methods (Kanis *et al.*, 1994). The structure of L_1 and L_2 Schiff base ligands were shown in Fig. 1.

THEORETICAL CALCULATIONS

Austin model 1 (AM1) (Dewar *et al.*, 1985) is one of the semi-empirical methods and it is a popular method for calculation of the electronic molecular properties such as ground state, geometry, molecular energy and molecular polarizability.

The geometry optimization and hyperpolarizability calculations were performed using MOPAC 7.0 Program on a Pentium III (550 MHz processor with 256 MB RAM). The optimized geometry with negative charge density on all coordination sites for L_1 and L_2 are shown in Fig. 2.

We report β_{tot} (total first hyperpolarizability) for L_1 and L_2 compounds has been calculated. The components of the first hyperpolarizability can be calculated using the following equation:

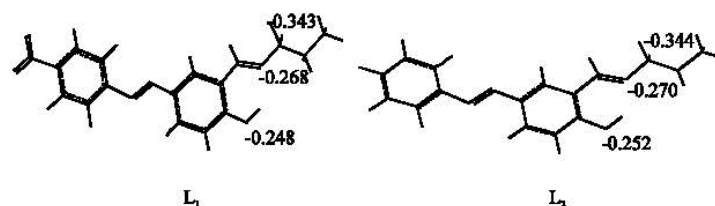


Fig. 2: Optimized geometry for L₁ and L₂ Schiff base compounds by the AM1 semi empirical method

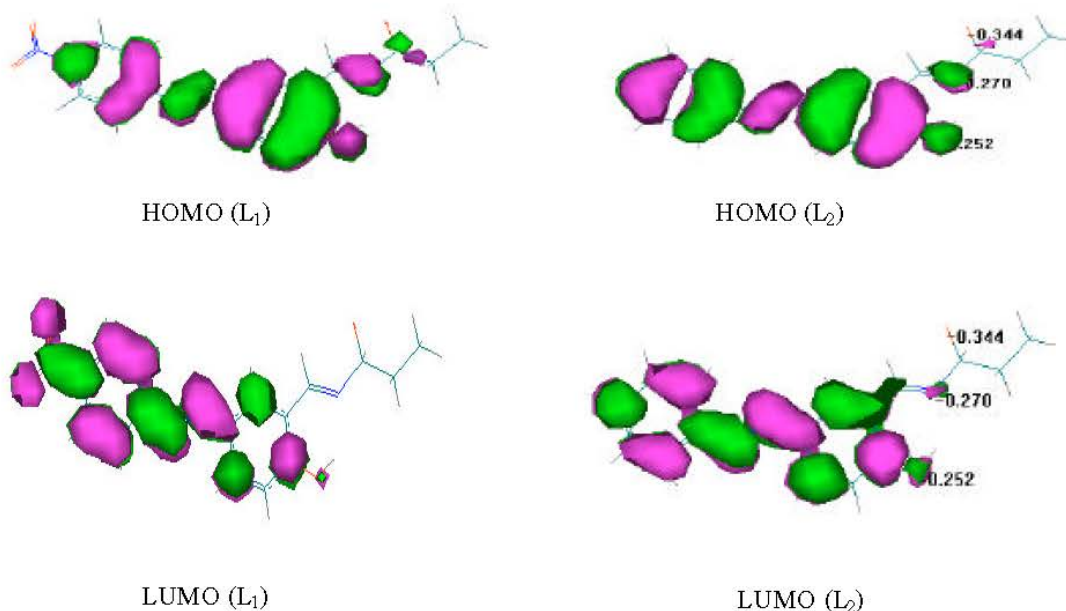


Fig. 3: The plot of HOMO and LUMO levels for L₁ and L₂ compounds

$$\beta_i = \beta_{iii} + 1/3 \sum_{i \neq j} (\beta_{ijj} + \beta_{jij} + \beta_{jji}) \quad (1)$$

Using the x, y and z components, the magnitude of the first hyperpolarizability tensor can be calculated by Eq. 2

$$\beta_{tot} = (\beta_x^2 + \beta_y^2 + \beta_z^2)^{1/2} \quad (2)$$

The complete equation for calculating the magnitude of first hyperpolarizability from MOPAC 7.0 out put is given as follows²:

$$\beta^{tot} = [(\beta_{xxx} + \beta_{xyy} + \beta_{xzz})^2 + (\beta_{yyy} + \beta_{yzz} + \beta_{yxx})^2 + (\beta_{zzz} + \beta_{zxx} + \beta_{zyy})^2]^{1/2} \quad (3)$$

The calculate all the electronic dipole moments and all the first hyperpolarizabilities, the origin of the cartesian coordinate system (x, y, z) = (0, 0, 0) has been chosen at own center of mass of L₁ and L₂ compounds in Fig. 1. Present calculations indicate that the L₁ compound might be the β -interesting material. It is shown that L₁ compound has great non-zero μ values (Table 1).

Table 1: The AM1 calculated total electric dipole moments μ (Debye) and dipole moment components (μ_x , μ_y and μ_z) for L₁ and L₂ imine compounds

Total μ (Debye) and dipole moment components	Compound	
	L ₁	L ₂
μ_x	6.306	2.785
μ_y	1.343	-1.968
μ_z	-0.124	-0.347
μ	6.448	3.427

Table 2: The AM1 calculated total first hyperpolarizability β_{tot} for L₁ and L₂ imine compounds

Compound	β_{tot}
L ₁	18.837×10^{-30} esu
L ₂	-1.820×10^{-30} esu

Some calculated structural properties like β_{tot} value calculated by AM1 semi-empirical method for L₁ and L₂ imines compounds are listed in Table 2.

The NLO responses can qualifiedly be understood by examining the energetic of frontier molecular orbitals [the highest molecular orbit (HOMO) and the lowest molecular orbit (LUMO)] of L₁ and L₂ imine compounds (Table 3). L₁ molecule has a NO₂ group in para position on phenyl group while L₂ molecule has H atom in this position. The

Table 3: The calculated energy of frontier molecular orbital (eV) for L₁ and L₂ compounds by AM1 semi-empirical method

Compound	E _(HOMO)	E _(LUMO)	ΔE (band gap)
L ₁	-9.2730	-1.5421	7.7309
L ₂	-8.7095	-0.7044	8.0051

NO₂ group possess strong electron-withdrawing action, when NO₂ was attached to the para position of phenyl ring, unshared electron-pair of the system could transfer to NO₂ along the conjugation system.

In the other hand the HOMO, largely dictates the source of charge transfer (CT), from the HOMO-LUMO energy calculation by MOPAC 7.0 it can be seen that the HOMO of the L₁ molecule is lower than the HOMO level of L₂ molecule. According to the HOMO-LUMO differences of above molecules, it can be seen that the HOMO-LUMO gap of L₁ molecule is relatively smaller than that of the L₂ molecule and shows higher β value than that of the L₂ molecule. It is evident that there should be an inverse relationship between HOMO-LUMO gap and the first of hyperpolarizability (Kanis *et al.*, 1994).

Figure 3 shows the electron density in HOMO and LUMO levels for L₁ and L₂ molecules.

CONCLUSION

- L₁ and L₂ compounds have three atoms as their coordination sites for metal complex formation (O₁, N₂ and O₃, Fig. 1).
- The geometry of L₁ and L₂ compounds are flat and there is a hydrogen bond between O₁ and N₂ atom in these structures.
- Our calculations show that L₁ and L₂ compounds have NLO property, but Table 2 shows that L₁ compound is a good candidate for second harmonic generation.

- β (NLO property) calculated for L₁ compound is 134.55 times of that Urea (β for Urea is 0.14 × 10⁻³⁰ esu).
- NO₂ group has a good role in the NLO property of these compounds (Table 2).

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