DFT Studies on Factors Affecting Non-Linear Optical
Properties of N-Salicylidene-Chloroaniline Schiff Bases

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The different molecular structure, electronic and spectroscopic aspects affect the non-linear optical properties of N-salicylidene-chloroaniline Schiff bases (**1-3**) were calculated using DFT/B3LYP method and 6-31G(d,p) basis set. The TD-DFT method has been used to calculate the electronic spectra of these Schiff bases. The longest wavelength π-π* transition band was calculated at 344.0 nm (f = 0.3944) for compound **3**. It was found that N-salicylidene-4-chloroaniline (**3**) has the highest polarizability (α_0 = 178.700 a.u.), hyperpolarizability (β_{tot} = 820.299 a.u.) and lower energy gap (ΔE = 4.046 eV). As a result compound **3** is predicted to have the highest non-linear optical activity between the studied compounds. The correlation equation that relate these electronic parameters with their SHG values were predicted.

Keywords: Optical nonlinearity, SHG, DFT, Schiff base.

INTRODUCTION

Schiff bases are of great importance in diverse fields of chemistry and biochemistry owing to their biological activity[1,2]. These Schiff bases are used as starting materials in the synthesis of important drugs such as antibiotics, antiallergics, antitumors and antifungals[1,3]. In addition, their nonlinear properties have an importance for the design of various molecular electronic devices such as optical switches and optical data storage devices[4,5]. For Schiff bases, non-linear optical studies provide the key functions of frequency shifting, optical modulation, optical switching, optical logic and optical memory for the emerging technologies in areas such as telecommunications, signal processing and optical interconnections[6-8].

Moreover, organic compounds such as Schiff bases which have conjugated π-systems are of great interest as potential materials for optical nonlinearity[9-11]. In the present work, the molecular structure and electronic properties of N-salicylidene-chloroaniline were performed using DFT/B3LYP method. The computed electronic parameters were correlated with their SHG values to deduce the equations that relate their non-linear optical properties with the predicted electronic parameters.

CALCULATION METHODS

All the calculations for the studied Schiff bases were calculated using Gaussian-03 software[12] on Pentium IV processor personal computer. The calculations were performed using the B3LYP/6-31G(d,p) level. The geometries were optimized by minimizing the energies with respect to all the geometrical parameters without imposing any molecular symmetry constraints. GaussView[13] and chemcraft[14] softwares have been used to draw the structures of the optimized geometries and to draw the HOMO and LUMO pictures.

RESULTS AND DISCUSSION

The calculated optimized molecular geometries of the studied Schiff bases showed that all these structures are nonplanar (Fig. 1). The calculations predicted O-H…N intramolecular H-bonding interaction between the hydroxyl proton and the N-atom of the Schiff base. The intramolecular N12…H26-O25 bond distances are calculated to be 1.754, 1.756 and 1.767 Å for the *para-*, *meta-* and *ortho-*substituted derivatives, respectively. It is the strongest in case of the N-salicylidene-3-chloroaniline. It was found that, the C14-C13-N12-C11 and C15-C13-N12-C11 dihedral angels between the two rings are in the range 32.54° to 38.68°. It is the maximum for N-salicylidene-2-chloroaniline, where the presence of the Cl-group substituent in *ortho-*position increases the deviation of the two ring planes from one another. The C6-C9-C11-N12 and C7-C9-C11-N12 dihedral angels do not exceed 1°. On other hand, the angles between the aryl and salicylidene ring planes are in the range 35.68° to 38.44°. These results indicate
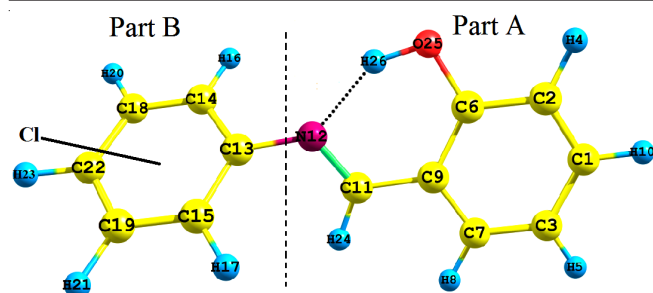
Fig. 1. Calculated optimized geometry of the studied N-salicylidene-chloroaniline Schiff bases **1**; *m*-Cl, **2**; *o*-Cl and **3**; *p*-Cl

the high conjugacy between the salicylidene rings and the Schiff base moiety but less extended to the other aryl ring. As a whole, the salicylidene group is almost coplanar for all Schiff bases but the two ring moieties are not. The substituent position would lead to remarkable variation in conjugacy where it is the best for N-salicylidene-4-chloroaniline.

The calculated natural atomic charges using the NBO method at the DFT/B3LYP level of theory for all the studied compounds were presented in Table-1. For the SHG more active molecules, the second-order polarizability caused by charge transfer of the whole system would generally get enhanced by the stronger intramolecular charge transfer (ICT). In order to investigate the strength of the intramolecular charge transfer interaction, the studied systems were divided into two parts A and B (Fig. 1). It is obvious that part A have negative

charge (electronic acceptors) while part B are positively charged (electronic donors). The substituent position on part B play an important role in the charge distribution and their effects could be sorted as **3 > 1 > 2**. It seems that for **3**, the electron donating ability of the Cl-group through the resonance effect overcame its inductive effect as electron withdrawing group. In contrast, the inductive effect is the dominant in the *o*- and *m*-positions.

The properties of the frontier molecular orbitals (FMOs) like energy are very useful for physicists and chemists[15-17]. The HOMO and LUMO pictures are shown in Fig. 2. It was found that the HOMO and LUMO levels are localized on the π-system of the studied molecules. The HOMO-LUMO energy gap (ΔE) represents the lowest energy electronic transition. In the studied compounds, the energy gaps (ΔE) are calculated to be 4.086, 4.077 and 4.046 eV for compounds **1-3**, respectively. These electron excitations are mainly described as π-π* transitions. The more accurate electronic transitions were calculated using the TD-DFT method. The calculated electronic spectra are shown in Fig. 3. The results of the TD-calculations are given in Table-2. The studied compounds **1-3** showed the longest wavelength absorption band predicted at 341.9, 343.7 and 344.0 nm for compounds **1-3**, respectively. These bands are mainly due to H→L excitations and the maximum wavelength value is for compound **3**. The effect of the substituent position on these bands is very small.

Several organic materials were used for non-linear optical applications[7,18]. These organic compounds were characterized by their high polarizability (α_0) and low HOMO-LUMO gap (ΔE). The calculated α_0 and ΔE values of the studied

TABLE-1
CALCULATED NATURAL ATOMIC CHARGES
OF THE STUDIED COMPOUNDS

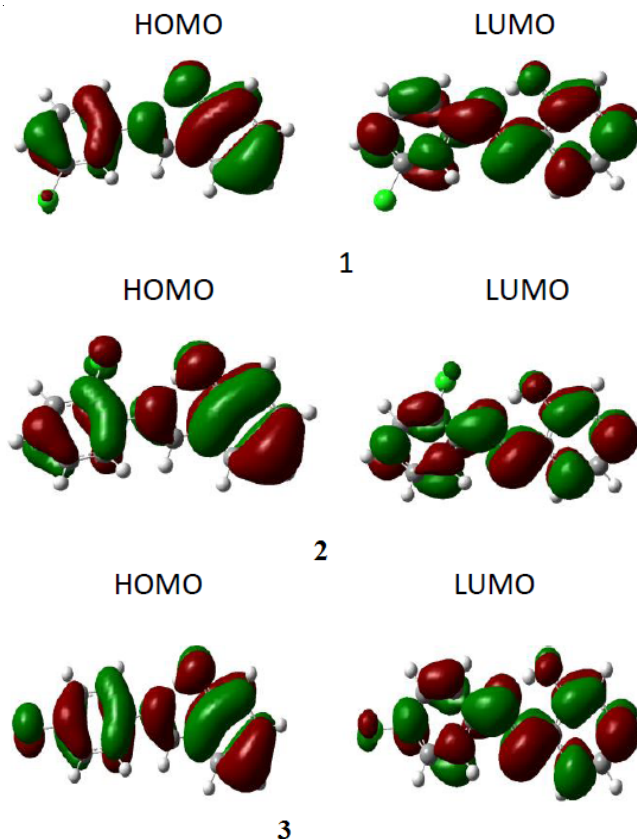| Atom	1	2	3
Part A			
C1	-0.1933	-0.1938	-0.1942
C2	-0.2897	-0.2894	-0.2897
C3	-0.2732	-0.2742	-0.2734
H4	0.2507	0.2508	0.2505
H5	0.2407	0.2400	0.2404
C6	0.3888	0.3907	0.3882
C7	-0.1822	-0.1829	-0.1833
H8	0.2352	0.2340	0.2344
C9	-0.1998	-0.2000	-0.1992
H10	0.2407	0.2403	0.2406
C11	0.1342	0.1362	0.1320
N12	-0.5214	-0.5166	-0.5213
H24	0.2001	0.1986	0.1982
O25	-0.6858	-0.6825	-0.6863
H26	0.5157	0.5201	0.5154
Net charge	-0.1393	-0.1287	-0.1477
Part B			
C13	0.1517	0.1248	0.1357
C14	-0.2325	-0.0431	-0.2154
C15	-0.2724	-0.2445	-0.2438
H16	0.2485	0.0082[a]	0.2505
H17	0.2529	0.2418	0.2425
C18	-0.2152	-0.2399	-0.2408
C19	-0.0336[a]	-0.2294	-0.2388
H20	0.2458	0.2550	0.2560
H21	-0.0065	0.2423	0.2551
C22	-0.2539	-0.2297	-0.0498
H23	0.2545	0.2435	-0.0034[a]
Net charge	0.1393	0.1287	0.1477

[a]Cl

Fig. 2. Ground state isodensity surface plots for the frontier molecular orbitals of the studied Schiff bases
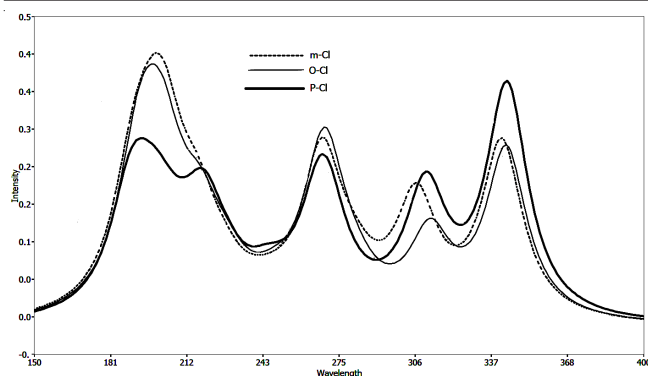
Fig. 3.   Calculated electronic spectra of the studied compounds using TD-DFT method

TABLE-2
CALCULATED ELECTRONIC TRANSITION
BANDS USING TD-DFT METHOD

	λ_{max} (nm)	f_{Osc}	Major contributions
1	341.9	0.2982	H→L (82 %)
	268.1	0.2668	H-4→L (16 %), H-3→L (55 %)
	217.0	0.1215	H→L+3 (63 %)
	201.5	0.2086	H-1→L+3 (46 %)
2	343.7	0.2887	H→L (83 %)
	269.0	0.2923	H-4→L (10 %), H-3→L (54 %), H-2→L (12 %)
	218.1	0.1191	H→L+3 (63 %)
	202.2	0.1953	H-2→L+1 (11 %), H-1→L+3 (50 %)
3	344.0	0.3944	H→L (82 %)
	267.1	0.1359	H-4→L (18 %), H-3→L (22 %), H→L+1 (35 %)
	219.3	0.1622	H-1→L+2 (18 %), H-1→L+4 (15 %), H→L+4 (57 %)
	200.9	0.1075	H-2→L+3 (22 %), H→L+5 (45 %)

compounds are given in Table-3. It is found that N-salicylidene-4-chloroaniline (**3**) has the highest polarizability (α_0 = 178.700 a.u.), hyperpolarizability (β_{tot} = 820.299 a.u.) and lower energy gap (ΔE = 4.046 eV). We performed multiple linear regression analysis of the experimental SHG values as a measure of the optical non-linearity with the studied electronic parameters[19]. The resulting equations showed good correlations between the experimental SHG and these parameters. The following equations have been obtained:

$$SHG = 1.4894 - 0.0017 \, \beta_{tot} \qquad R^2 = 0.964$$
$$SHG = 8.453 - 0.0461 \, \alpha_0 \qquad R^2 = 0.851$$
$$SHG = -48.357 + 11.973 \, \Delta E \qquad R^2 = 0.966$$
$$SHG = -365.129 - 0.004 \, \beta_{tot} + 0.200 \, \alpha_0 + 80.603 \, \Delta E \qquad R^2 = 0.999$$

TABLE-3
AVERAGE POLARIZABILITY (α_0, a.u.), FIRST
HYPERPOLARIZABILITY (β_0, a.u.), E_{HOMO} AND
E_{LUMO} OF THE STUDIED COMPOUNDS

Parameter	1	2	3
β_{tot}	395.963	646.936	820.299
α_0	174.410	172.040	178.700
E_{HOMO}	-6.004	-5.926	-5.947
E_{LUMO}	-1.918	-1.849	-1.901
ΔE	4.086	4.077	4.046

Conclusion

The molecular structure, electronic and spectral properties of N-salicylidene-chloroaniline Schiff bases (**1-3**) were calculated using DFT/B3LYP method and 6-31G(d,p) basis set. The TD-DFT method has been used to calculate the electronic spectra of these Schiff bases. The longest wavelength π-π* transition bands were calculated at 341.9 (f = 0.2982), 343.6 (f = 0.2887) and 344.0 nm (f = 0.3944) for compounds **1-3**, respectively. It was found that N-salicylidene-4-chloroaniline (**3**) has the highest polarizability (α_0 = 178.700 a.u.), hyperpolarizability (β_{tot} = 820.299 a.u.) and lower energy gap (ΔE = 4.046 eV). As a result, compound **3** is predicted to have the highest non-linear optical activity between the studied compounds. The correlation equation that relate these electronic parameters with their SHG values were predicted.

REFERENCES

1. R.H. Lozier, R.A. Bogomolni and W. Stoeckenius, *J. Biophys.*, **15**, 955 (1975).
2. A.D. Garnovskii, A.L. Nivorozhkin and V.I. Minkin, *Coord. Chem. Rev.*, **126**, 1 (1993).
3. E.M. Hodnett and W.J. Dunn, *J. Med. Chem.*, **13**, 768 (1970).
4. A.P. Alivisatos, P.F. Barbara, A.W. Castleman, J. Chang, D.A. Dixon, M.L. Klein, G.L. McLendon, J.S. Miller, M.A. Ratner, P.J. Rossky, S.I. Stupp and M.E. Thompson, *Adv. Mater.*, **10**, 1297 (1998).
5. L. Dalton, *Adv. Polym. Sci.*, **158**, 1 (2002).
6. V.M. Geskin, C. Lambert and J.L. Bredas, *J. Am. Chem. Soc.*, **125**, 15651 (2003).
7. D. Sajan, H. Joe, V.S. Jayakumar and J. Zaleski, *J. Mol. Struct.*, **785**, 43 (2006).
8. S. Di Bella, I. Fragala, I. Ledoux, M.A. Diaz-Garcia, P.G. Lacroix and T.J. Marks, *Chem. Mater.*, **6**, 881 (1994).
9. J. Zyss and D.S. Chemla, Nonlinear Optical Properties of Organic Molecules and Crystals, Academic Press, New York, vol. 1, pp. 23 (1987).
10. A.F. Garito, K.D. Singer and C.C. Teng, in ed.: D.J. Williams, Nonlinear Optical Properties of Organic and Polymeric Materials, American Chemical Society, Washington, ACS Symposium Series, vol. 233, 1 (1983).
11. R.A. Hahn and D. Bloor, eds., Organic Materials for Non-linear Optics II, The Royal Society of Chemistry, Cambridge (1991).
12. M.J. Frisch, *et al.*, Gaussian-03, Revision C.01, Gaussian, Inc., Wallingford, CT (2004).
13. R. Dennington II, T. Keith and J. Millam, GaussView, Version 4.1, Semichem Inc., Shawnee Mission, KS (2007).
14. G.A. Zhurko and D.A. Zhurko, Chemcraft: Lite Version Build 08 (Freeware) (2005).
15. K. Fukui, T. Yonezawa and H.J. Shingu, *J. Chem. Phys.*, **20**, 722 (1952).
16. L. Padmaja, C. Ravikumar, D. Sajan, I.H. Joe, V.S. Jayakumar, G.R. Pettit and O. Faurskov Nielsen, *J. Raman Spectrosc.*, **40**, 419 (2009).
17. C. Ravikumar, I.H. Joe and V.S. Jayakumar, *Chem. Phys. Lett.*, **460**, 552 (2008).
18. P. Gnanasekaran and J. Madhavan, *Asian J. Chem.*, **22**, 109 (2010).
19. K. Bhat, K.J. Chang, M.D. Aggarwal, W.S. Wang, B.G. Penn and D.O. Frazier, *Mater. Chem. Phys.*, **44**, 261 (1996).