Preparation, Characterization, Electronic Structures and Non-linear Optical Properties of Some Asymmetrical Schiff Base Compounds as Model Compounds for Non-Linear Optical Organic Materials

IRAN SHEIKHSHOAIE

Department of Chemistry
Shahid Bahonar University of Kerman, P.O. Box 76175-133, Kerman, Iran
E-mail: ishoae@yahoo.com

Three mono azo asymmetrical bidentate Schiff base compounds (1–3) were synthesized and their structures characterized by some spectroscopic methods and C, H and N elemental analyses. Also some theoretical calculations about the electronic properties of the structures of synthesized compounds have been performed. The theoretical non-linear optical properties (β values) of these compounds were calculated with AM1 semi-empirical method by using MOPAC 7.0 program package and the electronic analysis of the electron density distribution was used to explain an increase of the molecular hyperpolarizabilities.

Key Words: Schiff-base, Second-order non-linear optical property, AM1, Hyperpolarizability.

INTRODUCTION

The donor-acceptor groups in the structures of organic compounds have an important role in the non-linearoptical (NLO) properties of these compounds[1,2]. These compounds were tested as examples of organic NLO-active materials[3–5].

In particular, *p*-nitroaniline (*p*-NA), *m*-nitroaniline (*m*-NA), 2-methyl-4-nitroaniline (MNA). *p*-nitro-N,N-dimethylaniline (*p*-NDMA) and other similar choromophores were found to exhibit rather large NLO properties.

On the other hand, an interest in explanation to non-linear optical behaviour has grown in recent years, primarily because of the telecommunication industry's need for high-bandwidth optical switching and processing devices to service the information and data transmission needs of the computer age, and of the proliferation of sophisticated laser tools. Non-linear optical properties constitute a valuable sensitive probe of the organic compounds electronic structure and as a consequence they find various applications in many areas of optoelectronics[5–8].

The synthesis and characterization of new organic compounds with non-linear

optical property is a time consuming and costly process. On the other hand, quantum chemistry calculations have proved to be useful in the description of the relationship among the electronic structure of molecular systems and their non-linear optical response[9, 10].

However, in this work, the three novel mono-azo Schiff base compounds[1-3] were synthesized and performed some calculations about the hyperpolarizability, ground stage, dipole moment, bond length, bond angle and charge density on all atoms in the structures of these compounds.

The β values obtained from theoretical calculations are compared with those for a standard choromophore, *p*-nitroaniline (PNA) (B = 34.5 $\times$ 10^{-30} esu)[11]. The calculated ground state dipole moment and the localization of the biggest value of electron density for the first compound are shown. This Schiff base ligand is a good NLO material.
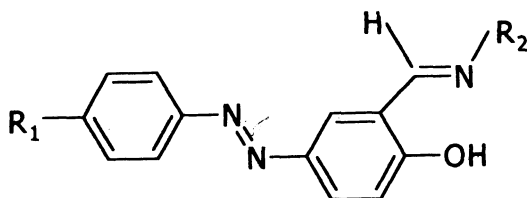
Compound 1. $R_1 = NO_2$, $R_2 = C_6H_{13}$;   Compound 2. $R_1 = OC_3H_7$, $R_2 = C_6H_{13}$;
Compound 3. $R_1 = OC_6H_{13}$, $R_2 = C_6H_{13}$

Structures of 1,3-monoazo bidentate Schiff base gands

EXPERIMENTAL

All chemicals were of reagent grade and used as purchased from the commerical sources. The starting materials (precursor ligand) were prepared as described in the literature[12, 13]. Elemental analyses were performed on a Perkin-Elmer analyzer. The UV-Vis spectra were recorded with a Beckman DU-7000 spectrometer and λ_{max} values were considered accurate to 0.1 nm. The FTIR spectra were recorded on a Shimadzu DR-8001 spectrophotometer in the range of 4000–400 cm^{-1}.

Syntheses of Schiff base ligands

Compounds were prepared in high yield by Schiff reaction[14]. Precursor ligand (1.00 mol) with 1-hexylamine (1.00 mol) in dry methanol (20 mL) were refluxed for 1.5 h, then filtered and washed the precipitate several times with hot ethanol and dried in vacuum at 90°C.

Satisfactory microanalyses, UV-Vis, ^{1}H NMR and FTIR characterised all the prepared Schiff base ligands. Inspection of the IR spectra of precursor ligands and corresponding Schiff bases[1-3] reveals that the absorption band of CO group

(1670–1667 cm^{-1}) was omitted and a new absorption band (1625–1623 cm^{-1}) due to C=N group appeared upon condensation.

Ligand 1. Dark red. m.p.: 103.9°C : Anal. (%) Calcd. for $C_{19}H_{22}N_4O_3$: C, 64.406; H, 6.214; N, 15.81. Found: C, 64.00; H, 6.07; N, 15.61. Yield: 67%.

Ligand 2. Yellow. m.p.: 66°C. Anal. (%) Calcd. for $C_{25}H_{35}N_3O_2$: C, 73.449; H, 8.557; N, 10.268. Found: C, 73.01; H, 8.11; N, 9.98. Yield: 80%.

Ligand 3. Orange. m.p.: 70°C. Anal. (%) Calcd. for $C_{22}H_{29}N_3O_2$: C, 78.805; H, 8.656; N, 12.537. Found: C, 87.31; H, 8.50; N, 12.01. Yield: 52%.

The structures and electronic properties of the synthesized compounds were investigated by using the SCF-MO method. Also, the molecular hyperpolarizability of these ligands is calculated and compared with the other structures.

Second-order non-linear optical property

The recent recognition that organic materials with conjugated π-electron systems exhibit extremely large optical non-linear responses has led to rapid growth of interest in a field which is currently dominated by inorganic materials such as lithium niobate[15]. In general, the microscopic polarization induced in a given molecule by an external field can be expressed as eqn. (1).

$$\mu_i(\text{ind.}) = \mu_i - \mu_{0i} = \alpha_{ij}E_j + \beta_{ijk}E_jE_k + \gamma_{ijkl}E_jE_kE_l + \dots \qquad (1)$$

where $\mu_i(\text{ind.})$ is the ith component of the induced dipole, μ_i and μ_{0i} refer to the perturbed and unperturbed ground-state dipoles, respectively, and β and γ are the second- and third-order polarizability (or hyperpolarizability) tensors, respectively.

Molecules with large second-order polarizabilities give rise to large second-order susceptibility $\chi^{(2)}$, in non-centrosymmetric crystals. These materials are useful in a variety of electro-optical devices[16], of which the conventional poker cell might be considered the progenitor. For characterization of materials the experimental techniuqe usually used is second-harmonic generation (SHG), where the E^2 term in the polarization leads to a component at double the incident frequency.

Method of calculation

Molecular structure of **1–3** has been calculated at the AM1[17] method with full geometry optimization. The AM1 calculations have been done using the MOPAC 7.0 and Hyperchem 5.0 programs[18]. We have calculated their hyperpolarizability and ground state dipole moment, which is a measure of their capability for orientation in a poled polymer, which is a common material in second-order NLO devices. The values obtained are compared which those for a standard NLO chromophore, *p*-nitroaniline (PNA)[19, 20]. PNA molecules possessing large second-order NLO coefficients consist of a conjugated delocalized π-electron system joining strong donor (CH$_3$) and strong acceptor (NO$_2$) groups. Direction of dipole moment for PNA molecule and charge density on all atoms are shown in Fig. 1.
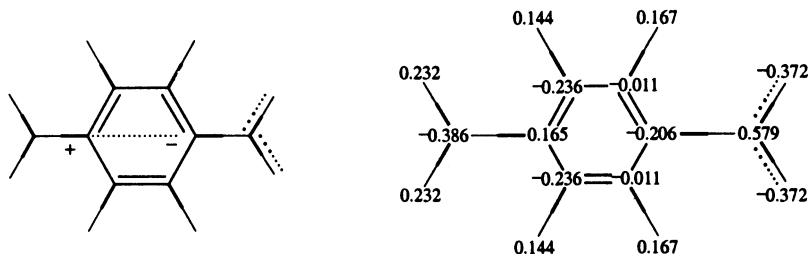
Fig. 1. Dipole moment and net charge density on *p*-nitroaniline molecule

Programs that use the sum-over-state approach calculate β as function of the frequency of light, whereas finite-field methods generally assume zero frequency. In other words, calculations regarding second-order optical non-linearity of these salicylaldiminato Schiff base compounds are frequency independent. The values reported in this work are all energy values rather than dipole moment values.

The calculated molecular hyperpolarizabilities of compounds **1-3** are given in Table-1. These values are energy values, which tend to have greater numerical stability than dipole moment values.

TABLE-1
NON-LINEAR OPTICAL PROPERTIES FOR SCHIFF BASE LIGANDS 1, 2 AND 3

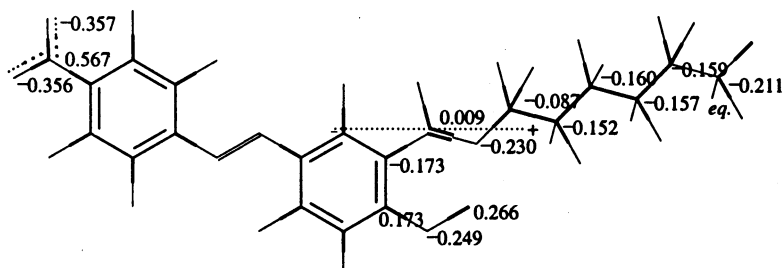| Compound	μ (debye)		$\beta \times 10^{-30}$ esu
1	μ_x	-6.096	18.835
	μ_y	1.042	
	μ_z	0.000	
	μ^a	6.184	
2	μ_x	-0.446	0.603
	μ_y	-3.714	
	μ_z	0.000	
	μ^a	3.740	
3	μ_x	-0.459	0.608
	μ_y	-3.731	
	μ_z	0.000	
	μ^a	3.760	

$\mu^a = (\mu_x^2 + \mu_y^2 + \mu_z^2)^{1/2}$

Fig. 2. The geometry optimization with charge density for some important atoms of compound no. 1
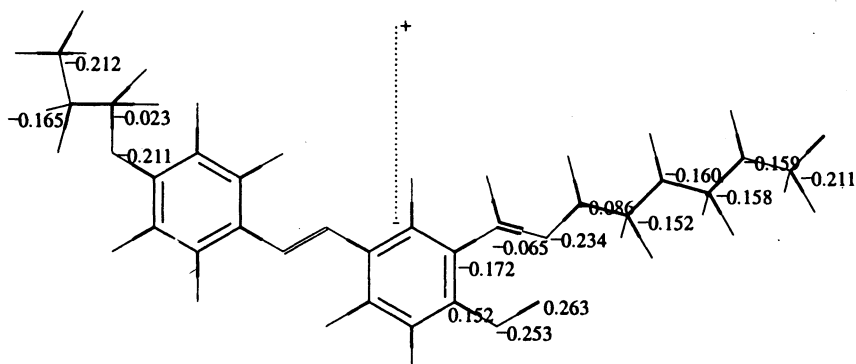
Fig. 3.   The geometry optimization with charge density for some important atoms of compound 2
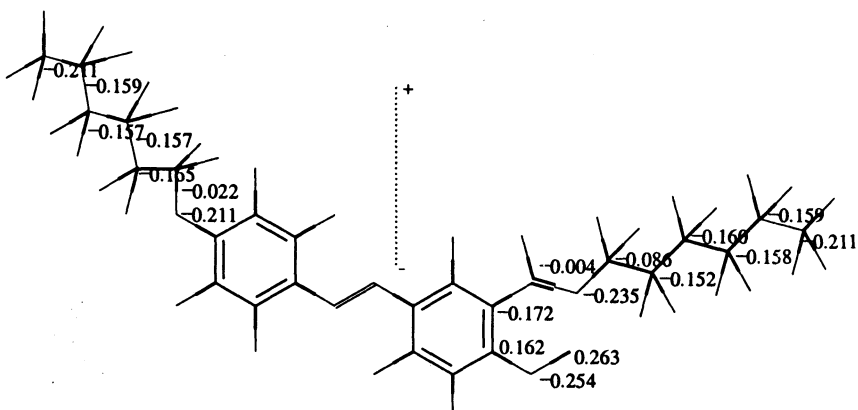

Fig. 4.   The geometry optimization with charge density for some important atoms of compound 3

The optimized structures of 1–3 Schiff base ligands with also the dipole moments for these compounds were shown in Figs. 2–4.

RESULTS AND DISCUSSION

1. From Figs. 1–3, the highest β values should be expected for compound 1 while the lowest ones for compound 3 as long as the benzene ring is substituted in para position NO_2 and OC_6H_{13} groups.

2. The hydroxyl groups haven't any important role in NLO property for these compounds.

3. The nitrogen atoms in imine group and oxygen atom in hydroxyl group are coordination sites in these compounds because they have a lot of negative charge density.

4. Table-1 shows that donor and acceptor groups have an important role in the NLO properties of these Schiff base compounds.

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