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Theoretical Study of Second-Order Non-Linear Optical Properties of Two Imino Chromophores Containing Salicylidine Group

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Two new tridentate imine compounds 4-nitrophenylazo-N-(2-hydroxy propylamine) salicylidine [$\mathbf{L_1}$] and phenylazo-N-(2-hydroxy propylamine) salicylidine [$\mathbf{L_2}$] have been synthesized and characterized by some spectroscopic techniques. The dipole moment (μ) and the first hyperpolarizabilty (β) and amount of charge density on all coordination atoms, HOMO energy and LUMO energy of $\mathbf{L_1}$ and $\mathbf{L_2}$ compounds were calculated by using AM1 semi-empirical method. The calculation results reveal this π-conjugated systems have a good nonlinear optical (NLO) property in second harmonic generation technique (SHG). The calculated β (NLO property) for $\mathbf{L_1}$ compound is 134.55 times of that urea.

Key Words: Nonlinear optical property, AM1, Schiff base, Semi-empirical methods.

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[1] 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[2].

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

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the molecule at a appropriate positions on the ring to enhance the conjugation. We have reported some compounds with NLO property[3-5].

Nonlinear optics (NLO) 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[6].

In this present study we synthesized two new tridentate Schiff base ligands **L_1** and **L_2** (Fig. 1) and characterized the structures and studied the structural properties by using AM1 semi-empirical methods[7].

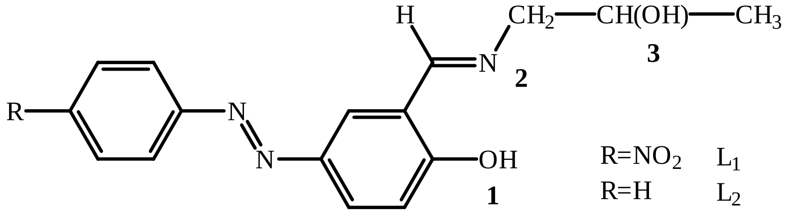
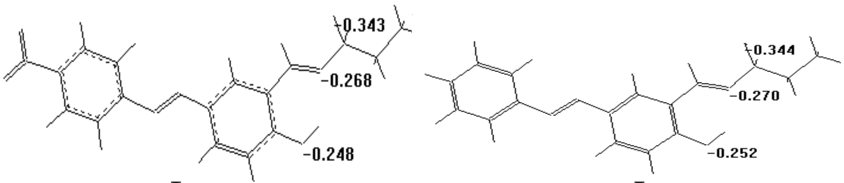


Fig. 1. Chemical structure of **L_1** and **L_2** imine compounds

Theoretical calculations

Austin model 1 (AM1)[7] 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 geometrical optimization and hyperpolarazibility calculations were performed using MOPAC 7.0 Program[8] on a Pentium III (550 MHz processor with 256 MB RAM). The optimized geometry with negative charge density on coordination sites for **L_1** and **L_2** compounds are shown in Fig. 2.



L_1 **L_2**

Fig. 2. Optimized geometry for **L_1** and **L_2** Schiff base compounds by the AM1 semi empirical method

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

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

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

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

The complete equation for calculating the magnitude of first hyperpolarizability from MOPAC 7.0 out put is given as follows[8]:

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

The dipole moments and all the first hyperpolarizabilities (β_{tot}), the origin of the cartesian coordinate system (x, y, z) = (0, 0, 0) has been chosen at own center of mass of $\mathbf{L_1}$ and $\mathbf{L_2}$ compounds in Fig.1. Our calculations indicate that the $\mathbf{L_1}$ compound might be the β-interesting material. It is shown that $\mathbf{L_1}$ compound has great non-zero μ values (Table-1).

TABLE-1
AM1 CALCULATED TOTAL ELECTRIC DIPOLE MOMENTS (μ)
AND DIPOLE MOMENT COMPONENTS (μ_x, μ_y AND μ_z)
FOR $\mathbf{L_1}$ AND $\mathbf{L_2}$ IMINE COMPOUNDS

Dipole moment μ (Debye) components	Compound	
	$\mathbf{L_1}$	$\mathbf{L_2}$
μ_x	6.306	2.785
μ_y	1.343	-1.968
μ_z	-0.124	-0.347
μ	6.448	3.427

β_{tot} value calculated by AM1 semi-empirical method for $\mathbf{L_1}$ and $\mathbf{L_2}$ imines compounds are listed in Table-2.

TABLE-2
FIRST HYPERPOLARIZABILITY β_{tot} FOR $\mathbf{L_1}$ AND $\mathbf{L_2}$
IMINE COMPOUNDS

Compound	β_{tot}
$\mathbf{L_1}$	18.837×10^{-30} esu
$\mathbf{L_2}$	-1.820×10^{-30} esu

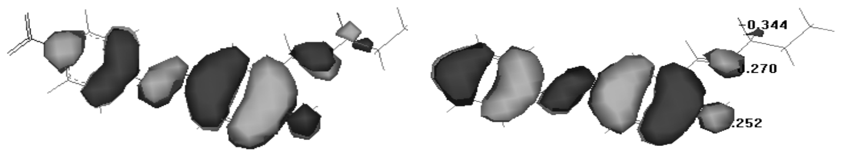
The NLO responses can be checked by examining the energetic of frontier molecular orbitals [the highest molecular orbit (HOMO) and the lowest molecular orbit (LUMO)] of $\mathbf{L_1}$ and $\mathbf{L_2}$ imine compounds (Table-3). $\mathbf{L_1}$ molecule has a NO_2 group in *para* position on phenyl group while $\mathbf{L_2}$ molecule has H atom in this position. The NO_2 group possesses strong electron-withdrawing action, when NO_2 was attached to the *para* position of phenyl ring, unshared electron-pair of the system could transfer to NO_2 along the conjugation system.

TABLE-3
CALCULATED ENERGY OF FRONTIER MOLECULAR ORBITAL (eV)
FOR $\mathbf{L_1}$ AND $\mathbf{L_2}$ COMPOUNDS BY AM1 SEMI-EMPIRICAL METHOD

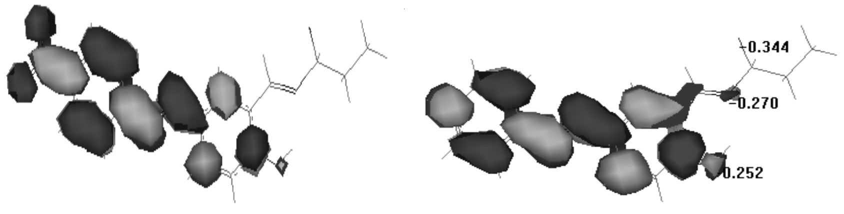
Compound	$E_{(HOMO)}$	$E_{(LUMO)}$	ΔE (band gap)
$\mathbf{L_1}$	-9.2730	-1.5421	7.7309
$\mathbf{L_2}$	-8.7095	-0.7044	8.0051

On the other hand, the HOMO largely influenced 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 $\mathbf{L_1}$ molecule is lower than the HOMO level of $\mathbf{L_2}$ molecule. According to the HOMO-LUMO differences of above molecules, it can be seen that the HOMO-LUMO gap of $\mathbf{L_1}$ molecule is relatively smaller than that of the $\mathbf{L_2}$ molecule and shows higher β value than that of the $\mathbf{L_2}$ molecule. It is evident that there should be an inverse relationship between HOMO-LUMO gap and the first of hyperpolarizability[7, 8].

Fig. 3 shows the electron density in HOMO and LUMO levels for $\mathbf{L_1}$ and $\mathbf{L_2}$ molecules.



HOMO ($\mathbf{L_1}$) HOMO ($\mathbf{L_2}$)



LUMO ($\mathbf{L_1}$) LUMO ($\mathbf{L_1}$)

Fig. 3. Plot of HOMO and LUMO levels for $\mathbf{L_1}$ and $\mathbf{L_2}$ compounds

Conclusion

(1) $\mathbf{L_1}$ and $\mathbf{L_2}$ compounds have three atoms as their coordination sites for metal complex formation (O1, N2 and O3, Fig. 1), (2) The geometry of $\mathbf{L_1}$ and $\mathbf{L_2}$ compounds are flat and there is a hydrogen bond between O1 and N2 atoms in these structures, (3) Our calculations show that $\mathbf{L_1}$ and $\mathbf{L_2}$ compounds have NLO property, but Table-2 shows that $\mathbf{L_1}$ compound is a good candidate for second harmonic generation, (4) β (NLO property) calculated for $\mathbf{L_1}$ compound is 134.55 times of that urea (β for urea is 0.14

× 10^{-30} esu) and (5) So NO_2 group has a good role in the NLO property of these compounds.

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