Asian Journal of Chemistry; Vol. 28, No. 2 (2016), 351-354

ASIAN JOURNAL OF CHEMISTRY

http://dx.doi.org/10.14233/ajchem.2016.19326

QSAR and DFT Studies on Non-Linear Optical Properties of Some Schiff Bases Derived from Salicylaldehyde and Nitroanilines

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Received: 5 May 2015; *Accepted*: 14 August 2015; *Published online*: 3 November 2015; AJC-17607

QSAR on the non-linear optical properties of some Schiff bases derived from salicylaldehyde and nitroanilines have been performed. All the studied structures are noncentrosymmetric with C_1 point group, hence are second harmonic generation (SHG) active. Quantum chemical parameters such as polarizability (α_0), hyperpolarizability (β_{tot}) and the frontier molecular orbital energy gap (ΔE) were used in this study. The separate stepwise selection-based multiple linear regression (MLR) analyses were performed using these descriptors. The selected multiple linear regression equations, those having the highest correlation coefficient values ($R^2 > 0.9$), showed the importance of the polarizability and energy gap quantum chemical parameters on the second harmonic generation values of the studied compounds. The hyperpolarizability showed almost insignificant improvement to the correlation coefficient (R^2). It could be seen from the best multiple linear regression equation ($R^2 = 0.955$) that there is enhancement in the second harmonic generation values with the decrease of α_0. The opposite is true for the energy gap (ΔE).

Keywords: Second harmonic generation, Quantum chemical descriptors, Non-linear optical, DFT, Schiff base.

INTRODUCTION

Organic compounds having conjugated π-systems are of great interest as potential materials for optical non-linearity [1-3]. In addition, these non-linear optical (NLO) 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]. The high optical non-linearity arises from extended π-conjugated systems, as well as the presence of asymmetrical charge transfer processes. The latter depends on the electron donating and electron accepting properties of the aromatic ring substituents. It is generally known by molecular orbital calculations that substituted aromatic molecules having large optical non-linearities is enhanced if the molecule has donor and acceptor groups bonded at opposite ends of a conjugated system within the molecule. Other important requirements for efficient non-linear optical materials are the lack of center of symmetry and small to moderate excitation energy [9].

The nature and position of substituent on the conjugated system affect the electronic properties such as polarizability, hyperpolarizability as well as HOMO-LUMO energy gap of molecular systems. In the present work, a series of Schiff bases derived from salicylaldehyde and *ortho*-, *meta*- or *para*-nitroaniline were used to predict the different electronic properties that govern their non-linear optical properties. Also, QSAR were performed on the non-linear optical properties of the studied Schiff bases in order to evaluate quantitatively the relation between the studied quantum chemical parameters and the second harmonic generation (SHG) of the studied Schiff bases. Such investigation could help in the understanding of the different factors affecting their non-linear optical (NLO) activity. In this work, we applied density functional calculations at the B3LYP level of theory using 6-31G(d,p) basis set.

CALCULATION METHODS

All the calculations for the studied Schiff bases were calculated using Gaussian-03 software [10] 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 [11] and chemcraft [12] softwares have been used to draw the structures of the optimized geometries.

RESULTS AND DISCUSSION

Molecular structure: The calculated optimized molecular geometries of the studied Schiff bases are shown in Fig. 1. All the studied compounds have nonplanar structure. The C14-C13-N12-C11 and C15-C13-N12-C11 dihedral angels between the two rings are calculated in the range of 35.79° to 41.38° for all the studied compounds. Moreover, the angles between the aryl and salicylidene ring planes are in the range 32.55° to 42.95°. It is the maximum for N-salicylidene-2-nitroaniline where the presence of the NO_2-group substituent at *ortho*-position increases the deviation of the two ring planes from each other. The C6-C9-C11-N12 and C7-C9-C11-N12 dihedral angels do not exceed 1°. These results indicate the strong conjugation in the salicylidene moiety (ring A) but less extended to the other aryl ring (ring B). As a result, the moiety A is almost planar but the two rings are not coplanar with respect to each other. The substituent position would lead to remarkable variation in conjugacy where it is the best for N-salicylidene-3-nitroaniline. Moreover, the calculations predicted O-H···N intramolecular H-bonding interaction between the hydroxyl proton and the N-atom of the Schiff base. The H···N intramolecular distance is in the order **1** < **2** < **4** < **3**. The nitro group seems to weaken this H···N bond where **3** showed the weakest H···N interaction probably due to steric effect.

Natural atomic charges: The charge populations at the different atomic sites are calculated using the DFT/B3LYP level of theory. For a noncentrosymmetric molecule which is second harmonic generation active, the second-order polarizability caused by charge transfer of the whole system would generally affected by the nature of substituent and its position. As a result, the non-linear optical activities will change. In this paper, each designed molecule was divided into two parts to evaluate the charge distribution, Part A for salicylidene group and Part B is the aryl ring with its substituent. The ground state charge distributions of all compounds, which obtained *via* natural bond orbital methods, were presented in Table-1. It is obvious that Part A have negative charge and serve as electronic acceptors, while Part B are positively charged and serve as electronic donors. The substituent position on part A plays vital role in the charge distribution and their effects could be sorted as **1** > **2** > **4** > **3**. It seems that the electron withdrawing character of the nitro group through both the resonance and inductive effects decrease the strength of the intramolecular charge transfer from ring B to A. This decrease has the maximum effect for **3**.

Frontier molecular orbitals: The properties of the frontier molecular orbitals (FMOs) like energy are very useful [13-15] for physicists and chemists. The electron densities of these FMOs were used for predicting the nature of electronic transitions. The energy gap (ΔE) between the HOMO and LUMO levels represents the lowest energy needed for electronic excitation which belongs to one electron transfer from the HOMO to LUMO. The HOMO-LUMO energy gap for the studied compounds were calculated by B3LYP/6-31G(d,p) and the results are collected in Table-2. The HOMO and LUMO pictures are shown in Fig. 2. It is found that the HOMO and LUMO levels are localized on the π-system of the studied molecules. Interestingly, the presence of the nitro group strongly stabilizes the LUMO level more than HOMO which

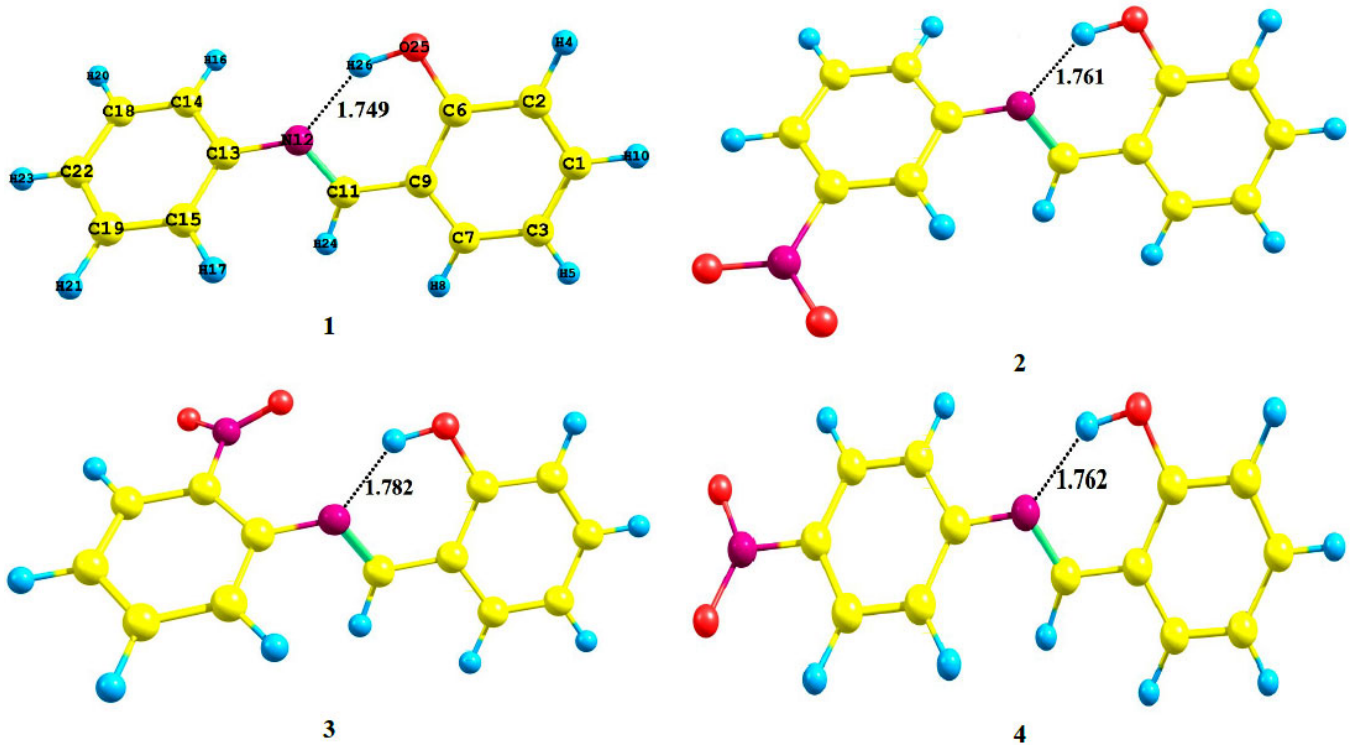

Fig. 1. Calculated optimized geometry of studied compounds

TABLE-1
CALCULATED NATURAL ATOMIC CHARGE OF THE STUDIED COMPOUNDS

Atom	1	2	3	4	Atom	1	2	3	4
C1	-0.196	-0.190	-0.191	-0.189	C13	0.137	0.146	0.165	0.168
C2	-0.290	-0.289	-0.288	-0.289	C14	-0.228	-0.201	0.054	-0.226
C3	-0.274	-0.272	-0.274	-0.272	C15	-0.256	-0.237	-0.254	-0.255
H4	0.250	0.252	0.252	0.253	H16	0.244	0.252	–	0.254
H5	0.239	0.242	0.241	0.243	H17	0.236	0.271	0.247	0.246
C6	0.387	0.391	0.396	0.392	C18	-0.228	-0.223	-0.203	-0.204
C7	-0.185	-0.180	-0.182	-0.180	C19	-0.226	0.063	-0.200	-0.201
H8	0.234	0.237	0.234	0.236	H20	0.239	0.250	0.272	0.274
C9	-0.198	-0.202	-0.203	-0.202	H21	0.238	-	0.246	0.273
H10	0.240	0.242	0.241	0.243	C22	-0.239	-0.218	-0.241	0.047
C11	0.130	0.139	0.140	0.141	H23	0.238	0.272	0.248	–
N12	-0.518	-0.528	-0.510	-0.526	N	–	0.514	0.513	0.511
H24	0.198	0.202	0.199	0.202	O	–	-0.380	-0.387	-0.386
O25	-0.688	-0.684	-0.675	-0.682	O	–	-0.384	-0.370	-0.388
H26	0.515	0.516	0.528	0.516	–	–	–	–	–
Net charge (A)	-0.158	-0.124	-0.091	-0.114	Net charge (B)	0.158	0.124	0.091	0.114

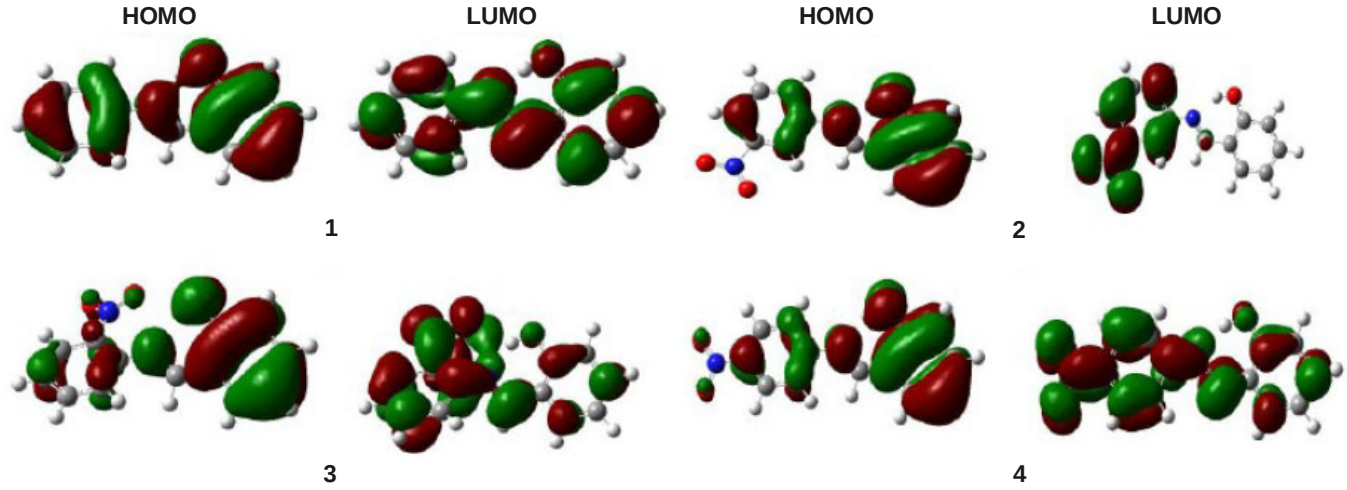

Fig. 2. Ground state isodensity surface plots for the frontier molecular orbitals

TABLE-2
AVERAGE POLARIZABILITY (α_0, a.u), FIRST HYPERPOLARIZABILITY (β_{tot}, a.u.), E_{HOMO} AND E_{LUMO} OF THE STUDIED COMPOUNDS

Parameter	1	2	3	4
β_{tot}	338.05	1248.19	1649.12	4385.34
α_0	161.24	37.08	301.11	348.96
E_{HOMO}	-5.8260	-6.0666	-6.1901	-6.29
E_{LUMO}	-1.7010	-2.4730	-2.5086	-2.6556
ΔE	4.1250	3.5936	3.6815	3.6366

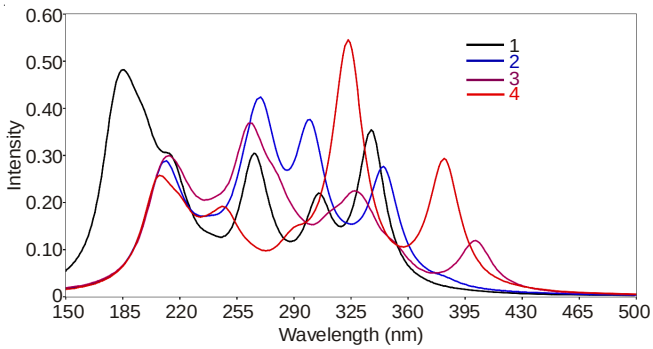

Fig. 3. Calculated electronic spectra of the studied compounds using TD-DFT method

lowers the energy gap between the frontier molecular orbitals (ΔE). This effect is the maximum for **3**. In the studied compounds, the energy gap (ΔE) values are calculated to be 4.125, 3.682, 3.594 and 3.637eV for compounds **1-4** respectively. These electron excitations are mainly described as π-π^* transitions.

The more accurate electronic transitions could be calculated using the time dependant density functional theory (TD-DFT). The calculated electronic spectra using the TD-DFT method is shown in Fig. 3. The results of the TD-calculations are given in Table-3. Compound **1** showed five intense electronic transition bands at 180.1 nm (f = 0.1073), 215.1 nm (sh, f = 0.1518), 265.5nm (f = 0.2490), 305.3 nm (f = 0.1652) and 337.6 nm (f = 0.3298). The most interesting in electronic spectra is the longest wavelength band. This transition band (337.6 nm) undergoes significant bathochromic shift in case of the nitro-substituted derivatives. This band occurs at 382.0, 401.6, 382.3 nm for compounds **2**-**4**, respectively. The presence of nitro group at *ortho* position strongly eases the electron transfer from the ground to excited state. This band are mainly due to (H→L ~ 82 %) which belongs to π-π^* transition.

TABLE-3
CALCULATED ELECTRONIC TRANSITION SPECTRA OF THE STUDIED COMPOUNDS

λ_{max}	f_{Osc}	Maximum contribution
		1
337.6	0.3298	H→L (82 %)
305.3	0.1652	H-1→L (77 %)
265.5	0.249	H-4→L (16 %), H-3→L (61 %)
215.1	0.1518	H→L+3 (76 %)
180.1	0.1073	H-8→L (10 %), H-7→L (17 %), H-6→L (26 %), H-2→L+1 (12 %)
		2
382.0	0.0113	H→L (96 %)
345.2	0.2405	H→L+1 (82 %)
300.1	0.2997	H-2→L+1 (14 %), H-1→L+1 (68 %)
269.7	0.2690	H-3→L (11 %), H-2→L+1 (54 %), H-1→L+1 (12 %)
211.9	0.1356	H-7→L+1 (14 %), H→L+4 (58 %)
		3
401.6	0.1055	H→L (91 %)
326.2	0.1050	H-3→L (12 %), H→L+1 (73 %)
261.0	0.1425	H-5→L (15 %), H-4→L (16 %), H-3→L (27 %), H-1→L+1 (11 %)
207.8	0.139	H-2→L+2 (56 %), H-1→L+3 (12 %)
		4
382.3	0.2716	H→L (89 %)
323.3	0.5172	H-1→L (82 %)
248.1	0.1068	H-6→L (32 %), H-2→L+1 (29 %)
206.4	0.1496	H-8→L (11 %), H→L+4 (51 %)

Non-linear optical properties: Non-linear optical materials were used as key materials for photonic communications which use light instead of electron for data transmission. With the development of laser technology, non-linear optical materials have been extensively applied to industry, national defense, medicine and research [6,16]. Several organic materials were used for such applications. Different quantum chemical parameters such as polarizability (α_0), hyperpolarizability (β_{tot}) as well as HOMO-LUMO gap (ΔE) have strong relation to the non-linear optical activity. The calculated α_0, β_{tot} and ΔE values of the studied compound are given in Table-2. The polarizability and hyperpolarizability of the studied nitro compounds (**2**-**4**) are higher than those for **1**. Also, the energy gaps of compounds **2**-**4** are lower than **1**. In order to find a mathematical relation which correlates the non-linear optical with these quantum chemical parameters, we performed multiple linear regression (MLR) analysis. Separate stepwise selection-based multiple linear regression (MLR) analyses were performed using these descriptors (β_{tot}, α_0 and ΔE). The obtained multiple linear regression equations are collected in Table-4. The correlation analyses of the second harmonic generation values of the studied compounds with each of the calculated β_{tot}, α_0 and ΔE descriptors gave poor to moderate correlations (eqns. 1-3) with correlation coefficient (R^2) values ranging from 0.335 to 0.514. With the exception of equation 6, the multiple linear regression with two parametric regression equations gave moderate correlations. In eqn. 6, the second harmonic generation showed good correlation with the α_0 and ΔE quantum chemical parameters. The addition of the β_{tot} showed no sense to the correlation coefficient. As a result, one could observe that the non-linear optical of the studied Schiff bases are strongly dependant on the α_0 and ΔE rather than β_{tot}. It could be seen from eqn. 6 that the coefficient of the α_0 is negative indicated the increase of the non-linear optical activity with decreasing the polarizability (α_0) parameter. In contrast, the non-linear optical activity is found directly proportional with the frontier molecular orbital energy gap (ΔE).

TABLE-4
RESULTS OF THE MULTIPLE LINEAR REGRESSION (MLR) ANALYSIS

Eqn. No.	Equations	R^2
1	$SHG = 0.8426-0.0002\beta_{tot}$	0.514
2	$SHG = 1.0672-0.0027\alpha_0$	0.335
3	$SHG = -3.4790+1.0558\Delta E$	0.335
4	$SHG = 1.0730-0.0000(06)\ \beta_{tot}-0.0022\alpha_0$	0.761
5	$SHG = -0.9060-0.0002\beta_{tot}+0.4465\Delta E$	0.555
6	$SHG = -2.2488-0.0025\alpha_0+0.8712\Delta E$	0.955
7	$SHG = -3.6638+0.0001\beta_{tot}-0.0003\alpha_0+1.2403\Delta E$	1.000

SHG = Second harmonic generation

Conclusion

In this work, the different quantum chemical parameters affect the non-linear optical (NLO) activity of the studied Schiff bases were calculated using the 6-31G(d,p). The molecular structure and spectroscopic properties of these systems were also predicted. The quantum chemical parameters of the studied Schiff bases such as polarizability (α_0), hyperpolarizability (β_{tot}) and energy gap (ΔE) were introduced for multiple linear regression (MLR) analysis with their second harmonic generation values. The multiple linear regression showed the importance of the polarizability (α_0) and the frontier orbital energy gap (ΔE) on the second harmonic generation. The hyperpolarizability (β_{tot}) has insignificant effect on the non-linear optical activity of the studied systems. The non-linear optical is enhanced with the decrease of the α_0 while the frontier molecular orbital energy gap (ΔE) is directly proportional with the second harmonic generation.

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