



Quantum Chemical Calculations on Molecular Structure and Non-Linear Optical Properties of Some Schiff Bases

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The molecular structure of four Schiff bases derived from salicylaldehyde and methylanilines were calculated using the DFT/B3LYP method and 6-311G(d,p) basis set. All these structures are non-planar and have no center of symmetry. The electronic and spectroscopic properties were used to predict the non-linear optical properties of the studied systems. The time dependent density functional theory (TD-DFT) calculations showed intense absorption bands at 337.6, 337.8, 339.6 and 340.7 nm for compounds **1-4** respectively. These bands are mainly due to H→L (about 82 %) excitation. It is found that N-salicylidene-4-methylaniline (**4**) has the highest polarizability (α_0), hyperpolarizability (β_{tot}) and lower energy gap (ΔE). As a result **4** is predicted to have the highest non-linear optical activity amongst the studied compounds.

Keywords: Schiff base, DFT, Non-linear optical, Charge transfer.

INTRODUCTION

Organic compounds having conjugated π -systems are of great interest as potential materials for optical non-linearity¹⁻³. The high non-linear optical activity arises from extended π -conjugated systems having asymmetrical charge transfer processes where the presence of donor-acceptor groups on the opposite ends of a conjugated system enhances the intramolecular charge transfer (ICT) which leads to high optical non-linearity. Other important requirements for efficient non-linear optical materials are (1) absence of center of symmetry; (2) changeable dipole moment upon excitation⁴ and (3) small to moderate excitation energies⁵. The nature and position of substituent on the conjugated system affect its electronic properties such as dipole moment, HOMO, LUMO energies and polarizability. These electronic parameters are strongly related to the non-linear optical (NLO) activity of compound. 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 and medicine^{6,7}. Several organic materials were used for such applications. In the present work, a series of Schiff bases derived from salicylaldehyde and methylanilines were used to predict the different electronic properties that

govern their non-linear optical properties. The aniline moiety has methyl substitution at 2-, 3- or 4-position. The effect of the methyl group substituent position of the aniline moiety on the non-linear optical properties has been studied. In this work, we applied density functional calculations at the B3LYP level of theory using 6-311G(d,p) basis set.

CALCULATION METHODS

All the calculations for the studied Schiff bases were calculated using Gaussian-03 software⁸. The calculations were performed using the B3LYP/6-311G(d,p) level. The geometries were optimized by minimizing the energies with respect to all the geometrical parameters without imposing any molecular symmetry constraints. GaussView⁹ and chemcraft¹⁰ softwares have been used to draw the structures of the optimized geometries. Frequency calculations at the optimized geometry confirmed that the optimized structures are true energy minimum where no imaginary frequency modes were obtained.

RESULTS AND DISCUSSION

The calculated optimized molecular geometries of the studied Schiff bases are shown in Fig. 1. It is worth noting that, all these structures are non-planar. The C14-C13-N12-C11 and C15-C13-N12-C11 dihedral angles are calculated in

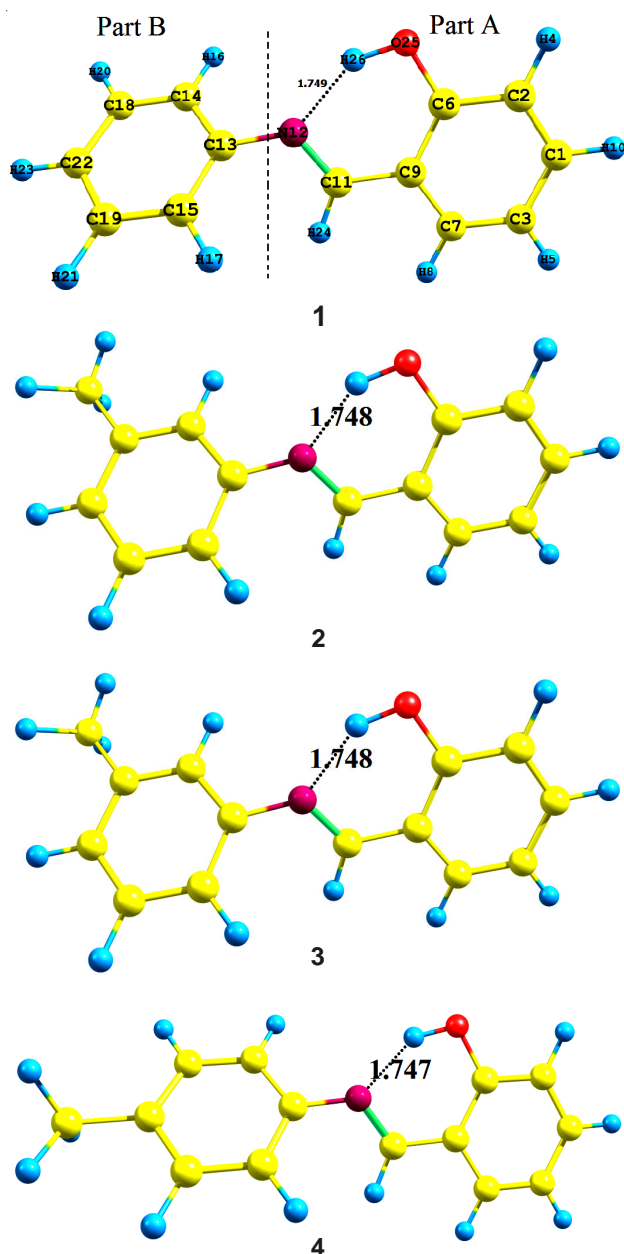


Fig. 1. Calculated optimized geometry of the studied compounds

the range 31.76° to 38.86° for all the studied compounds. It is the maximum for N-salicylidene-2-methylaniline (**3**) where the presence of the methyl group substituent at the *ortho*-position increases the deviation of the two rings from coplanarity. The C6-C9-C11-N12 and C7-C9-C11-N12 dihedral angles do not exceed 1° . On other hand, the angles between the aryl and salicylidene ring planes are in the range 31.76° to 38.86° . These results indicate the high conjugacy of the salicylidene moiety but less extended to the other aryl ring. As a whole, the salicylidene group is almost planar 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-methylaniline (**4**). Moreover the calculation 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 the shortest in case of **4** where the methyl group at the *p*-position.

Natural atomic charges: The charge populations at the different atomic sites are calculated using the DFT/B3LYP level of theory. For a non-centrosymmetric molecule which is SHG active, the second-order polarizability caused by charge transfer of the whole system would generally get enhanced by the strong intramolecular charge transfer (ICT). As a result, better non-linear optical activities could be further achieved. In this paper, each designed molecule was divided into two parts to evaluate the charge distribution, part A (salicylidene moiety) and part B (aniline moiety). 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 electron acceptors, while part B are positively charged and serve as electron donors. The substituent position on part B play a vital role in the charge distribution and their effects could be sorted as $p\text{-CH}_3 > o\text{-CH}_3 > m\text{-CH}_3 > \text{H}$. Moreover, the methyl group substituent as electron donor through inductive effect increase the electron donating ability of part B through the conjugated π -system hence high electron densities are predicted on part A.

Frontier molecular orbitals: The properties of the frontier molecular orbitals (FMOs) like energy are very useful for physicists and chemists¹¹⁻¹³. The HOMO-LUMO energy

TABLE-1
CALCULATED NATURAL ATOMIC CHARGES OF THE STUDIED COMPOUNDS

Atom	1	2	3	4	Atom	1	2	3	4	
		Part A					Part B			
C1	-0.1964	-0.1970	-0.1968	-0.1974	C13	0.1371	0.1432	0.1422	0.1302	
C2	-0.2902	-0.2903	-0.2902	-0.2904	C14	-0.2278	-0.2257	-0.0259	-0.2203	
C3	-0.2743	-0.2744	-0.2741	-0.2745	C15	-0.2559	-0.2630	-0.2505	-0.2486	
H4	0.2495	0.2492	0.2494	0.2491	H16	0.2442	0.2360	0.2363	0.2439	
H5	0.2393	0.2390	0.2393	0.2389	H17	0.2365	-0.0260	-0.2251	0.2361	
C6	0.3869	0.3865	0.3859	0.3861	C18	-0.2276	-0.2194	-0.2332	-0.2238	
C7	-0.1845	-0.1849	-0.1846	-0.1853	C19	-0.2255	0.2381	-0.2345	-0.2232	
H8	0.2338	0.2336	0.2340	0.2334	H20	0.2394	-0.2350	0.2376	0.2355	
C9	-0.1979	-0.1975	-0.1979	-0.1971	H21	0.2384	0.2338	-0.2325	0.2344	
H10	0.2395	0.2393	0.2395	0.2391	C22	-0.2387	0.2402	0.2372	-0.0353	
C11	0.1297	0.1291	0.1290	0.1277	H23	0.2378	-0.6876 ^a	-0.6896 ^a	-0.6884 ^a	
N12	-0.5182	-0.5171	-0.5194	-0.5174			0.2400 ^b	0.2478 ^b	0.2422 ^b	
H24	0.1980	0.1979	0.1990	0.1970			0.2453 ^b	0.2362 ^b	0.2443 ^b	
O25	-0.6881	-0.6887	-0.6891	-0.6890			0.2402 ^b	0.2469 ^b	0.2374 ^b	
H26	0.5154	0.5154	0.5142	0.5152						
Net charge	-0.1577	-0.1602	-0.1619	-0.1644	Net charge	0.1577	0.1602	0.1619	0.1644	

^aC(methyl), ^bH(methyl)

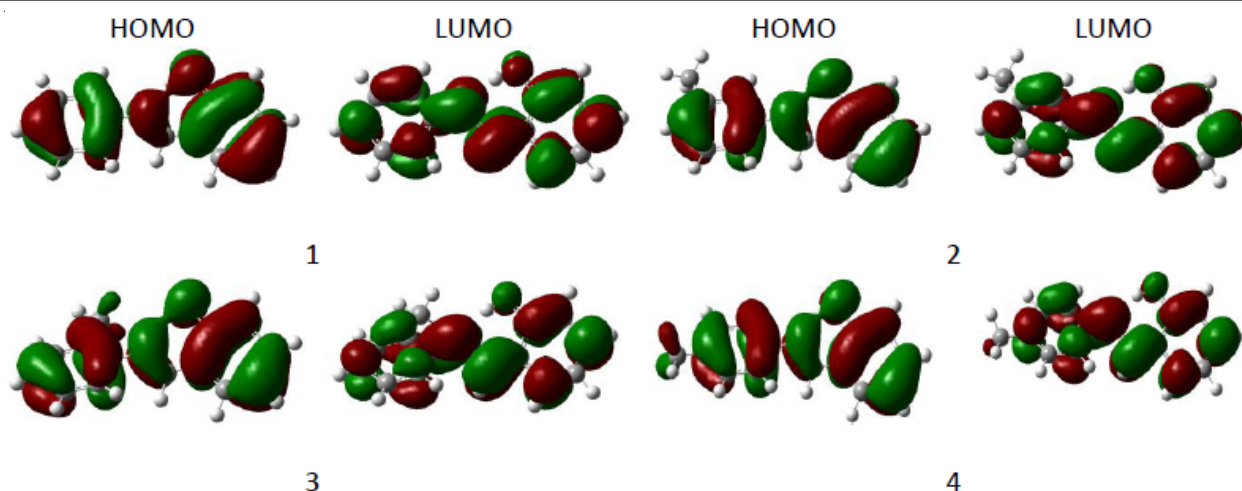


Fig. 2. Ground state isodensity surface plots for the frontier molecular orbitals of the studied compounds

gap represents the least energy needed for electronic transition (ΔE). Hence, the electron densities of these FMOs were used for predicting the nature of electronic transition. The HOMO-LUMO energy gap for the studied compounds were calculated by B3LYP/6-311G(d,p). 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. In the studied compounds, the energy gap values (ΔE) are calculated to be 4.1250, 4.1201, 4.1239 and 4.0763 eV for compounds **1-4** respectively. The ease of the electronic transition is in the order **4** > **2** > **3** > **1**. The ΔE value is the least for **4** indicating the easiest electronic transition in case of *p*-substituted derivative, **4** (Table-2). These electron excitations are mainly described as π - π^* transitions.

TABLE-2
AVERAGE POLARIZABILITY (α_0 , a.u.³), FIRST
HYPERPOLARIZABILITY (β_0 , a.u.), E_{HOMO}
AND E_{LUMO} OF THE STUDIED COMPOUNDS

Parameter	1	2	3	4
β_{tot}	338.0527	402.7085	379.4513	696.2870
α_0	161.2400	175.1700	172.1900	178.2400
E_{HOMO}	-5.826	-5.77974	-5.79662	-5.72614
E_{LUMO}	-1.701	-1.65964	-1.6727	-1.64984
ΔE	4.125	4.120	4.124	4.076

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. The studied compounds **1-4** showed intense absorption bands at 337.6, 337.8, 339.6 and 340.7 nm, respectively. These bands are mainly due to H \rightarrow L (about 82 %)

TABLE-3
CALCULATED ELECTRONIC TRANSITION
BANDS USING TD-DFT METHOD

	Wavelength (nm)	f	Major contributions
1	337.6	0.3298	H \rightarrow L (82 %)
2	337.8	0.3558	H \rightarrow L (82 %)
3	339.6	0.3535	H \rightarrow L (83 %)
4	340.7	0.4330	H \rightarrow L (82 %)

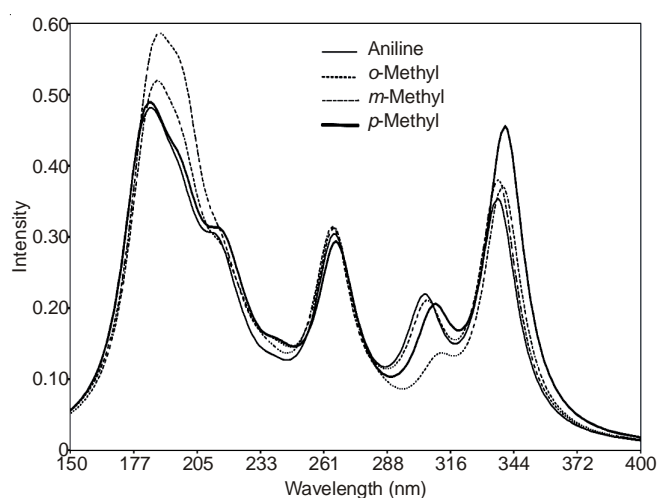


Fig. 3. Calculated electronic spectra of the studied compounds using TD-DFT method

excitation. These results are in good agreement with our prediction that **4** has the easiest intra-molecular charge transfer (ICT) and so the best NLO activity.

Moreover, the electronic parameters such as polarizability (α_0) and hyperpolarizability (β_{tot}) are important factors for non-linear optical materials. Organic materials having high polarizability (α_0) and hyperpolarizability (β_{tot}) are good candidates for non-linear optical activity. The calculated α_0 and β_{tot} values of the studied compounds are given in Table-2. The polarizability (α_0) and hyperpolarizability (β_{tot}) of the studied compounds are in the order **4** > **2** > **3** > **1**. As a result compound **4** is considered as a better non-linear optical material than the others.

Conclusion

The molecular structure of Schiff bases derived from salicylaldehyde and methylanilines have been predicted using DFT/B3LYP-6-311G(d,p) method. The results indicate the planarity (high conjugacy) of the salicylidene moiety but less extended to the other aryl ring. The natural electronic charge calculated using NBO method showed that the intramolecular charge transfer interaction from part B to A is in the order **4** > **2** > **3** > **1**. The electronic properties such as polarizability (α_0),

hyperpolarizability (β_{tot}) and energy gap (ΔE) indicated that **4** has the highest non-linear optical activity of the studied compounds.

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