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## Structural and Optical Properties of Some 5, 8-Diaminoquinoxaline Schiff Bases: Quantum Chemical Calculations

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### ABSTRACT

The molecular structure and optical properties of Schiff bases derived from condensation 4-substituted benzaldehyde (1) and 5, 8-diaminoquinoxaline were researched. These Schiff bases were survived using DFT/B3LYP method and 6-311++G (d, p) basis sets. This is the first report on the linear, non-linear optical properties and HOMO-LUMO molecular orbitals analysis of these compounds. Also, some quantum chemical parameters derived from frontier molecular orbitals were studied.

**Keywords:** Dipole moment, Polarizability, Density functional theory (DFT), Optical properties, Hyperpolarizability, 5, 8-diaminoquinoxaline, Frontier molecular orbitals, Schiff bases

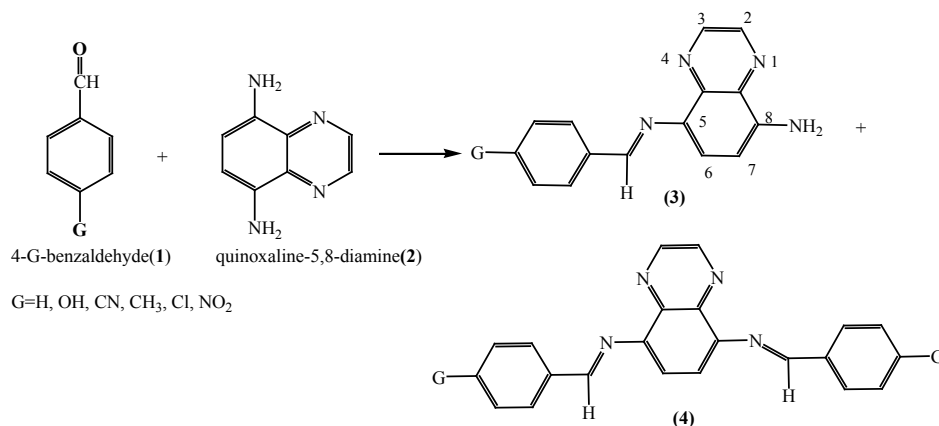
### INTRODUCTION

During the past decades optical organic compounds have been much fascinating because materials with non-linear optical (NLO) properties have potential applications in the field of optoelectronic such as optical communication, optical computing, optical switching and dynamic image processing [1-3]. The molecular first hyperpolarizability ( $\beta$ ) value is showing NLO property of a compound, so theoretical calculations and practical measurements on NLO property is a key factor in designing the optical materials. The practical measurements of  $\beta$  are difficult. But theoretical resolve of it is quite useful in understanding the relationship between the structure and NLO properties. The present study is dedicated to perform a theoretical investigation about the linear and nonlinear optical properties of these Schiff bases, represented as dipole moment ( $\mu$ ), polarizability ( $\alpha$ ), hyperpolarizability, and frontier molecular orbitals.

Several organic derivatives are designed with large first hyperpolarizability. Among the interesting type of organomaterials, Schiff bases have recently been identified as promising NLO materials due to long range conjugation and mesomeric effect in the molecules [4-8].

A Schiff base or azomethine, named after Hugo Schiff, is a functional group that contains a carbon-nitrogen double bond with the nitrogen atom connected to an aryl or alkyl group-but not hydrogen [9].

In this work our designed Schiff bases were obtained from imaginary following reaction (**Scheme 1**). Then molecular geometry and properties of mono- and di-Schiff bases (3 and 4) were studied. Our aim is designing new NLO materials that can be synthesized in future.



**Scheme 1:** Synthetic reaction of 4-substituted benzaldehyde (1) derived Schiff bases of 5, 8-diaminoquinoxaline

## MATERIALS AND METHODS

### Computational details

At first all the molecules were drawn by Gaussview05 program [10] for creation input files. All the ground state geometries of the molecules were optimized by Gaussian09 program [11] and opt keyword without imposing any symmetry constraint. The stationary points of all structures were found and potential energy surfaces (PES) were characterized using freq keyword and standard analytical harmonic vibrational analysis. There are no imaginary (negative) frequencies so all molecules correspond to local true minima of PES. The dipole moment ( $\mu$  value), polarizability ( $\alpha$  value), the first static hyperpolarizability ( $\beta$  value) and molecular orbitals of all aimed molecules were obtained by polar keyword after optimization, in an alternative step as separately. Polar may not be combined for methods lacking analytic gradients (MP4(SDTQ), QCISD(T), CCSD(T), DFT and so on).

Optimization and calculating the molecular orbitals and optical properties were carried by Density functional theory [12] using Becker's three parameter hybrid exchange functional [13] with Lee-Yang-Parr correlation functional [14,15] and 6-311G++ (d, p) basis sets.

## RESULTS AND DISCUSSION

### Optimization of molecular geometries

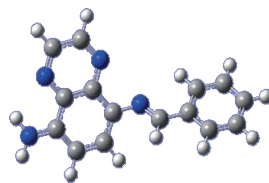
Our molecules are formed from reaction between 4-substituted benzaldehydes (1) and 5, 8-diaminoquinoxaline (2) (**Scheme 1**). As shown in **Scheme 1** these molecules can be classified into two series: mono-Schiff bases (3) and di-Schiff bases (4). All of these Schiff bases have been optimized to study of their electronic and optical properties. The equilibrium geometry optimization for all the molecules has been achieved by energy minimization, using DFT / B3LYP/ 6-311G++ (d, p) level of theory. The optimized geometries of all molecules under study are minima on PES, because all of them have no imaginary (negative) frequency in the vibrational spectra. Three dimensional structures and IUPAC names of mono-Schiff bases (3) and for di-Schiff bases (4) are shown in **Figures 1 and 2**.

Schiff bases have the general formula of  $RR'C=N-R''$ , where  $R''$  is an alkyl or aryl moiety. These two latter groups make the Schiff base a stable imine, because of absence imine-enamine tautomerization. Imine bonds ( $N=CH$ ) in Schiff bases from aldehydes have two geometrical configurations, so our molecules can have two geometrical isomers (i.e. Z and E isomers). There is steric hindrance between aryl moieties, so E-isomers are more stable in all molecules. Because of this, only properties of E-isomers were studied in this research.

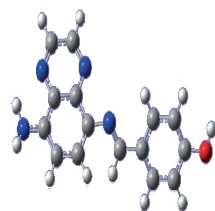
Some structural parameters for these molecules are listed in **Tables 1 and 2**. Imine bonds lengths approximately in all molecules are 1.27-1.28 angstrom, imine bond length in literature is 1.279Å. There is good agreement between calculated  $r_{C=N}$  and its normal value.

The torsional angle ( $\Phi_{CCNC5}$ ) values in these molecules are in range 175-180 degree that represents imine bonds have E-configurations (**Tables 1 and 2**). The values of  $\Phi_{NC5CN4}$  show coplanarity of imine bond and quinoxaline

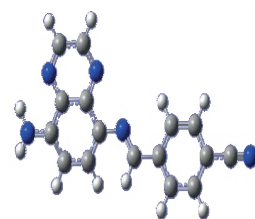
ring. The values of  $\Phi_{\text{NC5CN4}}$  are near zero (0-5 to 5 degree). This coplanarity is necessary for resonance and electron delocalization occurrence in the Schiff bases. Resonance increases optical properties in compounds. It must be remind, di-Schiff bases (4) are symmetrical molecules and both of imine bonds lengths, and dihedral angles ( $\Phi_{\text{NCCN}}$ ,  $\Phi_{\text{CCNC}}$ ) are same, so they are not repeated. Atomic numbering for the aimed Schiff bases are shown in **Scheme 1**



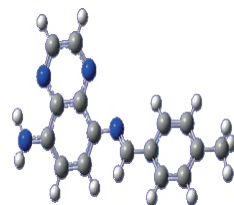
(*E*)- $\text{N}^2$ -benzylidenequinoxaline-5,8-diamine (**3a**).



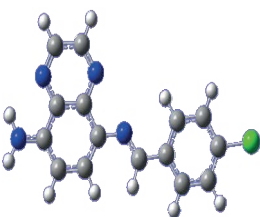
(*E*)-4-((8-aminoquinoxaline-5-yl)imino)methylphenol (**3b**).



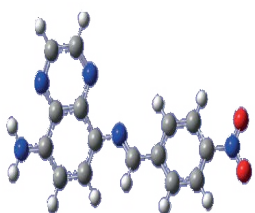
(*E*)-4-((8-aminoquinoxaline-5-yl)imino)methylbenzotrile (**3c**).



(*E*)- $\text{N}^2$ -(4-methylbenzylidene)quinoxaline-5,8-diamine (**3d**).

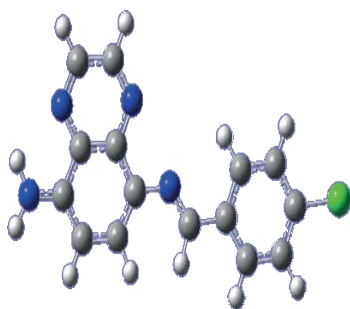
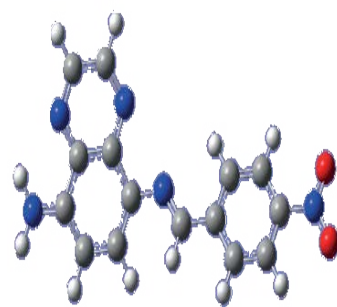
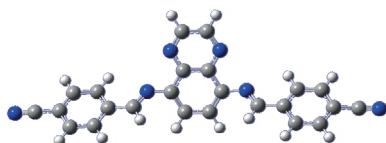
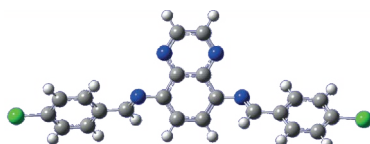
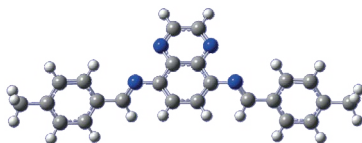
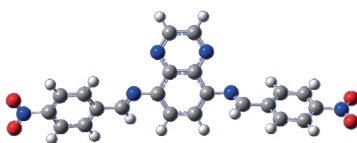


(*E*)- $\text{N}^2$ -(4-chlorobenzylidene)quinoxaline-5,8-diamine (**3e**).



(*E*)- $\text{N}^2$ -(4-nitrobenzylidene)quinoxaline-5,8-diamine (**3f**).

**Figure 1:** Three dimensional structures and IUPAC names for mono- Schiff bases (3).

*(E)*-N<sup>5</sup>-(4-chlorobenzylidene) quinoxaline-5,8- diamine (**3e**)*(E)* - N<sup>5</sup> - (4-Nitrobenzylidene) quinoxaline -5,8- diamine (**3f**).4,4'-((1E,1'E)-(quinoxaline-5,8-diybis (azanylylidene))bis(methanylylidene)) dibenzonitrile (**4c**)*(N'E, N'E)*-N<sup>5</sup>, N<sup>8</sup>-bis (4-methylbenzylidene) quinoxaline-5, 8-diamine (**4d**)*(N'E, N'E)*-N<sup>5</sup>, N<sup>8</sup>-bis (4-chlorobenzylidene) quinoxaline-5, 8-diamine (**4e**)*(N'E, N'E)*-N<sup>5</sup>, N<sup>8</sup>-bis (4-nitrobenzylidene)quinoxaline-5, 8-diamine (**4f**)**Figure 2:** Three dimensional structures and IUPAC names for di- Schiff bases (**4**).**Electric dipole moments**

Polarity refers to the distribution of partial electric charge in molecules or more technically, the degree to which a molecule has a dipole moment which relates to its inherent electric field. Polarity is a fixed property of the molecule that doesn't depend on the external field. A dipole moment implies a permanent charge separation across a distance.

It is an important molecular property that is mainly used to study the intermolecular interactions involving the non-bonded type dipole-dipole interactions.

**Table 1:** Calculated of some structural parameters (bond lengths ( $r$ ) and torsional angles ( $\Phi$ )) by DFT/B3LYP/ 6-311++G (d, p) theoretical method for the mono- Schiff bases (3).

Schiff bases	G	$r_{C=N}$ (in angstrom unit)	$\Phi_{NCSCN4}$ (in degree)	$\Phi_{CCNC5}$ (in degree)
3a	H	1.276	3.8	175.5
3b	OH	1.277	3.7	175.6
3c	CN	1.276	3.4	176
3d	CH <sub>3</sub>	1.277	3.7	175.6
3e	Cl	1.278	0	180
3f	NO <sub>2</sub>	1.277	3.5	176.1

**Table 2:** Calculated of some structural parameters (bond lengths ( $r$ ) and torsional angles ( $\Phi$ )) by DFT/B3LYP/ 6-311++G (d, p) theoretical method for the di-Schiff bases (4).

Schiff bases	G	$r_{C=N}$ (in angstrom unit)	$\Phi_{NCSCN4}$ (in degree)	$\Phi_{CCNC5}$ (in degree)
4a	H	1.275	5.4	175.3
4b	OH	1.277	5.2	175.3
4c	CN	1.275	5.5	175.6
4d	CH <sub>3</sub>	1.276	5.4	175.3
4e	Cl	1.275	3.9	175.4
4f	NO <sub>2</sub>	1.274	4	175.5

The dipole moments ( $\mu$ ) of twelve molecules in Debye (D) are given in **Tables 3 and 4**. It can be order molecules on increasing polarity as follows:

**Table 3:** Calculated molecular dipole moment, the polarizability tensors ( $\alpha$ ) and average polarizability ( $\alpha_{ave}$ ) of mono-Schiff bases (3) by DFT/B3LYP/ 6-311++G (d, p) theoretical method.

Schiff base	$\mu$ (in Debye, D)	$\alpha_{xx}$	$\alpha_{xy}$	$\alpha_{yy}$	$\alpha_{xz}$	$\alpha_{yz}$	$\alpha_{zz}$	$\alpha_{ave}$ (in a.u.)	$\alpha_{ave}$ (in esu)
3a	1.6814	380.776	3.154	226.879	1.508	-6.648	120.292	242.649	$35.96 \times 10^{-24}$
3b	1.1902	401.837	-4.053	229.804	-0.85	-6.764	122.48	251.374	$37.25 \times 10^{-24}$
3c	7.382	477.386	9.685	235.461	1.616	-5.787	121.628	278.158	$41.22 \times 10^{-24}$
3d	1.3287	415.189	4.215	236.789	1.783	-6.275	129.296	260.424	$38.59 \times 10^{-24}$
3e	4.9084	467.569	-3.708	246.329	-0.016	0.007	107.862	273.92	$40.59 \times 10^{-24}$
3f	8.6955	499.728	4.971	243.974	5.633	-7.051	121.462	288.387	$42.74 \times 10^{-24}$

**Table 4:** Calculated molecular state dipole moment, the polarizability tensors ( $\alpha$ ) and average polarizability ( $\alpha_{ave}$ ) of di- Schiff bases (4) by DFT/B3LYP/ 6-311++G (d, p) theoretical method.

Schiff base	$\mu$ (in Debye, D)	$\alpha_{xx}$	$\alpha_{xy}$	$\alpha_{yy}$	$\alpha_{xz}$	$\alpha_{yz}$	$\alpha_{zz}$	$\alpha_{ave}$ (in a.u.)	$\alpha_{ave}$ (in esu)
4a	2.7082	586.452	0	298.385	0	-16.437	174.884	353.24	$52.35 \times 10^{-24}$
4b	0.5955	645.747	-0.002	302.955	0.001	-17.408	178.401	375.701	$55.68 \times 10^{-24}$
4c	2.5529	761.282	0	307.431	0	-17.838	183.105	417.272	$61.84 \times 10^{-24}$
4d	2.7377	666.841	0.016	315.573	-0.023	17.032	193.463	391.959	$58.09 \times 10^{-24}$
4e	1.7253	699.636	-0.007	295.243	-1.914	0	198.421	397.766	$58.95 \times 10^{-24}$
4f	0.9415	753.811	0.001	305.457	0.162	-0.001	206.889	422.052	$62.55 \times 10^{-24}$

3f (8.6955 D) > 3c (7.3820 D) > 3e (4.9084 D) > 3a (1.6814 D) > 3d (1.3287 D) > 3b (1.1902 D)

4d (2.7377D) > 4a (2.7082D) > 4c (2.5529D) > 4e (1.7253D) > 4f (0.9415D) > 4b (0.5955D)

These dipole moments values show that mono- Schiff bases (3) have generally bigger electrical moments than di-Schiff bases (4). Whereas dipole moment is a vector, in symmetrical molecules such as di- Schiff bases (4) bond dipole moments with same value cancel each other's. For example in **Figures 3 and 4** dipole moments of 3c and 4c can be compared.

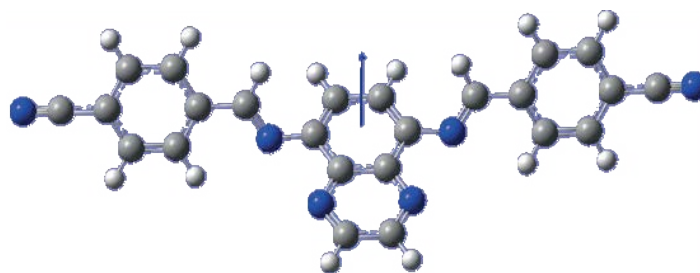


Figure 3: Dipole moment vector for 4c according to Molliken atomic charges.

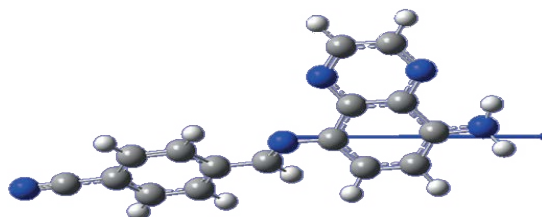


Figure 4: Dipole moment vector for 3c according to calculated Molliken atomic charges.

Moreover, the dipole moment of 3f (8.6955 D) is the biggest. The reason is that  $\text{NO}_2$  is very strong acceptor (-M, -I) group and creates bigger opposite charges on molecule. Also 3c have big dipole moment (7.3820 D) because of cyanide group as good acceptor (-M, -I). The dipole moment equals the distance between the centres' of charge multiply the charge of negative center (or positive center). Schiff base have more charges on each part of molecule so have bigger dipole moment.

### Polarizability

Polarizability refers to the degree to which the electron clouds in a molecule or atom can be influenced by an external electric field. Polarizability allows us to better understand the interactions between nonpolar atoms and molecules and other electrically charged species, such as ions or polar molecules with dipole moments. In the presence of an electric field, electron clouds can be distorted. The created distortion of the electron cloud causes the molecule or atom to acquire a dipole moment. This induced dipole moment is related to the polarizability and the strength of the electric field by the following equation:

$$\mu_{\text{ind}} = \alpha E$$

Polarizability is a property of matter. This property determines not only the strength molecular interactions (long-range intermolecular induction, dispersion forces, etc.) as well as the cross sections of different scattering and collision processes, but also the nonlinear optical properties of the system [16,17].

Polarizability was calculated at B3LYP/ 6-311++G (d, p) level of theory using the standard Gaussian09w keyword 'Polar' [18]. This keyword means that the polarizabilities were obtained analytically rather than by numerical differentiation.

The polarizability is presented in the output file from Gaussian09w in the standard direction in lower triangular order:  $\alpha_{xx}, \alpha_{xy}, \alpha_{yy}, \alpha_{xz}, \alpha_{yz}, \alpha_{zz}$ . The average polarizability ( $\alpha_{\text{ave}}$ ), using xx, yy, and zz tensors are described as the following equation [19]:

$$\alpha_{\text{ave}} = (\alpha_{xx} + \alpha_{yy} + \alpha_{zz}) / 3$$

The values of polarizability tensors on output files are reported in atomic units (a.u.), so the calculated values ( $\alpha_{\text{ave}}$ ) were converted into electrostatic units. (1 a.u. equals with  $0.1482 \times 10^{-24}$  esu) [20]. Results for studied molecules are mentioned in **Tables 3 and 4**. Polarizability values can be order as following:

3f ( $42.74 \times 10^{-24}$ ) > 3c ( $41.22 \times 10^{-24}$ ) > 3e ( $40.59 \times 10^{-24}$ ) > 3d ( $38.59 \times 10^{-24}$ ) > 3b ( $37.25 \times 10^{-24}$ ) > 3a ( $35.96 \times 10^{-24}$ )

4f ( $62.55 \times 10^{-24}$ ) > 4c ( $61.84 \times 10^{-24}$ ) > 4e ( $58.95 \times 10^{-24}$ ) > 4d ( $58.09 \times 10^{-24}$ ) > 4b ( $55.68 \times 10^{-24}$ ) > 4a ( $52.35 \times 10^{-24}$ )

Polarizability values show linear optical property for di-Schiff bases (4) are more than mono-Schiff bases (3) because conjugated systems in these bases are longer.

### Hyperpolarizability

The first order hyperpolarizability is the measure of the nonlinear optical of a molecule activity it measures the second order response of the molecular electric dipole moment to the action of an external electric field and is thus often referred to as dipole hyperpolarizability. In the presence of an applied electric field, the energy of a system is a function of the electric field. Investigation of molecular NLO properties is very important, because of the key functions on information technology and industrial applications.

The first hyperpolarizability is a third order symmetric tensor which can be elucidated by a  $3 \times 3 \times 3$  matrix. The 27 constituents of the 3D matrix can be diminished to 10 constituents as a result of the Kleinman symmetry [21,22]. The value of the total first static hyperpolarizability is calculated by the following equation [22]:

$$\beta_{\text{total}} = [(\beta_{xxx} + \beta_{xyy} + \beta_{zzz})^2 + (\beta_{yyy} + \beta_{yzz} + \beta_{yxx})^2 + (\beta_{zzz} + \beta_{zyy} + \beta_{zxx})^2]^{1/2}$$

The first-order hyperpolarizability ( $\beta$ ) of these novel molecular systems (3 and 4) were calculated using B3LYP level of theory with the standard 6-311++G (d, p) basis set. Since calculated values of the hyperpolarizability ( $\beta$ ) are in atomic units (a.u), these values have been converted into electrostatic units (esu). The conversion factor between atomic units and esu is as follows:

$$1 \text{ atomic unit} = 8.641 \times 10^{-33} \text{ cm}^5 \cdot \text{esu}^{-1} = \text{esu}$$

The results of hyperpolarizability for molecules 3 and 4 are mentioned in **Tables 5 and 6**. In generally  $\beta_{\text{tot}}$  values for mono-Schiff bases (3) are greater than for di-Schiff bases (4). Nevertheless  $\beta_{\text{tot}}$  values of all these molecules are 7 to 240 times more than that of urea ( $0.77 \times 10^{-30}$ ) at the same level of theory B3LYP/6-311++G(d, p) (Urea is one of the prototypical compounds used for comparison NLO properties of other molecules).

**Table 5:** Calculated values of hyperpolarizability components (in a.u.) and total hyperpolarizability using DFT/B3LYP/6-311++G (d, p) level of theory for mono-Schiff bases (3).

Schiff base	$\beta_{xxx}$	$\beta_{xyy}$	$\beta_{xyy}$	$\beta_{yyy}$	$\beta_{xxz}$	$\beta_{xyz}$	$\beta_{yyz}$	$\beta_{xzz}$	$\beta_{yzz}$	$\beta_{zzz}$	$\beta_{\text{total}}$ (in esu)
3a	3486.43	571.03	-151.67	249.32	171.16	-21.21	61.99	15.72	-37.9	17.74	$29.80 \times 10^{-30}$
3b	-1064.1	228.42	194.69	271.34	261.48	75.21	47.77	16.42	-35.36	17.44	$8.85 \times 10^{-30}$
3c	10092.57	938.73	-266.97	212.29	268.71	-29.24	54.71	-63.81	-43.01	16.65	$84.93 \times 10^{-30}$
3d	2694.11	394.24	-178.26	261.09	235.16	-50.2	63.63	-2.23	-35.77	11.6	$22.53 \times 10^{-30}$
3e	-3955.38	159.65	342.59	237.09	-0.013	0.007	0.0013	81.43	-37.14	0.027	$30.67 \times 10^{-30}$
3f	21640.45	1890.12	-293.55	203.39	304.98	-15.92	74.75	-102.42	-43.03	21.29	$184.43 \times 10^{-30}$

**Table 6:** Calculated values of hyperpolarizability components (in a.u.) and total hyperpolarizability (in esu) using DFT/B3LYP/6-311++G (d, p) level of theory for di-Schiff bases (4).

Schiff base	$\beta_{xxx}$	$\beta_{xyy}$	$\beta_{xyy}$	$\beta_{yyy}$	$\beta_{xxz}$	$\beta_{xyz}$	$\beta_{yyz}$	$\beta_{xzz}$	$\beta_{yzz}$	$\beta_{zzz}$	$\beta_{\text{total}}$ (in esu)
4a	0.02	-475.89	0	206.46	395.82	0	130.07	0	-56.39	52.35	$5.73 \times 10^{-30}$
4b	0.38	228.25	-0.01	248.7	541.62	0	158.48	-0.01	-34.73	52.01	$7.54 \times 10^{-30}$
4c	-0.33	-1456.41	0	211.12	437.15	0	116.6	0	-37.03	64.6	$12.30 \times 10^{-30}$
4d	-1.27	-220.29	0	224.91	-487.03	-0.04	-163.71	-0.01	-54.27	-41.4	$6.00 \times 10^{-30}$
4e	-24.41	-1914.45	-4.22	-14.54	-8.84	-714.22	-1.61	-2.78	-274.86	-1.13	$19.04 \times 10^{-30}$
4f	-3.57	-2893.56	-0.03	263.66	-0.16	-15.6	-0.01	0.03	-53.03	-0.04	$23.18 \times 10^{-30}$

The magnitude of hyperpolarizability depends on the strength of donor and acceptor unit substituted across conjugated system, to investigate the effect of the substitution on nonlinear behavior variety of donor and acceptor groups have been substituted on Schiff bases.  $\beta$  values have the following order:

$$3f (184.43 \times 10^{-30}) > 3c (84.93 \times 10^{-30}) > 3e (30.67 \times 10^{-30}) > 3a (29.80 \times 10^{-30}) > 3d (22.53 \times 10^{-30}) > 3b (8.85 \times 10^{-30})$$

$$4f (23.18 \times 10^{-30}) > 4e (19.04 \times 10^{-30}) > 4c (12.30 \times 10^{-30}) > 4b (7.54 \times 10^{-30}) > 4d (6.00 \times 10^{-30}) > 4a (5.73 \times 10^{-30})$$

Mono-Schiff bases have more  $\beta$  values. It seems in these compounds NH<sub>2</sub> group as electron donating (-M) and G-C<sub>6</sub>H<sub>4</sub> group (especially when G=NO<sub>2</sub> and CN) as electron withdrawing increase charge transfer and as a result the first hyperpolarizability (**Figure 5**).

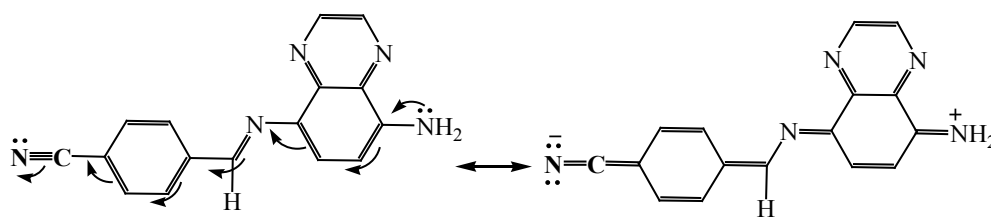


Figure 5: intramolecular charge transfer for **3c**.

### Frontier molecular orbitals

The interaction of two atomic or molecular orbitals produces two new molecular orbitals. One of the new orbital is termed LUMO (lowest unoccupied molecular orbital) and other is HOMO (highest occupied molecular orbital). These orbitals are sometimes referred as frontier molecular orbitals (FMOs), because they lie at the furthest borders of the compound's electrons. HOMO and LUMO figure how the molecule interacts with other species. Highest occupied and lowest unoccupied orbitals in atoms participate in the bonding more than any other levels. The energy difference between frontier molecular orbitals is known as the HOMO-LUMO energy gap ( $\Delta E$ ). The frontier orbitals energy gap helps individualize the chemical reactivity of molecule. The lower the energy of the HOMO and the higher the energy of the LUMO, the more stable the species is thermodynamically. A molecule which have more orbital gap is less polarized and less chemically reactive [23]. According to the present DFT calculations, among aimed molecules **3a** and **4a** have the biggest  $\Delta E$  value.

The hard-soft-acid-base (HSAB) principle was used by Pearson to rationalize a variety of chemical information. The qualitative definition of HSAB was converted to a quantitative one by using the idea of polarizability. A less polarizable molecule or ion is "hard" and a more easily polarized species are "soft". The quantitative definition of hardness is the average of ionization potential and electron affinity. The concepts of hardness and softness of molecules are intimately linked with their polarizabilities and also the sizes. Softness and polarizability are assumed to be related "a soft species is also more polarizable." Global hardness and softness are important properties to measure the molecular stability and reactivity. Evaluating the values of the hardness in **Tables 7 and 8** shows that **3a** and **4a** are harder, this means that **3f** has the largest potential chemical resistance to change the number of electrons among the other molecules. Also, it can be seen in **Tables 7 and 8** compounds **3f** and **4f** have the high value of global softness that show the greater reactivity in relationship to the others.

Table 7: Calculated molecular orbital energies and other quantum chemistry parameters using DFT/B3LYP/6-311++G (d, p) level of theory for mono- Schiff bases (**3**).

Schiff base	$E_{\text{HOMO}}$	$E_{\text{LUMO}}$	$\Delta E$	$\chi$ (in eV)	PI (in eV)	$\eta$ (in eV)	$\omega$ (in eV)	$\sigma$ (in eV <sup>-1</sup> )	S (in eV <sup>-1</sup> )
<b>3a</b>	-0.1993	-0.0807	0.1186	0.14	-0.14	0.5928	0.1653	16.8705	8.4352
<b>3b</b>	-0.1962	-0.0785	0.1177	0.1373	-0.1373	0.0588	0.1602	16.9952	8.4976
<b>3c</b>	-0.2099	-0.0968	0.1131	0.1534	-0.1534	0.0566	0.2079	17.6803	8.8394
<b>3d</b>	-0.1971	-0.0788	0.1183	0.138	-0.138	0.0591	0.1609	16.9118	8.4559
<b>3e</b>	-0.2017	-0.0879	0.1138	0.1448	-0.1448	0.0569	0.1877	17.5762	8.7881
<b>3f</b>	-0.2099	-0.1116	0.0984	0.1605	-0.1607	0.0492	0.2626	20.3273	10.1636

Table 8: Calculated molecular orbital energies (in eV) and some quantum chemistry parameters using DFT/B3LYP/6-311++G (d, p) level of theory for di- Schiff bases (**4**).

Schiff base	$E_{\text{HOMO}}$	$E_{\text{LUMO}}$	$\Delta E$	X (in eV)	$\eta$ (in eV)	$\sigma$ (in eV <sup>-1</sup> )	PI (in eV)	S (in eV <sup>-1</sup> )	$\omega$ (in eV)
<b>4a</b>	-0.2135	-0.0871	0.1264	0.1503	0.0632	15.8252	-0.1503	7.9126	0.1787
<b>4b</b>	-0.2070	-0.0825	0.1245	0.1447	0.0623	16.0604	-0.1447	8.0301	0.1682
<b>4c</b>	-0.2333	-0.1131	0.1202	0.1732	0.0601	16.6458	-0.1732	8.3229	0.2496
<b>4d</b>	-0.2090	-0.0833	0.1257	0.1461	0.0626	15.9108	-0.1461	7.9554	0.1699
<b>4e</b>	-0.2195	-0.0938	0.1257	0.1566	0.0628	15.9146	-0.1566	7.9573	0.1952
<b>4f</b>	-0.2372	-0.1266	0.1106	0.1819	0.0553	18.0831	-0.1819	-9.0415	0.2991

One can relate hardness to the gap between the HOMO and LUMO: The energy gap ( $\Delta E$ ) is directly involved with hardness/softness of a chemical species. A hard molecule has a large energy gap, and a soft molecule has a small one.



Soft molecules are more reactive than hard ones because they could easily offer electrons to an acceptor.

The physical and chemical behaviours of systems can be described by conceptual Density Functional Theory (DFT). With the availability and increased uses of DFT several new quantum chemistry-based descriptors such as electronic chemical potential ( $P_i$ ) or absolute electronegativity ( $\chi$ ) and absolute or chemical hardness ( $\eta$ ) were defined to quantitatively depict the reactivity of organomaterials. These two parameters have particular importance to the organists. Chemical potential measures the escaping tendency of an electron cloud, while chemical hardness determines the resistance of the species to lose electrons. Both  $P_i$  and  $\eta$  are global properties at the ground state, that is, they are molecular properties. The approximately definition of  $\mu$  and  $\eta$  are obtained in following equations:

$$-P_i = (IP + EA) / 2 = \chi$$

$$\eta = (IP - EA) / 2$$

Where IP is the ionization potential ( $E_{LUMO}$ ) and  $E_A$  ( $E_{HOMO}$ ) is the electron affinity of the system.

The low IP creates a better electron donor, and the large  $E_A$  makes a better acceptor. The obtained values of IP and  $E_A$  were considered for the calculation of some quantum chemical parameters such as electronegativity ( $\chi$ ), Chemical hardness ( $\eta$ ), global softness ( $S$ ), chemical potentials ( $P_i$ ), and global electrophilicity ( $\omega$ ). These quantum chemical parameters have been used by a number of workers [24,25] to assess a priori of the reactivity of chemical properties from their intrinsic electrical properties, which have been calculated according to the following equations:

$$\Delta E = E_{LUMO} - E_{HOMO}$$

$$P_i = -\square$$

$$\omega = P_i^2 / 2\eta$$

$$\sigma = 1/\eta$$

$$S = 1/2\eta$$

To evaluate the relations between values of FMOs and the first static hyperpolarizability of the molecules, the calculated values of HOMO and LUMO energy, energy gap ( $\Delta E$ ) and reminded quantum chemical parameters of compounds 3 and 4 using B3LYP/6311++G (d, p) method are listed in **Tables 7 and 8**. It can be seen from these Tables, the calculated values of  $\beta_{tot}$  for the similar compounds increase with decreasing values of the energy gap. There is an inverse relationship between the  $\beta_{tot}$  and  $\Delta E$ . The frontier molecular orbital energies, helps to use intramolecular charge transfer to explain the hyperpolarizability. The HOMO orbital acts as an electron donor, while the LUMO orbital is an electron acceptor.  $E_{HOMO}$  is often associated with the electron-donating ability of a molecule, whereas  $E_{LUMO}$  indicates its ability to accept electrons. In a molecule, the electron transfers from electron donator (ED) groups to the efficient electron acceptor (EA) groups through p conjugated path. The HOMO and LUMO energy gap explains the fact that eventual charge transfer interaction is taking place within the molecule.

As depicted in **Tables 7 and 8** compounds 3a and 4a have a largest energy gap which decreases in the following order in the bases:

$$3a (0.1186 \text{ eV}) > 3d (0.1183 \text{ eV}) > 3b (0.1177 \text{ eV}) > 3e (0.1138 \text{ eV}) > 3c (0.1131 \text{ eV}) > 3f (0.0984 \text{ eV})$$

And

$$4a (0.1264 \text{ eV}) > 4d=4e (0.1257 \text{ eV}) > 4b (0.1245 \text{ eV}) > 4c (0.1202 \text{ eV}) > 4f (0.1106 \text{ eV})$$

The global reactivity parameter chemical potential which is represented by HOMO energy occurs from charge distribution between two systems having different chemical potential. Here all the compounds act as electrophiles and hence their electronic potentials are negative. Another global reactivity descriptor that is electrophilicity index depicts the electron accepting ability of the species. The electrophilicity index encompasses both; the propensity of the electrophile to acquire an additional electronic charge driven by  $P_i$  (the square of chemical potential) and the resistance of the system to exchange an electronic charge with the environment described by  $\eta$  simultaneously. Therefore, a good electrophile is characterized by a high absolute value of  $P_i$  and a low value of  $\eta$ . Computed the electrophilicity indexes and the corresponding values indicate (**Tables 7 and 8**) 3f and 4f have the highest value of electrophilicity, which show their high ability to accept electrons.

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## CONCLUSION

Theoretical calculations provide another method to research essential properties of organic compounds. As hyperpolarizability is difficult to measure directly, computational method is a useful choice.

The molecular structures of 4-substituted benzaldehyde (1) derived Schiff bases of 5, 8-diaminoquinoxaline were studied using DFT/ B3LYP level of theory and 6-311++ G (d, p) basis sets. Linear and non-linear optical properties of mono- Schiff bases (3) and di- Schiff bases (4) were calculated by calculating the dipole moment, the mean polarizability and the first hyperpolarizability with this method. This research showed that the investigated Schiff bases are good candidates as non-linear optical materials. Especially mono- Schiff bases (3) have larger the first hyperpolarizability  $\beta$  values ( $\beta$  for 3f is 240 times more than  $\beta$  for urea), which makes these compounds attractive objects for future studies of nonlinear optics.

Also frontier molecular orbitals energies ( $E_{\text{HOMO}}$  and  $E_{\text{LUMO}}$ ), HOMO-LUMO energy gap ( $\Delta E$ ) and quantum chemical descriptors of compounds 3 and 4 using the same method were calculated. The HOMO-LUMO energy gap is one of important stability indexes. The energy gap ( $\Delta E$ ) represents the chemical reactivity of compounds and is an important stability index. For a system lower value of  $\Delta E$  makes it more reactive or low kinetic stability. The more  $\Delta E$  makes the material more stable for optical devices. The Schiff bases 3a and 4a have largest energy gap so they are more stable materials for optical devices such as solar cell.

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