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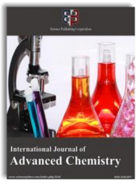

Synthesis, spectral characterization, molecular structure, HOMO-LUMO, MEP and NLO analysis of some (E)-N-(4-Fluoro-3-Phenoxybenzylidene)-substituted benzenamines

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Abstract

In this work, (E)-N-(4-Fluoro-3-Phenoxybenzylidene)-substituted benzenamines (1-6) have been synthesized and characterized by IR, ^{1}H and ^{13}C NMR spectral studies. Density functional theory (DFT) has been used to optimize geometrical parameters, atomic charges, vibrational wavenumbers and intensity of vibrational bands. The molecular properties HOMO-LUMO, MEP and atomic charges of carbon, nitrogen and oxygen were calculated using B3LYP/6-311G (d, p) basis set. The polarizability and first order hyperpolarizability of the title Compounds were calculated and interpreted.

Keywords: *DFT; HOMO – LUMO Energies; NLO; MEP; Substituted Benzenamines.*

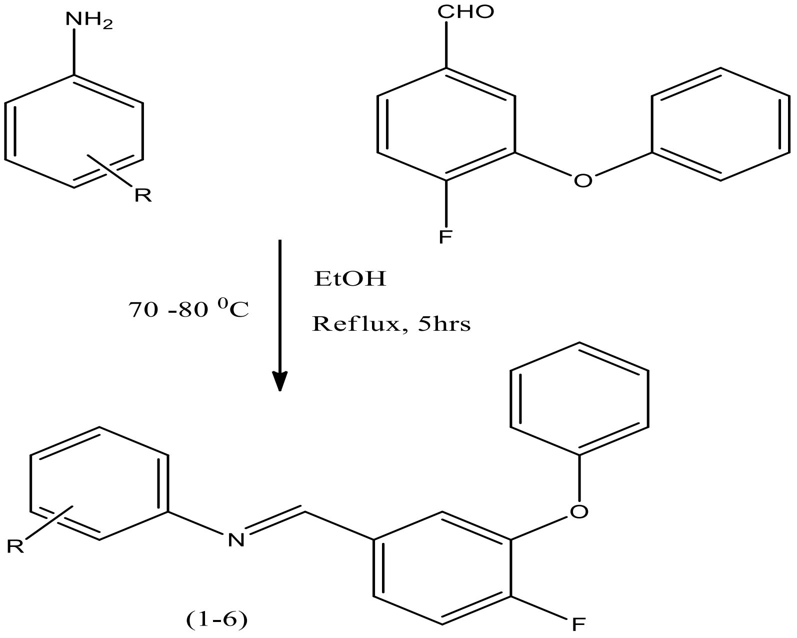
1. Introduction

Compounds containing an azomethine group (-CH=N-), known as Schiff bases, are formed by the condensation of a primary amine with a carbonyl compound. Schiff bases of aliphatic aldehydes are relatively unstable which are readily undergoes polymerization while those of aromatic aldehydes having an effective conjugation system are found to be more stable. Schiff bases have been reported to play a very important role in many biological and chemical reactions, due to the presence of the imine linkage. They are facing a growing interest due to their various applications as anticancer (Sinha et al. 2008; Crowe et al. 1980; Wang et al. 2001; Przybylski et al. 2008; Desai et al. 2001), antibacterial (Shivakumar et al. 2008; Przybylski et al. 2009; Pandeya et al. 1999; Karthikeyan et al. 2006), antiviral (Holla et al. 2001; Jarrahpour et al. 2007; da Silva et al. 2011) and antifungal (Singh et al. 1981; Saravanan et al. 2010; Panneerselvam et al. 2005). Intra-molecular hydrogen bonding between OH hydrogen and C=N nitrogen atoms of Schiff bases determines the properties of various molecular systems and plays a significant role in many biochemical mechanisms (Singh et al. 2001). C=N linkage in the azomethine derivatives is essential for biological activity (Walsh et al. 1996). The proton transfer is known to be crucial for physicochemical properties and practical application of Schiff bases, this process has been widely studied in literature (Odabasoglu et al. 2007). Schiff bases have been used extensively as ligands for the synthesis of novel organometallic compounds (Vicini et al. 2003; Pandeya et al. 1999). Inspite of these synthetic utility, Schiff bases have good electronic, linear and non-linear optical properties (Szady-Chelmieniecka et al. 2001; Dhanaraj et al. 2009; Schilf et al. 2002). Several theoretical analyses have been carried out for isomeric forms of these Schiff bases (Yuan et al. 2000). The present investigation is focused on the synthesis and theoretical investigation of the molecular structures and their vibrational frequencies analysis and charges of newly synthesized Schiff bases derived from 4-Fluoro-3-phenoxybenzaldehyde having extended conjugation. HOMO– LUMO energies, dipole moments, polarizabilities and first hyperpolarizabilities were determined by density functional theory (DFT) method.

2. Experimental details

General Procedure for Preparation of (E)-N-(4-Fluoro-3-Phenoxybenzylidene)-Substituted Benzenamine.

The Schiff bases were obtained by refluxing equimolar quantities of the substituted aromatic amine, 4-Fluoro-3-phenoxybenzaldehyde and few drops of glacial acetic acid, (0.01 mole of each in 25 mL ethanol) on a water bath for 5-6 hrs. After the completion of the reaction, as monitored by TLC, the resulting solution was cooled to room temperature, and then poured in crushed ice with constant stirring. The precipitate was filtered and washed with cold water. Then this was recrystallized using ethanol to obtain pale yellow solid. The analytical and spectral data of synthesized Schiff bases are presented in Table-1.



R= 4-Cl, 4-Br, 4-OCH, 3-NO_2, 4-NO_2, 2-NO_2- 4-OCH_3

Table 1: The Physical Analytical, Melting Point and Spectral Data of (E)-N-(4-Fluoro-3- Phenoxybenzylidene)-Substituted Benzenamines (1-6)

Entry	X	M. F.	M. W.	Yield (%)	m. p. (°C)	IR	^{1}H NMR	^{13}C NMR
						C=N	CH=N	C=N
1	4-Cl	$C_{19}H_{13}ClFNO$	325.8	88	60 - 61	1589.34	8.353	159.22
2	4-Br	$C_{19}H_{13}BrFNO$	370.2	91	63 - 64	1589.34	8.296	159.21
3	4-OCH_3	$C_{20}H_{16}FNO_2$	321.3	87	66 - 68	1589.34	8.398	158.51
4	3-NO_2	$C_{19}H_{13}FN_2O_3$	336.3	83	81 - 82	1591.27	8.398	160.56
5	4-NO_2	$C_{19}H_{13}FN_2O_3$	336.3	91	96 - 97	1589.34	9.892	159.2
6	2-NO_2-4-OCH_3	$C_{20}H_{15}FN_2O_4$	366.1	85	92 - 93	1598.99	9.887	156.09

2.1. Spectral measurements

Infrared spectra (KBr, 4000–400 cm^{-1}) have been recorded on Avatar-330 FT-IR spectrophotometer. The NMR spectra of all synthesized compounds have been recorded on Bruker 400 MHz spectrometer operating at 400 MHz for recording ^{1}H spectra and 100 MHz for ^{13}C spectra in $CDCl_3$ solvent using TMS as internal standard.

2.2. Computational studies

All calculations were done at density functional theory (DFT) level on a personal computer using Gaussian-03 package using B3LYP/6-311G (d, p) basis set (Frisch et al. 2004). The polarizabilities and hyperpolarizabilities were determined from the DFT optimized structure by finite field approach using B3LYP/6-311 G (d, p) basis set. Vibrational frequencies and Mulliken charges have also characterized using the B3LYP/6-311 G (d, p) available in Gaussian-03 package.

3. Results and discussion

3.1. Molecular geometry

The optimized structural parameters such as bond lengths, bond angle and dihedral angle of (1 – 6) were determined at B3LYP level theory with 6-311G (d, p) basis set and are presented in Table - 2. Optimized structure of (E)-N-(4-Fluoro-3-Phenoxybenzylidene)-substituted benzenamines (1-6) shown in Fig. 1. Overall, the C9-C8-N7 bond angles of compound (1-6) illustrate the double bond character and the sp^2 hybridization of the imine carbon atom and the torsion angles [C6-N7-C8–C9 of -177.6] in title compounds, indicate an almost planar E-configuration with respect to the imine C=N bond. As a result from optimized structural parameters such as bond lengths, bond and dihedral angles, we can conclude the E-configuration with respect to the imine C=N bond is more stable compound.

3.2. Mulliken analysis

The Mulliken atomic charges of synthesized molecules calculated by the same basic set and are tabulated in Table-3. Results from Mulliken charge analysis shows that all the hydrogen atoms have a net positive charge. The obtained atomic charge shows that the H2 atom has bigger positive atomic charge than the other hydrogen atoms. This is due to the presence of electronegative group. In order to have an easy look at the charge changes a column chart is illustrated as Fig. 2. From Tables-3, we can observed that most of the carbons having negative values compare to C6, C8, C9, C12, C13, C16. This is due to adjacent electronegative atoms. These data clearly shows that (1-6) are the most reactive towards substitution reactions.

3.3. Molecular electrostatic potential analysis

Molecular electrostatic potential (MEP) is a helpful descriptor used to visualize the electrophilic or nucleophilic reactive sites of molecules (Prasad et al. 2010] and to show the electrostatic potential regions in terms of color grading.

In MEP map Fig. 3, different values of the electrostatic potential are represented by different colors: red and blue represents the regions of the most negative and positive electrostatic potential whereas green represents the region of zero potential. Potential increases in the order of: red < orange < yellow < green < blue. The positive regions are placed around all hydrogen atoms, which are related to nucleophilic reactivity (Kavitha et al. 2010). The nitrogen and oxygen atoms in compounds (1-6) exhibit a negative charge, which are donor atoms. From these data we conclude from this our title molecules are ready for both electrophilic and nucleophilic reactions.

3.4. Frontier molecular orbital analysis

As seen from HOMO-LUMO Fig. 4, in the title compounds (1-6), the electron cloud distribution in HOMO is localized on whole benzene ring, while the LUMO is localized mainly on the azomethine and azomethine side benzene group. The difference of the charge separation between the HOMO and LUMO of those structure play important role in the internal charge transfer (ICT). Furthermore, the difference on the values of ΔE of compounds (1-6) was observed, which has different substituent at 1or 2 or 3- sites of the phenyl core.

For a system having lower value of ΔE makes it more reactive or less stable and also has a direct influence on the electron density difference for the stabilizing ICT process. In this sense, it seems that the selection of a compound 6 containing substituent has a beneficial effect among the designed candidate. It may be due to the presence of both electron-donating and electron-withdrawing present in the phenyl core. As a result, the trend of ΔE gap of inspected compounds becomes 6<4<5<3<2 < 1. We can observe from HOMO-LUMO Tables, the introduction of different substituent at 1or 2 or 3- sites of the phenyl core significantly change the ΔE value.

Chemical hardness is related with the stability and reactivity of a chemical system, it measures the resistance to change in the electron distribution or charge transfer. In this sense, chemical hardness corresponds to the gap between the HOMO and LUMO. The larger the HOMO–LUMO energy gap, the harder and more stable/less reactive the molecule. The higher value of ΔE represents more hardness or less softness of a compound, thus compound 1 referred as hard molecule when compared to 2-6 (Koopmans, 1934). Another global reactivity descriptor electrophilicity index (ψ) describes the electron accepting ability of the systems quite similar to hardness and chemical potential. High values of electrophilicity index increases electron accepting abilities of the molecules. Thus, electron accepting abilities of compounds (1-6) are arranged in following order: 4>6 >5 >1 ≈ 2 >3.

Table 2: Selected Bond Lengths, Bond Angles and Dihedral Angles of (E)-N-(4-Fluoro-3-Phenoxybenzylidene)-Substituted Benzenamines (1-6)

Bond length (Å)	XRD[a]	1	2	3	4	5	6
C1-C2	1.395	1.393	1.39	1.396	1.386	1.388	1.407
C2-C3	1.378	1.394	1.396	1.399	1.397	1.395	1.398
C3-Cl3		1.758	1.911	1.364	1.467		
C3-C4		1.397	1.393	1.406	1.394	1.393	1.393
C4-C5	1.4	1.39	1.393	1.384	1.389	1.395	1.407
C5-C6	1.386	1.406	1.401	1.409	1.404	1.403	1.382
C6-N7	1.419	1.405	1.404	1.404	1.401	1.404	1.388
N7-C8	1.257	1.251	1.251	1.25	1.253	1.252	1.248
C8-C9	1.387	1.456	1.455	1.457	1.452	1.452	1.455
C9-C10		1.409	1.409	1.409	1.409	1.402	1.409
C10-C11		1.39	1.39	1.39	1.39	1.394	1.39
C11-C12		1.39	1.391	1.391	1.39	1.385	1.391
C12-C13		1.391	1.401	1.4	1.403	1.408	1.402
C12-F12		1.342	1.342	1.343	1.341	1.342	1.342
C13-C14		1.393	1.393	1.394	1.393	1.389	1.393
C14-O15		1.371	1.371	1.373	1.369	1.369	1.372
O15-C16		1.387	1.387	1.385	1.389	1.393	1.387
C16-C17		1.395	1.397	1.396	1.397	1.394	1.397
C17-C18		1.395	1.395	1.394	1.395	1.396	1.395
C18-C19		1.396	1.396	1.396	1.397	1.396	1.396
C19-C20		1.396	1.396	1.396	1.396	1.396	1.396
C20-C21		1.395	1.395	1.395	1.395	1.396	1.395
C21-C16		1.397	1.395	1.397	1.394	1.394	1.395
Bond angle (°)							
C1-C6-N7	118.8	123.2	123.2	123.3	123.1	123	121.3
C9-C8-N7	122.6	127.6	127.6	127.9	127.3	127.6	121.8
C6-N7-C8	117.8	127.8	127.8	128.3	127.4	127.1	130
C8-C9-C10	122.2	121.6	121.6	121.7	121.5	120.9	121
C8-C9-C14	119.2	118.7	118.7	118.8	118.7	119.1	119
C12-C13-O15		116.8	116.8	117.1	116.5	115.7	116.8
C14-C13-O15		124.5	124.5	124	124.9	125.7	124.4
F12-C12-C13		118.7	118.7	118.9	118.6	118.3	118.6
C17-C16-O15		116.7	116.7	116.2	121.7	119.3	116.6
C21-C16-C15		122.2	122.2	122.8	117	119.3	122.3
Dihedral(°)							
C9-C8-N7-C6	-173.4	-179.8	-179.8	-179.9	-179.5	-170	-177.6
C14-C9-C8-N7	0.4	0.7	0.6	0.9	0.6	0.8	0.9
C10-C9-C8-N7	0.2	0.7	0.8	0.3	0.8	0.1	14.1
C8-N7-C6-C1	0.6	0.6	0.7	-0.4	1.8	0.5	4
H8-C8-N7-C6	4	0.2	0.2	0.1	0.5	0.8	0.4
H8-C8-C9-C10	-131	-179.3	-179.2	-179.7	-179.2	-170	-165.9
H8-C8-C9-C14	-49	0.3	0.3	-0.3	0.4	0.5	12.1

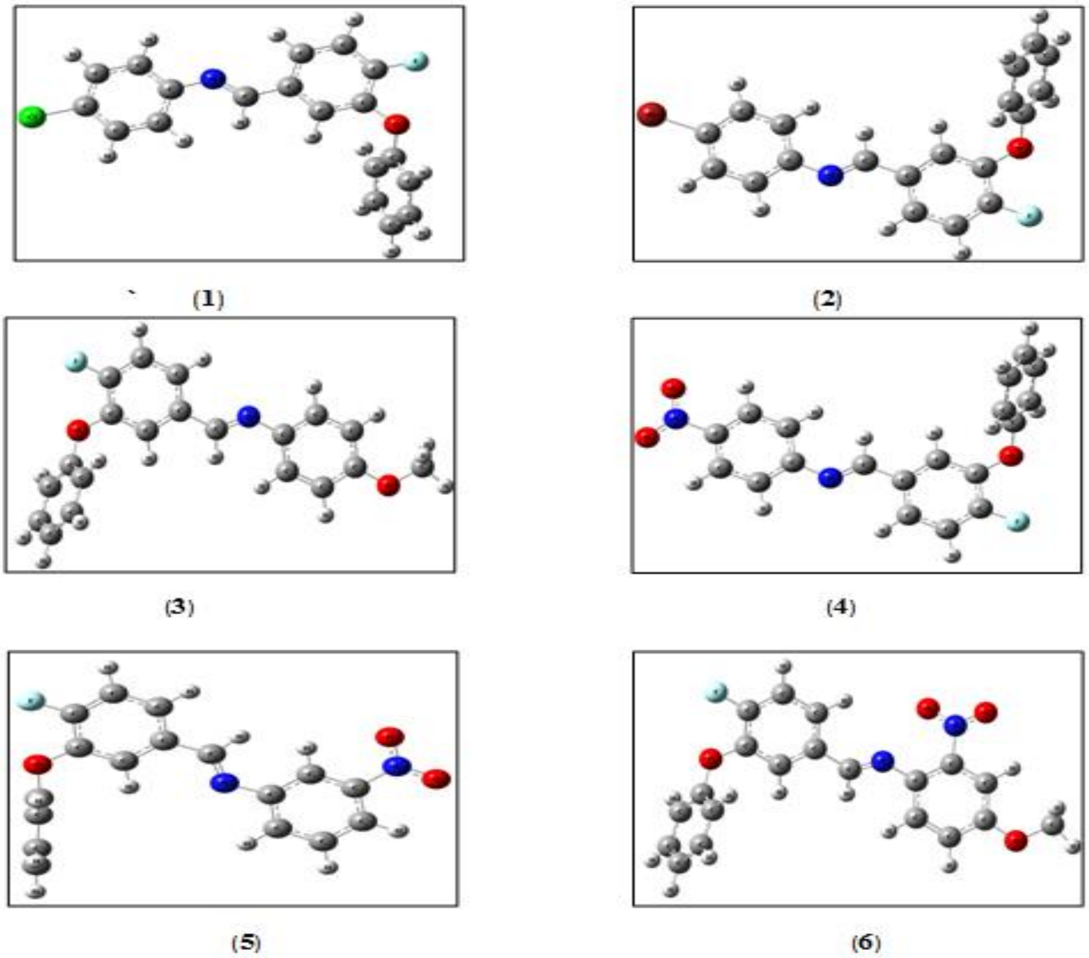
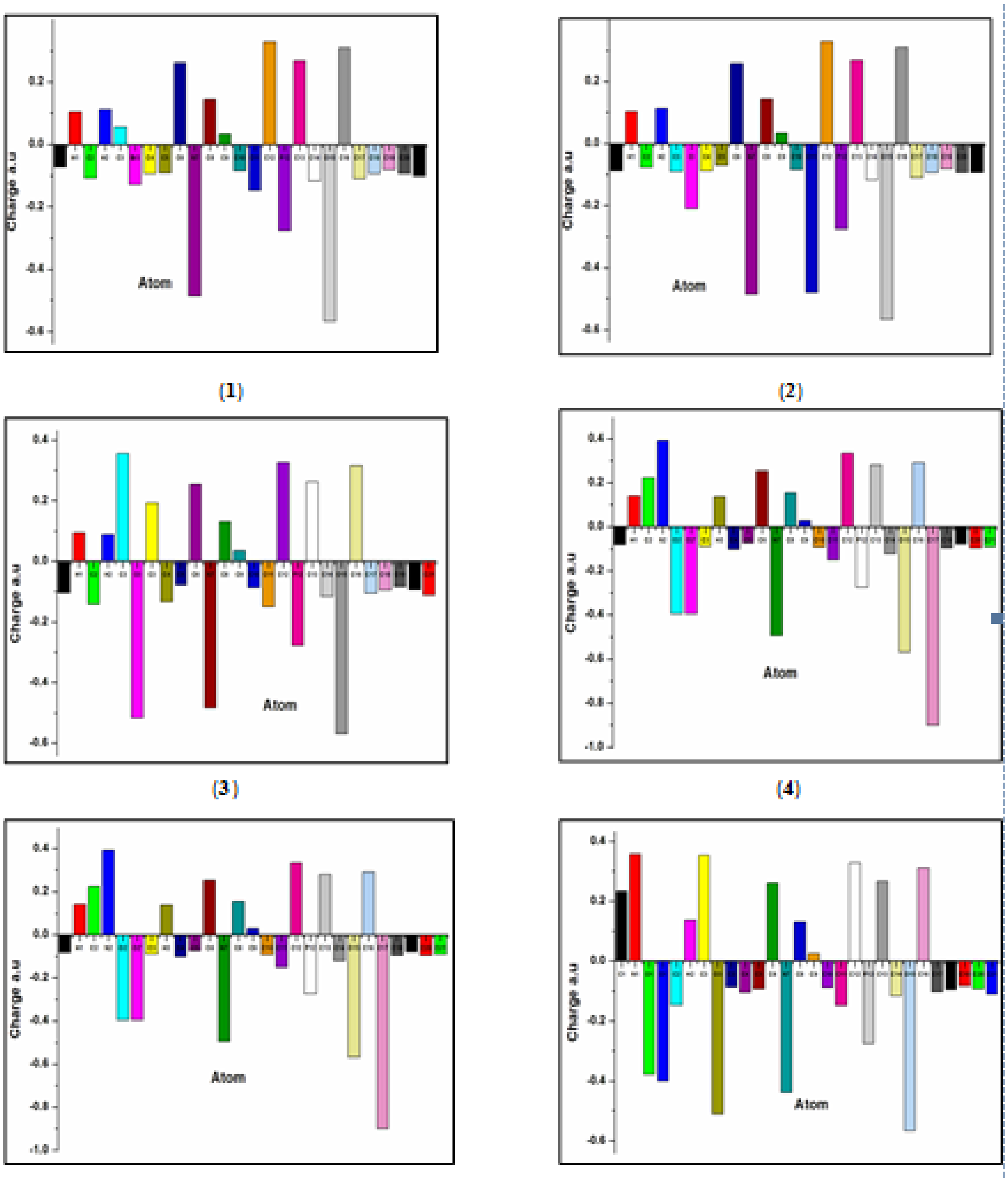

(1) (2) (3) (4) (5) (6)

Fig. 1: Optimized Structureof (E) – N – (4 – Fluoro – 3 – Phenoxybenzylidene) – Substituted Benzenamines (1 - 6).

Table 3: Mulliken Atomic Charges of (E)-N-(4-Fluoro-3-Phenoxybenzylidene)-Substituted Benzenamines (1-6)

Atom	Atom Charge (a. u)		Atom	Atom Charge (a. u)	Atom	Atom Charge (a. u)	Atom	Atom Charge (a. u)	Atom	Atom Charge (a. u)
	1	2		3		4		5		6
C1	-0.089	-0.073	C1	-0.104	C1	-0.087	C1	-0.081	C1	0.233
H1	0.103	0.104	H1	0.094	H1	0.109	H1	0.141	N1	0.357
C2	-0.077	-0.107	C2	-0.14	C2	-0.108	C2	0.223	O1	-0.379
H2	0.113	0.112	H2	0.088	H2	0.14	N2	0.392	O1	-0.4
C3	-0.091	0.056	C3	0.356	C3	0.25	O2	-0.396	C2	-0.147
Cl	-0.21	-0.128	O3	-0.516	N3	0.384	O2’	-0.396	H2	0.136
C4	-0.089	-0.095	C3	0.192	O3	-0.4	C3	-0.089	C3	0.353
C5	-0.07	-0.092	C4	-0.133	O3	-0.4	H3	0.137	O3	-0.51
C6	0.258	0.261	C5	-0.078	C4	-0.094	C4	-0.102	C3	-0.087
N7	-0.485	-0.486	C6	0.254	C5	-0.108	C5	-0.073	C4	-0.105
C8	0.142	0.143	N7	-0.484	C6	0.282	C6	0.253	C5	-0.092
C9	0.032	0.032	C8	0.13	N7	-0.491	N7	-0.494	C6	0.261
C10	-0.085	-0.085	C9	0.035	C8	0.156	C8	0.155	N7	-0.44
C11	-0.48	-0.148	C10	-0.086	C9	0.027	C9	0.027	C8	0.13
C12	0.328	0.328	C11	-0.149	C10	-0.082	C10	-0.092	C9	0.025
F12	-0.275	-0.275	C12	0.326	C11	-0.147	C11	-0.151	C10	-0.088
C13	0.267	0.267	F12	-0.278	C12	0.331	C12	0.335	C11	-0.148
C14	-0.117	-0.117	C13	0.262	F12	-0.272	F12	-0.274	C12	0.328
O15	-0.567	-0.567	C14	-0.116	C13	0.27	C13	0.28	F12	-0.275
C16	0.309	0.309	O15	-0.568	C14	-0.117	C14	-0.122	C13	0.266

C17	-0.11	-0.11	C16	0.315	O15	-0.566	O15	-0.569	C14	-0.117
C18	-0.094	-0.094	C17	-0.105	C16	0.304	C16	0.29	O15	-0.567
C19	-0.082	-0.082	C18	-0.095	C17	-0.098	C17	-0.9	C16	0.31
C20	-0.095	-0.095	C19	-0.084	C18	-0.095	C18	-0.096	C17	-0.102
C21	-0.095	-0.101	C20	-0.093	C19	-0.081	C19	-0.078	C18	-0.095
			C21	-0.112	C20	-0.094	C20	-0.096	C19	-0.083
					C21	-0.108	C21	-0.09	C20	-0.093
									C21	-0.11

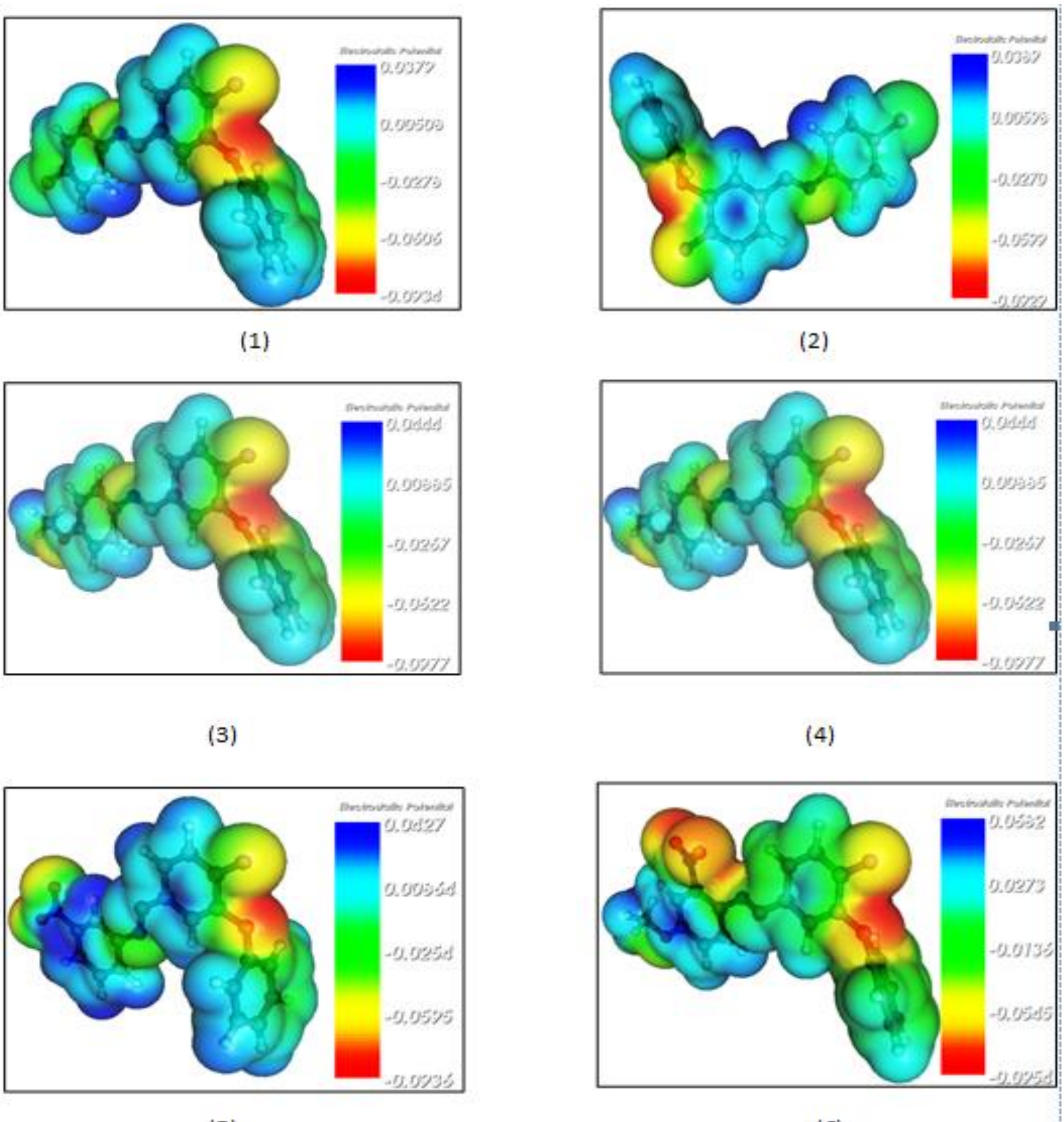


(1) (2)

(3) (4)

(5) (6)

Fig. 2: Mulliken Charges of (E) – N – (4 – Fluoro – 3 – Phenoxybenzylidene) – Substituted Benzenamines (1 - 6).



(1) (2)

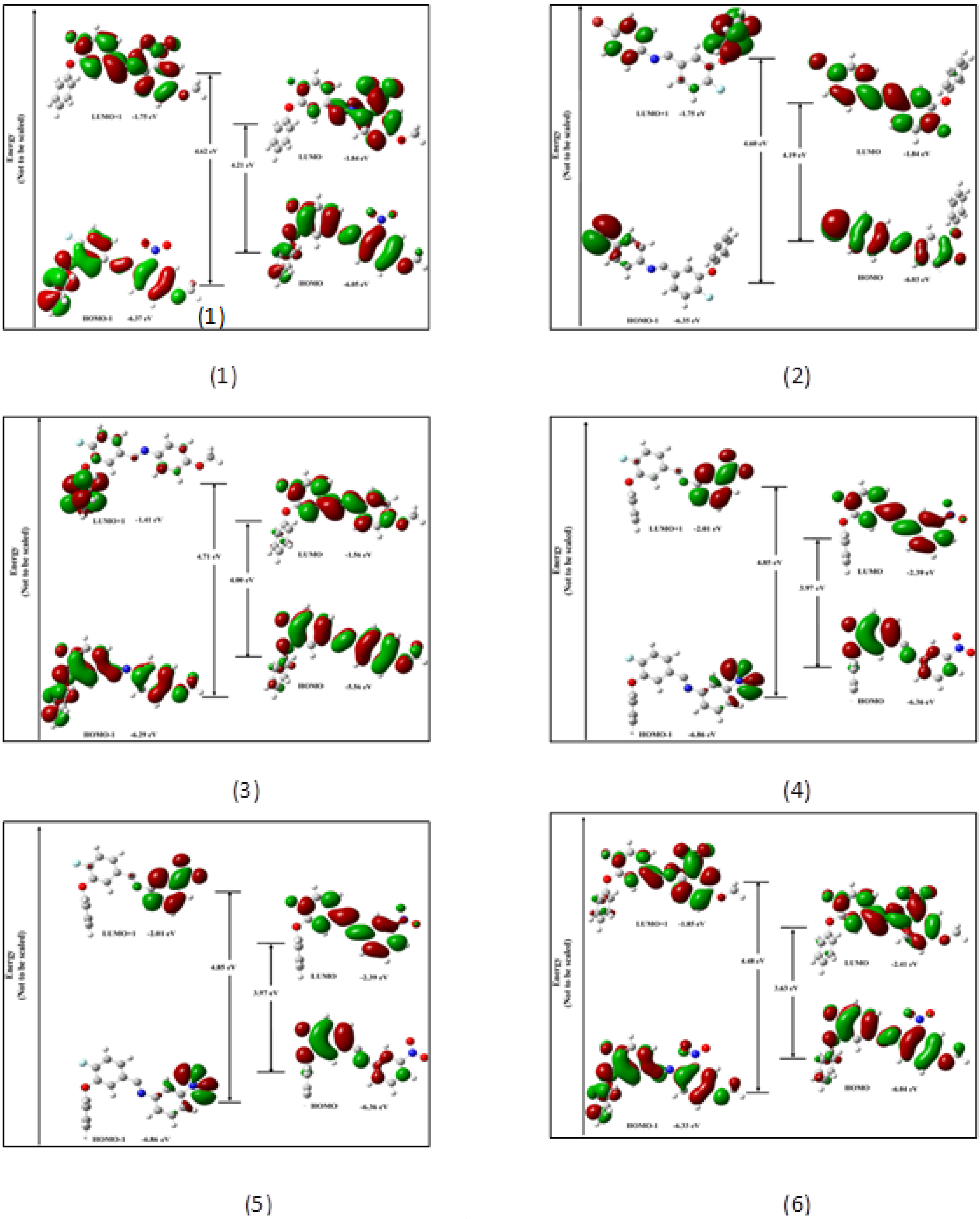
(3) (4)

(5) (6)

Fig. 3: Molecular electrostatic Potential Diagrams of (E) – N – (4 – Fluoro – 3 – Phenoxybenzylidene) – Substituted Benzenamines (1 - 6).

Table 4: Calculated Energy Values (EV) of (E)-N-(4-Fluoro-3-Phenoxybenzylidene)-Substituted Benzenamines (1-6) In Gas Phase

B3LYP / 6-311 G(d,p)	1	2	3	4	5	6
E_{HOMO}	-6.05	-6.03	-5.56	-6.38	-6.36	-6.04
E_{LUOMO}	-1.84	-1.84	-1.56	-2.59	-2.39	-2.41
ELUMO-HOMO	4.21	4.19	4	3.78	3.97	3.63
E_{HOMO-1}	-6.37	-6.35	-6.12	-6.75	-6.86	-6.33
$E_{LUOMO+1}$	-1.75	-1.75	-1.41	-2.14	-2.01	-1.85
$E_{(LUMO+1)-(HOMO-1)}$	4.62	4.6	4.71	4.6	4.85	4.48
Electrinegativity(χ)	-3.95	-3.94	-3.56	-4.49	-4.38	-4.22
Hardness(η)	2.11	2.09	2	1.89	1.99	1.82
Electrophilicity index(ψ)	3.7	3.7	3.16	5.32	4.82	4.91
Softness(s)	175.79	176.88	184.98	195.64	186.29	203.85



(1) (2)

(3) (4)

(5) (6)

Fig. 4: Molecular Orvitals and Energies for the HOMO and LUMO in Gas Phase (1 - 6).

3.5. Non-linear optical activity

NLO is important property providing key for areas such as telecommunications, signal processing and optical interactions (Arockia doss et al. 2015; Arockia doss et al. 2015). A large variety of NLO switches exhibiting large changes in the first order hyperpolarizability (β), the molecular second-order NLO response. In this context, the design of NLO switches, that is, molecules computed for their first hyperpolarizability by alternate their substitution at 1 or 2 or 3- sites in phenyl core.

From Tables-5, the order of dipole moments for 1-6 is 5 > 4 > 6 > 3 > 1> 2. The dipole moment in a molecule is an important property that is mainly used to study the intermolecular interactions involving the non-bonded type dipole–dipole interactions. Polarizability is proportional with molecular volume. The bigger molecular polarizability means the more interaction with the electric field of light. Thus, molecular electronic charge distributions have been rearranged by interaction with electric field of light.

As the results mentioned previously, similar derivatives may have significance nonlinear optical property. In this sense a series of new molecules possessing nonlinear optical property are designed which includes Cl, Br, NO_2, and OCH_3 groups at 1 or 2 or 3- sites of the phenyl core. According to hyperpolarizability tables, all values of each mentioned molecules are greater than their urea values. Therefore, NLO properties of our compounds are better than urea. Results from Tables, the general ranking of NLO properties should be as follows: 4 > 5 > 3 > 2 > 6 > 1. With results in hand, molecule 5 is the best candidate for NLO properties.

To sum up, it can be concluded that the presence of an electron withdrawing group (nitro) in the Meta position at the phenyl ring contributes to decrease the dipole moments, mean polarizability and first order hyperpolarizability of the (1-6) probably because of an inductive competition between the nitro group and the electronic density available in the molecule. The above results show that (1-6) can be best material for NLO applications.

Table 5: Non-Linear Optical Properties of (1–6) Calculated Using B3LYP Method Using 6-311G (D, P) Basis Set

NLO behavior	1	2	3	4	5	6
Dipole moment(μ) D	1.447	1.384	2.672	4.989	5.06	4.918
Mean polarizability (α) x10^{-23}esu	2	2.1	1.9	2.2	2.2	2.1
Anisotropy of the Polarizability ($\Delta\alpha$) x10-24 esu	4.75	4.19	4.67	9.81	6.75	2.89
First order polarizability (β_0) x10^{-30}esu	1.03	2.13	2.19	3.62	2.25	2.11

4. Conclusions

Structures of (E)-N-(4-Fluoro-3-Phenoxybenzylidene)-substituted benzenamines (1-6) were analyzed by IR, ^{1H} and ^{13}C NMR spectroscopy. In addition, molecular geometry and Mulliken charge analysis predicts the most reactive parts in the molecule. The electronic transitions and states were investigated computationally and show good agreement with the experimental data. The calculated HOMO and LUMO energies were used to analyze the charge transfer within the molecule. The calculated dipole moment and first order hyperpolarizability results indicate that the molecule has a reasonably good nonlinear optical behavior.

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